

Wolfgang Nolting

# Theoretical Physics 8

Statistical Physics



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# General Preface

The nine volumes of the series *Basic Course: Theoretical Physics* are thought to be textbook material for the study of university-level physics. They are aimed to impart, in a compact form, the most important skills of theoretical physics which can be used as basis for handling more sophisticated topics and problems in the advanced study of physics as well as in the subsequent physics research. The conceptual design of the presentation is organized in such a way that

*Classical Mechanics (volume 1)*  
*Analytical Mechanics (volume 2)*  
*Electrodynamics (volume 3)*  
*Special Theory of Relativity (volume 4)*  
*Thermodynamics (volume 5)*

are considered as the theory part of an *integrated course* of experimental and theoretical physics as is being offered at many universities starting from the first semester. Therefore, the presentation is consciously chosen to be very elaborate and self-contained, sometimes surely at the cost of certain elegance, so that the course is suitable even for self-study, at first without any need of secondary literature. At any stage, no material is used which has not been dealt with earlier in the text. This holds in particular for the mathematical tools, which have been comprehensively developed starting from the school level, of course more or less in the form of recipes, such that right from the beginning of the study, one can solve problems in theoretical physics. The mathematical insertions are always then plugged in when they become indispensable to proceed further in the program of theoretical physics. It goes without saying that in such a context, not all the mathematical statements can be proved and derived with absolute rigor. Instead, sometimes a reference must be made to an appropriate course in mathematics or to an advanced textbook in mathematics. Nevertheless, I have tried for a reasonably balanced representation so that the mathematical tools are not only applicable but also appear at least ‘plausible’.

The mathematical interludes are of course necessary only in the first volumes of this series, which incorporate more or less the material of a bachelor program. In the second part of the series which comprises the modern aspects of Theoretical Physics,

*Quantum Mechanics: Basics (volume 6)*

*Quantum Mechanics: Methods and Applications (volume 7)*

*Statistical Physics (volume 8)*

*Many-Body Theory (volume 9),*

mathematical insertions are no longer necessary. This is partly because, by the time one comes to this stage, the obligatory mathematics courses one has to take in order to study physics would have provided the required tools. The fact that training in theory has already started in the first semester itself permits inclusion of parts of quantum mechanics and statistical physics in the bachelor program itself. It is clear that the content of the last three volumes cannot be part of an *integrated course* but rather the subject matter of pure theory lectures. This holds in particular for *Many-Body Theory* which is offered, sometimes under different names as, e.g., *Advanced Quantum Mechanics*, in the eighth or so semester of study. In this part new methods and concepts beyond basic studies are introduced and discussed, which are developed in particular for correlated many particle systems which in the meantime have become indispensable for a student pursuing master's or a higher degree and for being able to read current research literature.

In all the volumes of the series *Basic Course: Theoretical Physics* numerous exercises are included to deepen the understanding and to help correctly apply the abstractly acquired knowledge. It is obligatory for a student to attempt on his own to adapt and apply the abstract concepts of theoretical physics to solve realistic problems. Detailed solutions to the exercises are given at the end of each volume. The idea is to help a student to overcome any difficulty at a particular step of the solution or to check one's own effort. Importantly these solutions should not seduce the student to follow the *easy way out* as a substitute for his own effort. At the end of each bigger chapter I have added self-examination questions which shall serve as a self-test and may be useful while preparing for examinations.

I should not forget to thank all the people who have contributed one way or other to the success of the book series. The single volumes arose mainly from lectures that I gave at the universities of Muenster, Wuerzburg, Osnabrueck, and Berlin (Germany), Valladolid (Spain), and Warangal (India). The interest and constructive criticism of the students provided me the decisive motivation for preparing the rather extensive manuscripts. After the publication of the German version I received a lot of suggestions from numerous colleagues for improvement and this helped to further develop and enhance the concept and the performance of the series. In particular I appreciate very much the support by Prof. Dr. A. Ramakanth, a long-standing scientific partner and friend, who helped me in many respects, e.g., what concerns the checking of the translation of the German text into the present English version.

Special thanks are due to the Springer company, in particular to Dr. Th. Schneider and his team. I remember many useful motivations and stimulations. I have the feeling that my books are well taken care of.

Berlin, Germany  
December 2017

Wolfgang Nolting

# Preface to Volume 8

In the prefaces of the preceding volumes I have already set out the goal of the basic course in *Theoretical Physics*. This goal, explained and justified in the *General Preface*, remains of course unchanged for the present eighth volume of the series on Statistical Physics also.

The *Statistical Physics* represents in almost all courses of study on physics the closure of the basic education in *Theoretical Physics* and is offered, as a rule, in the sixth semester, at least when the training in Theoretical Physics starts already in the first semester. It belongs, besides *Quantum Mechanics* (Vols. 6 and 7), to the modern disciplines of Theoretical Physics, whose understanding is mandatory either in elementary form for the bachelor program or in an advanced version for the master program. In contrast, *Classical and Analytical Mechanics* (Vols. 1 and 2), *Electrodynamics* (Vol. 3), *Special Theory of Relativity* (Vol. 4), and *Thermodynamics* (Vol. 5) are ascribed to the *classical* disciplines. Normally they are parts of the bachelor program in the course of study on physics.

The underlying volume on *Statistical Physics* is subdivided into four larger chapters. In the first chapter, the most important concepts and methods for classical systems are explained and exercised. It is demonstrated how the large number of degrees of freedom of macroscopic systems can lead to completely novel phenomena. As an example it may be mentioned here the irreversible transition of a thermodynamic system into equilibrium, which, although actually all microscopic equations of motion are time-reversal invariant, has to, as everyday observation, be accepted and understood. The *Method of Statistical Ensembles* (*microcanonical, canonical, grandcanonical*) turns out to be a successful approach for the description of macroscopic physical systems. The proof of the equivalence of these three ensembles is an important subject of the first chapter.

The second chapter deals with *Quantum Statistics*. A double indeterminacy is characteristic of it, which requires two averaging processes of completely different nature. Besides the indeterminacy due to the large number of degrees of freedom, which is of course present also for classical systems, there appears the principally unavoidable quantum-mechanical uncertainty (*measurement process!*). This fact necessitates the development of genuine quantum-statistical concepts.



A first important application of the general theory concerns the *Ideal Quantum Gases* in Chap. 3, for which the quantum-mechanical *Principle of Indistinguishability of Identical Particles* plays an extraordinary role. Systems of identical *Fermions* and systems of identical *Bosons* underlie different physical principles, which lead to physical behaviors strongly deviating from one another. As a further important application of the *Statistical Physics* I have chosen the highly topical branch of the *Phase Transitions and Critical Phenomena* in Chap. 4.

This volume on *Statistical Physics* arose from lectures I gave at the German universities in Würzburg, Münster, and Berlin. The animating interest of the students in my lecture notes has induced me to prepare the text with special care. The present one as well as the other volumes are thought to be the textbook material for the study of basic physics, primarily intended for the students rather than for the teachers.

I am thankful to the Springer company, especially to Dr. Th. Schneider, for accepting and supporting the concept of my proposal. The collaboration was always delightful and very professional. A decisive contribution to the book was provided by Prof. Dr. A. Ramakanth from the Kakatiya University of Warangal (India), a long-standing scientific partner and friend, who helped me in many respects. Many thanks for it!

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Wolfgang Nolting

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# Chapter 1

## Classical Statistical Physics



### 1.1 Preparations

#### 1.1.1 Formulation of the Problem

The **Thermodynamics**, discussed in Vol. 5 of this basic course in **Theoretical Physics**, is a phenomenological theory, which, being based on a few fundamental postulates (*laws of thermodynamics*), describes macroscopic systems *in equilibrium* with the help of a few variables as, for instance, pressure, volume, temperature, particle density, ... . However, Thermodynamics is not at all a closed, complete theory. So it finds, by reason of empirical findings, that macroscopic systems strive to go from the non-equilibrium into the equilibrium. Thermodynamics, though, is not able to reenact the irreversible setting of the equilibrium. The facts of experience, gathered in the laws of thermodynamics, build the basis of Thermodynamics, but are not explained by it. Fundamental terms such as *temperature* and *heat* count, in a certain sense, to the *elementary equipment*, but their existence must be postulated (*zeroth law of thermodynamics*) or must be '*justified*' by an *intuitive self-understanding*. The actual *justification* of the Thermodynamics is delegated to

#### **Statistical Physics .**

The macroscopic systems, to which Thermodynamics is addressed, consist of many individual entities (atoms, molecules, clusters,...), the behavior of which is fixed by microscopic, classical or quantum-mechanical equations of motion. It is therefore thinkable, at least in principle, to derive the laws and rules of Thermodynamics from *microscopic data*, and exactly that is the concern of Statistical Physics. Because of the unimaginably great number of particles (typically  $10^{23}$  in a few cubic centimeters of a crystal), however, an exact solution is almost always out of reach. Even if a super-computer of sufficient capacity were available, from where should one take the information about the huge set of initial conditions necessary for the solution of the equations of motion? Who should be able to evaluate the horseload of single data with an acceptable expenditure of time? Since, particularly

the available *initial information*, is thus in any case incomplete, the attempt of a **precise** microscopic description must be given up from the very beginning.

**postulate of the equal ‘a-priori’-probabilities ,**

which implies that the system can be in any of these *thinkable* states with equal probability. This hypothesis is not provable. It takes its justification only in retrospect (‘*a posteriori*’) from the unambiguous comparison of the *statistical results* with the empirical findings. On the other hand, it is surely indeed the only *plausible* assumption, any other assumption would be tainted with the ‘*aura of arbitrariness*’.

Let us consider once more the above conclusion from another point of view, namely, that Statistical Physics, and therefore also Thermodynamics, can be reasonable only for *asymptotically large* systems. Let us think about the term *equilibrium*, which is so important for Thermodynamics, and again about the example of the *isolated* system. When the system is, according to *macroscopic criteria*, in its equilibrium, i.e., its macroscopic observables do not change with the time, then this does not at all mean that it is also microscopically valid. To the best of our knowledge, in the *micro-world* it can not be spoken of *temporal constancy*, if one has in mind, e.g., the rapid motion of gas molecules. But how does the state of equilibrium now really manifest itself, and in particular what concerns the irreversible evolution of the system into this state? It seems that we reached here a decisive question of Statistical Physics. The theory will have to explain, how the empirically uniquely manifested *irreversibility* of macroscopic systems is to be understood, although all microscopic equations of motion are time-reversal invariant and therewith *reversible*. We can solve the dilemma, for the present, only by the supposition that the macroscopic description of the phenomenological Thermodynamics and the exact microscopic analysis must distinctly be bordered to each other. In the following chapters we will indeed get to know that in the case of very large systems ( $N \rightarrow \infty$ ) certain observables, which we then will denote as *macroscopic*, obey other laws, by which *irreversible tendency into equilibrium* is admitted and explainable, in contrast to *microscopic observables*, by which *equilibrium* can not be defined. Although the *finite* system and the *asymptotic* system ( $N \rightarrow \infty, V \rightarrow \infty, N/V \rightarrow \text{const}$ ) are microscopically subject to exactly the same laws of Classical Mechanics or Quantum Mechanics, only the huge number of degrees of freedom of the *asymptotic* system thus leads to the special *behavioral codes*, which dominate the *Thermodynamics*. The microscopic justification of the, in this sense, *asymptotic correctness* of the Thermodynamics is executed in the framework of Statistical Physics. That involves, in particular, a *microscopic-mechanical* justificatin of the basic quantities *temperature* and *entropy*, by which the basic relation of Thermodynamics can be formulated as a **provable** statement. But that also means, on the other hand, that Thermodynamics is **not** applicable to systems of only a few particles.

One distinguishes **Classical Statistical Physics** and **Quantum Statistics**, depending on whether the microscopic equations of motion are taken from Classical Mechanics or from Quantum Mechanics. At first, it is an interesting fact that the general rules and connections of the phenomenological Thermodynamics, which

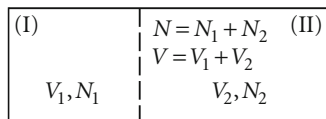
we are going to justify in the framework of Statistical Physics, are independent of whether we derive them classically or quantum-mechanically. That is the reason why we could discuss Thermodynamics already in Vol. 5 of this basic course in Theoretical Physics, i.e., before the Quantum Mechanics, without putting up with any restrictions. This statement of course refers only to the **general** laws and equations. It is clear that, for instance, special forms of the equations of state, and therewith also explicit dependencies of the thermodynamic potentials on their *natural variables* can very well be different, depending on whether they are seen in the framework of Classical Mechanics or in the framework of Quantum Mechanics. In the following first chapter we will at first deal with **Classical Statistics**, while from Chap. 2 on the focus is exclusively on the super-ordinate **Quantum Statistics**.

One has to divide Statistical Physics into a *theory of equilibrium states* and a theory of *non-equilibrium processes*. In the first case one is focused on quantities, which are not time-dependent (probabilities, distributions, average values, . . . !), in the second case one is focused on those with time-dependencies. The more comprehensive, but also rather involved *Non-Equilibrium Statistical Physics* exceeds the framework of this basic course in Theoretical Physics, and is regarded, if at all, only in the form of side-remarks.

### 1.1.2 Simple Model System

By inspecting a very simple abstract model system we want to prepare ourselves for the above mentioned problems, and in particular we try to get a certain visualization how the large number of degrees of freedom (large particle number) of macroscopic systems can lead to extraordinary effects. We will use this model system every now and then for later statements as a ‘*view help*’, for instance, when we discuss in Sect. 1.3.2 the fundamental concepts of *entropy* and *temperature* in the framework of Statistical Physics.

$N$  particles of a classical ideal gas are enclosed in an **isolated** container of the volume  $V$ . The container consists of two chambers (I) and (II) with the volumes  $V_1$  and  $V_2$ , respectively (Fig. 1.1). We assume that the particles of the gas can arbitrarily change the chambers, where, however, a certain particle property  $A$  has in (I) the value  $a_1$  and in (II) the value  $a_2$ . That one can imagine to be realized by any electric or magnetic field. Details of the realizations, though, do not play any role for the



**Fig. 1.1** Classical ideal gas (particle number  $N$ ) in an isolated container (volume  $V$ ) with a wall, permeable for particles



following. In addition, it is for our purposes here sufficient to know that a given particle is either in chamber (I) or in chamber (II). Its actual position within the respective chamber, however, is unimportant. Since for each of the  $N$  particles it holds that it must be in (I) or in (II), one finds

$$2^N \text{ different states}$$

of the total system. On the other hand, the observable  $A$  of the total system can take  $(N + 1)$  values, namely:

$$Na_1, (N - 1)a_1 + a_2, (N - 2)a_1 + 2a_2, \dots, a_1 + (N - 1)a_2, Na_2 .$$

The measured value

$$N_1 a_1 + N_2 a_2 = N_1 a_1 + (N - N_1) a_2 ,$$

except for  $N_1 = 0$  and  $N_2 = N$ , will be highly degenerate, because it is only decisive that  $N_1$  particles are in chamber (I) and  $N_2$  particles in chamber (II), while it does not matter which individual particle is in which chamber. There are

$$\Gamma_N(N_1) = \frac{N!}{N_1! N_2!} = \frac{N!}{N_1! (N - N_1)!} \quad (1.1)$$

different possibilities to bring, out of  $N$  particles,  $N_1$  into (I) and  $N_2 = N - N_1$  into (II). The degree of degeneracy of the above measured value is correspondingly high. We check:

$$\sum_{N_1=0}^N \frac{N!}{N_1! (N - N_1)!} = \sum_{N_1=0}^N \binom{N}{N_1} 1^{N_1} 1^{N-N_1} = (1 + 1)^N = 2^N .$$

We see that indeed all states are encompassed. We denote the probability that a given particle is in  $V_1$  or  $V_2$  by  $p_1$  and  $p_2$ , respectively. These probabilities are of course for all particles the same and easily be given:

$$p_1 = \frac{V_1}{V} ; \quad p_2 = \frac{V_2}{V} = 1 - p_1 . \quad (1.2)$$

When we now pick out  $N_1$  particles and ask for the probability that these given particles are all in  $V_1$ , and the other  $N_2 = N - N_1$  all in  $V_2$ , then we find

$$p_1^{N_1} p_2^{N_2} .$$

If one is *only* interested in the **probability**  $w_N(N_1)$  that *anyhow*  $N_1$  and  $N_2$  particles are in  $V_1$  and  $V_2$ , respectively, then one has to simply multiply this expression by

the number of possibilities of realization (1.1):

$$w_N(N_1) = \frac{N!}{N_1!(N-N_1)!} p_1^{N_1} p_2^{N-N_1} . \quad (1.3)$$

We check the normalization:

$$\sum_{N_1=0}^N w_N(N_1) = \sum_{N_1=0}^N \binom{N}{N_1} p_1^{N_1} p_2^{N-N_1} = (p_1 + p_2)^N = 1^N = 1 .$$

Since the binomial series is used here, one calls (1.3) a **binomial distribution**.

We get the *average value*  $\langle N_1 \rangle$  of the particle number in  $V_1$  in such a way that each number  $N_1$  is multiplied by its probability  $w_N(N_1)$ , and then it is added up over all possible numbers:

$$\langle N_1 \rangle = \sum_{N_1=0}^N N_1 w_N(N_1) . \quad (1.4)$$

In the same manner one calculates the average value of the square of the particle number,

$$\langle N_1^2 \rangle = \sum_{N_1=0}^n N_1^2 w_N(N_1) ,$$

and therewith the *mean square deviation*:

$$\overline{\Delta N_1} \equiv \sqrt{\langle N_1^2 \rangle - \langle N_1 \rangle^2} = \sqrt{\langle (N_1 - \langle N_1 \rangle)^2 \rangle} . \quad (1.5)$$

For the binomial distribution (1.3) one finds:

$$\langle N_1 \rangle = N p_1 ; \quad \overline{\Delta N_1} = \sqrt{N p_1 (1 - p_1)} . \quad (1.6)$$

The explicit derivation of these expressions is offered as Exercise 1.1.1.

The maximum of the distribution  $w_N(N_1)$  defines the *most probable* particle number  $\widehat{N}_1$ . For its calculation it is more comfortable to inspect the logarithm of  $w_N$ , which of course becomes maximal at the same position:

$$\ln w_N(N_1) \Big|_{N_1=\widehat{N}_1} \stackrel{!}{=} \text{maximum} .$$

Here we can exploit the extremely useful **Stirling formula**,

$$N! = \sqrt{2\pi N} N^N \exp\left(-N + \frac{1}{12N} + \dots\right) , \quad (1.7)$$

the derivation of which is offered in many textbooks on advanced mathematics. For very large  $N$  (1.7) permits the simple estimation

$$\ln N! \approx N(\ln N - 1) \quad (1.8)$$

(Exercise 1.1.2), which is acceptable, though, only for the logarithm, for which one can confidently neglect terms of the order of magnitude  $\ln N$  compared to  $N$ . (Example:  $N = 10^{10} \implies \ln N = 10 \cdot \ln 10 = 10 \cdot 1.370 = 13.70 \lll N$ ). It thus holds to a good approximation for  $N, N_1, N_2 \gg 1$ :

$$\begin{aligned} \ln w_N(N_1) &\approx \\ &\approx N \ln N - N - N_1 \ln N_1 + N_1 - N_2 \ln N_2 + N_2 + N_1 \ln p_1 + N_2 \ln p_2 \\ &= N \ln N - N_1 \ln N_1 - (N - N_1) \ln(N - N_1) + N_1 \ln p_1 + (N - N_1) \ln p_2 . \end{aligned}$$

We consider  $N_1$  approximately, and for the moment, as a continuous variable and exploit the extreme value condition:

$$\begin{aligned} \left. \frac{d \ln w_N}{dN_1} \right|_{\widehat{N}_1} &\stackrel{!}{=} 0 = -\ln \widehat{N}_1 - 1 + \ln(N - \widehat{N}_1) + 1 + \ln p_1 - \ln p_2 \\ \iff \ln \frac{\widehat{N}_1}{N - \widehat{N}_1} &\stackrel{!}{=} \ln \frac{p_1}{p_2} . \end{aligned}$$

For the binomial distribution (1.3), the *most probable* value of the particle number is thus identical to the *average* one:

$$\widehat{N}_1 = Np_1 = \langle N_1 \rangle . \quad (1.9)$$

Because of

$$\left. \frac{d^2}{dN_1^2} \ln w_N \right|_{\widehat{N}_1} = -\frac{1}{\widehat{N}_1} - \frac{1}{N - \widehat{N}_1} < 0$$

$w_N$  becomes indeed **maximal** at the position  $N_1 = \widehat{N}_1$ .

We now come across the property of the model system, which is most decisive for our considerations, when we inspect a bit more carefully the behavior of the binomial distribution in the neighborhood of the maximum. It will turn out that  $w_N(N_1)$  has an extremely sharp peak there.

Let  $x$  be in the following the deviation of the particle number  $N_1$  from its most probable value  $\widehat{N}_1$ :

$$N_1 = \widehat{N}_1 + x; \quad N_2 = N - \widehat{N}_1 - x; \quad 1 \ll x \ll \widehat{N}_1 .$$

This we insert into (1.3) and discuss then successively the single terms:

$$N_1! = \widehat{N}_1! (\widehat{N}_1 + 1) \dots (\widehat{N}_1 + x),$$

$$(N - N_1)! = (N - \widehat{N}_1)! \left[ (N - \widehat{N}_1)(N - \widehat{N}_1 - 1) \dots (N - \widehat{N}_1 - x + 1) \right]^{-1}.$$

It follows therewith:

$$\ln N_1! = \ln \widehat{N}_1! + \sum_{y=1}^x \ln(\widehat{N}_1 + y),$$

$$\ln(N - N_1)! = \ln(N - \widehat{N}_1)! - \sum_{y=1}^x \ln(N - \widehat{N}_1 - y + 1).$$

In the last term we could confidently neglect the 1 compared to  $N - \widehat{N}_1$ :

$$\ln[N_1!(N - N_1)!] = \ln[\widehat{N}_1!(N - \widehat{N}_1)!] + \sum_{y=1}^x \ln \frac{\widehat{N}_1 + y}{N - \widehat{N}_1 - y}.$$

One can apply for the logarithm of the last summand, because of  $\ln(1 \pm z) \approx \pm z$  for  $z \ll 1$ , the following estimation:

$$\ln \frac{\widehat{N}_1 + y}{N - \widehat{N}_1 - y} = \ln \frac{\widehat{N}_1}{N - \widehat{N}_1} + \ln \frac{1 + \frac{y}{\widehat{N}_1}}{1 - \frac{y}{N - \widehat{N}_1}}$$

$$\stackrel{(1.9)}{\approx} \ln \frac{p_1}{p_2} + y \left( \frac{1}{\widehat{N}_1} + \frac{1}{N - \widehat{N}_1} \right) = \ln \frac{p_1}{p_2} + \frac{y}{N p_1 (1 - p_1)}.$$

If we insert this into the above sum, it remains:

$$\ln[N_1!(N - N_1)!] \approx \ln[\widehat{N}_1!(N - \widehat{N}_1)!] + x \ln \frac{p_1}{p_2} + \frac{1/2 x(x+1)}{N p_1 (1 - p_1)}.$$

According to (1.3) it holds then for  $N_1$  close to  $\widehat{N}_1$ :

$$\ln w_N(N_1) \approx \ln N! - \left\{ \ln(\widehat{N}_1!(N - \widehat{N}_1)!) + x \ln \frac{p_1}{p_2} + \frac{x(x+1)}{2N p_1 (1 - p_1)} \right\}$$

$$+ (\widehat{N}_1 + x) \ln p_1 + (N - \widehat{N}_1 - x) \ln p_2$$

$$= \ln w_N(\widehat{N}_1) - \frac{x(x+1)}{2N p_1 (1 - p_1)}.$$

We still neglect the 1 compared to  $x$  and recognize then that for the here assumed large particle numbers the binomial distribution (1.3) represents, at least near its maximum, a *Gaussian bell*:

$$w_N(N_1) \approx w_N(\widehat{N}_1) \exp\left(-\frac{(N_1 - \widehat{N}_1)^2}{2Np_1(1-p_1)}\right). \quad (1.10)$$

The maximum value  $w_N(\widehat{N}_1)$  directly arises from an insertion of  $\widehat{N}_1 = Np_1$  into the definition (1.3). Sometimes, however, it is more convenient to fix the coefficient of the exponential function in (1.10) by the normalization condition

$$\sum_{N_1} w_N(N_1) = 1.$$

If we replace the sum by an integral, where the limits of integration for  $x = N_1 - \widehat{N}_1$  can be put without substantial mistake to  $\pm\infty$ , then it results with the standard integral,

$$\int_{-\infty}^{+\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}},$$

an alternative expression for  $w_N(N_1)$ ,

$$w_N(N_1) = \frac{1}{\sqrt{2\pi Np_1(1-p_1)}} \exp\left(-\frac{(N_1 - \widehat{N}_1)^2}{2Np_1(1-p_1)}\right), \quad (1.11)$$

which approximates the exact formula 1.3 not so well as (1.10), but is instead suitably normalized. Both approximations, (1.10) and (1.11), are called **Gaussian distributions** and exhibit equally well what is here essential for us.

The Gaussian distribution is symmetrically concentrated around the maximum  $N_1 = \widehat{N}_1$ . One defines appropriately as *width* of the distribution the distance between  $\widehat{N}_1$  and the  $N_1$ -values, at which  $w_N$  has dropped to the  $e$ -th part of the maximum value:

$$|\Delta N_1|_{-1} = \sqrt{2Np_1(1-p_1)}.$$

Absolutely seen, that is for the macroscopic systems, we are interested in, a very large number. However, related to the full interval of values  $0 \leq N_1 \leq N$ ,

$$\frac{|\Delta N_1|_{-1}}{N} = \sqrt{\frac{2p_1(1-p_1)}{N}}, \quad (1.12)$$

it is negligibly small.

*Example*

$$p_1 = \frac{1}{2}; \quad N = \frac{1}{2} \cdot 10^{22} \implies |\Delta N_1|_{-1} = \frac{1}{2} 10^{11},$$

$$\frac{|\Delta N_1|_{-1}}{N} = 10^{-11}.$$

$|\Delta N_1|_{-1}/N$  is a measure for the **relative width** of the Gaussian distribution. The distribution possesses a very sharp peak at the most probable value  $\widehat{N}_1$ . That is now the decisive point for the fact that Statistical Physics *really works*. For the macroscopic measurement of the observable  $A$ , the actual particle numbers in the chambers (I) and (II) are not decisive, but rather, with which *relative accuracy* the macroscopic measuring value can be predicted. The *relative deviation* of the measuring value from

$$\widehat{N}_1 a_1 + (N - \widehat{N}_1) a_2$$

is given by (1.12) and therewith almost zero for the *asymptotically large* system. Hence, although the microscopic uncertainty increases with increasing particle number, the relative accuracy of the measurement becomes better and better. In this sense, for macroscopic systems in the framework of Statistical Physics, it will be allowed to speak of **definite** values of the observables. They are fixed '*practically fluctuation-free*'.

Let us finally consider once more the above numerical example. What is the probability that a measuring value is observed, which deviates from the most probable value only by

$$\frac{N_1 - \widehat{N}_1}{N} = 10^{-10},$$

i.e., extremely slightly? According to (1.10) we find with

$$\frac{w_N(N_1)}{w_N(\widehat{N}_1)} = e^{-100}$$

a probability which has already dropped off to its  $e^{100}$ -th part. The **total probability** to obtain with a measurement a value outside the interval

$$-10^{-10} \leq \frac{N_1 - \widehat{N}_1}{N} \leq +10^{-10},$$

amounts to

$$1 - \frac{1}{\sqrt{\pi}} \int_{-100}^{+100} e^{-t^2} dt < 10^{-4000}$$

and is therewith unimaginably small. —Let us assume that a particle of the gas changes the chamber  $10^{10}$ -times per second. This means  $10^{10} \cdot 10^{22} = 10^{32}$  changes of the micro-state per second. According to that we would have to wait  $10^{-32} \cdot e^{100} \text{ s} \approx 10^{-32} \cdot 10^{44} \text{ s} = 10^{12} \text{ s}$ , in order to find a relative deviation of the measuring value of the order of magnitude  $10^{-10}$ . This corresponds to about the 100 to 1000-fold of an average human age. We can definitely presume that we will **never** observe such an occurrence:

It goes without saying that the presented estimations can be valid only for *asymptotically large* particle systems. For small numbers the deviations will become pretty substantial.

### 1.1.3 Exercises

#### Exercise 1.1.1

Consider the binomial distribution (1.3)!

1. Calculate the average values

$$\langle N_1 \rangle = \sum_{N_1=0}^n N_1 w_N(N_1),$$

$$\langle N_1^2 \rangle = \sum_{N_1=0}^n N_1^2 w_N(N_1)$$

and therewith the mean square deviation:

$$\overline{\Delta N_1} = \sqrt{\langle N_1^2 \rangle - \langle N_1 \rangle^2}.$$

What follows for the *relative deviation*  $\overline{\Delta N_1} / \langle N_1 \rangle$  in the limit  $N \rightarrow \infty$ ?

2. Assume  $p_1 = p_2 = 1/2$ . Calculate  $w_N(N_1)$  explicitly for  $N = 4$ .
3. Assume  $p_1 = p_2 = 1/2$  and  $N = 10^{23}$ . How large are  $\langle N_1 \rangle$ ,  $\overline{\Delta N_1}$ ,  $\overline{\Delta N_1} / \langle N_1 \rangle$ ?  
Give the probability for the situation where all the particles are found in the volume  $V_1$  ( $N_1 = N$ ,  $N_2 = 0$ ).

#### Exercise 1.1.2

The *Stirling formula* (1.7) turns out to be very useful for the Statistical Physics. Find simple reasons for the estimation

$$\ln m! \approx m \ln m - m \quad (m \in \mathbf{N}, \quad m \gg 1).$$

**Exercise 1.1.3**

Show that for  $p_1 \ll 1$ ,  $N_1 \ll N$  the binomial distribution (1.3) becomes a *Poisson distribution*:

$$w_N(N_1) = \frac{\langle N_1 \rangle^{N_1}}{N_1!} \exp(-\langle N_1 \rangle)$$

**Exercise 1.1.4**

Let a book of 500 pages contain 500 misprints, which are distributed completely randomly over the book. Calculate by means of the *Poisson distribution* (Exercise 1.1.3) the probability that a given page contains

1. no mistake,
2. at least three mistakes.

**Exercise 1.1.5**

1.  $N$  uniform but numbered bullets can arbitrarily be distributed over  $N$  boxes, from which  $k$  are red and  $N - k$  are blue. Each box can receive exactly one bullet. For a random distribution of the bullets over the boxes, how large is the probability that  $k$  pre-given bullets occupy just the  $k$  red boxes?
2. We again pick out  $k$  bullets and search for the probability that in the case of an arbitrary distribution  $k' < k$  bullets are in the red boxes and the other  $k - k'$  ones in the blue boxes.
3. Use the results of part 2., in order to determine the probability to correctly forecast in a lottery (6 from 49) six (five, four, three) numbers.

**Exercise 1.1.6**

Let a system consist of  $N = 4$  particles. The *advance information* is so that for each particle two states  $a$  and  $b$  are realizable. Let  $n_a$  and  $n_b$  be the numbers of the particles in the states  $a$  and  $b$ .

1. List the possible distributions  $(n_a, n_b)$ .
2. Give explicitly all the *thinkable* states of the system, which belong to the individual distributions  $(n_a, n_b)$ .
3. Determine the probabilities of the distributions  $(n_a, n_b)$ .

## 1.2 Micro-Canonical Ensemble

### 1.2.1 State, Phase Space, Time Average

The system, which we are interested in, and for which we want to assume for the following considerations that it is **isolated**, may possess  $s$  degrees of freedom. For its description we therefore need an equally large number of *generalized coordinates*



(see section 1.1, Vol. 2),

$$\mathbf{q} = (q_1, q_2, \dots, q_s) ,$$

with the corresponding *generalized momenta*:

$$\mathbf{p} = (p_1, p_2, \dots, p_s) .$$

The generalized coordinates and the generalized momenta span, in the form of Cartesian axes, the so-called *phase space* (see subsection 2.4.1, Vol. 2). This in the Statistical Physics sometimes is also called the  $\Gamma$ -*space*. As independent variables of equal footing, momenta and coordinates can be combined to a *phase* and a *phase vector*, respectively:

$$\boldsymbol{\pi} = (\pi_1, \pi_2, \dots, \pi_{2s}) \equiv (q_1, q_2, \dots, q_s, p_1, \dots, p_s) .$$

Each micro-state then corresponds to a definite phase point  $\boldsymbol{\pi}$  of the phase space. In the framework of Classical Mechanics, the state of the system is completely defined by the phase  $\boldsymbol{\pi}$ . As *phase curve* or *phase trajectory* one denotes the set of all phase points  $\boldsymbol{\pi} \equiv (\mathbf{q}, \mathbf{p})$ , which the system passes through in course of time (Fig. 1.2). With given initial conditions

$$\boldsymbol{\pi}(t = 0) = (\mathbf{q}(0), \mathbf{p}(0))$$

these phase points  $\boldsymbol{\pi}(t)$  are uniquely calculable by the means of the *Hamilton's equations of motion* ((2.11), (2.12), Vol. 2),

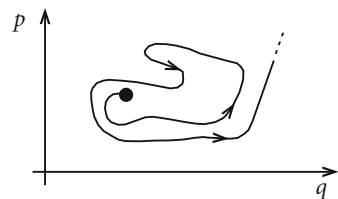
$$\dot{p}_i = -\frac{\partial H}{\partial q_i} ; \quad \dot{q}_i = \frac{\partial H}{\partial p_i} ; \quad i = 1, \dots, s , \quad (1.13)$$

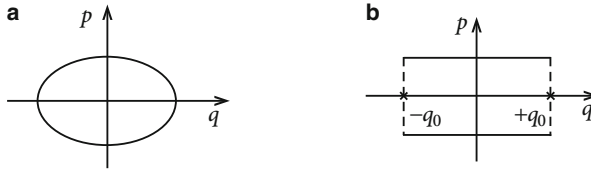
provided the *Hamilton function*,

$$H = H(q_1, \dots, q_s, p_1, \dots, p_s)$$

is known. For an isolated, conservative system,  $H$  can not be explicitly time-dependent. When there are in addition *holonomic-scleronomic constraints* ((1.3),

**Fig. 1.2** Phase trajectory in the two-dimensional phase space





**Fig. 1.3** (a) Phase trajectory of the linear harmonic oscillator, (b) phase trajectory for the particle motion in a potential well with ideally reflecting walls

Vol. 2), then  $H$  is identical to the total energy of the system:

$$H = H(\mathbf{q}, \mathbf{p}) \equiv E. \quad (1.14)$$

Hamilton's equations of motion (1.13) are differential equations of the first order, and hence have unique solutions. The trajectory therefore never intersects itself and represents a closed curve. Furthermore, it is bound to the  $(2s - 1)$ -dimensional hyper-surface of the phase space (*energy-surface*), defined by (1.14). As is known (subsection 2.4.1, Vol. 2), the trajectory of the linear harmonic oscillator represents an ellipse in its two-dimensional phase space, with semi-axes determined by the energy  $E$  (Fig. 1.3). Since the state of the system is uniquely determined by  $\boldsymbol{\pi}(t)$ , all quantities of Classical Mechanics, which are measurable on the system (*observables*), can of course also be interpreted as phase-space functions:

$$F = F(\mathbf{q}, \mathbf{p}, t) = F(\boldsymbol{\pi}, t). \quad (1.15)$$

These functions obey the equation of motion ((2.105), Vol. 2):

$$\frac{dF}{dt} = \{F, H\} + \frac{\partial F}{\partial t}. \quad (1.16)$$

$\{\dots, \dots\}$  means here the *Poisson bracket* ((2.104), Vol. 2):

$$\{F, H\} = \sum_{j=1}^s \left( \frac{\partial F}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial F}{\partial p_j} \frac{\partial H}{\partial q_j} \right). \quad (1.17)$$

The bracket possesses several remarkable properties, for instance the one that its value does not depend on the special choice of the *canonically conjugate* coordinates and momenta.  $(\mathbf{Q}, \mathbf{P})$  are also canonically conjugate like  $(\mathbf{q}, \mathbf{p})$ , if for them, after insertion of  $\mathbf{q} = \mathbf{q}(\mathbf{Q}, \mathbf{P})$  and  $\mathbf{p} = \mathbf{p}(\mathbf{Q}, \mathbf{P})$  into the Hamilton function  $H(\mathbf{q}, \mathbf{p})$ , equations of motion of the form (1.13) are valid. Further important properties of the Poisson bracket have been discussed in section 2.4 of Vol. 2.

The rigorous solution of the equation of motion (1.16) is out of question because of the reasons discussed in Sect. 1.1.1 for the macroscopic systems of Statistical Mechanics. In an isolated system, the observable  $F$  will not '*explicitly*' depend

on time, but the system will, in the course of time, change its position within the phase space ( $\pi = \pi(t)$ ). The actual values of  $F$  will therewith of course also change with time. It is, as mentioned, impossible to determine this time-dependence in a detailed manner, but perhaps also it is neither imperatively necessary, if one takes into consideration the fact that each experiment indeed lasts a finite time. The experimental measuring value thus is already an *average value*. Quantities, which are by no means (!) measurable, are, strictly speaking, also for the theory not interesting. From the very beginning thus, only the determination of the **time-average** appears to be of importance:

$$\bar{F}^{t_0} = \frac{1}{t_0} \int_0^{t_0} F(\mathbf{q}, \mathbf{p}) dt . \quad (1.18)$$

For finite  $t_0$  this will depend, though, on the initial conditions. In this sense,  $\bar{F}^{t_0}$  is not determinable, either, because the complete *pre-information* about the considered system is lacking. Therefore we (have to) postulate that at least the limiting value

$$\bar{F} = \lim_{t_0 \rightarrow \infty} \bar{F}^{t_0} \quad (1.19)$$

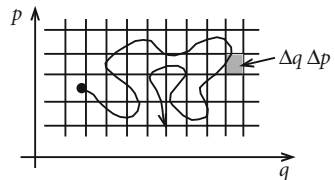
does exist and is **independent** of the initial conditions. Later we will realize that the validity of this postulate is fundamental for Statistical Physics. The statement of the postulate appears indeed quite plausible, but is nevertheless not at all a matter of course. A strict mathematical proof does not exist up to now. It is just a special formulation of the **quasi-ergodic hypothesis** (P. and T. Ehrenfest, 1911):

*The phase trajectory, bound in the phase space to the  $H(\mathbf{q}, \mathbf{p})=E$ -hyper-surface, approaches in the course of time each point of this surface arbitrarily closely!*

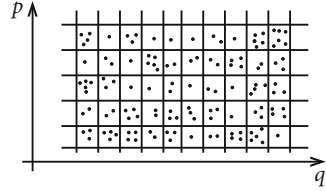
On the  $H(\mathbf{q}, \mathbf{p})=E$ -hyper-surface, around a phase point  $\pi = (\mathbf{q}, \mathbf{p})$ , when one puts a raster  $\Delta^s q \Delta^s p$  (Fig. 1.4), then one can indicate a time  $t_0$ , surely co-determined by the size of the raster, within which the trajectory has at least once traversed the raster.—As plausible as this hypothesis may appear, it is nevertheless unprovable. Indeed, there are even a few counter-examples (*non-ergodic systems*), which, however, are of such special kind that we will not further consider them here.

We can now decompose, as indicated in Fig. 1.4, the phase space into small *volume elements*  $\Delta^s q \Delta^s p$ , and can then simply count, how often the trajectory of

**Fig. 1.4** Cross-line screen (rasterization) of the two-dimensional phase space



**Fig. 1.5** Illustration of the density distribution function



the system has traversed within the time  $t_0$  the individual elements (see Fig. 1.5). This can be expressed by a

**density-distribution function**

$$\bar{\bar{\rho}}(\mathbf{q}, \mathbf{p}, t_0)$$

in such a sense that

$$\bar{\bar{\rho}}(\mathbf{q}, \mathbf{p}, t_0) \Delta^s q \Delta^s p$$

represents the frequency, with which the trajectory has passed within the time  $t_0$  the *volume element*  $\Delta^s q \Delta^s p$  around the phase point  $(\mathbf{q}, \mathbf{p})$ . The actual number of events of course depends on  $t_0$  and will increase with  $t_0$  over all limits. It is therefore recommendable to normalize the density distribution, where we simultaneously make the phase-space volume element become infinitesimally small ( $\Delta^s q \Delta^s p \rightarrow d^s q d^s p$ ):

$$\bar{\rho}(\mathbf{q}, \mathbf{p}, t_0) = \frac{\bar{\bar{\rho}}(\mathbf{q}, \mathbf{p}, t_0)}{\iint d^s q d^s p \bar{\bar{\rho}}(\mathbf{q}, \mathbf{p}, t_0)} . \tag{1.20}$$

If  $t_0$  is sufficiently large, then  $\bar{\rho}$  will represent, to a good approximation, a continuous phase space function, and

$$\bar{\rho}(\mathbf{q}, \mathbf{p}, t_0) d^s q d^s p$$

can be interpreted as the probability that, at a given point of time in between 0 and  $t_0$ , the system can be found in the *volume element*  $d^s q d^s p$  at  $(\mathbf{q}, \mathbf{p})$ . As soon as the system is in the element  $d^s q d^s p$  at  $(\mathbf{q}, \mathbf{p})$ , the observable  $F$  adopts the value  $F(\mathbf{q}, \mathbf{p})$ . Its time-average value (1.18) can therewith be expressed also by the distribution function, because, for getting the average value, it does not matter, at which concrete point of time in the interval  $[0, t_0]$  the observable  $F$  has adopted a certain value:

$$\bar{F}^{t_0} = \iint d^s q d^s p \bar{\rho}(\mathbf{q}, \mathbf{p}, t_0) F(\mathbf{q}, \mathbf{p}) . \tag{1.21}$$

This representation, of course, is still a *time average*, because  $\bar{\rho}$  results from the time-behavior of the trajectory of the system. But it already delivers a clear hint

to the concept of the *statistical ensemble*, which traces back to Boltzmann and Gibbs, and turns out to be basic for Statistical Physics. We will refer to it in the next subsection.

The quasi-ergodic hypothesis (1.19) now requires that for  $t_0 \rightarrow \infty$  the distribution function of macroscopic systems ( $s \rightarrow \infty$ ) becomes independent of the initial conditions:

$$\lim_{t_0 \rightarrow \infty} \bar{\rho}(\mathbf{q}, \mathbf{p}, t_0) \equiv \bar{\rho}(\mathbf{q}, \mathbf{p}) . \quad (1.22)$$

This is a decisive precondition for the validity of the Statistical Physics of macroscopic systems. As already mentioned, this hypothesis can not be proven in a mathematically strict sense. It gets its justification exclusively by the consistency of the Statistical Physics, developed on the basis of this hypothesis, compared to the experimental observations.

## 1.2.2 Statistical Ensemble, Ensemble Average

The goal consists of describing a system, about which we have only an incomplete information. The exact (micro-) state can not be precisely specified. In a way, we can only ‘*delimit*’ it, and can therefore also hope only for statements, which are ‘*correct on average*’, as explained in detail in Sect. 1.1.1. It is therefore particularly an issue of calculating average values. In order that these become independent of the (unknown) initial conditions, we need the validity of the quasi-ergodic hypothesis (1.19), and an, in principle, infinitely long *observation time*. In general, however, the Hamilton’s equations of motion (1.13) can not be integrated in closed form, and therewith the phase  $\pi(t)$  can not at all be given explicitly as function of time. That excludes then of course also the time-integration needed for the average value (1.18). It therefore seems so as if we would not have made yet any substantial progress by the considerations of the last section.

The reformulation of the time-average value (1.18) to the equivalent version (1.21), with the aid of a distribution function  $\bar{\rho}$ , however, gives first indications to an alternative method of calculating average values. The idea consists in the introduction of the concept of a

### **statistical ensemble .**

By this one understands a ‘*family*’ of ‘*thought*’ systems, which are all identical copies of the actual real system, and therewith are physically completely identical to it. Each member of the family is in one of the micro-states, which are *conceivable* (*possible*) for the real system, and which are compatible with its (incomplete) boundary conditions, and which evolve according to suitable equations of motion. If there are  $Z$  *conceivable* micro-states, which, according to our pre-information, are, *in principle*, accessible to the real system, and which the system will indeed occupy, according to the quasi-ergodic hypothesis, somewhere along the way, then

the ensemble consists of  $Z$  members, each of them completely equivalent to the real system. At a single definite moment, the entirety of ensemble systems simulates the full time evolution of the real system, however, only then, when the quasi-ergodic hypothesis is indeed valid. Exactly then it is possible to replace the time averaging (1.19) by an *instantaneous* averaging over the members of the ensemble. That corresponds to the formulation (1.21) of the time-average, when we replace the distribution function (1.22) by a respective one over the ensemble systems. The statement

$$\text{time-average} \stackrel{!}{=} \text{ensemble-average}$$

is indeed the basic presumption of the Gibb's method of the construction of Statistical Physics. But if it is so, then the necessity to completely integrate the Hamilton's equations of motion is done away with, because we perform the ensemble averaging at a **fixed** point of time. This shall now be formulated in more detail.

At a given point of time the ensemble systems occupy definite points in the phase space. These points build something like an amount of a liquid (*liquid drop*), which moves through the phase space in a form, which is still to be investigated. Other than in a real liquid, however, there are of course no interactions between the *single constituents*, i.e. between the members of the ensemble. Especially, it is the *local density* of this phase-space liquid, which is now interesting. For this purpose we decompose, as in the last subsection, the phase space into small *volume elements*,

$$d\Gamma \equiv d^s q d^s p \equiv dq_1 dq_2 \dots dq_s dp_1 dp_2 \dots dp_s = \prod_{j=1}^s dq_j dp_j, \quad (1.23)$$

and define a **distribution function**,

$$\widehat{\rho}(q_1, \dots, q_s, p_1, \dots, p_s, t) = \widehat{\rho}(\mathbf{q}, \mathbf{p}, t),$$

by the requirement that

$$dZ = \widehat{\rho}(\mathbf{q}, \mathbf{p}, t) d^s q d^s p$$

represents the number of systems, which are located in the *volume element*  $d\Gamma$  around the phase point  $(\mathbf{q}, \mathbf{p})$  at the time  $t$ . It is clear then that

$$Z = \int \dots \int \widehat{\rho}(\mathbf{q}, \mathbf{p}, t) d^s q d^s p \quad (1.24)$$

must be the time-independent total number of the ensemble members. The **normalized distribution function**,

$$\rho(\mathbf{q}, \mathbf{p}, t) = \frac{1}{Z} \widehat{\rho}(\mathbf{q}, \mathbf{p}, t), \quad (1.25)$$

will change almost continuously, for sufficiently large  $Z$ , from volume element to volume element, and can then be interpreted as **probability density** for the fact that at the time  $t$  one ensemble member can be found in the phase  $\pi = (\mathbf{q}, \mathbf{p})$ . Using this consideration, we can express each observable  $F(\mathbf{q}, \mathbf{p})$  by the distribution function  $\rho(\mathbf{q}, \mathbf{p}, t)$ :

$$\langle F \rangle_t = \int \cdots \int dq_1 \dots dp_s F(\mathbf{q}, \mathbf{p}) \rho(\mathbf{q}, \mathbf{p}, t) . \quad (1.26)$$

This representation strongly resembles that in (1.21), although the starting points are different. The formulation (1.21) represents a **time-average**, while (1.26) means an **ensemble-average**. Their equivalence appears, according to our pre-considerations, to be rather plausible. However, it is not strictly provable, because its validity needs the validity of the quasi-ergodic hypothesis.

To the question, which value the property  $F$  gets in our system, about which only incomplete information is available, the Statistical Physics gives the answer : ' $\langle F \rangle$  !'. Of course, we can not assume that this is in any case really exact. In order to make the scattering around this value *sufficiently small*, we will later demand that the **relative, mean square deviation** is a very small quantity:

$$\sqrt{\frac{\langle F^2 \rangle - \langle F \rangle^2}{\langle F \rangle^2}} \ll 1 \quad (1.27)$$

We recognize with (1.26) that *stationary* distributions ( $\partial\rho/\partial t = 0$ ) yield for all not explicitly time-dependent observables **time-independent** ensemble-average values. It will be the task in the following to find ways for the determination of the density-distribution function  $\rho(\mathbf{q}, \mathbf{p}, t)$  for physically relevant situations. Systems in *thermodynamic equilibrium* must obviously be described by *stationary* distributions. Only these are therefore of interest in the following.

### 1.2.3 Liouville Equation

We want to derive in this subsection some very general properties of the density-distribution function  $\rho(\mathbf{q}, \mathbf{p}, t)$ , especially the laws and concepts, which determine its time-dependence. With the  $2s$ -dimensional *phase-space velocity*

$$\mathbf{v} = (\dot{q}_1, \dot{q}_2, \dots, \dot{q}_s, \dot{p}_1, \dot{p}_2, \dots, \dot{p}_s) \quad (1.28)$$

a *current density* of the phase points, which are occupied by the ensemble systems, can be defined:

$$\mathbf{j} = \rho \mathbf{v} . \quad (1.29)$$

This current density is to be understood completely along the lines of the more familiar *electric current density* (see subsection 2.1.1, Vol. 3). The only difference is that there are not electric charges, which move through the real position space, but phase points moving in the phase space. Let now  $G$  be an arbitrary region in the phase space with the surface  $S(G)$ , then

$$\int_{S(G)} d\mathbf{S} \cdot \mathbf{j} \quad (d\mathbf{S} = dS \mathbf{n}; \quad \mathbf{n}: \text{surface normal})$$

is the number of phase points, which *are flowing* per unit time through the surface  $S$ . Since there are no sources and sinks for ensemble systems, this number is of course equal to the change in the number of phase points in the region  $G$  per time unit:

$$\int_{S(G)} d\mathbf{S} \cdot \mathbf{j} = -\frac{\partial}{\partial t} \int_G d^s q d^s p \rho(\mathbf{q}, \mathbf{p}, t) .$$

The *surface integral* on the left side can be changed, by the use of the Gauss theorem ((1.59), Vol. 3), into a *volume integral*:

$$\int_G d^s q d^s p \left[ \frac{\partial}{\partial t} \rho(\mathbf{q}, \mathbf{p}, t) + \text{div} \mathbf{j} \right] = 0 . \quad (1.30)$$

The *divergence* is to be built by the  $2s$ -dimensional *gradient* in the phase space,

$$\nabla \equiv \left( \frac{\partial}{\partial q_1}, \dots, \frac{\partial}{\partial q_s}, \frac{\partial}{\partial p_1}, \dots, \frac{\partial}{\partial p_s} \right) : \quad (1.31)$$

$$\text{div} \mathbf{j} = \nabla \cdot \mathbf{j} = \sum_{j=1}^s \left[ \frac{\partial}{\partial q_j} (\rho \dot{q}_j) + \frac{\partial}{\partial p_j} (\rho \dot{p}_j) \right] . \quad (1.32)$$

The relation (1.30) must hold for arbitrary regions  $G$  of the phase space, which enforces the conclusion that the integrand must already vanish. The density-distribution function thus fulfills a **continuity equation**,

$$\frac{\partial}{\partial t} \rho(\mathbf{q}, \mathbf{p}, t) + \text{div}(\mathbf{v} \cdot \rho(\mathbf{q}, \mathbf{p}, t)) = 0 , \quad (1.33)$$

which, of course, implies nothing but the conservation of the total number of ensemble systems. It can further be reformulated with (1.32):

$$-\frac{\partial \rho}{\partial t} = \sum_{j=1}^s \left( \dot{q}_j \frac{\partial \rho}{\partial q_j} + \dot{p}_j \frac{\partial \rho}{\partial p_j} \right) + \rho \sum_{j=1}^s \left( \frac{\partial \dot{q}_j}{\partial q_j} + \frac{\partial \dot{p}_j}{\partial p_j} \right) .$$



All ensemble systems are of course described by the same (not explicitly time-dependent) Hamilton function  $H(\mathbf{q}, \mathbf{p})$ . If one then inserts the Hamilton's equations of motion (1.13) into the above equation, one recognizes that each term of the second sum is equal to zero. It results the

### Liouville Equation

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{j=1}^s \left( \frac{\partial\rho}{\partial q_j} \dot{q}_j + \frac{\partial\rho}{\partial p_j} \dot{p}_j \right) = 0 . \quad (1.34)$$

The total time-differential of the density-distribution function vanishes. It holds therefore for **all** times  $t$ :

$$\rho(\mathbf{q}(t), \mathbf{p}(t), t) \equiv \rho(\mathbf{q}(0), \mathbf{p}(0), 0) . \quad (1.35)$$

Illustratively, this relation states that an observer, co-moving with the *ensemble flow*, sees in its surroundings always the same, i.e., temporally constant, density of phase points. The ensemble '*liquid*' moves in the phase space as an **incompressible** liquid.

The Liouville equation can also be formulated with (1.17), in a compact manner, with the help of the Poisson bracket:

$$\frac{\partial\rho}{\partial t} + \{\rho, H\} = 0 . \quad (1.36)$$

A further equivalent representation follows with (1.28) and (1.31):

$$\frac{\partial\rho}{\partial t} + \mathbf{v} \cdot \nabla\rho = 0 . \quad (1.37)$$

It depends on the actual type of problem which of the three formulations of the Liouville equation, (1.34), (1.36) or (1.37) is the more convenient one. For Quantum Statistics, to be discussed in Chap. 2, in particular the representation (1.36) turns out to be interesting, since the *principle of correspondence* ((3.229), Vol. 6) uniquely prescribes how the Poisson bracket has to be transferred into Quantum Mechanics.

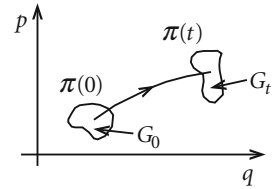
The idea of the *incompressible liquid*, mediated by the Liouville equation, can further be formulated a bit more precisely:

### Liouville Theorem

Let  $G_0$  be a region of the phase space with the volume  $\Gamma_0$ , whose points are all occupied by ensemble systems at the time  $t = 0$ . These are moving in the phase space and fill at the time  $t$  the region  $G_t$  of the volume  $\Gamma_t$ . In general,  $G_t$  will be different from  $G_0$ . It holds, however, for all times  $t$ :

$$\Gamma_t = \Gamma_0 . \quad (1.38)$$

**Fig. 1.6** Illustration of the Liouville theorem



Note that the statement of the theorem refers only to the *conservation of the phase space volume* (Fig. 1.6). Nothing is said about the **shape** of the region  $G_t$  in comparison to that of  $G_0$ . Arbitrary deformations are allowed. We perform the rigorous proof of (1.38) as Exercise 1.2.3, and restrict ourselves here to an *illustrative* explanatory statement: Starting point is, at first, a region  $\Delta G_0$  around  $\pi(0) = (\mathbf{q}(0), \mathbf{p}(0))$ , which is so small that the density  $\rho$  in the inside can be assumed to be practically constant. All points of this region move according to the Hamilton's equations of motion, and reach at the time  $t$  the region  $\Delta G_t$  around  $\pi(t) = (\mathbf{q}(t), \mathbf{p}(t))$ . During the motion the trajectories of the individual points **do not intersect**. In particular, the trajectories of the *surface points* of  $\Delta G_0$  can not be intersected by those of the *inner points* of  $\Delta G_0$ , and of course also not by the trajectories of any phase points, which at  $t = 0$  were outside of  $\Delta G_0$ .  $\Delta G_0$  and  $\Delta G_t$  thus contain exactly the same number of phase points! On the other hand, according to (1.35), the point **density** is the same for  $\Delta G_0$  and  $\Delta G_t$ . Consequently, the volumes  $\Delta \Gamma_0$  and  $\Delta \Gamma_t$  must be of equal size. The same is then also valid for the volumes  $\Gamma_0$ ,  $\Gamma_t$  of finite regions  $G_0$ ,  $G_t$ , when we divide these finite regions, for the proof, into small regions  $\Delta G_0$ ,  $\Delta G_t$  in the above described form.

As already mentioned at the end of Sect. 1.2.2, one speaks of a **stationary distribution** or of a **static equilibrium**, if, beyond the always valid statement (1.34), also the local temporal change of density vanishes:

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} = 0 . \quad (1.39)$$

The probability, to find ensemble systems at definite positions of the phase space, is then the same for all times. That is trivially the case, when the ensemble-*liquid* is homogeneously 'smeared' over the entire phase space, i.e., when the density-distribution function  $\rho$  is everywhere constant:

$$\frac{\partial \rho}{\partial q_j} = \frac{\partial \rho}{\partial p_j} = 0 \quad \forall j .$$

With (1.34) it follows then immediately (1.39).

A distribution is, however, also stationary, when  $\rho$  depends on  $\mathbf{q}$  and  $\mathbf{p}$  only via an *integral of motion*  $c$ :

$$\rho = \rho(c, t); \quad c = c(\mathbf{q}, \mathbf{p}) . \quad (1.40)$$

Integral of motion means:

$$0 = \frac{dc}{dt} = \sum_{j=1}^s \left( \frac{\partial c}{\partial q_j} \dot{q}_j + \frac{\partial c}{\partial p_j} \dot{p}_j \right),$$

where of course on the right-hand side each summand need not necessarily be equal to zero. It follows then from the Liouville theorem (1.34),

$$0 = \frac{d\rho}{dt} = \left( \frac{\partial \rho}{\partial c} \right)_t \frac{dc}{dt} + \left( \frac{\partial \rho}{\partial t} \right)_c = \left( \frac{\partial \rho}{\partial t} \right)_c,$$

and therewith in particular:

$$\left( \frac{\partial \rho}{\partial t} \right)_{\mathbf{q}, \mathbf{p}} = 0.$$

The Hamilton function  $H(\mathbf{q}, \mathbf{p}) = E = \text{const}$  is an important constant of motion of an isolated system. If the density-distribution function thus depends on  $\mathbf{q}$  and  $\mathbf{p}$  only via  $H$ ,

$$\rho = \rho(H(\mathbf{q}, \mathbf{p})), \quad (1.41)$$

then the distribution is *stationary* (see Exercise 1.2.2). Stationary distributions are, as already mentioned, important for the description of systems in the thermodynamic equilibrium. All the concrete distribution functions, which we discuss in the following sections, will therefore be of the type (1.41).

### 1.2.4 Micro-Canonical Ensemble

According to the pre-considerations of the last subsections, the main problem of Statistical Physics consists obviously of finding the density-distribution function  $\rho(\mathbf{q}, \mathbf{p}, t)$  of a statistical ensemble, where, for the equilibrium statistics, only *stationary* distributions are of interest. Our considerations so far concerned isolated, or better, *quasi-isolated* systems for which we have

$$E < H(\mathbf{q}, \mathbf{p}) < E + \Delta \quad (\Delta \ll E). \quad (1.42)$$

We had asserted in Sect. 1.1.1 that for realistic macroscopic systems the exact energy constancy ( $H = E$ ) can not be guaranteed. On the other hand, it goes without saying that in an isolated system particle number and volume are strictly constant ( $N = \text{const}$ ,  $V = \text{const}$ ).

All *conceivable* micro-states, which are compatible with (1.42), appear, according to the postulate agreed upon in Sect. 1.1.1, with the same *a priori*-probability. On the other hand, according to (1.25),  $\rho(\mathbf{q}, \mathbf{p}, t)$  is the probability density to find at the time  $t$ , an ensemble member at the phase  $\boldsymbol{\pi} = (\mathbf{q}, \mathbf{p})$ . Together with (1.42) this means for the density-distribution function of a statistical ensemble of quasi-isolated systems:

$$\rho(\mathbf{q}, \mathbf{p}, t) = \begin{cases} \rho_0 = \text{const} , & \text{if } E < H(\mathbf{q}, \mathbf{p}) < E + \Delta , \\ 0 & \text{otherwise .} \end{cases} \quad (1.43)$$

The constant  $\rho_0$  is determined by the normalization of the distribution. The density function (1.43) is dependent on coordinates and momenta only via the Hamilton function, and describes therewith according to (1.41) a *stationary* distribution. The corresponding ensemble averages (1.26) are therefore time-independent. This is important, because we want to link them later to the observables of the equilibrium-thermodynamics. One calls the statistical ensemble, defined by (1.43), a

**micro-canonical ensemble .**

This occupies, *homogeneously smeared*, the so-called **phase volume**

$$\Gamma(E) = \alpha \iint_{E < H(\mathbf{q}, \mathbf{p}) < E + \Delta} d^s q d^s p . \quad (1.44)$$

For the following considerations it is advantageous to incorporate a factor  $\alpha$  directly into the definition. In particular, it shall make  $\Gamma(E)$  dimension-less.  $d^s q d^s p$  has the dimension [action]<sup>s</sup>. We therefore choose

$$\alpha = \frac{\alpha^*}{h^s} , \quad (1.45)$$

where  $h$  is Planck's quantum of action ((1.3), Vol. 6). In the framework of the classical theory that is more or less playing around, and can of course not yet point to any quantum property. For systems of  $N$  particles without constraints, which represent the normal case for the following considerations

$$s = 3N . \quad (1.46)$$

We still leave open in (1.45) a dimensionless constant  $\alpha^*$ , which will be fixed only later. With the choice  $\alpha^* = 1$  contradictions can be constructed in the further course of our considerations, which appear to be unsolvable in the framework of Classical Statistical Physics. Only the take over of certain quantum-mechanical aspects will lead to an ansatz for  $\alpha^*$ , which removes the dilemma (*correct Boltzmann-counting*, Sect. 1.3.7). Let us not specify, however,  $\alpha^*$  before it becomes really necessary.

For the constant  $\rho_0$  of the micro-canonical ensemble (1.43) it now holds obviously:

$$\rho_0 = \frac{\alpha}{\Gamma(E)} . \quad (1.47)$$

Sometimes one denotes as **phase volume** also the total volume, enclosed in the phase space by the hyper-surface  $H(\mathbf{q}, \mathbf{p}) = E$ :

$$\varphi(E) = \alpha \iint_{H(\mathbf{q}, \mathbf{p}) \leq E} d^s q d^s p . \quad (1.48)$$

The comparison with (1.44) yields the connection:

$$\Gamma(E) = \varphi(E + \Delta) - \varphi(E) . \quad (1.49)$$

Eventually, we still define the **density of states**:

$$D(E) = \frac{d\varphi(E)}{dE} = \lim_{\Delta \rightarrow 0} \frac{1}{\Delta} \Gamma(E) . \quad (1.50)$$

For  $\Delta \ll E$ , which is always assumed, we have to a good approximation:

$$\Gamma(E) \approx \Delta D(E) . \quad (1.51)$$

For the classical observable  $F = F(\mathbf{q}, \mathbf{p})$  the *ensemble-average value* over the *micro-canonical ensemble*, now reads, if one inserts (1.43), (1.44) and (1.47) into (1.26):

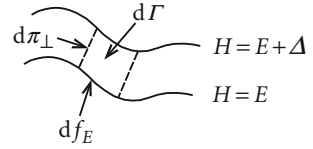
$$\langle F \rangle = \frac{\iint_{E < H(\mathbf{q}, \mathbf{p}) < E + \Delta} d^s q d^s p F(\mathbf{q}, \mathbf{p})}{\iint_{E < H(\mathbf{q}, \mathbf{p}) < E + \Delta} d^s q d^s p} . \quad (1.52)$$

For certain purposes it still makes sense to represent the phase volume  $\Gamma(E)$ , occupied by the micro-canonical ensemble, by a manner somewhat different from that in (1.44). The phase-space volume  $\Gamma(E)$ , enclosed by the hyper-surfaces  $H = E + \Delta$  and  $H = E$ , results from a summing up of the volume elements (Fig. 1.7)

$$d\Gamma = df_E d\pi_\perp .$$

$df_E$  is the surface element of the  $H = E$ -surface and  $d\pi_\perp$  the perpendicular distance between the two hyper-surfaces. The vector  $\nabla H$  stands perpendicularly on the

**Fig. 1.7** Volume element  $d\Gamma$  in the phase space between two infinitesimally neighboring hyper-surfaces



$H=E=\text{const}$ -surface. For the change of  $H$  with the transition from the one to the other surface it must therefore be:

$$\Delta \stackrel{!}{=} |\nabla H d\pi_{\perp}| .$$

The volume element  $d\Gamma$  can therewith be represented as:

$$d\Gamma = \Delta \frac{df_E}{|\nabla H|} . \quad (1.53)$$

In the case of sufficiently small  $\Delta$  the volume integral in (1.44) can thus be replaced by a surface integral:

$$\Gamma(E) \approx \Delta \alpha \int_{H=E} \frac{df_E}{|\nabla H(\mathbf{q}, \mathbf{p})|} . \quad (1.54)$$

According to (1.51) this means for the density of states:

$$D(E) = \alpha \int_{H=E} \frac{df_E}{|\nabla H(\mathbf{q}, \mathbf{p})|} . \quad (1.55)$$

We have therewith found, in particular, an alternative representation of the ensemble-average value, when we insert (1.53) and (1.55) into (1.52):

$$\langle F \rangle \approx \frac{\alpha}{D(E)} \int_{H(\mathbf{q}, \mathbf{p})=E} df_E \frac{F(\mathbf{q}, \mathbf{p})}{|\nabla H(\mathbf{q}, \mathbf{p})|} . \quad (1.56)$$

In this version, the averaging is carried out by a surface integral. That looks actually more complicated than (1.52), but can be, in certain cases, more comfortable for application. A special phase-space observable is the Hamilton function. For the average value via the micro-canonical ensemble it follows from (1.56):

$$\langle H \rangle \approx E . \quad (1.57)$$

We will identify in the next chapter the average value  $\langle H \rangle$  with the **internal energy**  $U$  of the respective system.

We now have rounded up the most important basic concepts of Classical Statistical Physics. The next topic of the program consists in creating the link to the equilibrium thermodynamics. Especially it is required to statistically justify the terms *entropy* and *temperature*, which are of central importance for Thermodynamics, so that the *basic relation of thermodynamics* ((2.55), Vol. 5), which corresponds to a combination of the first two laws of Thermodynamics, becomes a **provable** assertion.

## 1.2.5 Exercises

### Exercise 1.2.1

Show that the classical linear harmonic oscillator with the Hamilton function

$$H(q, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

fulfills the quasi-ergodic hypothesis. Calculate for this purpose the phase-space trajectory

$$\pi(t) = (q(t), p(t)) .$$

### Exercise 1.2.2

Let the density-distribution function  $\rho$  of a statistical ensemble depend on  $\mathbf{q}$  and  $\mathbf{p}$  only via the Hamilton function  $H = H(\mathbf{q}, \mathbf{p})$ . By using the Liouville equation in the form of (1.37),

$$\frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho = 0 ,$$

show that  $\rho$  must be a stationary distribution.

### Exercise 1.2.3

Let  $G_0$  be a region of the phase space, which is occupied at the time  $t = 0$  by the members of a statistical ensemble.  $G_0$  may have the volume  $\Gamma_0$ :

$$\Gamma_0 = \int_{G_0} d^s q(0) d^s p(0) .$$

The region  $G_t$ , which arises after the time  $t$  by the motions of the points from  $G_0$ , then possesses the volume:

$$\Gamma_t = \int_{G_t} d^s q(t) d^s p(t) .$$

Prove the Liouville theorem (1.38):

$$\Gamma_t = \Gamma_0 .$$

Because of

$$\Gamma_t = \int_{G_0} \det F^{(t,0)} d^s q(0) d^s p(0)$$

it will be mandatory to show that the functional determinant (Jacobian determinant) ((1.363), Vol. 1),

$$\det F^{(t,0)} \equiv \frac{\partial(q_1(t), \dots, q_s(t), p_1(t), \dots, p_s(t))}{\partial(q_1(0), \dots, q_s(0), p_1(0), \dots, p_s(0))} ,$$

is equal to one.

#### Exercise 1.2.4

Consider the classical linear harmonic oscillator:

$$H(q, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2 .$$

1. Determine the normalized density-distribution function of the micro-canonical ensemble.
2. Calculate therewith the average values of the potential and the kinetic energy.

#### Exercise 1.2.5

A particle of the mass  $m$  moves **freely** in the one-dimensional interval  $0 \leq x \leq x_0$ , and is elastically reflected by the walls at  $x = 0$  and  $x = x_0$ .

1. Sketch the trajectory of the system in the phase space.
2. Calculate the classical phase volume  $\varphi(E)$ .

#### Exercise 1.2.6

$N$  noninteracting particles, each of the same mass  $m$ , move on a plane in the potential

$$V(x, y) = \begin{cases} 0, & \text{if } 0 \leq x \leq x_0 \text{ and } 0 \leq y \leq y_0 , \\ \infty & \text{otherwise .} \end{cases}$$

Calculate the classical normalized density distribution  $\rho(\mathbf{q}, \mathbf{p})$  of the micro-canonical ensemble.



**Exercise 1.2.7**

Discuss the phase volume and the phase trajectory

1. of a particle, which, on its linear motion, is subject only to a frictional force, which is proportional to the particle velocity,
2. of a linear harmonic oscillator with weak friction.

**Exercise 1.2.8**

Calculate the phase volume  $\varphi(E)$  of a relativistic particle of the energy  $E$ , which moves in a box of the volume  $V$ .

**Exercise 1.2.9**

For  $N$  classical particles there are available two energy levels

$$\varepsilon_1 = \varepsilon > 0 ; \quad \varepsilon_2 = -\varepsilon .$$

The energy  $E$  of the total system is then determined by the distribution of the particles over both the levels:

$$E = E(N_1, N_2) = N_1\varepsilon_1 + N_2\varepsilon_2 = (N_1 - N_2) \varepsilon ; \quad N = N_1 + N_2 = \text{const.}$$

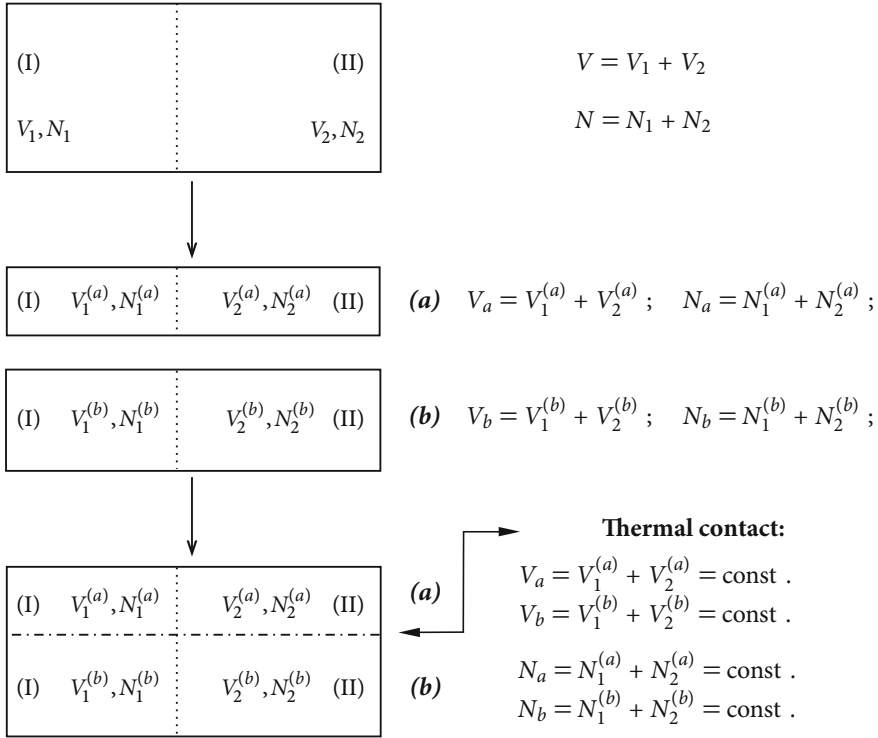
Determine the phase volume  $\Gamma_N(E)$  as function of the particle numbers  $N_i$ . Show that

$$\ln \Gamma_N(E) \propto N .$$

**1.3 Connection to Thermodynamics****1.3.1 Considerations on Thermal Equilibrium**

We now want to bring the elements of Statistics, as we have introduced them in the last section, into contact with the fundamental quantities of the Phenomenological Thermodynamics. That is conceptually not a trivial task, and it therefore needs some preparation. For this purpose we will come back once again to the simple and exactly solvable model system, which we introduced in Sect. 1.1.2. It concerns a gas of  $N$  particles in an *isolated* container of the volume  $V$ , which is divided into two chambers (I) and (II) (volumes:  $V_1, V_2$ ). The particles can arbitrarily change the chambers, where, however, certain properties take different values in (I) and (II). That holds, in particular, for the energy, which is equal to  $\varepsilon$  for a particle in chamber (I) and  $(-\varepsilon)$  for a particle in chamber (II). The total energy of the system is then determined by the *excess*

$$y = N_1 - \frac{1}{2}N \tag{1.58}$$



**Fig. 1.8** Schematic decomposition of a gas of  $N$  particles in a volume  $V$  into several subsystems

of particles in chamber (I) ( $N = N_1 + N_2$ ):

$$E = N_1 \varepsilon - (N - N_1) \varepsilon = 2y \varepsilon . \tag{1.59}$$

We have commented on the accuracy of an energy measurement and the fluctuations around the *most probable* value in detail in Sect. 1.1.2.

We will now extend this *thought experiment* by an essential aspect. We let the system be composed of two partial systems (a) and (b) of the described kind (Fig. 1.8):

$$V_a + V_b = V ; \quad N_a + N_b = N .$$

The subdivision into the chambers (I) and (II) within the partial systems shall take place in such a way that the probability  $p_1$  for a particle to be in (I) (see (1.2)), is the

same for both the partial systems, and is equal to that of the total system:

$$p_1 = \frac{V_1^{(a)}}{V_a} = \frac{V_1^{(b)}}{V_b}$$

$$\iff p_1 = \frac{V_1}{V} = \frac{V_1^{(a)} + V_1^{(b)}}{V_a + V_b} .$$

The at first isolated partial systems have the energies,

$$E_a = 2y_a\varepsilon ; \quad E_b = 2y_b\varepsilon ,$$

which are fixed, as the energy of the total system (1.59), by the *particle excesses* in the respective chambers (I):

$$y_a = N_1^{(a)} - \frac{1}{2}N_a , \quad y_b = N_1^{(b)} - \frac{1}{2}N_b \quad (1.60)$$

To an energy  $E_\alpha$ , given by  $y_\alpha$ , the isolated  $\alpha$ -partial system possesses  $\Gamma_{N_\alpha}(y_\alpha)$  different micro-states. For macroscopic particle numbers  $N_\alpha$  ( $\alpha = a, b$ ) we get the previous result (1.10):

$$\Gamma_{N_\alpha}(y_\alpha) = 2^{N_\alpha} w_{N_\alpha}(N_1^{(\alpha)}) = \Gamma_\alpha^{\max} \exp \left[ -\frac{(N_1^{(\alpha)} - \widehat{N}_1^{(\alpha)})^2}{2p_1(1-p_1)N_\alpha} \right] \quad (1.61)$$

$$\alpha = a, b .$$

$2^{N_\alpha}$  is the total number of states of the partial system  $\alpha$ , and  $w_{N_\alpha}(N_1^{(\alpha)})$  is the probability that out of the  $N_\alpha$  particles  $N_1^{(\alpha)}$  are in chamber (I). According to (1.9) this probability distribution has its maximal value at

$$\widehat{N}_1^{(\alpha)} = N_\alpha p_1 \quad (\alpha = a, b) .$$

That is then also true for the number of micro-states

$$\Gamma_\alpha^{\max} = (\Gamma_{N_\alpha}(y_\alpha))_{\max} = 2^{N_\alpha} w_{N_\alpha}(\widehat{N}_1^{(\alpha)}) . \quad (1.62)$$

When the two partial systems (a) and (b) remain to be isolated, then, of course, nothing new will come out compared to that discussed in Sect. 1.1.2.

In the next step, however, a

### thermal contact

between (a) and (b) will be installed. That means that the partial systems can now exchange energy, without changing in the process their particle numbers and their volumes. We assume that the energy exchange is due to a replacement of particles between the chambers (I) and (II) within the respective container (a) and (b),

respectively. The *technical realization* of this process must not be of interest here. However, it should be guaranteed in particular that the energy exchange passes off in such a way that interactions between particles of (a) and those of (b) continue to be neglected. The total system (*super system*) remains to be *isolated*. Its energy (1.59) is thus strictly fixed, so that at the *thermal contact* of (a) and (b) the boundary condition

$$y = y_a + y_b \quad (1.63)$$

is to be fulfilled. But that can happen now in a variety of ways. We therefore ask ourselves what happens really as a consequence of the contact between the two partial systems? How is the energy  $E$  of the *super system* distributed over the subsystems under the boundary condition (1.63)? The **most probable** distribution will be the one, which guarantees a maximal number of micro-states for the *super system*. Let us at first search for this special distribution.

Each state of (a) can be combined with each state of (b) to result in a micro-state of the *super system*. The total number of states, compatible with (1.63), is therewith

$$\Gamma_N(y) = \sum_{y_a=-1/2N_a}^{+1/2N_a} \Gamma_{N_a}(y_a) \Gamma_{N_b}(y - y_a) , \quad (1.64)$$

if we presume  $N_b > N_a$ .  $\Gamma_{N_a}$  and  $\Gamma_{N_b}$  are defined by (1.61). Each summand belongs to a definite distribution of the energy  $E = 2y\varepsilon$  over the partial systems (a) and (b). Which summand in (1.64) is maximal? To answer this question we have to build, as for *quite a normal* extreme-value problem, the first derivative of the summand with respect to  $y_a$  and then to put the result equal to zero. We use for a better overview, transiently, the abbreviations:

$$\begin{aligned} \tilde{p}_1 &= p_1 (1 - p_1) , \\ z_\alpha &= N_1^{(\alpha)} - \widehat{N}_1^{(\alpha)} = y_\alpha + N_\alpha \left( \frac{1}{2} - p_1 \right) \quad (\alpha = a, b) , \\ z &= N_1 - \widehat{N}_1 = y + N \left( \frac{1}{2} - p_1 \right) = z_a + z_b . \end{aligned}$$

Then (1.61) reads

$$\Gamma_{N_\alpha}(z_\alpha) = \Gamma_\alpha^{\max} \exp \left( -\frac{z_\alpha^2}{2\tilde{p}_1 N_\alpha} \right) \quad (\alpha = a, b) ,$$

and it holds for the summands in (1.64):

$$\Gamma_{N_a}(z_a) \Gamma_{N_b}(z - z_a) = \Gamma_a^{\max} \Gamma_b^{\max} \exp \left[ -\frac{z_a^2}{2\tilde{p}_1 N_a} - \frac{(z - z_a)^2}{2\tilde{p}_1 N_b} \right] . \quad (1.65)$$

When seeking for the maximum, it is convenient to differentiate the logarithm of this expression, which of course becomes maximal at the same point:

$$\ln(\Gamma_{N_a}(z_a)\Gamma_{N_b}(z-z_a)) = \ln(\Gamma_a^{\max}\Gamma_b^{\max}) - \frac{z_a^2}{2\tilde{p}_1N_a} - \frac{(z-z_a)^2}{2\tilde{p}_1N_b}.$$

The zero of the first derivative,

$$0 \stackrel{!}{=} \left. \frac{\partial \ln(\Gamma_{N_a}(z_a)\Gamma_{N_b}(z-z_a))}{\partial z_a} \right|_{\hat{z}_a} = -\frac{\hat{z}_a}{\tilde{p}_1N_a} + \frac{(z-\hat{z}_a)}{\tilde{p}_1N_b},$$

yields the extreme-value condition:

$$\frac{\hat{z}_a}{N_a} = \frac{\hat{z}_b}{N_b} \stackrel{!}{=} \frac{z}{N}.$$

If we revoke the above agreed abbreviations, we get

$$\frac{\hat{y}_a}{N_a} = \frac{\hat{y}_b}{N_b} = \frac{y}{N}, \quad (1.66)$$

and we recognize that the *most probable configuration* is acclaimed by the fact that the relative *excess* of particles in chamber (I) is the same for the partial systems (a) and (b), and is identical to that of the *super system*. We further check whether the extremum is really a maximum:

$$\frac{\partial^2}{\partial z_a^2} \ln[\Gamma_{N_a}(z_a)\Gamma_{N_b}(z-z_a)] = -\frac{1}{\tilde{p}_1N_a} - \frac{1}{\tilde{p}_1N_b} < 0.$$

The *most probable* (maximal) summand in (1.64) is therefore of the following form:

$$[\Gamma_{N_a}(z_a)\Gamma_{N_b}(z-z_a)]_{\max} = \Gamma_a^{\max}\Gamma_b^{\max} \exp\left[-\frac{1}{2\tilde{p}_1} \cdot \frac{z^2}{N}\right]. \quad (1.67)$$

Of decisive importance for the validity of Statistical Physics is now the observation that the distribution of the number of micro-states, which are summed up in (1.64), is similarly sharply bunched around the maximum (1.67), as we already could recognize it for the isolated single system (Sect. 1.1.2). This has namely the consequence that only a few configurations (summands in (1.64)) do really influence the physical properties of the *super system*. To confirm this fact let us investigate the number of micro-states near the maximum:

$$\Delta z_\alpha = z_\alpha - \hat{z}_\alpha = y_\alpha - \hat{y}_\alpha = \Delta y_\alpha \quad (\alpha = a, b).$$

Instead of (1.65) we write:

$$\Gamma_{N_a}(z_a)\Gamma_{N_b}(z_b) = \Gamma_a^{\max}\Gamma_b^{\max} \exp\left[-\frac{1}{2\tilde{p}_1} \left\{ \frac{1}{N_a} (\hat{z}_a^2 + 2\hat{z}_a\Delta z_a + \Delta z_a^2) + \frac{1}{N_b} (\hat{z}_b^2 + 2\hat{z}_b\Delta z_b + \Delta z_b^2) \right\}\right].$$

Because of  $y = y_a + y_b = \hat{y}_a + \hat{y}_b = \text{const}$  we have  $\Delta y_a = -\Delta y_b$  and therewith also  $\Delta z_a = -\Delta z_b$ . Furthermore it holds (1.66):

$$\Gamma_{N_a}(z_a)\Gamma_{N_b}(z_b) = \left\{ \Gamma_a^{\max}\Gamma_b^{\max} \exp\left(-\frac{z^2}{2N\tilde{p}_1}\right) \right\} \exp\left[-\frac{\Delta z_a^2}{2\tilde{p}_1} \left(\frac{1}{N_a} + \frac{1}{N_b}\right)\right].$$

The term in the curly bracket is, according to (1.67), the maximal summand in (1.64). When we replace again the  $z$ -variable by the original  $y$ -variable, then we have found with

$$\Gamma_{N_a}(y_a)\Gamma_{N_b}(y - y_a) = \left[ \Gamma_{N_a}(y_a)\Gamma_{N_b}(y - y_a) \right]_{\max} \exp\left[-\frac{N\Delta y_a^2}{2\tilde{p}_1 N_a N_b}\right] \quad (1.68)$$

a representation, which indeed demonstrates, that the number of micro-states, which are available for the isolated *super system*, and which are possible, according to (1.64), in the case of thermal contact of its two subsystems (a) and (b), exhibits a distinct maximum as function of  $y_a$  at the point  $\hat{y}_a = (N_a/N)y$ . As measure of the width of the distribution we take, as in (1.12), the distance between  $\hat{y}_a$  and the two  $y_a$ -values, which are symmetrically located to the maximum, and for which the distribution (1.68) drops down to the  $e$ -th part of its maximal value (1.67). This distance amounts to:

$$|\Delta y_a|_{-1} = \sqrt{\frac{2}{N} N_a N_b p_1 (1 - p_1)}.$$

In relation to the total range of values of  $y_a$  it results as *relative width*:

$$\frac{|\Delta y_a|_{-1}}{N_a} = \sqrt{\frac{2N_b p_1 (1 - p_1)}{N_a N}}. \quad (1.69)$$

With a characteristic numerical example such as

$$p_1 = \frac{1}{2}; \quad N_a = N_b = \frac{1}{2}N = 10^{22}$$

one finds:

$$\frac{|\Delta y_a|_{-1}}{N_a} = \frac{1}{2}10^{-11}.$$

The distribution of the number of micro-states is thus extremely *sharply bunched*. Already for such a minor relative deviation as

$$\frac{\Delta y_a}{N_a} = 10^{-10}$$

the distribution  $\Gamma_{N_a}(y_a)\Gamma_{N_b}(y - y_a)$  would have dropped in our numerical example, according to (1.68), onto the

$e^{-400}$ -fold of the maximal value.

What is the conclusion that can be drawn from this?

When the macroscopic partial system (a), within an isolated *super system*, is brought into thermal contact with another macroscopic partial system (b), then there are at its disposal unimaginably many micro-states (order of magnitude  $2^{10^{22}}$ ), and accordingly great is our lack of knowledge about the *micro-structure* of this system. But if we are interested only in the macroscopic property *energy*  $E_a$ , then we can say with utmost probability that a measurement of the energy yields a result, which deviates, at the very most, by  $10^{-10}$  relatively from the *most probable* value. The measuring value

$$\widehat{E}_a = 2\hat{y}_a\varepsilon = 2y\frac{N_a}{N}\varepsilon \quad (1.70)$$

can be predicted, except for a completely unimportant relative error.

After these *exemplary* considerations we can get now a first conception of the important term

### **thermal equilibrium .**

Two partial systems, which are being in *thermal contact*, have reached *thermal equilibrium*, as soon as the isolated *super system*, composed by them, is found in its *most probable configuration* (1.66, 1.67). When we prepare partial system (a) to be in any initial state, and bring it into *thermal contact* with partial system (b), then energy will be exchanged between (a) and (b) until, after a certain *relaxation time*, the *super system* has reached its *most probable* configuration. According to the quasi-ergodic hypothesis, in the course of time it approaches each state, which is compatible with the boundary conditions, arbitrarily closely. As demonstrated at the end of Sect. 1.1.2 in another context, here also it can be estimated that the system will not leave this *most probable* configuration in a time that exceeds our expectation of life by several orders of magnitude. Thus we can speak of an

### **irreversible transition into thermal equilibrium .**

In the introductory Sect. 1.1.1 we had already pointed out the difficulty, to microscopically justify *thermal equilibrium* and the *irreversible transition* into it, because all microscopic equations of motion are time-reversal invariant. We see here with the example of our model system, how the large number of degrees of freedom of the macroscopic systems opens quite novel possibilities of explanation.

The essential statements, derived in this subsection from a very abstract, very simple model, are confirmed by all the other exactly calculable models. The

assumption that they are even generally valid, has, up to now, not yet led to any contradiction between theory and experiment.

### 1.3.2 Entropy and Temperature

We know from the considerations on Phenomenological Thermodynamics in Vol. 5 that the *entropy* is a very important, but also a rather abstract (not easy to visualize) physical quantity. ‘*Most imaginative*’ is, if at all, its characterization as *measure for the disorder of a system*. For the statistical reasoning of the entropy, we therefore can **not** start from a *plausibility ansatz* for this basic quantity, but have to proceed essentially more formally. We will put the statistical definition of the entropy at the very beginning, and that, too, without further justification, i.e., without any hint by what this definition is actually motivated. By the discussion of the consequences of this ‘arbitrary’ definition we will then convince ourselves that it is indeed the same quantity as that, which we used in the Phenomenological Thermodynamics.

For an isolated system with  $N$  particles in the volume  $V$  (without constraints, therefore  $s = 3N$ ), we define the **entropy** as the natural logarithm of the phase volume (1.44) of the corresponding micro-canonical ensemble:

$$S(E, V, N) = k_B \ln \Gamma_N(E, V) . \quad (1.71)$$

The definition (1.44) immediately reveals that the phase volume is determined, besides by the energy  $E$ , also by the particle number  $N$  and the volume  $V$  of the considered systems. We therefore write here, more precisely than in (1.44),  $\Gamma_N(E, V)$  instead of  $\Gamma(E)$ . The constant  $k_B$  is conveniently identified with the universal **Boltzmann constant** ((1.6), Vol. 5),

$$k_B = 1.3805 \cdot 10^{-23} \text{ J/K} , \quad (1.72)$$

which at this stage, however, does not yet have any deeper meaning. We achieve therewith that the *statistical temperature*, later to be derived from (1.71), agrees with the absolute temperature of Thermodynamics, even including the unit (Kelvin-, Celsius-degree). For the now immediately following considerations  $k_B$  in (1.71) is, at first, only a constant, which is not specified any further.—More problems could arise from another detail of the definition (1.71). The phase volume  $\Gamma_N(E, V)$  of the micro-canonical ensemble follows, according to (1.44), from a phase-space integration over an energy shell of the thickness  $\Delta$ . The *statistical entropy*, introduced with (1.71), seems therefore to be dependent on a further parameter, namely  $\Delta$ . That would be fatal, though, since we do not know any *thermodynamic analog* to it. However, we will be able to show at the end of this subsection that for the macroscopic system ( $N \rightarrow \infty$ ) the dependence on  $\Delta$  becomes *asymptotically unimportant*. That has a consequence, which appears *somewhat strange* at first, that the following two representations of the *statistical entropy* are completely equivalent



to (1.71):

$$S(E, V, N) = k_B \ln \varphi_N(E, V) , \quad (1.73)$$

$$S(E, V, N) = k_B \ln D_N(E, V) . \quad (1.74)$$

Thereby,  $\varphi_N(E, V)$  in (1.48) and  $D_N(E, V)$  in (1.50) are defined as *phase volume* and *density of states*, respectively. The equivalence of (1.71), (1.73) and (1.74) results, in the last analysis, from the *mathematical fact* that in a (phase) space of high dimension, the volume, which is confined by a closed area, lies almost exclusively within a very thin surface layer (see Exercise 1.3.1). The more precise reasoning of (1.73) and (1.74) at the end of this section will yield a further indication, how the large number of degrees of freedom of macroscopic systems can lead to *unexpected* phenomena. What microscopically is certainly wrong, can turn out to be *asymptotically (macroscopically)* correct.

In order to show that the *statistical entropy* (1.71) can be identified with the thermodynamic entropy, two essential statements are to be verified:

1.  $S$  is extensive (additive) (section 3.3, Vol. 5),
2.  $S$  fulfills the second law of Thermodynamics: *For all (irreversible) processes, which take place even in an isolated system, the entropy does not decrease ( $dS \geq 0$ , subsection 3.7.1, Vol. 5)!*

We will deal with point 2 in the next subsection. Here we will at first consider the *additivity* and *extensivity*, respectively, of the *statistical entropy* (1.71).

We first consider two **isolated** systems, each of which defines a micro-canonical ensemble:

$$\begin{aligned} E_1 < H_1(\mathbf{q}, \mathbf{p}) < E_1 + \Delta_1, \\ E_2 < H_2(\mathbf{q}, \mathbf{p}) < E_2 + \Delta_2 . \end{aligned} \quad (1.75)$$

They have the entropies:

$$\begin{aligned} S_1(E_1, V_1, N_1) &= k_B \ln \Gamma_{N_1}(E_1, V_1), \\ S_2(E_2, V_2, N_2) &= k_B \ln \Gamma_{N_2}(E_2, V_2) . \end{aligned} \quad (1.76)$$

The phase volume of the total system ( $N = N_1 + N_2$ ,  $V = V_1 + V_2$ ),

$$E = E_1 + E_2 < H(\mathbf{q}, \mathbf{p}) = H_1(\mathbf{q}_1, \mathbf{p}_1) + H_2(\mathbf{q}_2, \mathbf{p}_2) < E + \Delta , \quad (1.77)$$

is, for the case that there does not exist any exchange-contact between the systems, nothing else but the product of the two partial phase volumes, because each *conceivable* state of system 1 can be combined with every *conceivable* state of

system 2 to give a *thinkable* state of the total system:

$$\begin{aligned}
 \Gamma_N(E, V) &= \frac{\alpha^*}{h^{3N}} \int \cdots \int_{E < H < E + \Delta} d^{3N} q d^{3N} p \\
 &= \frac{\alpha^*}{h^{3N}} \int \cdots \int_{\substack{E_1 < H_1(\mathbf{q}_1, \mathbf{p}_1) < E_1 + \Delta_1 \\ E_2 < H_2(\mathbf{q}_2, \mathbf{p}_2) < E_2 + \Delta_2}} d^{3N_1} q_1 d^{3N_1} p_1 d^{3N_2} q_2 d^{3N_2} p_2 \\
 &= \frac{\alpha_1^*}{h^{3N_1}} \int \cdots \int_{E_1 < H_1 < E_1 + \Delta_1} d^{3N_1} q_1 d^{3N_1} p_1 \frac{\alpha_2^*}{h^{3N_2}} \int \cdots \int_{E_2 < H_2 < E_2 + \Delta_2} d^{3N_2} q_2 d^{3N_2} p_2 \\
 &= \Gamma_{N_1}(E_1, V_1) \Gamma_{N_2}(E_2, V_2) .
 \end{aligned} \tag{1.78}$$

(The justification for  $\alpha^* \rightarrow \alpha_1^* \alpha_2^*$  will be later presented (Sect. 1.3.7).) The entropy is therewith trivially additive:

$$S(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) . \tag{1.79}$$

However, what happens when we allow *thermal contact* between the partial systems? A case such as the one we had defined, in connection with our model system in Sect. 1.3.1, a contact, by which the systems 1 and 2 can exchange energy, while their particle numbers and volumes stay constant. Furthermore, there shall not be *any significant* interactions between the systems, so that the Hamilton function of the *super system* is composed additively by those of the partial systems:

$$H(\mathbf{q}, \mathbf{p}) = H(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) = H_1(\mathbf{q}_1, \mathbf{p}_1) + H_2(\mathbf{q}_2, \mathbf{p}_2) . \tag{1.80}$$

It is clear that in principle the energy exchange **can not take place** without interaction. However, since we are developing here the *Statistical Equilibrium Physics*, the time, which the system needs to reach equilibrium, does not play a role. We can therefore assume that, in the framework of a *thought experiments*, the exchange is brought about by a few particles only, which interact with those of system 1 as well as those of system 2. These very few particles contribute such a minor interaction energy that (1.80) can be seen as practically exact.

The isolated total system defines, in the sense of (1.77), a micro-canonical ensemble. However, since energy exchange is now possible between the partial systems, the conditions (1.75) are no longer valid. But the weaker condition (1.77) can be satisfied in manifold ways.

For simplifying the following considerations let us decompose the energy  $E$  into small, *atomic* units  $\varepsilon$ , and let us assume that the energy exchange between the two systems, which are in thermal contact, takes place in *packets* of this quantity  $\varepsilon$ :

$$E = n_0 \varepsilon; \quad E_m = m \varepsilon; \quad 0 \leq m \leq n_0 . \tag{1.81}$$

With the discrete energies of the quantum systems, this decomposition is manageable without any difficulty. For the continuous energies of the classical systems it means, though, a certain simplification. If, however, the decomposition is sufficiently fine ( $\varepsilon \rightarrow 0$ ), then a negligible error arises, when  $E_m$  is considered as the average energy of the respective interval. Because of  $H = E$ ,  $E$  must be bounded below, and the always free choice of the energy zero allows to identify it with the lowest energy of the total system. Since the energy  $E$  can be distributed in all possible ways over the two partial systems ( $E_1 = E_m, E_2 = E - E_m, m = 0, \dots, n_0$ ), it follows with the same justification as that for (1.78):

$$\Gamma_N(E, V) = \sum_{m=0}^{n_0} \Gamma_{N_1}(E_m, V_1) \Gamma_{N_2}(E - E_m, V_2) . \quad (1.82)$$

The statistical entropy of the total system therefore reads:

$$S(E, V, N) = k_B \ln \sum_{m=0}^{n_0} \Gamma_{N_1}(E_m, V_1) \Gamma_{N_2}(E - E_m, V_2) \\ (V = V_1 + V_2; \quad N = N_1 + N_2) . \quad (1.83)$$

We know from our discussion of the model system in the preceding subsection that the distribution  $[\Gamma_{N_1}(E_m, V_1) \Gamma_{N_2}(E - E_m, V_2)]$  will exhibit an extremely sharp maximum at the *most probable configuration*, which defines the *thermal equilibrium*. (One may think about the fact that the *phase volume*  $\Gamma_N(E, V)$  in the case of *discrete* states is identical to the number of these states for  $E < H < E + \Delta!$ ) In (1.82) there will thus exist a dominating summand,

$$\Gamma_{N_1}(\widehat{E}_m, V_1) \Gamma_{N_2}(E - \widehat{E}_m, V_2) ,$$

which admits the estimation

$$\Gamma_{N_1}(\widehat{E}_m, V_1) \Gamma_{N_2}(E - \widehat{E}_m, V_2) \leq \Gamma_N(E, V) \leq \\ \leq n_0 \Gamma_{N_1}(\widehat{E}_m, V_1) \Gamma_{N_2}(E - \widehat{E}_m, V_2) . \quad (1.84)$$

This means for the entropy:

$$S_1(\widehat{E}_m, V_1, N_1) + S_2(E - \widehat{E}_m, V_2, N_2) \leq S(E, V, N) \leq \\ \leq k_B \ln n_0 + S_1(\widehat{E}_m, V_1, N_1) + S_2(E - \widehat{E}_m, V_2, N_2) . \quad (1.85)$$

We had found for the model system in Sect. 1.3.1 with (1.61), (1.62) or (1.67) (see also Exercise 1.2.9):

$$\ln \Gamma_{N_1}(\widehat{E}_m, V_1) \sim N_1 , \\ \ln \Gamma_{N_2}(E - \widehat{E}_m, V_2) \sim N_2 . \quad (1.86)$$

$n_0$  is at most of the order of magnitude of the particle number  $N = N_1 + N_2$ . If now at least one of the two particle numbers  $N_1, N_2$  is *macroscopic*, i.e., of the order of magnitude  $10^{22}$ , for instance, then  $\ln N \approx 22 \ln 10 \approx 50$ , and thus in any case negligible compared to  $\ln \Gamma_{N_1} + \ln \Gamma_{N_2}$ . The estimation (1.86) holds for all exactly tractable model systems, making therewith, for the not exactly solvable general case, the assumption  $\ln([\Gamma_{N_1} \Gamma_{N_2}]_{\max}) \gg \ln N$  at least plausible. But that means according to (1.85) the

**extensivity of the entropy**

$$S(E, V, N) = S_1(\widehat{E}_1, V_1, N_1) + S_2(\widehat{E}_2, V_2, N_2) \quad (+\mathcal{O}(\ln N)) \quad (1.87)$$

for two macroscopic systems, which are in thermal contact, when the isolated *super system*, which is composed by them, is in its *most probable configuration*. The latter is equivalent to *thermal equilibrium* between the two partial systems.

The results of this section can be still extended to a further important aspect, which will lead us to the statistical concept of **temperature**. In Sect. 1.3.1, with the discussion of a model system, we used for the first time the term *thermal equilibrium*. In an isolated system  $(E, V, N)$ , this situation is given, when for each two subsystems, which can exchange energy with each other, the product  $\Gamma_{N_1}(E_1, V_1)\Gamma_{N_2}(E_2, V_2)$  is maximal, where the boundary conditions  $E = E_1 + E_2$ ,  $N = N_1 + N_2$  and  $V = V_1 + V_2$  are to be fulfilled.

That is, as we have seen above, the situation, for which the extensivity of the entropy (1.87) is valid. For fixed particle numbers  $N_1, N_2$  and fixed volumes  $V_1, V_2$ , especially the energy differentiation of the product  $\Gamma_{N_1}\Gamma_{N_2}$  must vanish:

$$d(\Gamma_{N_1}\Gamma_{N_2}) = \left(\frac{\partial\Gamma_{N_1}}{\partial E_1}\right)_{N_1, V_1} \Gamma_{N_2} dE_1 + \Gamma_{N_1} \left(\frac{\partial\Gamma_{N_2}}{\partial E_2}\right)_{N_2, V_2} dE_2 \stackrel{!}{=} 0.$$

After division by  $\Gamma_{N_1}\Gamma_{N_2}$ ,

$$\begin{aligned} 0 &= \frac{1}{\Gamma_{N_1}} \left(\frac{\partial\Gamma_{N_1}}{\partial E_1}\right)_{N_1, V_1} dE_1 + \frac{1}{\Gamma_{N_2}} \left(\frac{\partial\Gamma_{N_2}}{\partial E_2}\right)_{N_2, V_2} dE_2 \\ &= \left(\frac{\partial \ln \Gamma_{N_1}}{\partial E_1}\right)_{N_1, V_1} dE_1 + \left(\frac{\partial \ln \Gamma_{N_2}}{\partial E_2}\right)_{N_2, V_2} dE_2, \end{aligned}$$

and fulfilling the boundary condition,

$$dE = dE_1 + dE_2 = 0,$$

it can be recognized that ultimately the energy-dependence of the entropy determines thermal equilibrium:

$$\left(\frac{\partial S_1(E_1, V_1, N_1)}{\partial E_1}\right)_{V_1, N_1} (E_1 = \widehat{E}_1) \stackrel{!}{=} \left(\frac{\partial S_2(E_2, V_2, N_2)}{\partial E_2}\right)_{V_2, N_2} (E_2 = \widehat{E}_2). \quad (1.88)$$

We define:

$$\frac{1}{T} \equiv \left( \frac{\partial S(E, V, N)}{\partial E} \right)_{V, N} = \frac{k_B}{\Gamma_N(E, V)} \left( \frac{\partial \Gamma_N(E, V)}{\partial E} \right)_{V, N}, \quad (1.89)$$

***T*: temperature .**

*Temperature* thus corresponds, in the sense of Statistical Physics, to the relative change of the phase volume of a micro-canonical ensemble with the energy. That sounds rather abstract and far-fetched. The interpretation of the equilibrium condition (1.88) appears here to be more revealing. Two arbitrary subsystems of an isolated total system with thermal contact are *in thermal equilibrium*, if they possess the same temperature. However, the two mentioned subsystems are in no way specified up to now. We can therefore generalize:

*In an isolated system at thermal equilibrium,  
the temperature remains the same at all positions*

But exactly this actual situation we got to know in the Phenomenological Thermodynamics as the equilibrium condition for isolated systems. The quantity  $T$ , introduced by (1.89), is indeed the absolute temperature of Thermodynamics. Formally the same connection between temperature, entropy, and (internal) energy, we had also found there ((3.5), Vol. 5).

With (1.71), the product  $k_B T$ , which is usually abbreviated in Statistical Physics by

$$k_B T \equiv \frac{1}{\beta}, \quad (1.90)$$

has the dimension ‘energy’. The choice of the *Boltzmann constant*  $k_B$  as the coefficient in the definition (1.71) of the entropy takes care for the fact that  $T$  obtains the unit (*Celsius*-, *Kelvin*-)degree.

For the considerations, which led to the statements (1.87) and (1.88), we have used the representation (1.71) of the statistical entropy. Let us close this subsection with the proof that for the *asymptotically large* systems of Statistical Physics, the formulations (1.73) and (1.74) are equivalent to (1.71). The line of proof is very similar to that by which we have verified the additivity of the entropy.

When the hyper-surface  $H = E$  is closed, then we can divide the enclosed phase volume (1.48) into slices of the thickness  $\Delta$ , and can then estimate:

$$\varphi_N(E, V) \leq n_0 \Gamma_N(E, V) .$$

The *uppermost* layer is  $\Gamma_N(E, V)$ , which contains the largest volume.  $n_0$  is the number of *slices*. Since  $H$  is bounded below, for finite  $\Delta$ ,  $n_0$  will also be finite, and will be at most of the order  $N$ . (Remember the reasoning for the *energy-indeterminacy*  $\Delta$  in Sect. 1.1.1). In

$$\ln \varphi_N(E, V) \leq \ln n_0 + \ln \Gamma_N(E, V)$$

the first summand on the right-hand side, for macroscopic systems ( $N \rightarrow \infty$ ), can therefore be neglected compared to the other term, which is proportional to  $N$ , which proves the equivalence of (1.73) and (1.71). In addition, it holds, according to (1.51):

$$k_B \ln \Gamma_N(E, V) = k_B \ln(\Delta D_N(E, V)) = k_B \ln \Delta + k_B \ln D_N(E, V) .$$

Since  $\ln \Delta$  is independent of  $N$ , here the first summand is asymptotically ( $N \rightarrow \infty$ ) negligible with respect to the second summand. Therewith, (1.74) is also confirmed. The statistical entropy therefore does **not** depend on  $\Delta$ , in contrast to what the definition (1.71) at first let suppose.

### 1.3.3 Second Law of Thermodynamics

In order to be able to indeed identify the *statistical entropy* (1.71) with the *thermodynamical one*, we still have to establish the validity of the *second law of Thermodynamics*. Since our definitions and conclusions so far referred exclusively to isolated systems, it therefore remains to verify **that for all processes, which take place in an isolated system, the entropy can not decrease**. After the preparations of the last subsection the proof is no longer very difficult.

Given are two at first isolated systems 1 and 2 (Fig. 1.9), the corresponding micro-canonical ensembles of which possess the phase volumes

$$\Gamma_{N_1}(E_1, V_1) \quad \text{and} \quad \Gamma_{N_2}(E_2, V_2) .$$

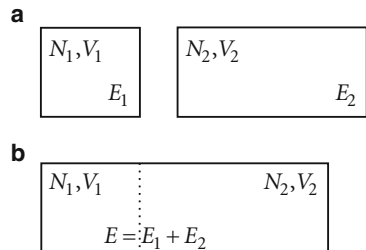
The phase volume ascribed to the total system then amounts to, according to (1.78):

$$\Gamma_N^{(a)}(E, V) = \Gamma_{N_1}(E_1, V_1)\Gamma_{N_2}(E_2, V_2) . \tag{1.91}$$

This leads to the entropy:

$$S^{(a)}(E, V, N) = k_B \ln \Gamma_{N_1}(E_1, V_1) + k_B \ln \Gamma_{N_2}(E_2, V_2) .$$

**Fig. 1.9** Composition of two at first isolated partial systems (a) to an isolated total system with thermal contact of the two subsystems (b)



In the next step (b) we allow **thermal contact** and therewith **energy fluctuations** between the systems (Fig. 1.9). The initial state corresponds to (1.91). The final state, after achieving thermal equilibrium, possesses, in contrast, a phase volume of the kind (1.82),

$$\Gamma_N^{(b)}(E, V) = \sum_{\Delta E} \Gamma_{N_1}(E_1 + \Delta E, V_1) \Gamma_{N_2}(E_2 - \Delta E, V_2), \quad (1.92)$$

where it is summed (or integrated) over all possible energy-exchange values  $\Delta E$ . The initial state (a) is represented in this sum by a single term, namely the term  $\Delta E=0$ . All the summands are positive, by what it becomes clear that, at the transition (a)  $\rightarrow$  (b), which means the irreversible transition into thermal equilibrium, the phase volume  $\Gamma_N(E, V)$ , and therewith also the entropy cannot decrease. When the two systems (a), before the process, are not at the same temperature, then there will be, according to our considerations for (1.87), among the summands in (1.92) a maximal term with  $\Delta E \neq 0$ , which strongly dominates the others, and which marks the equilibrium state. This will take care for the actual entropy increase. **The entropy thus has in any case the tendency to increase.** It is thereby actually not so decisive that in (1.92) there appear, compared to (1.91), additional positive-definite summands, but it is decisive that among them there is an extremely dominating one. Of course, the first part of the statement to the proof of the entropy increase is completely sufficient, we have to only note that we have not used for the entropy of the final equilibrium state the *exact* expression (1.92), but under the neglecting of the contributions of the order of magnitude  $(\ln N)$ , only the maximal summand. Otherwise, we could not have assumed the extensivity of the entropy (1.87).

The genuine cause of the entropy increase is qualitatively rather easy to understand. In the initial state (a) there are with  $E_1 < H_1 < E_1 + \Delta_1$  and  $E_2 < H_2 < E_2 + \Delta_2$  **two** conditions imposed, in the final state (b) still only **one**:  $E_1 + E_2 < H < E_1 + E_2 + \Delta$ . Less restrictive boundary conditions, however, mean that more states have access to the system. Hence, a greater phase volume is entitled to the system, which means a greater entropy. For this reason, the above considerations are not only valid for energy fluctuations, but also for particle and volume exchange.

After having satisfactorily shown the validity of the second law of Thermodynamics for the entropy defined in (1.71), we can also make statements about in which **direction** energy is exchanged between the systems. Before the contact let the two just discussed systems be at different temperatures, with  $T_1 > T_2$ . If now the energy exchange takes place without particle and volume changes and additionally with constant total energy ( $\Delta E_1 = -\Delta E_2$ ), then it must be:

$$\begin{aligned} \Delta S &= \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} \Delta E_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \Delta E_2 \\ &= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Delta E_1 \stackrel{!}{\geq} 0. \end{aligned}$$

This inequality can be fulfilled only for  $\Delta E_1 \leq 0$ . The energy of system 1 thus decreases. Energy has flown from the system of higher temperature to the system of lower temperature. Even this covers the statements of the Phenomenological Thermodynamics.

We have now already collected several important arguments, which documents that the *statistical entropy* is identical to the *thermodynamical entropy*.

The chain of proof, though, is not yet consistent. We have permitted up to now only energy fluctuations by thermal contact between the two subsystems of the isolated total system, while the particle exchange and the volume exchange were excluded. We could therewith statistically justify an important statement of Thermodynamics, namely that in an isolated system in the equilibrium the same temperature prevails at all positions. The equilibrium condition for isolated systems, however, includes, as is well-known, two further statements ((3.72), Vol. 5), which concern the *chemical potential* and the *pressure*. These terms have something to do with the up to now not considered particle fluctuations and volume fluctuations. That will be investigated in the next subsections.

### 1.3.4 Chemical Potential

In the test arrangement of Fig. 1.9 between the two subsystems 1 and 2 we now want to allow also a **particle-exchange contact**. Therewith, only the particle number  $N$  of the isolated *super system* is constant;  $N_1$  and  $N_2$ , however, are no longer constant:

$$\begin{aligned} E &= E_1 + E_2 = \text{const} \iff dE_1 = -dE_2, \\ N &= N_1 + N_2 = \text{const} \iff dN_1 = -dN_2. \end{aligned} \quad (1.93)$$

The initial state (a) is the same as in the preceding subsection. The phase volume (1.91) is ascribed to it. But for the final state (b) now instead of (1.92) holds:

$$\Gamma_N^{(b)}(E, V) = \sum_{E_1, N_1} \Gamma_{N_1}(E_1, V_1) \Gamma_{N_2=N-N_1}(E_2 = E - E_1, V_2). \quad (1.94)$$

The **equilibrium state** corresponds again to the configuration  $(E_1, N_1; E_2, N_2)$ , for which the maximal phase volume is available. We determine the maximal summand in (1.94) by the condition:

$$\begin{aligned} 0 \stackrel{!}{=} d(\Gamma_{N_1} \Gamma_{N_2}) &= \left[ \left( \frac{\partial \Gamma_{N_1}}{\partial N_1} \right)_{E_1, V_1} dN_1 + \left( \frac{\partial \Gamma_{N_1}}{\partial E_1} \right)_{N_1, V_1} dE_1 \right] \Gamma_{N_2} \\ &\quad + \Gamma_{N_1} \left[ \left( \frac{\partial \Gamma_{N_2}}{\partial N_2} \right)_{E_2, V_2} dN_2 + \left( \frac{\partial \Gamma_{N_2}}{\partial E_2} \right)_{N_2, V_2} dE_2 \right]. \end{aligned}$$



We divide by  $\Gamma_{N_1} \Gamma_{N_2}$ , exploit the boundary conditions (1.93), and use the definition (1.71) of the entropy:

$$0 = \left[ \left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} - \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} \right] dN_1 + \left[ \left( \frac{\partial S_1}{\partial E_1} \right)_{N_1, V_1} - \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} \right] dE_1 .$$

Since  $N_1$  and  $E_1$  are independent variables, each summand itself must already vanish. By the second summand it is then reproduced the *old* result (1.88), according to which in thermal equilibrium the two systems in contact exhibit the same temperature:

$$\frac{1}{T_1} = \frac{1}{T_2} .$$

On the other hand, the first summand leads to a *new* condition:

$$\left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} \stackrel{!}{=} \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} . \quad (1.95)$$

We formally define, as in Thermodynamics:

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{E, V} ; \quad \text{chemical potential.} \quad (1.96)$$

Therewith (1.95) reads:

$$\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$$

or equivalently because of  $T_1 = T_2$ :

$$\mu_1 = \mu_2 . \quad (1.97)$$

As already shown after (1.88) with respect to the temperature, this statement can be generalized:

**In an isolated system at thermal equilibrium  
there prevails the same chemical potential at all positions**

This statement coincides with that of the corresponding Phenomenological Thermodynamics. For us, this is a further hint that the *statistical* definitions of entropy, temperature, and chemical potential are consistent with the *thermodynamic concepts*. The chemical potential  $\mu$ , however, can now be calculated *microscopically* with the Hamilton function of the system, via the phase volume, when (1.71) and (1.89) are inserted into (1.96):

$$\mu = - \left( \frac{\partial \Gamma_N}{\partial N} \right)_{E, V} \left[ \left( \frac{\partial \Gamma_N}{\partial E} \right)_{N, V} \right]^{-1} . \quad (1.98)$$

For the complete equivalence of the equilibrium conditions of the isolated system in Statistical Physics and Thermodynamics we still need a statement, corresponding to (1.97) and (1.88), about the *pressure*. For this, though, we do no longer have the freedom, to *statistically define* it like  $T$  and  $\mu$ . *Pressure* is a mechanical quantity and is therewith, in contrast to  $\mu$  and  $T$ , already undisputedly preset by the concepts and laws of Classical Mechanics. According to the rules of Statistical Physics, we will have to average the corresponding phase-space function with the micro-canonical ensemble. We show in the next subsection that the *thermodynamic relation*

$$p = T \left( \frac{\partial S}{\partial V} \right)_{E,N} \quad (1.99)$$

remains also *statistically correct*. That means that, when we insert into the right-hand side of this relation the *statistical* definitions of  $T$  and  $S$ , we get the *mechanical* definition of the pressure.

### 1.3.5 Basic Relation of Thermodynamics

The Hamilton function of a system can depend on, in addition to its dynamical variables  $(\mathbf{q}, \mathbf{p})$ , also on the so-called **external parameters**. By these one understands such quantities, which do not change during the dynamical movement of the system in the phase space due to the Hamilton's equations of motion (1.13), which, however, are *externally adjustable*, and whose variation of course influences the properties of the system. The most obvious example is the volume  $V$  of a container, in which the  $N$  particles of a gas are moving around:

$$H = H(\mathbf{q}, \mathbf{p}; V). \quad (1.100)$$

If an interference into the physical system takes place exclusively via the *external parameters*, then it is called **adiabatic** (see Exercise 1.3.7). In order to see, how the *pressure* is to be incorporated into the statistical description, we consider such an adiabatic change of the state for a system, which is described by a Hamilton function of the type (1.100). In Classical Mechanics the pressure represents the negative partial derivative of  $H$  with respect to the external parameter *volume*. That means for Statistical Physics, **pressure**

$$p = - \left\langle \frac{\partial H}{\partial V} \right\rangle, \quad (1.101)$$

where the bracket  $\langle \dots \rangle$  means, according to (1.26), averaging over the micro-canonical ensemble. This definition is mandatory for us. We want to investigate whether (1.101) is equivalent to (1.99), that is whether the pressure can indeed

be expressed by the *statistical* quantities  $S$  and  $T$ . Let the starting point be the representation (1.99), into which we insert (1.73) for the entropy and (1.48) for the phase volume:

$$\begin{aligned} p &= T \left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{k_B T}{\varphi_N(E, V)} \frac{\partial}{\partial V} \varphi_N(E, V) \\ &= \frac{k_B T}{\varphi_N(E, V)} \lim_{\Delta V \rightarrow 0} \frac{\alpha}{\Delta V} \left[ \iint_{H(\mathbf{q}, \mathbf{p}; V + \Delta V) \leq E} d^{3N} q d^{3N} p - \iint_{H(\mathbf{q}, \mathbf{p}; V) \leq E} d^{3N} q d^{3N} p \right]. \end{aligned}$$

With

$$H(\mathbf{q}, \mathbf{p}; V + \Delta V) = H(\mathbf{q}, \mathbf{p}; V) + \Delta V \frac{\partial H}{\partial V} + \dots$$

it further follows:

$$p = \frac{k_B T}{\varphi_N(E, V)} \lim_{\Delta V \rightarrow 0} \frac{\alpha}{\Delta V} \iint_{E \leq H(\mathbf{q}, \mathbf{p}; V) \leq E - \Delta V (\partial H / \partial V)} d^{3N} q d^{3N} p.$$

For the volume integral on the right-hand side we use, in analogy to (1.54), the formulation as surface integral:

$$\begin{aligned} p &= \frac{k_B T}{\varphi_N(E, V)} \lim_{\Delta V \rightarrow 0} \frac{\alpha}{\Delta V} \int_{H(\mathbf{q}, \mathbf{p}; V) = E} \frac{df_E}{|\nabla H|} \int_E^{E - \Delta V (\partial H / \partial V)} dE' \\ &= \frac{k_B T}{\varphi_N(E, V)} \alpha \int_{H(\mathbf{q}, \mathbf{p}; V) = E} \frac{df_E}{|\nabla H|} \left( -\frac{\partial H}{\partial V} \right) \\ &= \frac{k_B T}{\varphi_N(E, V)} D_N(E, V) \left\langle -\frac{\partial H}{\partial V} \right\rangle. \end{aligned}$$

In the last step we have applied the representation (1.56) of the micro-canonical ensemble-average. It follows further with the density of states  $D_N(E, V)$  according to (1.50):

$$\begin{aligned} p &= \left\langle -\frac{\partial H}{\partial V} \right\rangle \frac{k_B T}{\varphi_N(E)} \left( \frac{\partial \varphi_N(E, V)}{\partial E} \right)_{V,N} \\ &= \left\langle -\frac{\partial H}{\partial V} \right\rangle T \left( \frac{\partial (k_B \ln \varphi_N(E, V))}{\partial E} \right)_{V,N} \end{aligned}$$

$$\stackrel{(1.73)}{=} \left\langle -\frac{\partial H}{\partial V} \right\rangle_T \left( \frac{\partial S(E, V, N)}{\partial E} \right)_{V, N}$$

$$\stackrel{(1.89)}{=} \left\langle -\frac{\partial H}{\partial V} \right\rangle.$$

The *statistical definition* (1.99) of the pressure is therewith indeed traced back to the mechanical formulation (1.101). The pressure  $p$  is now introduced by (1.99) into the Statistical Physics, where we have just convinced ourselves of the consistency of it with respect to the presetting of Classical Mechanics.

The term

### quasi-static change of state

is of great importance for Thermodynamics as well as for the Statistical Physics of the equilibrium. By this one understands a continuous and sufficiently slow variation of  $E$ ,  $V$ , and  $N$ , so that at each moment a *micro-canonical ensemble* can be defined. When these quantities are changing, then of course, strictly speaking, the system is no longer isolated. Such a change can indeed be caused only by ‘*influence from the outside*’. As already explained in connection with the justification of (1.80), the time, which the process needs, does not matter in the equilibrium statistics. The process can therefore be executed so extremely slowly that a minimal ‘*influence from the outside*’ is sufficient, and at each moment the system can be considered as isolated and being in equilibrium. In particular, an entropy is thus definable at each moment of the course of the *quasi-static change of state*. For an infinitesimal change of the entropy it must then hold:

$$dS = \left( \frac{\partial S}{\partial E} \right)_{V, N} dE + \left( \frac{\partial S}{\partial V} \right)_{E, N} dV + \left( \frac{\partial S}{\partial N} \right)_{E, V} dN.$$

But with (1.89), (1.96) and (1.99) this is nothing else but the **first law of Thermodynamics**,

$$TdS = dE + pdV - \mu dN, \quad (1.102)$$

which we have **derived** here for the special case of a gas of  $N$  particles in the volume  $V$ .—If we also assume the validity of the second law of Thermodynamics (Sect. 1.3.3), then the **basic relation of Thermodynamics** is confirmed, which corresponds to a combination of the first two laws of Thermodynamics ((2.55), Vol. 5):

$$TdS \geq dE + pdV - \mu dN. \quad (1.103)$$

The third law of Thermodynamics is of *quantum-mechanical nature*. We therefore consider it only in Chap. 2.

Therewith we have reached our goal. The basic relation, and hence the full macroscopic Thermodynamics, could be *statistically justified*. All observables can be traced back, by the use of the *phase volume* and the *Hamilton function*, to microscopic interactions.

The **implementation concept** of the Statistical Physics thus consists in the following partial steps:

1. Formulation of the **Hamilton function**

$$H = H(\mathbf{q}, \mathbf{p}; z)$$

$$z : \text{external parameter, e.g. } z = V$$

by specification of the microscopic interactions.

2. Determination of the **phase volume**  $\varphi_N(E, V)$  and  $\Gamma_N(E, V)$ , respectively, by using  $H$ !
3. Derivation of the **entropy**  $S = S(E, V, N)$  from  $\varphi_N(E, V)$  with (1.73) or from  $\Gamma_N(E, V)$  with (1.71)!
4. Fixing the **temperature**  $T$  according to (1.89), the **chemical potential**  $\mu$  according to (1.98), and the **pressure**  $p$  according to (1.99)!
5. Determination of the

$$\text{internal energy:} \quad U = \langle H \rangle. \quad (1.104)$$

Because of (1.57),  $\langle H \rangle = E$ ,  $U$  results from solving the entropy expression in 3. for  $E$ :

$$U = E(S, V, N). \quad (1.105)$$

6. By Legendre transformation fixing the other **thermodynamic potentials**:

$$\text{free energy:} \quad F(T, V, N) = U - TS, \quad (1.106)$$

$$\text{enthalpy:} \quad \widehat{H}(S, p, N) = U + pV, \quad (1.107)$$

$$\text{free (Gibbs) enthalpy:} \quad G(T, p, N) = U + pV - TS. \quad (1.108)$$

7. For further evaluation, application of the well-known laws of Phenomenological Thermodynamics (Vol. 5)!

The motivation for the introduction and the discussion of the pressure, at the beginning of this chapter, was the still lacking third equilibrium condition for the isolated system. Because of 7., the proof for the fact that there is

***in an isolated system at equilibrium, at each point of the volume,  
the pressure is the same***

can now be taken over word-for-word from Thermodynamics ((3.71), (3.72), Vol. 5).

### 1.3.6 Equipartition Theorem

With the Statistical Physics, developed so far, we are already able to derive, in the framework of the micro-canonical ensemble, some important thermodynamic consequences. This will be demonstrated in this subsection with the example of a *generalized equipartition theorem*.

For a classical system with the Hamilton function  $H(\mathbf{q}, \mathbf{p})$  let us calculate the statistical average

$$\left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle; \quad \pi_i \in \{\mathbf{q}, \mathbf{p}\}$$

in the framework of the micro-canonical ensemble. According to (1.52) one therefore has to evaluate:

$$\begin{aligned} \left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle &= \frac{\iint_{E < H < E + \Delta} d^s q d^s p \pi_i (\partial H / \partial \pi_j)}{\iint_{E < H < E + \Delta} d^s q d^s p} \\ &= \frac{\alpha \Delta}{\Delta D(E)} \frac{\partial}{\partial E} \left\{ \iint_{H < E} d^s q d^s p \pi_i \frac{\partial H}{\partial \pi_j} \right\}. \end{aligned} \quad (1.109)$$

We reformulate at first the curly bracket with the aid of an integration by parts:

$$\begin{aligned} \iint_{H < E} d^s q d^s p \pi_i \frac{\partial H}{\partial \pi_j} &= \iint_{H < E} d^s q d^s p \pi_i \frac{\partial}{\partial \pi_j} (H - E) \\ &= \iint_{H < E} d^s q d^s p \frac{\partial}{\partial \pi_j} (\pi_i (H - E)) - \iint_{H < E} d^s q d^s p (H - E) \frac{\partial \pi_i}{\partial \pi_j}. \end{aligned}$$

In the second step we could insert the constant  $E$  into the integrand, since, because of  $dE/d\pi_j = 0$ , its contribution vanishes.  $\pi_j$  is one of the  $2s$  integration variables  $\{q_1, \dots, q_s, p_1, \dots, p_s\}$ . The integrated first summand is therefore equal to zero, because, with the other variables  $\{\pi_i, i \neq j\}$  fixed, the limits of integration are just given by  $H(\dots, \pi_j, \dots) = E$ . The remaining second summand is inserted into (1.109):

$$\begin{aligned} \left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle &= \delta_{ij} \frac{\alpha}{D(E)} \frac{\partial}{\partial E} \iint_{H < E} d^s q d^s p (E - H) \\ &= \delta_{ij} \frac{\alpha}{D(E)} \left[ \left(1 + E \frac{\partial}{\partial E}\right) \iint_{H < E} d^s q d^s p - \lim_{\Delta E \rightarrow 0} \frac{1}{\Delta E} \iint_{E < H < E + \Delta E} d^s q d^s p H \right]. \end{aligned}$$

The second and the third term cancel each other:

$$\left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle = \delta_{ij} \frac{\varphi(E)}{D(E)} = \frac{\delta_{ij}}{(1/\varphi(E))(\partial/\partial E)\varphi(E)} = \frac{\delta_{ij}}{(\partial/\partial E) \ln \varphi(E)} \stackrel{(1.73)}{=} \frac{\delta_{ij} k_B}{(\partial/\partial E)S(E)} .$$

When we now insert the definition (1.89) of the temperature, then we finally get the **generalized equipartition theorem**

$$\left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle = \delta_{ij} k_B T; \quad (\pi_i \in \{\mathbf{q}, \mathbf{p}\}) , \quad (1.110)$$

which, with the Hamilton's equations of motion (1.13), can also be written as follows:

$$\langle p_i \dot{q}_i \rangle = -\langle q_i \dot{p}_i \rangle = k_B T; \quad i = 1, 2, \dots, s \quad (1.111)$$

If one evaluates (1.110) especially for an  $N$ -particle system,

$$\begin{aligned} q_i &= x_i; & i &= 1, \dots, 3N: \text{ Cartesian position coordinates,} \\ p_i &= m_i \dot{x}_i; & \dot{p}_i &= -\frac{\partial \widehat{V}}{\partial x_i}; & \widehat{V}: & \text{potential,} \end{aligned}$$

it results the statement that the statistical average of the *virial of forces* ((3.33), Vol. 1) is proportional to the number of degrees of freedom ( $3N$ ) and proportional to the temperature:

$$\left\langle \sum_{i=1}^{3N} x_i \frac{\partial \widehat{V}}{\partial x_i} \right\rangle = -\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3N k_B T . \quad (1.112)$$

When we also calculate the average of the kinetic energy,

$$\langle \widehat{T} \rangle = \left\langle \sum_{i=1}^{3N} \frac{m_i}{2} \dot{x}_i^2 \right\rangle = \frac{1}{2} \sum_{i=1}^{3N} \langle \dot{q}_i p_i \rangle = \frac{3N}{2} k_B T , \quad (1.113)$$

we obtain the **equipartition theorem of the energy**, which states that each degree of freedom contributes, *on an average*,  $1/2 k_B T$  to the kinetic energy. One notes in passing that the result (1.113) makes the statistical temperature, defined abstractly in (1.89), for the first time *illustrative* and measurable.

When we finally combine (1.112) and (1.113), then we recognize the **virial theorem**, known from Classical Mechanics ((3.33), Vol. 1), according to which the average of the kinetic energy is just half the virial of the system:

$$\langle \widehat{T} \rangle = \frac{1}{2} \left\langle \sum_{i=1}^{3N} x_i \frac{\partial \widehat{V}}{\partial x_i} \right\rangle . \quad (1.114)$$

Note that we have proved this statement in the Classical Mechanics (Vol. 1) for the corresponding **time**-averages. The fundamental presumption of Statistical Physics, *time-average = ensemble-average*, thus finds its confirmation in this special case.

### 1.3.7 Ideal Gas

We consider as a further example the classical ideal gas, i.e., the noninteracting gas consisting of  $N$  atoms ( $\cong$  mass points) in the volume  $V$ . Let us choose the line of solution in the way, as was described in the form of a 'recipe' at the end of Sect. 1.3.5. In this sense, the first point of program consists in the formulation of the Hamilton function:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \widehat{V}(q_1, \dots, q_{3N}). \quad (1.115)$$

The potential  $\widehat{V}$  shall realize the *constraint*, which keeps the particles within the volume  $V$ , which we can assume to be a cuboid with the edge length  $L$ . The concrete shape of the container, though, does not play any role for the following. It is important that the particles are *elastically* reflected at the walls, so that their kinetic energy thereby does not change. The walls then need not be explicitly included in the considerations. They only realize the potential

$$\widehat{V}(\mathbf{q}) = \begin{cases} 0, & \text{if all } |q_i| < \frac{L}{2}, \\ \infty & \text{otherwise.} \end{cases} \quad (1.116)$$

In the next step the phase volume,

$$\varphi_N(E, V) = \alpha \iint_{H < E} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N},$$

has to be calculated. The space integrations can immediately be done, because of (1.116). They obviously yield a factor  $V^N$ :

$$\varphi_N(E, V) = \alpha V^N \iint_{H < E} dp_1 \dots dp_{3N}. \quad (1.117)$$

The Hamilton function depends, for particles within the volume  $V$ , only on the squares of the particle momenta. For all combinations, which fulfill

$$\sqrt{p_1^2 + \dots + p_{3N}^2} < \sqrt{2mE},$$



$H < E$  holds. The corresponding phase points thus belong to  $\varphi_N(E, V)$ . The remaining multifold integral in (1.117) hence represents a sphere in the  $3N$ -dimensional momentum space with the radius

$$R = \sqrt{p_1^2 + \dots + p_{3N}^2} = \sqrt{2mE} .$$

We have calculated the volume of such a sphere as Exercise 1.3.1:

$$V_{3N}^{(p)} = C_{3N} (2mE)^{3N/2} .$$

We can assume, w.l.o.g.,  $N$  to be an even number. If the particle number is actually odd, then we add (subtract) a particle, without influencing *the physics* of the system even in the least, because of  $N \approx 10^{22}$ . For even  $N$ ,  $3N$  is also even, and we take from Exercise 1.3.1:

$$C_{3N} = \frac{\pi^{3N/2}}{(3N/2)!} .$$

The phase volume of the ideal gas is therewith determined:

$$\varphi_N(E, V) = \alpha^* \left( \frac{V}{h^3} \right)^N \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} . \quad (1.118)$$

We have also inserted here  $\alpha = \alpha^*/h^{3N}$ , according to (1.45). With the definition (1.73) and the Stirling formula

$$\ln \left( \frac{3N}{2} \right)! \approx \frac{3N}{2} \left( \ln \frac{3N}{2} - 1 \right) ,$$

we now have found the **entropy** of the ideal gas:

$$S(E, V, N) = k_B \ln \alpha^* + Nk_B \left\{ \ln \left[ V \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{3}{2} \right\} . \quad (1.119)$$

In this form, the entropy is determined only up to the term  $k_B \ln \alpha^*$ . If one assumes that here it is only an arbitrary constant, then this fact would not bother us too much. We also know from Thermodynamics (Vol. 5) that only entropy-**differences** are relevant. One would then take, out of convenience,  $\alpha^* = 1$ . But this choice leads to contradictions. For instance, Phenomenological Thermodynamics deduces from the extensivity of the entropy the so-called *homogeneity relation* ((3.39), Vol. 5):

$$S(\lambda E, \lambda V, \lambda N) \stackrel{!}{=} \lambda S(E, V, N); \quad \lambda \in \mathbf{R} . \quad (1.120)$$

This is violated by (1.119) if  $\alpha^* = 1$  (or  $\alpha^* = \text{const}$ ). The  $\ln V$ -term in (1.119) is *disturbing*. The still undetermined quantity  $\alpha^*$  must therefore represent something more than an unessential constant. Let us try to collect additional information about  $\alpha^*$ .

The energy-differentiation of the entropy should, according to (1.89), lead to the temperature. With the assumption that  $\alpha^*$  **does not** depend on  $E$ , it follows from (1.119):

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{3}{2} \frac{Nk_B}{E}.$$

This leads with

$$U = E = \frac{3}{2} Nk_B T \quad (1.121)$$

to the exact thermodynamic relation for the **internal energy** of the ideal gas (*caloric equation of state*). The assumption of the energy-**independence** of  $\alpha^*$  thus seems to be justified. It does not come into conflict with Thermodynamics.—Let us investigate in the same manner the volume-dependence! Presuming that  $\alpha^*$  **does not** depend on  $V$ , one finds, with (1.99), from (1.119) for the pressure:

$$p = T \left( \frac{\partial S}{\partial V} \right)_{E,N} = TNk_B \frac{1}{V}.$$

But this is just the correct *thermal equation of state* of the ideal gas:

$$pV = Nk_B T. \quad (1.122)$$

We conclude therefrom that  $\alpha^*$  can **not** be a function of  $V$ , either. It remains then only a possible dependence on the particle number. How might this look like?

The *homogeneity relation* (1.120) will be violated, because of the factor  $V$  in the argument of the logarithm in (1.119), if one takes  $\alpha^* = 1$ . If there stood the *intensive* quantity  $V/N$  instead of  $V$ , everything would obviously be in order. But that can be achieved by the choice

$$\alpha^* = \frac{1}{N!}, \quad (1.123)$$

and by the use of the Stirling formula  $\ln \alpha^* \approx -N(\ln N - 1)$ . Hence, (1.119) reads:

$$S(E, V, N) = Nk_B \left\{ \ln \left[ \frac{V}{N} \left( \frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right\}. \quad (1.124)$$

This equation turns out to be indeed the correct entropy expression for the ideal gas. According to its *discoverers* it is called the **Sackur-Tetrode equation**. From this equation it follows, by solving for  $E$ , the thermodynamic potential *internal energy*  $U = E$  as function of its *natural* variables  $S$ ,  $V$  and  $N$ :

$$U(S, V, N) = N \left( \frac{3h^2}{4\pi m} \right) \left( \frac{N}{V} \right)^{2/3} \exp \left( \frac{2S}{3Nk_B} - \frac{5}{3} \right). \quad (1.125)$$

One easily realizes that this result agrees with that of the Phenomenological Thermodynamics ((3.44), Vol. 5), which must be considered as a further support of the ansatz (1.123). In contrast to (1.124), though, in Thermodynamics, we had to still let an entropy constant  $\sigma$  free.—Nevertheless, there is some evidence that (1.123) indeed is the correct choice for  $\alpha^*$ . But we will not yet be content therewith and look for further arguments for (1.123).

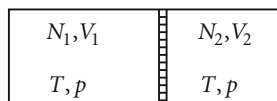
Already for the Phenomenological Thermodynamics there appeared a major problem in connection with the *mixing of two ideal gases*, which is known under the keyword **Gibb's paradox**. Let us briefly recall the situation. An isolated system (volume  $V = V_1 + V_2$ , particle number  $N = N_1 + N_2$ ) may at first be divided by a wall into two chambers, in which there are at the same temperature  $T$  two ideal gases ( $V_{1,2}$ ,  $N_{1,2}$ ) (Fig. 1.10). The wall shall be mobile, so that in both the chambers the same pressure  $p$  arises. One is now interested in the change of entropy (**entropy of mixing**), which results as a consequence of the mixing of the two gases after the removal of the wall. Since both the gases had before the mixing the same pressure and the same temperature, these two quantities will not have changed after the mixing. In particular, it holds because of (1.122):

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}. \quad (1.126)$$

For the entropy change one finds with formula (1.119) and with  $\alpha^* = 1$ , when we replace  $E/N$  according to (1.121) by  $(3/2)k_B T$ :

$$\begin{aligned} \Delta S &= S_{\text{after}} - S_{\text{before}} \\ &= \sum_{i=1}^2 (S(T, V, N_i) - S(T, V_i, N_i)) \\ &= k_B \left[ N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] \end{aligned} \quad (1.127)$$

**Fig. 1.10** Arrangement for the interpretation of the entropy of mixing of two ideal gases



(see (3.54), Vol. 5). For two **different** gases this expression is surely correct, and also experimentally verifiable. The same result, by the way, is given also by the *Sackur-Tetrode equation* (1.124).

The same experiment is now performed with two **identical** gases. The  $\alpha^* = 1$ -formula (1.119) then yields as entropy of mixing

$$\begin{aligned}\overline{\Delta S} &= S(T, V, N) - \sum_{i=1}^2 S(T, V_i, N_i) \\ &= Nk_B \ln V - N_1 k_B \ln V_1 - N_2 k_B \ln V_2 \\ &= k_B \left[ N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] > 0.\end{aligned}$$

That is the same expression as that, which is found in the case of the mixing of different gases (1.127). This fact is called the *Gibb's paradox*.  $\overline{\Delta S} > 0$  for the mixing of **identical** gases would indeed be fatal, since then the **state quantity entropy** would depend on the previous history of the system. Depending on whether or not the state  $(N, V, T)$  was prepared by removing a wall would yield another entropy. It would even be possible to create arbitrarily large entropies, simply by dividing the container into arbitrarily many chambers of the same pressure and the same temperature, *before* the removal of the corresponding walls.—The *right* formula (1.124) for the entropy, however, does not know the Gibb's paradox. Because of (1.126) it follows:

$$\overline{\Delta S} = S(T, V, N) - \sum_{i=1}^2 S(T, V_i, N_i) = 0. \quad (1.128)$$

This is a further hint that the choice (1.123) for  $\alpha^*$ , which is called the **correct Boltzmann-counting**, is exact.

With it, the **'right' phase volume** (1.44) of the micro-canonical ensemble for an  $N$ -particle system in the volume  $V$  reads:

$$\Gamma_N(E, V) = \frac{1}{h^{3N} N!} \iint_{E < H(\mathbf{q}, \mathbf{p}) < E + \Delta} d^{3N} q d^{3N} p. \quad (1.129)$$

Up to now we have justified the factor  $1/N!$  by physical evidence because without this factor certain basic properties of the entropy would be violated. It would of course be desirable, to be able to recognize its meaning somewhat more directly. In particular, it raises the question, what happens, when the system consists of two or more types of particles. Do we have then the same factor  $1/N!$ , where  $N = \sum_j N_j$  is the total particle number, or do we have to choose something different, maybe  $[\prod_j N_j!]^{-1}$ ?

For a deeper justification of the *correct Boltzmann-counting* some quantum-mechanical aspects must be taken into account. Quantum Mechanics teaches us that the physical properties of systems of *identical* particles and those of systems of *distinguishable* particles can be very different (section 8.2, Vol. 7). Typical phenomena result alone from the fact that the interchange of two identical particles can not yield a new state. More precisely: All states of systems, which consist of identical particles, are (anti)symmetric with respect to particle interchanges. The *principle of indistinguishability* is actually alien to Classical Physics. All *classical* particles are considered as distinguishable, being identifiable for all arbitrary later times by the use of the Hamilton's equations of motion. That means in particular, that the interchange of two particles of the same kind leads classically to a new state, although the corresponding states, arising out of each other, can by no means be distinguished macroscopically by a measurement. For  $N$  particles there are  $N!$  possibilities for interchanges of this kind. Each possibility corresponds to another classical state. The volume of the phase space is in this sense *inflated*; in particular also when by removal of separating walls, as in the above example, the possibilities of interchanges increase. The question is, whether this '*inflating*' of the phase space is really reasonable.

We have realized again and again, when dealing with Quantum Mechanics (Vol. 6,7), that Classical Mechanics can be considered, under certain conditions, as a correct limiting case of Quantum Mechanics. One therefore might suppose that, at least in the here interesting context, the quantum-mechanical *principle of indistinguishability* of identical particles does **not** get lost by the limiting process *Quantum Mechanics*  $\rightarrow$  *Classical Mechanics*. But if this were indeed the case, then the factor  $1/N!$  in (1.129) would just offset the mentioned '*inflating*' of the phase volume as a consequence of identical particles, and would therewith let the volume of the phase space correspond to the number of really different states. Furthermore, it would answer the above addressed question, what happens when the total system is composed by  $n_0$  **different** particle types. Of course, only the interchanges within one and the same sort will not change the state. The corresponding generalization of (1.129) thus reads:

$$\Gamma_N(E, V) = \frac{1}{h^{3N} \prod_{j=1}^{n_0} N_j!} \iint_{E < H(\mathbf{q}, \mathbf{p}) < E + \Delta} d^{3N}q d^{3N}p . \quad (1.130)$$

Equation (1.129) is contained herein as the  $n_0 = 1$ -special case.

The same conclusion, namely to see Classical Mechanics realized as the limiting case of Quantum Mechanics, also enforces the choice of the factor  $h^{3N}$ , where  $h$  is the well-defined Planck's quantum of action. This factor we had introduced in (1.45) at first only to *get the correct dimension*.

### 1.3.8 Exercises

#### Exercise 1.3.1

1. For the surface  $S_N(R)$  of an  $N$ -dimensional sphere of radius  $R$  it holds:

$$S_N(R) = NC_N R^{N-1} .$$

Verify:

$$C_N = \begin{cases} \frac{\pi^{N/2}}{(N/2)!} , & \text{if } N \text{ even,} \\ \frac{2(2\pi)^{(N-1)/2}}{N!!} , & \text{if } N \text{ odd} \end{cases}$$

(double factorial:  $N!! = 1 \cdot 3 \cdot 5 \cdots N$ ).

2. Show that for large dimensions  $N$ , practically the full volume of the sphere is compressed in a thin surface layer.

#### Exercise 1.3.2

For the two-level system determine from Exercise 1.2.9 the entropy  $S(E, N)$ . Derive the temperature-dependence of the (internal) energy  $E$  and show that the entropy can be expressed by

$$n(T) = \frac{1}{\exp(2\beta\varepsilon) + 1} .$$

Which meaning does  $n(T)$  have? How does  $S(T, N)$  behave for  $T \rightarrow 0$ ?

#### Exercise 1.3.3

Let the phase volume of a gas of  $N$  particles in the volume  $V$  be given by

$$\Gamma_N(E, V) = f(N) V^N E^{3N/2} .$$

1. Calculate the caloric equation of state:

$$U = E(T, V, N) .$$

2. Calculate the thermal equation of state:

$$p = p(T, V, N) .$$

3. Verify for an *adiabatic* change of state ( $S = \text{const}$ ,  $N = \text{const}$ ):

$$pV^{5/3} = \text{const}$$

**Exercise 1.3.4**

Consider two ideal gases in an isolated box of volume  $V$  (particle numbers  $N_1, N_2$ ; particle masses  $m_1, m_2$ ).

1. From the phase volume (partition function)  $\varphi_N(E, V)$  of the total system, derive the conditions for the thermal equilibrium!
2. How do the temperatures  $T_1, T_2$  of the two gases behave in relation to the temperature of the total system?
3. How does one get the total gas pressure  $p$  from the partial pressures  $p_1, p_2$  of the two partial gases?

**Exercise 1.3.5**

Consider, as in Exercise 1.2.6, a system of  $N$  noninteracting particles each of mass  $m$ , which move within the  $xy$ -plane in the potential

$$V(x, y) = \begin{cases} 0, & \text{if } 0 \leq x \leq x_0; 0 \leq y \leq y_0, \\ \infty & \text{otherwise} \end{cases} .$$

1. Demonstrate the equivalence of the two representations (1.71) and (1.73) of the entropy for large particle numbers  $N$ :

$$S(E, V, N) = k_B \ln \varphi_N(E, V) ,$$

$$S(E, V, N) = k_B \ln \Gamma_N(E, V) .$$

2. Calculate the temperature  $T$ , and represent the entropy  $S$  and the free energy  $F$  as functions of  $T, V$  and  $N$ . For this purpose choose the quantity  $\alpha^*$ , which is not yet fixed by the definition of the phase volume (1.45), as:

$$\alpha^* = \frac{1}{N!} \quad (\text{see (1.129)}) .$$

3. Determine the chemical potential  $\mu = \mu(E, V, N)$  and compare the result with the thermodynamic relation:

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T, V} = \mu(T, V, N) .$$

**Exercise 1.3.6**

Let a system of  $N$  independent linear harmonic oscillators be given.

1. Calculate the phase volume  $\varphi_N(E)$ .
2. Find the entropy  $S(E, N)$  and calculate the temperature  $T = T(E, N)$ . ( $V$  in this example is **not** an *external* parameter!)

**Exercise 1.3.7**

Let the Hamilton function of an isolated thermodynamic system depend, besides on the canonical variables  $\mathbf{q}$  and  $\mathbf{p}$ , also on the *external* parameters  $z_1, z_2, \dots, z_n$ :

$$H = H(\mathbf{q}, \mathbf{p}; z_1, z_2, \dots, z_n) .$$

Show that for the change  $(dU)_{ad}$  of the internal energy  $U = \langle H \rangle$ , it must be in the case of a *purely adiabatic* change of state:

$$(dU)_{ad} = \sum_{i=1}^n \left\langle \frac{\partial H}{\partial z_i} \right\rangle dz_i .$$

**Exercise 1.3.8**

1. For the system, described in the preceding exercise, calculate the change of the phase volume

$$\varphi(E; z_1, z_2, \dots, z_n) = \alpha \int \cdots \int_{H(\mathbf{q}, \mathbf{p}; z_1, \dots, z_n) \leq E} d^s q d^s p$$

due to a general change of the variables:

$$E \rightarrow E + dE; \quad z_i \rightarrow z_i + dz_i \quad (i = 1, 2, \dots, n) .$$

2. Show that for a *purely adiabatic* change of state ( $dE = (dU)_{ad}$ ) the phase volume remains uninfluenced. One speaks of *adiabatic invariance* of the phase volume.

**Exercise 1.3.9**

Consider a system of  $N$  noninteracting atoms of a gas in the volume  $V$  (cuboid of the edge length  $L$ ). This is described by a micro-canonical ensemble, where, under neglect of the *energy smearing*  $\Delta$ , it can be assumed for the density distribution function

$$\rho(\mathbf{q}, \mathbf{p}) \sim \delta[(p_1^2 + p_2^2 + \dots + p_{3N}^2) - 2mE] \quad \text{if all } |q_i| < \frac{L}{2} .$$

1. Show that the probability that a given particle has a velocity component in the interval  $(v_1, v_1 + dv_1)$  is given by *Maxwell's velocity distribution*

$$w(v_1)dv_1 = C \exp\left(-\frac{mv_1^2}{2k_B T}\right) dv_1$$

( $C =$  normalization constant).

2. How does the probability distribution read for the magnitude of the velocity  $v$  of a particle?



3. Which is the most probable magnitude of velocity?
4. Calculate  $\langle \mathbf{v} \rangle$ ,  $\langle v \rangle$  and  $\sqrt{\langle \mathbf{v}^2 \rangle}$ .

**Exercise 1.3.10**

The functions  $f(E) = E^N$  with  $N = \mathcal{O}(10^{23})$  and  $\ln f(E)$  are to be expanded around  $E = E_0$  in a Taylor series. Which conditions must be fulfilled, in order that the term of the first order is very much smaller than that of the zeroth order? For which of the two functions is thus a Taylor series more reasonable?

**Exercise 1.3.11**

Calculate the density of states  $D_N(E, V)$  of the ideal gas ( $N$  particles in the volume  $V$ ). Use the definition (1.74) of the entropy,

$$S(E, V, N) = k_B \ln D_N(E, V) ,$$

in order to calculate, by means of the density of states, the temperature of the gas. How does this differ from the temperature (1.121), which is calculated by using the phase volume  $\varphi_N(E, V)$ ?

## 1.4 Canonical Ensemble

In the *micro-canonical ensemble* the selecting point of view for the systems, which belong to this statistical ensemble, is that they have, except for a small *indeterminacy*  $\Delta$ , all the same energy:

**micro-canonical ensemble**

$$E \approx \text{const} , \quad V = \text{const} , \quad N = \text{const} .$$

This ensemble is thus suitable for the description of an isolated or quasi-isolated system. From the given quantities  $E$ ,  $V$  and  $N$  the entropy and the basic relation of Thermodynamics can be derived.

Frequently, however, the (experimental) starting situation is different, e.g., when the considered system is in thermal contact with a *heat bath*. *Heat bath* is to be understood here in the same manner as in Thermodynamics (subsection 1.1, Vol. 5), namely as a very much larger system, whose energy content practically will not change by the contact with our reference system, and by the therewith caused energy fluctuations. In particular, for the reference system, it defines a constant temperature. The corresponding statistical ensemble is called

**canonical ensemble**

$$T = \text{const} , \quad V = \text{const} , \quad N = \text{const} .$$

The canonical ensemble is characterized, as the micro-canonical ensemble, by a certain *density distribution function*  $\rho(\mathbf{q}, \mathbf{p})$ . To find this function and to motivate

it will be the first point of program of this section. The second point will consist in the effort to demonstrate the *statistical equivalence* of the micro-canonical and the canonical ensembles. The latter is indispensable, since the two ensembles actually correspond to physically completely different starting situations.—A third important *statistical ensemble*, namely the so-called *grand-canonical ensemble*, will be discussed in Sect. 1.5.

### 1.4.1 Partition Function

We choose as our reference system  $\Sigma_1$  a small, but nevertheless *macroscopic* part of a very large isolated system, for which a micro-canonical ensemble can be defined

$$E < H(\mathbf{q}, \mathbf{p}) < E + \Delta .$$

It shall be in its thermal equilibrium. That means (Sect. 1.3.2) that at each point of this *super system* the same temperature  $T$  has been established, thus in particular also in  $\Sigma_1$ . In the following we are exclusively interested in the properties of  $\Sigma_1$ , which is in *thermal contact* with the very much larger complementary partial system  $\Sigma_2$  (Fig. 1.11). It can therefore exchange energy, but **without** particle or volume fluctuations. A corresponding situation we have already discussed once, namely in connection with the proof of the additivity of the entropy, in Sect. 1.3.2. Now, however, the systems  $\Sigma_1$  and  $\Sigma_2$ , which come into question, shall be of very different orders of magnitude.

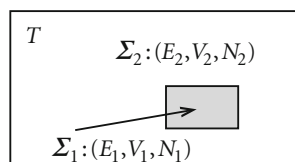
The *thermal contact* must of course be managed by interactions between  $\Sigma_1$  and  $\Sigma_2$ . As exemplified in connection with the reasoning of (1.82), these interactions can be assumed, however, as *asymptotically small*, since the time required to reach the equilibrium does not actually matter, so that to a good approximation holds:

$$H(\mathbf{q}, \mathbf{p}) = H(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) \approx H_1(\mathbf{q}_1, \mathbf{p}_1) + H_2(\mathbf{q}_2, \mathbf{p}_2) . \quad (1.131)$$

$H_1$  and  $H_2$  are the Hamilton functions of  $\Sigma_1$  and  $\Sigma_2$ , respectively. Since the *super system* is isolated, the energies  $E_1, E_2$  of the partial systems are restricted by

$$E < E_1 + E_2 < E + \Delta ,$$

**Fig. 1.11** Small system  $\Sigma_1$  within the heat bath of an isolated super system  $\Sigma_2$ . Schematic representation of the interpretation of the canonical ensemble



which, however, can be fulfilled in a manifold manner. The equilibrium state  $(\widehat{E}_1, \widehat{E}_2)$  is, as discussed in detail in Sects. 1.3.1 and 1.3.2, marked by the maximal number of possibilities of realization.

We now want to build a statistical ensemble consisting of systems which are identical to  $\Sigma_1$ , and have to derive, for this purpose, the corresponding **density distribution function**. According to (1.25) this function has the meaning of a probability density, which we will exploit for its determination. Let  $\bar{\rho}(\mathbf{q}, \mathbf{p})$  be the density distribution function of the micro-canonical ensemble of the *super system*. Then one can interpret

$$\bar{\rho}(\mathbf{q}, \mathbf{p}) = \bar{\rho}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2)$$

as the probability density to find the partial system  $\Sigma_1$  in the phase  $\pi_1 = (\mathbf{q}_1, \mathbf{p}_1)$  and the complementary partial system  $\Sigma_2$  in the phase  $\pi_2 = (\mathbf{q}_2, \mathbf{p}_2)$ . By this one gets the special probability density for  $\Sigma_1$  by *integrating* over all the  $\Sigma_2$ -possibilities:

$$\begin{aligned} \rho_1(\mathbf{q}_1, \mathbf{p}_1) &= \int \cdots \int d^{3N_2} q_2 d^{3N_2} p_2 \bar{\rho}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{p}_1, \mathbf{p}_2) \\ &= \frac{\alpha}{\Gamma_N(E, V)} \int \cdots \int d^{3N_2} q_2 d^{3N_2} p_2 \Theta(H(\mathbf{q}, \mathbf{p}) - E) \Theta(E + \Delta - H(\mathbf{q}, \mathbf{p})) . \end{aligned}$$

In the second step we have inserted (1.43) and (1.47) for the micro-canonical distribution  $\bar{\rho}$  of the *super system*.  $\Theta(x)$  is the *step function*:

$$\Theta(x) = \begin{cases} 1, & \text{if } x > 0, \\ 0, & \text{if } x < 0. \end{cases} \quad (1.132)$$

When we take  $H_1(\mathbf{q}_1, \mathbf{p}_1) = E_1$ , then it can further be reformulated:

$$\begin{aligned} \rho_1(\mathbf{q}_1, \mathbf{p}_1) &= \frac{\alpha}{\Gamma_N(E, V)} \int \cdots \int d^{3N_2} q_2 d^{3N_2} p_2 \\ &\quad \cdot \Theta[H_2(\mathbf{q}_2, \mathbf{p}_2) - (E - E_1)] \Theta(E - E_1 + \Delta - H_2(\mathbf{q}_2, \mathbf{p}_2)) \\ &= \frac{\Gamma_{N_2}(E - E_1, V_2)}{\Gamma_N(E, V)} . \end{aligned} \quad (1.133)$$

The reservoir  $\Sigma_2$  can in principle be made arbitrarily large ( $N_2 \gg N_1$ ). Furthermore, we know, due to previous considerations, that the distribution of the configurations  $\Gamma_{N_1}(E_1, V_1) \Gamma_{N_2}(E - E_1, V_2)$  will exhibit an extremely sharp maximum at the *most probable configuration*  $(\widehat{E}_1, E - \widehat{E}_1)$ , so that in reality only energies  $E_1 \approx \widehat{E}_1$  are of interest. In each case it will hold for the *relevant energies*  $E_1$

$$E_1 \approx \widehat{E}_1 \ll E - \widehat{E}_1 \approx E .$$

For the logarithm of the phase volume  $\Gamma_{N_2}(E - E_1, V_2)$  in (1.133) a Taylor expansion therefore offers itself:

$$\begin{aligned} k_B \ln \Gamma_{N_2}(E - E_1, V_2) &= S_2(E_2 = E - E_1, V_2, N_2) \\ &= S_2(E, V_2, N_2) - E_1 \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (E_2 = E) + \mathcal{O}(E_1^2) . \end{aligned}$$

The first summand is, with respect to  $\Sigma_1$ , a constant ( $S_0$ ). For the second summand we write with (1.89):

$$\left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (E_2 = E) = \frac{1}{T} .$$

Actually, on the right-hand side, there should appear the temperature, which the system  $\Sigma_2$  would take at the energy  $E$ . Because of  $\widehat{E}_2 = E - \widehat{E}_1 \approx E$  the deviation from the temperature  $T$  of the heat bath is, however, negligibly small:

$$\ln \Gamma_{N_2}(E - E_1, V_2) \approx \frac{S_0}{k_B} - \frac{E_1}{k_B T} .$$

This means, when we still use the abbreviation (1.90) ( $\beta = 1/k_B T$ ), usual in Statistical Physics:

$$\Gamma_{N_2}(E - E_1, V_2) \approx e^{S_0/k_B} e^{-\beta E_1} = e^{S_0/k_B} e^{-\beta H_1(\mathbf{q}_1, \mathbf{p}_1)} .$$

According to (1.133), we have therewith found for the density distribution function:

$$\rho_1(\mathbf{q}_1, \mathbf{p}_1) \sim \exp(-\beta H_1(\mathbf{q}_1, \mathbf{p}_1)) .$$

The index 1 can now be left out because it only served to distinguish from  $\Sigma_2$ . As a heat bath it fixes the temperature  $T$ , but otherwise it no longer influences the further considerations. The **canonical ensemble**, as a group of congeneric systems in thermal contact with a *heat bath* of the temperature  $T$ , is thus described by the following distribution function

$$\rho(\mathbf{q}, \mathbf{p}) = \frac{\exp(-\beta H(\mathbf{q}, \mathbf{p}))}{1/h^{3N} N! \int \dots \int d^{3N} q d^{3N} p \exp(-\beta H(\mathbf{q}, \mathbf{p}))} , \quad (1.134)$$

which, according to

$$\frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p \rho(\mathbf{q}, \mathbf{p}) = 1 ,$$

is normalized to one. The characteristic pre-factor is justified in the same manner as commented on in connection with (1.129). In contrast to the micro-canonical distribution function (1.43), it is here a function, which is continuous function in the entire phase space, a fact that can lead to substantial mathematical advantages.

The density distribution function  $\rho(\mathbf{q}, \mathbf{p})$  of the canonical ensemble depends on  $\mathbf{q}$  and  $\mathbf{p}$  only via the Hamilton function. It is therefore, according to (1.41), a distribution function of a **stationary** ensemble. With (1.26) the average of a phase-space observable  $F(\mathbf{q}, \mathbf{p})$  is now given by

$$\langle F \rangle = \frac{\int \dots \int d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})} F(\mathbf{q}, \mathbf{p})}{\int \dots \int d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})}}, \quad (1.135)$$

where a possible temperature-dependence is brought into play by  $\beta$ .

The central role, which in the micro-canonical ensemble is attached to the phase volume  $\Gamma_N(E, V)$  ((1.47), (1.71), ...), is adopted in the canonical ensemble by the **partition function**  $Z_N(T, V)$ .

$$Z_N(T, V) = \frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})}. \quad (1.136)$$

With respect to applications, this is probably the most important formula of the whole Classical Statistical Physics. We will demonstrate in the next subsection that all the relevant quantities of Thermodynamics can be directly derived from  $Z_N(T, V)$ . As soon as  $Z_N(T, V)$  is determined, the problem can already be considered as practically solved. The pre-factor can again be motivated as that of the phase volume (1.129) in the micro-canonical ensemble.

If the Hamilton function of the  $N$ -particle system has the *usual form*

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \widehat{V}(\mathbf{q}),$$

then the integrations over the momenta in (1.136) can directly be done. When we denote by  $p_1, p_2, \dots, p_{3N}$  the Cartesian components of the  $N$ -particle-momentum vectors  $\mathbf{p}_i$ , it follows:

$$\begin{aligned} & \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} dp_1 \dots dp_{3N} \exp \left[ -\frac{\beta}{2m} (p_1^2 + \dots + p_{3N}^2) \right] = \\ & = \left[ \int_{-\infty}^{+\infty} dp_1 \exp \left( -\frac{\beta}{2m} p_1^2 \right) \right]^{3N} = \left[ \sqrt{\frac{2m\pi}{\beta}} \right]^{3N} = (2\pi m k_B T)^{3N/2}. \end{aligned}$$

With the so-called  
**thermal de Broglie wavelength**

$$\lambda(T) = \frac{h}{\sqrt{2\pi mk_{\text{B}}T}}, \quad (1.137)$$

which has to be distinguished from the quantum-mechanical de Broglie wavelength ((2.14), Vol. 6), the partition function reads:

$$Z_N(T, V) = \frac{1}{\lambda^{3N}(T)N!} \int_V d^{3N}q e^{-\beta\widehat{V}(\mathbf{q})}. \quad (1.138)$$

Because of its fundamental meaning we will present also a third possibility of representation for the partition function, which uses the *density of states*  $D_N(E, V)$  defined in (1.50):

$$D_N(E, V)dE = \frac{1}{h^{3N}N!} \int_{E < H(\mathbf{q}, \mathbf{p}) < E + dE} \cdots \int d^{3N}q d^{3N}p. \quad (1.139)$$

The comparison with (1.136) leads to:

$$Z_N(T, V) = \int dE D_N(E, V) e^{-\beta E}. \quad (1.140)$$

$D_N(E, V)dE$  corresponds to the number of states in the energy interval  $(E; E + dE)$ . The full integrand in (1.140) therewith represents the number of states of this energy interval, which are at the temperature  $T$  **occupied** by the canonical ensemble.

### 1.4.2 Free Energy

In the micro-canonical ensemble the internal energy  $U$  is equated with the energy variable  $E$ . Strictly speaking, however, it is an ensemble average of the Hamilton function (1.104):

$$U = \langle H \rangle.$$

This definition holds very generally. It leads with (1.135) and (1.136) to the following connection with the partition function:

$$U = U(T, V, N) = -\frac{\partial}{\partial\beta} \ln Z_N(T, V) = k_{\text{B}}T^2 \frac{\partial}{\partial T} \ln Z_N(T, V). \quad (1.141)$$

It is, however, by no means clear from the beginning that the internal energy, calculated by the canonical ensemble, has anything to do with the energy, which is *micro-canonically* interpreted as *internal energy*. The equivalence of (1.141) and (1.104) is not at all trivial, because the physical starting situations of the two ensembles are simply too different. While, namely, in the micro-canonical ensemble all ensemble systems have the same energy, except for a small indeterminacy  $\Delta$ , so that  $\langle H \rangle \approx H \approx E$ , in the canonical ensemble **all** energies appear, so that  $\langle H \rangle$  is a *real* average. Only if the distribution of the system energies exhibit at  $\langle H \rangle$  a pronounced maximum, can we therefore expect that the two descriptions (canonical, micro-canonical) yield equivalent results. We will show that this is indeed the case, however, only for the *asymptotically large*, macroscopic system.

As discussed in connection with (1.99), the definition of the pressure is uniquely preset by Classical Mechanics. Using (1.101) one finds a rather simple connection with the partition function:

$$p = -\left\langle \frac{\partial H}{\partial V} \right\rangle = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N(T, V) . \quad (1.142)$$

The micro-canonical ensemble is determined by the variables  $U = E$ ,  $V$ , and  $N$ . These are, as we know from Thermodynamics ((3.9), Vol. 5), the *natural variables* of the thermodynamic potential *entropy*  $S = S(U, V, N)$ , which thus plays the central role in the micro-canonical ensemble.

The internal energy  $U$  (1.141), represented by the *canonical* variables  $T$ ,  $V$ ,  $N$ , is **not** a thermodynamical potential. These are in fact the *natural variables* of the **free energy**  $F(T, V, N)$ , which is therefore of similar importance for the canonical ensemble as the entropy is for the micro-canonical ensemble. In order to show, how the free energy arises from the partition function, we at first recall its thermodynamic definition ((3.10), Vol. 5):

$$F(T, V, N) = U(T, V, N) - TS(T, V, N) . \quad (1.143)$$

We use the total differential

$$dF = -SdT - pdV \quad (N = \text{const})$$

for the investigation of

$$d(-\beta F) = \frac{F}{k_B T^2} dT + \frac{1}{k_B T} (SdT + pdV) = \frac{1}{k_B T} \left[ \frac{U}{T} dT + pdV \right] .$$

From this we get after insertion of (1.141) for  $U$  and (1.142) for  $p$ :

$$d(-\beta F) = \left( \frac{\partial \ln Z_N(T, V)}{\partial T} \right)_{V, N} dT + \left( \frac{\partial \ln Z_N(T, V)}{\partial V} \right)_{T, N} dV .$$

Except for an unimportant constant one finds therewith the following important connection between the free energy and the partition function:

$$F(T, V, N) = -k_B T \ln Z_N(T, V) . \quad (1.144)$$

Sometimes one also writes:

$$Z_N(T, V) = \exp(-\beta F(T, V, N)) .$$

A further important requirement for the free energy concerns its **extensivity**. This can be relatively easily shown for (1.144). For two partial systems in thermal equilibrium, the interaction between which can be neglected in the sense of (1.131), the common partition function can be written as:

$$Z_N(T, V) = \frac{1}{h^{3N} N_1! N_2!} \int \dots \int d^{3N} q d^{3N} p e^{-\beta(H_1 + H_2)} \quad (N = N_1 + N_2) .$$

The pre-factor is justified as in (1.130). The interchange of a particle from the one partial system to the other partial system yields, though, a **new** state. Therefore the denominator is  $N_1! N_2!$  instead of  $N!$ :

$$\begin{aligned} Z_N(T, V) &= \frac{1}{h^{3N_1} N_1!} \int \dots \int d^{3N_1} q d^{3N_1} p e^{-\beta H_1(\mathbf{q}_1, \mathbf{p}_1)} \\ &\quad \cdot \frac{1}{h^{3N_2} N_2!} \int \dots \int d^{3N_2} q d^{3N_2} p e^{-\beta H_2(\mathbf{q}_2, \mathbf{p}_2)} \\ &= Z_{N_1}(T, V_1) Z_{N_2}(T, V_2) . \end{aligned}$$

Therewith, according to (1.144), the extensivity of the *statistical* free energy is evident:

$$F(T, V, N) = F_1(T, V_1, N_1) + F_2(T, V_2, N_2) . \quad (1.145)$$

The still remaining, distinctly more difficult task consists in proving the equivalence of the statements of Statistical Physics, which are, on the one hand, derivable with the micro-canonical ensemble, and on the other hand, with the canonical ensemble. We have formulated the problem for the *internal energy* already in connection with (1.141). A further important example is the **entropy**, which, in the concept of the canonical ensemble, can be derived from the partition function:

$$S(T, V, N) = - \left( \frac{\partial F}{\partial T} \right)_{V, N} = k_B \left[ \frac{\partial}{\partial T} (T \ln Z_N(T, V)) \right]_{V, N} . \quad (1.146)$$

We will have to demonstrate in Sect. 1.4.4 that the so determined entropy is consistent with the micro-canonical definition (1.71) and (1.73), respectively.



With (1.141), (1.142), (1.144), and (1.146) all thermodynamic potentials can be ultimately traced back to the partition function. The solution of a physical problem within the framework of the canonical ensemble therefore starts always with the attempt to determine the partition function  $Z_N(T, V)$ , with the Hamilton function  $H(\mathbf{q}, \mathbf{p})$  and the definition equation (1.136). As soon as this is achieved, the problem is practically already solved, because the thermodynamic potentials can be deduced from  $Z_N(T, V)$  in a rather simple manner. That is what was meant above, when we denoted the partition function as the probably most important quantity of the whole Statistical Physics.

### 1.4.3 Fluctuations

In Thermodynamics (see (4.33), Vol. 5) we had denoted as *thermal stability condition* the fact that the heat capacity  $C_V$  can not become negative:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V \geq 0. \quad (1.147)$$

This relation is surely plausible (*isochoric heat supply raises the temperature!*), but could not strictly be proven in the framework of Thermodynamics. Statistical Physics verifies (1.147) as a result of an energy fluctuation formula, which at this stage, though, helps us, above all, to recognize the equivalence of micro-canonical and canonical ensembles:

$$\begin{aligned} C_V &= \left( \frac{\partial U}{\partial T} \right)_{V,N} = -\frac{\partial}{\partial T} \frac{\partial}{\partial \beta} \ln Z_N(T, V) \\ &= k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z_N = k_B \beta^2 \frac{\partial}{\partial \beta} \left( \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta} \right) \\ &= k_B \beta^2 \left[ \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \frac{1}{Z_N^2} \left( \frac{\partial Z_N}{\partial \beta} \right)^2 \right]. \end{aligned}$$

Insertion of (1.135) and (1.136),

$$C_V = k_B \beta^2 (\langle H^2 \rangle - \langle H \rangle^2) = k_B \beta^2 \langle (H - \langle H \rangle)^2 \rangle \geq 0, \quad (1.148)$$

proves the *thermal stability* (1.147).—We can, however, get still further information from this important formula. Other than in the micro-canonical ensemble, the energies of the systems of the canonical ensemble are distributed around the average value  $U = \langle H \rangle$ . There appear in principle **all** energies. As already commented on in connection with (1.141), an equivalence of the statistical descriptions, given on the one hand by the micro-canonical ensemble and, on the other, by the canonical

ensemble, is to expect only for the case that the distribution of the *canonical* system energies has a pronounced maximum at the mean value  $\langle H \rangle$ . That can easily be checked with the *fluctuation formula* (1.148). The *relative mean square deviation* of a system energy from the mean value  $\langle H \rangle$  is given in a canonical ensemble by

$$\overline{(\Delta E)} = \frac{\sqrt{\langle H^2 \rangle - \langle H \rangle^2}}{\langle H \rangle} = \frac{\sqrt{C_V k_B T^2}}{U}. \quad (1.149)$$

Since one can always assume

$$C_V \propto N; \quad U \propto N,$$

(e.g., ideal gas (1.121):  $U = (3/2)Nk_B T$ ,  $C_V = (3/2)Nk_B$ ), (1.149) means a relative width of the energy distribution around  $\langle H \rangle$  of

$$\overline{(\Delta E)} \sim \frac{1}{\sqrt{N}} \xrightarrow{N \rightarrow \infty} 0,$$

which for macroscopic systems ( $N \approx 10^{22}$ ) becomes extraordinarily narrow. It is indeed true that in the canonical ensemble all energies appear, but, on the other hand, at a given temperature  $T$  *almost all* systems have obviously an energy, which deviates only non-essentially from  $U = \langle H \rangle$ . For *asymptotically large* systems the internal energy  $U$  must be considered as practically sharp. That is the decisive fact with respect to the statistical equivalence of micro-canonical and canonical ensemble. In the next subsection we develop the analogous considerations for the entropy.

#### 1.4.4 Equivalence of Micro-Canonical and Canonical Ensemble

The micro-canonical and the canonical ensemble are based on completely different starting situations. It can therefore not at all be considered as a matter of course that for the macroscopic systems, which we are here interested in, they come to consistent physical statements. We will convince ourselves in this subsection that this is indeed the case, because the whole concept of the Statistical Physics stands or falls therewith.

In both ensembles there are prescriptions (definitions or derivations) for the fundamental quantities *temperature* and *entropy*. To demonstrate the physical equivalence of micro-canonical and canonical descriptions we have therefore, above all, to prove that *entropy* and *temperature* do really mean exactly the same in both ensembles. According to our pre-considerations in the last subsection concerning the internal energy, we can consider the two ensembles as equivalent if *temperature*

and *entropy* of the canonical ensemble agree with the corresponding quantities of a micro-canonical ensemble with the energy  $E = U = \langle H \rangle$ :

$$\begin{aligned} T^{mce}(E = U = \langle H \rangle) &\longleftrightarrow T, \\ S^{mce}(E = U = \langle H \rangle, V, N) &\longleftrightarrow S^{ce}(T, V, N). \end{aligned} \quad (1.150)$$

Thereby it is to be taken into consideration that for the canonical ensemble the temperature  $T$  and for the micro-canonical ensemble the energy  $E$  are fixedly pre-given quantities. First condition for the proof of equivalence is thus that the energies of the systems, which are **not** fixedly pre-given in the canonical ensemble, are sharply concentrated around the mean value  $U = \langle H \rangle$ , so that *almost all* ensemble-systems have an energy, which differs only non-essentially from  $U$ . Then it is allowed to treat the internal energy  $U$  as a variable which characterizes the full ensemble. That this indeed is the case in the *asymptotically large* system, we have shown in the last subsection. But a sharply concentrated energy distribution means also that the quantity

$$D_N(E, V) e^{-\beta E} dE,$$

which is proportional to the probability that the considered system has an energy from the interval  $(E; E + dE)$ , possesses a sharp maximum at  $E = U = \langle H \rangle$ . That holds then of course also for the logarithm of this expression. We investigate the corresponding extreme-value condition:

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{\partial}{\partial E} \ln(D_N(E, V) e^{-\beta E}) \Big|_{E=U} \\ &= \frac{\partial}{\partial E} (\ln D_N(E, V) - \beta E) \Big|_{E=U} \\ &= -\beta + \frac{1}{k_B} \left( \frac{\partial}{\partial E} S^{mce}(E, V, N) \right)_{V, N} (E = U). \end{aligned}$$

In the last step we have inserted the definition (1.74) of the *micro-canonical* entropy. The extreme-value condition leads with (1.89) eventually to:

$$\left( \frac{1}{T^{mce}(E)} \right) (E = U) = \left( \frac{\partial}{\partial E} S^{mce}(E, V, N) \right)_{V, N} (E = U) = \frac{1}{T}. \quad (1.151)$$

This relation represents one of the two conditions of equivalence (1.150). The fixedly pre-given temperature  $T$  of the canonical ensemble corresponds exactly to the temperature, which belongs in the micro-canonical ensemble to the energy  $E = U = \langle H \rangle$ , i.e., to the energy, which *almost all* systems of the canonical ensemble possess.

We attach a Taylor expansion to the just investigated term around its maximum at  $E = U$ :

$$\begin{aligned} \ln(D_N(E, V)e^{-\beta E}) &= \ln D_N(E, V) - \beta E \\ &= \ln(D_N(U, V)e^{-\beta U}) + \frac{1}{2}(E-U)^2 \left( \frac{\partial^2}{\partial E^2} \ln D_N(E, V) \right)_{V,N} (E=U) + \dots \end{aligned}$$

The second summand can be evaluated as follows:

$$\begin{aligned} \left( \frac{\partial^2}{\partial E^2} \ln D_N(E, V) \right)_{V,N} (E=U) &= \frac{1}{k_B} \left( \frac{\partial}{\partial E} \frac{1}{T^{mce}(E)} \right)_{N,V} (E=U) \\ &= \frac{-1}{k_B(T^{mce}(U))^2} \left( \frac{\partial T^{mce}(E)}{\partial E} \right)_{V,N} (E=U). \end{aligned}$$

Because of (1.151) one can identify  $T^{mce}(U)$  with  $T$ :

$$\left( \frac{\partial}{\partial E} T^{mce}(E) \right)_{V,N} (E=U) \longrightarrow \left( \frac{\partial T}{\partial U} \right)_{V,N} = \frac{1}{C_V}.$$

It remains therewith for the above expansion:

$$\ln(D_N(E, V)e^{-\beta E}) = \ln(D_N(U, V)e^{-\beta U}) - \frac{1}{2}(E-U)^2 \frac{1}{k_B T^2 C_V} + \dots$$

The so estimated expression ,

$$D_N(E, V)e^{-\beta E} \approx D_N(U, V) \exp(-\beta U) \exp \left[ -\frac{k_B \beta^2}{2C_V} (E-U)^2 \right],$$

represents just the integrand of the partition function (1.140):

$$Z_N(T, V) \approx D_N(U, V) \exp(-\beta U) \int dE \exp \left[ -\frac{k_B \beta^2}{2C_V} (E-U)^2 \right].$$

On the right-hand side there appears a standard integral when we fix the integration limits at  $\pm\infty$ , which is always allowed because of the quickly decreasing exponential function:

$$Z_N(T, V) \approx D_N(U, V) e^{-\beta U} \sqrt{\frac{2\pi C_V}{k_B \beta^2}} \quad (U = \langle H \rangle). \quad (1.152)$$

This very useful formula leads us to an estimation for the free energy (1.144) of a macroscopic system:

$$F(T, V, N) = -\frac{1}{\beta} \ln Z_N(T, V) = U - \frac{1}{\beta} \ln D_N(U, V) + \frac{1}{2} \ln \frac{2\pi C_V}{k_B \beta^2}.$$

For the *asymptotically large* system the last summand ( $\ln C_V \sim \ln N$ ) can be neglected in comparison to the two others ( $U \sim N$ ,  $\ln D_N \sim N$ ). The free energy of the canonical ensemble,

$$F(T, V, N) = U(T, V, N) - TS^{ce}(T, V, N) ,$$

can therefore also be written as follows:

$$F(T, V, N) = U - TS^{mce}(E = U, V, N) . \quad (1.153)$$

We have thereby exploited the definition (1.74) for  $S^{mce}$ . The comparison of the last two equations reveals that for the macroscopic system the *entropy* of the canonical ensemble agrees with that of the micro-canonical ensemble, if the latter is defined to the energy  $E = U$ , where  $U = \langle H \rangle$  represents the extremely sharp maximum of the *canonical* energy distribution. The second of the two conditions of equivalence (1.150) is also therewith verified. However, it cannot be stressed often enough that this equivalence holds only for *asymptotically large* systems, because the neglect of  $\ln N$ -terms with respect to terms, which are proportional to the particle number  $N$ , is of course only *asymptotically correct*.

Hence, although the two ensembles correspond to two completely different starting situations, nevertheless for macroscopic systems they come to consistent statements. For the treatment of a concrete physical problem we can choose, according to expedience, the one or the other representation. In most cases the one that is *mathematically better tractable* is the canonical ensemble. The equivalence of the two ensembles obviously depends decisively on the fact, investigated in Sect. 1.4.3, that the distribution of the system energies of a canonical ensemble exhibits an extraordinarily sharp maximum at the energy  $E = \langle H \rangle = U$  so that *almost all* members of the ensemble have this energy. Hence, although in principle all energies appear in the canonical ensemble, nevertheless there is *de facto* a unique relation between the fixedly pre-given temperature  $T$  and the energy. From this reason, the canonical ensemble is *de facto* equivalent to a micro-canonical ensemble with the energy  $E = \langle H \rangle = U$ .

## 1.4.5 Exercises

### Exercise 1.4.1

Determine the classical canonical partition function of the linear harmonic oscillator!

### Exercise 1.4.2

Consider a classical ideal gas in an infinitely high cylindrical container. In the direction of the cylinder axis a homogeneous gravitational field acts. Calculate by

means of the canonical ensemble

1. the average kinetic energy of a particle of the gas,
2. the average potential energy of a particle of the gas.

### Exercise 1.4.3

A system of  $N$  noninteracting two-atomic molecules are encased at the temperature  $T$  in the volume  $V$ . The Hamilton function of a single molecule reads:

$$H_0(\mathbf{p}_1, \mathbf{p}_2; \mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2m}(\mathbf{p}_1^2 + \mathbf{p}_2^2) + \frac{1}{2}\alpha |\mathbf{r}_1 - \mathbf{r}_2|^2 \quad (\alpha > 0) .$$

Calculate

1. the classical canonical partition function,
2. the equation of state  $f(p, T, V, N) = 0$ ,
3. the heat capacity  $C_V$ ,
4. the mean square diameter of the molecule  $\langle \mathbf{r}^2 \rangle = \langle |\mathbf{r}_1 - \mathbf{r}_2|^2 \rangle$ .

### Exercise 1.4.4

Given is a classical ideal gas of  $N$  particles of the same kind in the volume  $V$ .

1. Calculate with the canonical ensemble the free energy  $F(T, V, N)$ .
2. Determine with  $F(T, V, N)$  the entropy  $S(T, V, N)$ , and compare the result with the *micro-canonically* derived Sackur-Tetrode equation (1.124).
3. Verify the thermal equation of state of the ideal gas.

### Exercise 1.4.5

Consider a system of  $N$  particles of the same kind in the volume  $V$ , which interact with each other by a repulsive pair potential of the form

$$\widehat{V}(\mathbf{r}_i, \mathbf{r}_j) = \frac{\alpha}{|\mathbf{r}_i - \mathbf{r}_j|^n}, \quad \alpha > 0, \quad n > 3 .$$

1. With the canonical ensemble calculate the partition function, except for the position integrals.
2. With the ansatz

$$\exp\left(-\beta \widehat{V}(|\mathbf{r}_i - \mathbf{r}_j|)\right) = 1 + f(|\mathbf{r}_i - \mathbf{r}_j|)$$

decompose the integrand of the position integral into a *reasonable* formation of products of the functions  $f(|\mathbf{r}_i - \mathbf{r}_j|)$ . Consider for this purpose how large the function values  $f(|\mathbf{r}|)$  can become.

3. Show that the canonical partition function can be written, for large  $N$  and for large  $V$ , as

$$Z_N(T, V) = Z_0(T) \left( 1 + \frac{N^2}{V} a_1(T) + \frac{N^4}{V^2} a_2(T) + \dots \right) ,$$

where  $Z_0$  is the partition function of the *free* system, and  $a_1(T)$  and  $a_2(T)$  are given by

$$a_1(T) = \frac{1}{2} \int d^3r f(|\mathbf{r}|),$$

$$a_2(T) = (a_1(T))^2.$$

4. Determine for the given pair potential the expansion coefficients  $a_1(T)$  and  $a_2(T)$ .

#### Exercise 1.4.6

A thermodynamic system consists of  $N$  atoms in the volume  $V$ , each of which carries a magnetic moment  $\boldsymbol{\mu}_i$  ( $|\boldsymbol{\mu}_i| = \mu$  for  $i = 1, 2, \dots, N$ ). The Hamilton function is composed of two parts

$$H(\mathbf{q}, \mathbf{p}) = H_0(\mathbf{q}, \mathbf{p}) + H_1(\mathbf{q}, \mathbf{p}).$$

$H_0(\mathbf{q}, \mathbf{p})$  describes the system in the absence of a magnetic field, while  $H_1(\mathbf{q}, \mathbf{p})$  comprises the influence of the homogeneous field  $\mathbf{B} = B\mathbf{e}_z$ . Let  $H_0$  be independent of the angles  $\varphi_i, \vartheta_i$  between the field  $\mathbf{B}$  and the moment  $\boldsymbol{\mu}_i$ .

1. How does the field term  $H_1$  read?
2. Calculate the canonical partition function.
3. Determine the temperature-dependence and the field-dependence of the average total magnetic moment:

$$\mathbf{m} = \left\langle \sum_{i=1}^N \boldsymbol{\mu}_i \right\rangle.$$

4. Discuss the total magnetic moment for the two limiting cases  $\beta\mu B \gg 1$  and  $\beta\mu B \ll 1$  (*Classical Langevin paramagnetism*).

#### Exercise 1.4.7

Consider a system of  $N$  particles in the volume  $V$ . Prove by means of the canonical ensemble the *generalized equipartition theorem* (1.110):

$$\left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle = \delta_{ij} k_B T$$

$$\pi_{i,j} \in \{q_1, \dots, q_{3N}, p_1, \dots, p_{3N}\}.$$

$\pi_i, \pi_j$  denote Cartesian components of one of the particle momenta or particle positions.

**Exercise 1.4.8**

$N$  classical particles of the mass  $m$  are moving, without any mutual interactions, with the potential energy

$$\widehat{V}(\mathbf{q}) = \alpha \sum_{i=1}^N (q_{ix}^4 + q_{iy}^4 + q_{iz}^4), \quad \alpha > 0$$

in the volume  $V$ . Calculate the temperature-dependencies of the internal energy  $U$  and the entropy  $S$ !

**Exercise 1.4.9**

Think of a system of  $N$  charged particles, for instance, a solid consisting of ions and electrons. Let this system be in a magnetic field  $\mathbf{B}$ . Its *magnetic moment*  $\mathbf{m}$  is calculated with the Hamilton function  $H$  according to

$$\mathbf{m} = -\nabla_{\mathbf{B}} H .$$

$\nabla_{\mathbf{B}}$  means the gradient with respect to the external magnetic field  $\mathbf{B}$ .

1. Express the average magnetic moment  $\langle \mathbf{m} \rangle$  by the canonical partition function  $Z_N$ . Find  $Z_N$  for the  $N$ -particle system (mass  $m_i$ , charge  $\bar{q}_i$ ,  $i = 1, 2, \dots, N$ ) in the magnetic field  $\mathbf{B}$ .
2. Show that in any case, even for  $\mathbf{B} \neq 0$ :

$$\langle \mathbf{m} \rangle \equiv 0$$

(*Bohr-van Leeuwen theorem*).

**Exercise 1.4.10**

$N$  noninteracting particles of a gas are at the temperature  $T$  in a volume  $V$ . Justify, by using the canonical ensemble, *Maxwell's velocity distribution* (see also Exercise 1.3.9),

$$w(\mathbf{v})d^3v = \left( \frac{m}{2\pi k_{\text{B}}T} \right)^{3/2} \exp\left( -\frac{m\mathbf{v}^2}{2k_{\text{B}}T} \right) d^3v ,$$

which indicates, with what a probability a particle of the gas has a velocity from the *volume element*  $d^3v$  at  $\mathbf{v}$ .

**Exercise 1.4.11**

In a box of the volume  $V$  there are at the temperature  $T$   $N$  atoms of a gas, all of the same mass  $m$ . The atoms are at first in an *excited state*. With the transition into the ground state they are emitting light, which is observed in  $z$ -direction by a spectrometer. An atom at rest would emit a single sharp line  $E_0$ . Because of the *Doppler effect*, and because of the finite temperature  $T$ , the detector receives an



energy band with an intensity distribution  $I(E)$ . Calculate

1. the average energy  $\langle E \rangle$  of the observed light,
2. the mean square deviation of the energy  $(\Delta E) = \sqrt{\langle (E - \langle E \rangle)^2 \rangle}$  of the observed light,
3. the intensity distribution  $I(E)$ .

#### Exercise 1.4.12

An ideal gas of  $N$  atoms is at the temperature  $T$  in a container (cuboid) of the volume  $V$  ( $V = L_x L_y L_z$ ). In the middle of one of the walls of the container there is a small hole of the area  $f$ . Outside the container there is vacuum.

1. How many atoms leave the container per unit time?
2. After how much time does the pressure drop in the inside to the  $1/e$ -fraction of the pressure value before the hole was opened?
3. How large is the average kinetic energy per particle in the exterior of the container relatively to that in the interior?

#### Exercise 1.4.13

1. An ideal gas of  $N$  atoms in the volume  $V$  is at the temperature  $T$  in an external potential  $\widehat{V}$ :

$$H(\mathbf{q}, \mathbf{p}) = T(\mathbf{p}) + \widehat{V}(\mathbf{q}) \longrightarrow \sum_{i=1}^N \left( \frac{\mathbf{p}_i^2}{2m} + v(\mathbf{r}_i) \right).$$

Calculate the position-dependence of the particle density  $n(\mathbf{r})$  (*barometric equation*). Hint:

$$n(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle; \quad \mathbf{r}_i: \text{position of the } i\text{-th atom.}$$

2. Let  $\widehat{V}$  be especially the gravitational field of the earth. Calculate how the pressure of the gas changes with the distance from the ground.

#### Exercise 1.4.14

A *relativistic* ideal gas consists of  $N$  particles, all with the mass  $m = 0$ , in the volume  $V$ .

1. Calculate the canonical partition function.
2. Calculate the internal energy  $U(T, V, N)$ .
3. Find the thermal equation of state  $p = f(T, V, N)$ .
4. Determine the free energy  $F = F(T, V, N)$  and test  $p = -(\partial F / \partial V)_{T, N}$  with part 3.
5. Give the enthalpy  $H$ .
6. Derive the entropy.
7. Calculate the heat capacities  $C_p, C_V$ .

**Exercise 1.4.15**

Consider a *classical* system of  $N$  particles in the volume  $V$ , described by the Hamilton function

$$H(\mathbf{q}, \mathbf{p}) = H_0(\mathbf{q}, \mathbf{p}) + H_1(\mathbf{q}, \mathbf{p}).$$

Expand the free energy  $F(T, V, N)$  as a functional of  $H_1$  around  $H_1 = 0$  up to quadratic terms in  $H_1$ . Present the result in dependence of the free energy  $F_0$  of the ‘*unperturbed*’ system ( $H_0$ ), and of suitable mean values of powers of  $H_1$ !

**1.5 Grand-Canonical Ensemble**

The *canonical ensemble* from Sect. 1.4 still admits a further generalization, namely to systems, which are subject, besides to energy fluctuations, also to particle fluctuations. A variable particle number can arise in the considered system by an exchange of particles with its *surroundings*, and also by *creation* and *annihilation* of particles of a certain type. One may think of the *magnons* of a ferromagnet, the *phonons* of a crystal lattice, or the *photons* of the electromagnetic radiation.

At first let us recall once more that for the **micro-canonical ensemble** the variables  $E = U$ ,  $V$ , and  $N$  are fixedly pre-given. These are, as we know from Thermodynamics (section 3.1, Vol. 5), the *natural* state variables of the **entropy**  $S(E, V, N)$ , which therefore represents the central thermodynamic function of the micro-canonical ensemble. In the experiment, though, in general, we have to do not with really isolated systems, but rather with those, which are in contact with a heat bath of the temperature  $T$ . The temperature is a relatively *manageable* parameter, i.e., experimentally easily adjustable. This motivates the concept of the **canonical ensemble**, for which the variables  $T$ ,  $V$ , and  $N$  are pre-given. These are the *natural* state variables of the **free energy**  $F(T, V, N)$ , which takes over the central role in the canonical ensemble, which is played in the micro-canonical ensemble by the entropy.—For all the other state quantities, which are not fixedly pre-given in the respective ensemble, Statistical Physics provides only average values.

Now one can naturally argue that also the particle number  $N$  of macroscopic systems may hardly be exactly known. Furthermore, there are physically important cases, as already mentioned above, for which  $N$  changes already with the variation of state variables, as, e.g., the temperature, by the *creation* and the *annihilation*, respectively, of particles. This fact is accounted for by the **grand-canonical ensemble**. Its fixedly pre-given variables are the **temperature**  $T$ , the **volume**  $V$ , and the **chemical potential**  $\mu$ . These are the *natural* state variables of the so-called **grand-canonical potential**  $\Omega(T, V, \mu)$ , which, up to now, we have not yet got to know. It is defined as the difference of free energy  $F$  and free enthalpy  $G$ :

$$\Omega = F - G = -pV . \quad (1.154)$$

When we now insert for  $G$  the *Gibbs-Duhem relation* ((3.35), Vol. 5)  $G = \mu N$  and build the total differential,

$$d\Omega = dF - \mu dN - Nd\mu = -SdT - pdV - Nd\mu, \quad (1.155)$$

then we explicitly recognize the  $(T, V, \mu)$ -dependence of the grand-canonical potential. This replaces in the grand-canonical ensemble the free energy of the canonical ensemble and the entropy of the micro-canonical ensemble, respectively. That will be discussed and worked out in the following subsections.

### 1.5.1 Grand-Canonical Partition Function

We had seen in Sect. 1.4 that all thermodynamic properties, we are interested in, are accessible by simple mathematical operations, as soon as the *canonical partition function*  $Z_N(T, V)$  is known. This function can, in principle, exactly be calculated by means of the Hamilton function  $H(\mathbf{q}, \mathbf{p})$  (1.136). For the grand-canonical ensemble, too, there exists such a central quantity, namely the *grand-canonical partition function*  $\Xi_\mu(T, V)$ . Its line of derivation is very similar to that of  $Z_N(T, V)$  in Sect. 1.4.1.

As in the case of a canonical ensemble, we investigate a reference system  $\Sigma_1$ , which shall be a small, but nevertheless *macroscopic* part of a very large **isolated super system**  $\Sigma$ . In difference to Sect. 1.4.1,  $\Sigma_1(E_1, V_1, N_1)$  shall be able to exchange with the surrounding *complementary system*  $\Sigma_2(E_2, V_2, N_2)$  besides energy also particles! The isolated *super system* ( $\Sigma = \Sigma_1 \cup \Sigma_2$ ), for which a micro-canonical ensemble is definable, shall be in its *thermal equilibrium*. According to (1.89) and (1.97) this means that at all points in  $\Sigma$  the same temperature  $T$  and the same chemical potential  $\mu$  must prevail. We assume once again, as justified more precisely in connection with (1.131), that the interactions, necessary for establishing the equilibrium between  $\Sigma_1$  and  $\Sigma_2$  are *asymptotically small*, so that they need not be taken into consideration for the following steps.

Except for the usual energy-indeterminacy  $\Delta$  of the micro-canonical ensemble, the energy of  $\Sigma_1$  is fixed by that of  $\Sigma_2$ . The same holds for the particle number  $N_1$ :

$$E = E_1 + E_2; \quad N = N_1 + N_2.$$

Of course, these boundary conditions ( $E, N$  fixedly pre-given) are again realizable in a manifold manner. According to our considerations in the Sects. 1.3.1 and 1.3.2 the equilibrium state,

$$E \longleftrightarrow \widehat{E}_1 + \widehat{E}_2; \quad N \longleftrightarrow \widehat{N}_1 + \widehat{N}_2,$$

is characterized by the maximal number of possibilities of realization. The interesting partial system  $\Sigma_1$  is very much smaller than  $\Sigma_2$ , so that

$$\widehat{E}_1 \ll \widehat{E}_2; \quad \widehat{N}_1 \ll \widehat{N}_2 \quad (1.156)$$

may be assumed. We look for a *statistical ensemble* consisting of systems which are equivalent to  $\Sigma_1$ . For this purpose, we need the corresponding density distribution function  $\rho_{N_1}(\mathbf{q}_1, \mathbf{p}_1)$ , for which it is to be taken into consideration, of course, that there belong to different particle numbers also different phase spaces. A change of  $N_1$  immediately provokes, e.g., a changed dimension of the phase space. This we will indicate by the index  $N_1$  at the symbol of the density distribution function. If, at first,  $N_1$  is kept constant, then the same argumentation as that for (1.133) leads to the following ansatz for  $\rho_{N_1}$  in the  $N_1$ -particle phase space:

$$\rho_{N_1}(\mathbf{q}_1, \mathbf{p}_1) \sim \Gamma_{N-N_1}(E - E_1, V_2) . \quad (1.157)$$

Because of (1.156), the phase-space volume on the right-hand side can be expanded around  $\Gamma_M(E, V_2)$ , at least for the actually interesting particle numbers and energies in the neighborhood of the equilibrium.  $V_2$ , in contrast, is fixed:

$$\begin{aligned} k_B \ln \Gamma_{N-N_1}(E - E_1, V_2) &\equiv S_2(E_2 = E - E_1, V_2, N_2 = N - N_1) \\ &= S_2(E, V_2, N) - E_1 \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (E_2 = E, N_2 = N) \\ &\quad - N_1 \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} (E_2 = E, N_2 = N) + \dots \end{aligned}$$

The first summand is, with respect to  $\Sigma_1$ , a constant  $S_0$ . For the second and the third summand we write because of (1.89) and (1.96), respectively, applying (1.156):

$$\begin{aligned} \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (E, N) &\approx \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (\widehat{E}_2, \widehat{N}_2) = \frac{1}{T} , \\ \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} (E, N) &\approx \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} (\widehat{E}_2, \widehat{N}_2) = -\frac{\mu}{T} . \end{aligned}$$

This leads to:

$$\ln \Gamma_{N-N_1}(E - E_1, V_2) \approx \frac{S_0}{k_B} - \frac{E_1}{k_B T} + \frac{\mu N_1}{k_B T}$$

or equivalently to:

$$\Gamma_{N-N_1}(E - E_1, V_2) \sim \exp(-\beta (E_1 - \mu N_1)) = \exp[-\beta (H_{N_1}(\mathbf{q}_1, \mathbf{p}_1) - \mu N_1)] .$$

This transfers to the **density-distribution function** in the  $N_1$ -particle phase space of the system  $\Sigma_1$ :

$$\rho_{N_1}(\mathbf{q}_1, \mathbf{p}_1) \sim \exp[-\beta (H_{N_1}(\mathbf{q}_1, \mathbf{p}_1) - \mu N_1)] . \quad (1.158)$$

Obviously, it is a *stationary* distribution, because the  $(\mathbf{q}, \mathbf{p})$ -dependence comes into play only by the Hamilton function  $H_N$  (see 1.43). We will fix the coefficients in (1.158) at a later stage.—From now on we can leave out the index ‘1’, which helped to distinguish  $\Sigma_1$  from the *complementary system*  $\Sigma_2$ , which, on its part, only served to fix  $T$  and  $\mu/T$ , and does not play any role in the following considerations.

We now define the **grand-canonical partition function**  $\Xi_\mu(T, V)$ , which has for the grand-canonical ensemble the same fundamental importance as  $Z_N(T, V)$  for the canonical ensemble

$$\begin{aligned}\Xi_\mu(T, V) &\equiv \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int \cdots \int d^{3N} q d^{3N} p e^{-\beta(H_N(\mathbf{q}, \mathbf{p}) - \mu N)} \\ &= \sum_{N=0}^{\infty} z^N Z_N(T, V) .\end{aligned}\tag{1.159}$$

One denotes the abbreviation

$$z = e^{\beta\mu}\tag{1.160}$$

as **fugacity**. The reason for the factor  $(h^{3N} N!)^{-1}$  is the same as for that explained in connection with (1.129). With a known Hamilton function  $H_N(\mathbf{q}, \mathbf{p})$  the grand-canonical partition function  $\Xi_\mu$  is in principle calculable. The summation over  $N$  runs up to infinity because the *super system* (heat bath and particle reservoir) can be, according to our preceding considerations, arbitrarily large.

Like  $Z_N(T, V)$  (1.140), we can of course express also the grand-canonical partition function by an energy integral over the density of states (1.50)  $D_N(E, V)$ :

$$\Xi_\mu(T, V) = \sum_{N=0}^{\infty} \int dE D_N(E, V) e^{-\beta(E - \mu N)} .\tag{1.161}$$

Since  $\rho_N(\mathbf{q}, \mathbf{p})$  represents the probability density to find the  $N$ -particle system in the phase  $\pi = (\mathbf{q}, \mathbf{p})$ , one gets with (1.158) for the ensemble-average of an arbitrary phase-space observable  $F_N(\mathbf{q}, \mathbf{p})$ :

$$\langle F \rangle = \frac{1}{\Xi_\mu(T, V)} \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int \cdots \int d^{3N} q d^{3N} p e^{-\beta(H_N(\mathbf{q}, \mathbf{p}) - \mu N)} F_N(\mathbf{q}, \mathbf{p}) .\tag{1.162}$$

If one compares this with the corresponding expression (1.135) of the canonical ensemble  $\langle F \rangle_{ce}$ , one realizes the following relationship:

$$\langle F \rangle = \frac{\sum_{N=0}^{\infty} z^N Z_N(T, V) \langle F_N \rangle_{ce}}{\sum_{N=0}^{\infty} z^N Z_N(T, V)} .\tag{1.163}$$

The representation (1.162) corresponds in the  $N$ -particle phase space to a **density-distribution function** of the form

$$\rho_N(\mathbf{q}, \mathbf{p}) = \frac{1}{\Xi_\mu(T, V)} \exp(-\beta (H_N(\mathbf{q}, \mathbf{p}) - \mu N)) \quad (1.164)$$

with the normalization:

$$\sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int \cdots \int d^{3N} q d^{3N} p \rho_N(\mathbf{q}, \mathbf{p}) = 1. \quad (1.165)$$

### 1.5.2 Connection to Thermodynamics

The next task consists in representing the state quantities, relevant for Thermodynamics, in the framework of the *grand-canonical ensemble*, i.e. ultimately, to express them by the grand-canonical partition function.

We begin with the **particle number**, which was in the *canonical ensemble* only a parameter, however, has now become in the *grand-canonical ensemble* a variable because of the particle fluctuations. From the very beginning, it appears therefore to be clear that a physical equivalence of *canonical* and *grand-canonical ensemble* is to be expected only when *almost all* the members of the grand-canonical ensemble possess the same particle number  $N$ . Thus the *particle-number distribution* should exhibit a sharp maximum at the average  $\langle N \rangle$ . For its calculation (1.163) appears to be convenient, where the *canonical average*  $\langle N \rangle_{ce}$  is trivially equal to  $N$  which is constant in a *canonical ensemble*:

$$\langle N \rangle = \frac{\sum_{N=0}^{\infty} N z^N Z_N(T, V)}{\sum_{N=0}^{\infty} z^N Z_N(T, V)} = \sum_{N=0}^{\infty} N w_N(T, V). \quad (1.166)$$

$w_N(T, V)$  denotes the probability that the considered system is found at the temperature  $T$  with  $N$  particles in the volume  $V$ :

$$w_N(T, V) = \frac{z^N Z_N(T, V)}{\Xi_\mu(T, V)}. \quad (1.167)$$

The comparison of (1.166) with (1.159) leads to an alternative representation of  $\langle N \rangle$ :

$$\langle N \rangle = \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \ln \Xi_\mu(T, V) \right)_{T, V}. \quad (1.168)$$

This relation can be used, at least in principle, to represent the chemical potential  $\mu$  in the variables  $T$ ,  $V$ , and  $\langle N \rangle$ :

$$\mu = \mu(T, V, \langle N \rangle) . \quad (1.169)$$

That will be needed at a later stage.—The second version of the grand-canonical partition function in (1.159) gives evidence that  $\Xi_\mu$  depends only via the fugacity  $z$  on the chemical potential. When one replaces  $\Xi_\mu(T, V)$  by the corresponding  $\Xi_z(T, V)$ , i.e., regarding  $z$  instead of  $\mu$  as variable,

$$\Xi_\mu(T, V) \xrightarrow{\mu=1/\beta \ln z} \Xi_z(T, V) , \quad (1.170)$$

then one also gets:

$$\langle N \rangle = z \left( \frac{\partial}{\partial z} \ln \Xi_z(T, V) \right)_{T, V} . \quad (1.171)$$

Next we investigate the **pressure**  $p$ , whose mechanical definition (1.101) reads with (1.162)

$$p = - \left\langle \frac{\partial H}{\partial V} \right\rangle = \frac{1}{\beta} \left( \frac{\partial}{\partial V} \ln \Xi_\mu(T, V) \right)_{T, \mu} . \quad (1.172)$$

Later we will find a still more direct way, by the use of the *grand-canonical potential* (1.154), in order to express  $p$  by the partition function  $\Xi_\mu$ .

The **internal energy**  $U$  is the average of the Hamilton function  $H$ , so that it immediately follows with (1.162):

$$U = \langle H \rangle = - \left( \frac{\partial}{\partial \beta} \ln \Xi_\mu(T, V) \right)_{\mu, V} + \mu \langle N \rangle \quad (1.173)$$

When we write the partition function, according to (1.170), as function of  $T$ ,  $V$ , and  $z$ , and insert Eq. (1.141) into (1.163) for the *canonical* average  $\langle H_N \rangle_{ce}$ , then it results an expression for the internal energy formally completely equivalent to (1.141)

$$U = - \left( \frac{\partial}{\partial \beta} \ln \Xi_z(T, V) \right)_{z, V} . \quad (1.174)$$

We have only to replace on the right-hand side the canonical by the grand-canonical partition function. Note, however, that  $U$  in (1.141) is to be read as  $U(T, V, N)$ , in (1.173) as  $U(T, V, \mu)$ , and in (1.174) as  $U(T, V, z)$ .

Let us at this stage briefly deviate from the subject in order to discuss some first considerations on the *statistical equivalence* of canonical and grand-canonical ensembles. As already mentioned, such an equivalence can be expected certainly

only when the probability (1.167)  $w_N(T, V)$  exhibits at  $N = \langle N \rangle$  a pronounced maximum, so that one can assume for *almost all* the systems the same particle number  $\langle N \rangle$ . For the grand-canonical partition function (1.159) one could then take approximately

$$\Xi_z(T, V) \approx z^{\langle N \rangle} Z_{\langle N \rangle}(T, V) , \quad (1.175)$$

so that with (1.173) the known result (1.141) of the canonical ensemble for the internal energy would be reproduced:

$$U(T, V, \langle N \rangle) \approx - \left( \frac{\partial}{\partial \beta} \ln Z_{\langle N \rangle}(T, V) \right)_{V, \langle N \rangle} . \quad (1.176)$$

Under the discussed presumptions canonical and grand-canonical ensemble are thus equivalent with respect to  $U$ , if one interprets the average  $\langle N \rangle$  as the thermodynamic state variable *particle number*.

The central role, which is played in the *micro-canonical* ensemble by the entropy  $S(E, V, N)$ , and in the *canonical* ensemble by the free energy  $F(T, V, N)$ , is taken over in the grand-canonical ensemble from the so-called

**grand-canonical potential**  $\Omega(T, V, \mu)$  .

For its differential  $d\Omega$  it holds according to (1.155) with  $\langle N \rangle$  as ‘*particle number*’:

$$d\Omega = -SdT - pdV - \langle N \rangle d\mu . \quad (1.177)$$

This is equivalent to

$$\begin{aligned} d \left( \frac{\Omega}{k_B T} \right) &= - \frac{\Omega}{k_B T^2} dT - \frac{1}{k_B T} (SdT + pdV + \langle N \rangle d\mu) \\ &= - \frac{U - \mu \langle N \rangle}{k_B T^2} dT - \frac{1}{k_B T} (pdV + \langle N \rangle d\mu) . \end{aligned}$$

Here we now insert (1.168), (1.172) and (1.173):

$$\begin{aligned} d \left( \frac{\Omega}{k_B T} \right) &= - \left( \frac{\partial}{\partial T} \ln \Xi_\mu(T, V) \right)_{\mu, V} dT - \left( \frac{\partial}{\partial V} \ln \Xi_\mu(T, V) \right)_{\mu, T} dV \\ &\quad - \left( \frac{\partial}{\partial \mu} \ln \Xi_\mu(T, V) \right)_{T, V} d\mu = -d \ln \Xi_\mu(T, V) . \end{aligned}$$

Except for an unimportant additive constant it must therefore hold:

$$\Omega(T, V, \mu) = -k_B T \ln \Xi_\mu(T, V) . \quad (1.178)$$



This relation is frequently also used in the form

$$\Xi_\mu(T, V) = \exp(-\beta \Omega(T, V, \mu)) . \quad (1.179)$$

Between the grand-canonical potential  $\Omega$  and the grand-canonical partition function  $\Xi_\mu$  there thus exists formally the same connection as in the canonical ensemble between  $Z_N(T, V)$  and the free energy  $F(T, V, N)$ . With (1.154) the relation (1.178) can also be written as follows:

$$\frac{pV}{k_B T} = \ln \Xi_\mu(T, V) . \quad (1.180)$$

From Thermodynamics we know the connection

$$p = -\frac{\partial F}{\partial V} .$$

$F$  is the central quantity of the *canonical ensemble*,  $pV$  that of the *grand-canonical ensemble*. Equivalence of the statistical descriptions then means in particular the fulfilling of the above relation, where  $p$  is determined *grand-canonically* and  $F$  *canonically*. To prove this we formulate at first the free energy  $F$  in the sense of the grand-canonical ensemble, where we interpret  $\langle N \rangle$  again as the state variable ‘particle number’:

$$F(T, V, \langle N \rangle) = \mu \langle N \rangle + \Omega(T, V, \mu) = \mu \langle N \rangle - k_B T \ln \Xi_\mu(T, V) . \quad (1.181)$$

In order that the right-hand side is really a function of  $T$ ,  $V$  and  $\langle N \rangle$ ,  $\mu$  must be inserted according to (1.169), i.e., (1.168) must be solved for  $\mu$ . That sounds quite complicated, and in principle it is so. The *natural* variables of the free energy are indeed not identical with the variables  $(T, V, \mu)$  of the grand-canonical ensemble. If we can assume, however, as we have already done once, above in connection with the internal energy, that *almost all* ensemble systems possess the same particle number  $\langle N \rangle$ , then we can approximately apply for the partition function (1.175) in (1.181), finding then with

$$F(T, V, \langle N \rangle) \approx -k_B T \ln Z_{\langle N \rangle}(T, V) \quad (1.182)$$

a representation, which exactly corresponds to that of the canonical ensemble.

When we substitute in the free energy (1.181) by the use of a suitable *Legendre transformation* the variable  $\langle N \rangle$  by  $\mu$ ,

$$F(T, V, \langle N \rangle) = \widehat{F}(T, V, \mu) - \mu \frac{\partial \widehat{F}}{\partial \mu} ,$$

we recognize, if we still include (1.168), that the Legendre transform  $\widehat{F}$  is identical to the grand-canonical potential:

$$\widehat{F}(T, V, \mu) = -k_B T \ln \Xi_\mu(T, V) = \Omega(T, V, \mu) . \quad (1.183)$$

The partial differentiations with respect to the *passive* variables  $T$  and  $V$  must therefore be the same for  $F$  and  $\Omega$  (see (2.5), Vol. 2), if one still inserts (1.169) for  $\mu$ :

$$\left( \frac{\partial F}{\partial T} \right)_{V, \langle N \rangle} = \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu=\mu(T, V, \langle N \rangle)} , \quad (1.184)$$

$$\left( \frac{\partial F}{\partial V} \right)_{T, \langle N \rangle} = \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu=\mu(T, V, \langle N \rangle)} . \quad (1.185)$$

We now use the second relation for the determination of the **pressure**. *Grand-canonically* it holds at first for the pressure, according to (1.177):

$$p = p(T, V, \langle N \rangle) = - \left( \frac{\partial \Omega}{\partial V} \right)_{T, \mu=\mu(T, V, \langle N \rangle)} = - \left( \frac{\partial F}{\partial V} \right)_{T, \langle N \rangle} . \quad (1.186)$$

If we eventually are still allowed to use for the macroscopic systems, we are interested in, approximately (1.182), then we obtain with

$$p(T, V, \langle N \rangle) \approx k_B T \left( \frac{\partial}{\partial V} \ln Z_{\langle N \rangle}(T, V) \right)_{T, \langle N \rangle} \quad (1.187)$$

an expression, which agrees exactly with the *canonical* result (1.142). On the left there is the *grand-canonical* pressure, on the right the *canonical* partition function. Under the mentioned presumptions, (1.187) thus testifies the equivalence of the statistical descriptions in the framework of, respectively, the canonical and the grand-canonical ensemble.

Let us finally check the **entropy**:

$$\begin{aligned} S(T, V, \langle N \rangle) &\stackrel{(1.177)}{=} - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu=\mu(T, V, \langle N \rangle)} \stackrel{(1.184)}{=} - \left( \frac{\partial F}{\partial T} \right)_{V, \langle N \rangle} \\ &\stackrel{(1.182)}{\approx} k_B \left( \frac{\partial}{\partial T} \ln Z_{\langle N \rangle}(T, V) \right)_{V, \langle N \rangle} . \end{aligned} \quad (1.188)$$

The comparison with the *canonical* result (1.146) confirms also in this case the statistical equivalence of the two ensembles.

Using the example of important thermodynamic state quantities as the internal energy (1.176), the free energy (1.182), the pressure (1.187), and the entropy (1.188), we were able to demonstrate in this subsection that the results

of the *grand-canonical ensemble* agree with those of the *canonical ensemble*, if the grand-canonical average  $\langle N \rangle$  can be identified with the particle number  $N$  of the canonical ensemble. That is surely the case when *almost all* systems of the grand-canonical ensemble have the same particle number  $\langle N \rangle$ , so that, in spite of the admitted particle fluctuations,  $\langle N \rangle$  represents a quantity, which is characteristic for the physical system. Exactly this fact remains to be shown. It will indeed turn out to be correct in the next subsection, again, however, only for macroscopic, *asymptotically large* systems.

### 1.5.3 Particle Fluctuations

We had denoted in Thermodynamics (see (2.71), (4.34), Vol. 5) as *mechanical stability condition* the requirement that the compressibility cannot be negative:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \geq 0. \quad (1.189)$$

It is of course plausible that a system can be stable only when a volume reduction ( $\Delta V < 0$ ) is accompanied by an enhancement of the pressure ( $\Delta p > 0$ ). Nevertheless, the criterion is not provable by the means of Phenomenological Thermodynamics. The Statistical Physics verifies (1.189) via a formula of particle-number fluctuations, which here, however, will help us above all to close the last gap in our chain of conclusions for the proof of the equivalence of canonical and grand-canonical ensemble.

We start with the expression (1.168) for  $\langle N \rangle$  as well as the average of the square of the particle number:

$$\langle N^2 \rangle = \frac{\sum_{N=0}^{\infty} N^2 z^N Z_N(T, V)}{\sum_{N=0}^{\infty} z^N Z_N(T, V)} = \frac{1}{\Xi_\mu} \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \Xi_\mu. \quad (1.190)$$

We find therewith:

$$\begin{aligned} \frac{\partial}{\partial \mu} \ln \Xi_\mu &= \frac{1}{\Xi_\mu} \frac{\partial}{\partial \mu} \Xi_\mu = \beta \langle N \rangle, \\ \frac{\partial^2}{\partial \mu^2} \ln \Xi_\mu &= -\frac{1}{\Xi_\mu^2} \left( \frac{\partial}{\partial \mu} \Xi_\mu \right)^2 + \frac{1}{\Xi_\mu} \frac{\partial^2}{\partial \mu^2} \Xi_\mu = -\beta^2 \langle N \rangle^2 + \beta^2 \langle N^2 \rangle. \end{aligned}$$

Then comes out the important intermediate result:

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \left( \frac{\partial^2}{\partial \mu^2} \ln \Xi_\mu(T, V) \right)_{T, V} = \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \langle N \rangle \right)_{T, V}. \quad (1.191)$$

Let us evaluate this formula at first for the simplest thermodynamic system, namely the **ideal gas**. As Exercise 1.5.1 we determine its grand-canonical partition function:

$$\Xi_{\mu}^{(0)}(T, V) = \exp\left(z_0 \frac{V}{\lambda^3(T)}\right). \quad (1.192)$$

$\lambda(T)$  is the thermal de Broglie wavelength (1.137). The particle number  $\langle N \rangle_0$  can easily be found with (1.171):

$$\langle N \rangle_0 = z_0 \frac{V}{\lambda^3(T)} = e^{\beta\mu_0} \frac{V}{\lambda^3(T)} = \frac{pV}{k_B T}. \quad (1.193)$$

In the last step we still have applied (1.180) to find therewith the thermal equation of state in the well-known form. The fluctuation formula (1.191) can directly be evaluated via (1.193):

$$\langle N^2 \rangle_0 - \langle N \rangle_0^2 = \langle N \rangle_0. \quad (1.194)$$

The *relative mean square deviation* of the particle number

$$\overline{(\Delta N)}_r \equiv \frac{\overline{(\Delta N)}}{\langle N \rangle} = \sqrt{\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2}} \quad (1.195)$$

tends for the ideal gas to zero for the *asymptotically large* system:

$$\overline{(\Delta N)}_r^{(0)} = \frac{1}{\sqrt{\langle N \rangle_0}} \xrightarrow{N \rightarrow \infty} 0. \quad (1.196)$$

For the special case of the *ideal gas* it can therefore indeed be assumed that *almost all* systems of the grand-canonical ensemble have the same *particle number*  $\langle N \rangle_0$ , by which the decisive precondition for the statistical equivalence of canonical and grand-canonical ensemble is fulfilled.

That this assertion is correct not only for the ideal gas, but is very generally valid for all macroscopic systems, can be recognized, if one reformulates a bit the right-hand side of (1.191) by a suitable transformation of the state variables. Applying purely thermodynamic considerations we prove as Exercise 1.5.5 the relation:

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial V}{\partial p}\right)_{T,\langle N \rangle} \left[\left(\frac{\partial p}{\partial \mu}\right)_{T,V}\right]^2. \quad (1.197)$$

The first factor is essentially the compressibility (1.189). The second factor can be evaluated with (1.180) and (1.168):

$$\left(\frac{\partial p}{\partial \mu}\right)_{T,V} = \frac{k_B T}{V} \left(\frac{\partial}{\partial \mu} \ln \Xi_{\mu}(T, V)\right)_{T,V} = \frac{\langle N \rangle}{V}.$$

Hence

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = \frac{\kappa_T}{V} \langle N \rangle^2. \quad (1.198)$$

When one inserts this result into (1.191),

$$\frac{\kappa_T}{\beta V} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle^2}, \quad (1.199)$$

then, for a start, the validity of the stability criterion (1.189) is proven. If we still normalize  $\kappa_T$  with respect to the compressibility of the ideal gas,

$$\kappa_T^{(0)} = \frac{1}{p} = \frac{\beta V}{\langle N \rangle},$$

then it follows for the *relative mean square deviation* of the particle number:

$$\overline{(\Delta N)}_r = \sqrt{\frac{\kappa_T}{\kappa_T^{(0)}}} \frac{1}{\sqrt{\langle N \rangle}}. \quad (1.200)$$

If one excludes points of phase transitions, then the first factor is always finite. The relative mean square deviation of the particle number thus becomes unimaginably small for macroscopic systems. That means that *almost all* systems of a grand-canonical ensemble possess the same particle number  $\langle N \rangle$ . The *statistical equivalence* of canonical and grand-canonical ensembles is therewith proven.

When we add the considerations from Sect. 1.4.4 then it is now certain that for **macroscopic systems** all the three ensembles (micro-canonical, canonical, grand-canonical) are physically equivalent. For the solution of a concrete problem one can therefore decide on one or the other, only with respect to expedience. However, it should warningly be stressed once more that the consistency of all the so far derived formulas and functions is guaranteed really only for macroscopic systems. Of course, they can purely formally be calculated also for **small** systems, but it can then **not** be expected that the laws and concepts of Thermodynamics and the Statistical Physics keep their validity.

## 1.5.4 Exercises

### Exercise 1.5.1

An ideal gas of identical particles each of mass  $m$  is at the temperature  $T$  in the volume  $V$ .

1. Calculate the classical grand-canonical partition function  $\Xi_\mu(T, V)$ .
2. Determine the equation of state  $p = f(T, V, \langle N \rangle)$ .

3. Represent the chemical potential as a function of the temperature and the pressure.
4. Show that the probability  $w_N(T, V)$  to find the gas at the temperature  $T$  with  $N$  particles in the volume  $V$ , obeys a Poisson distribution.

**Exercise 1.5.2**

In the framework of the grand-canonical ensemble prove the thermodynamic relation:

$$\left( \frac{\partial F}{\partial \langle N \rangle} \right)_{T, V} = \mu .$$

**Exercise 1.5.3**

Calculate *grand-canonically* for an ideal gas of identical particles each of mass  $m$  the entropy and compare the result with the *micro-canonically* derived *Sackur-Tetrode equation* (1.124).

**Exercise 1.5.4**

Let a system (e.g. a gas) be at the temperature  $T$  in the volume  $V$ . Let it consist of  $n$  different particle components. They may differ, for instance, by the particle masses  $m_1, m_2, \dots, m_n$ .

1. As generalization of (1.159), how does the grand-canonical partition function  $\Xi_{\{\mu_i\}}(T, V)$  read?
2. Show that the grand-canonical partition functions factorizes,

$$\Xi_{\{\mu_i\}}(T, V) = \Xi_{\mu_1}(T, V) \cdots \Xi_{\mu_n}(T, V) ,$$

if particles of different components do not interact with each other.

3. Calculate especially the grand-canonical partition function for an  $n$ -component ideal gas.
4. How does the thermal equation of state of the ideal gas-mixture read?

**Exercise 1.5.5**

Prove the relation (1.197):

$$\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T, V} = - \left( \frac{\partial V}{\partial p} \right)_{T, \langle N \rangle} \left[ \left( \frac{\partial p}{\partial \mu} \right)_{T, V} \right]^2 .$$

**Exercise 1.5.6**

1. Express the relative mean square energy-deviation

$$(\overline{\Delta E})_r = \sqrt{\frac{\langle (H - \langle H \rangle)^2 \rangle}{\langle H \rangle^2}}$$

by the grand-canonical partition function  $\Xi_z(T, V)$ .

2. In the case of the ideal gas, how is  $(\overline{\Delta E})_T$  connected with the particle number  $\langle N \rangle$ ?

## 1.6 Self-Examination Questions

### To Section. 1.1

1. Why can *Thermodynamics* not be considered as a closed, complete theory?
2. What is the main goal of Statistical Physics?
3. Why can Statistical Physics yield trusted statements actually only for the *asymptotically large* systems?
4. What is the hypothesis of the same ‘a-priori’-probabilities? To which systems does it refer?
5. Can *thermal equilibrium* be explained microscopically?
6. Is Thermodynamics valid also for systems of few particles?
7. What does one understand by a *binomial distribution*?
8. How does the *Stirling formula* read?

### To Section. 1.2

1. Which meanings do the terms *phase vector*, *phase trajectory*, and *phase space* have?
2. How is the *time-average* of the classical observable  $F(\mathbf{q}, \mathbf{p})$  defined?
3. What is the statement of the quasi-ergodic hypothesis?
4. What does one understand by a *statistical ensemble*?
5. What is expressed by the catch phrase *time-average*  $\stackrel{!}{=} \textit{ensemble-average}$ ?
6. Which relation exists between the assumption *time-average*  $\stackrel{!}{=} \textit{ensemble-average}$  and the quasi-ergodic hypothesis?
7. How does Statistical Physics answer the question which value the property of the system  $F(\mathbf{q}, \mathbf{p})$  possesses?
8. What does  $\text{div } \mathbf{v}$  yield, when  $\mathbf{v} = \dot{\boldsymbol{\pi}}$  means the  $2s$ -dimensional phase-space velocity, and  $\text{div}$  the divergence in the phase space?
9. Which continuity equation is fulfilled by the density-distribution function  $\rho(\mathbf{q}, \mathbf{p}, t)$  of the statistical ensemble? What is its physical background?
10. How does the Liouville equation read, and how can it be interpreted?
11. Why do the ensemble systems move in the phase space like an *incompressible liquid*?
12. The Liouville theorem speaks of the conservation of the phase-space volume. What does that mean?
13. When do we call a density distribution *stationary*?

14. How does the density-distribution of a micro-canonical ensemble read?
15. Which type of system is represented by the micro-canonical ensemble?
16. How are the phase volumes  $\Gamma(E)$  and  $\varphi(E)$ , respectively, defined?

### To Section. 1.3

1. How can one exemplarily explain *thermal equilibrium*?
2. In what way is the *irreversible transition into thermal equilibrium* understandable only for systems with very many degrees of freedom?
3. How does Statistical Physics define entropy?
4. How can one justify the equivalence of the expressions  $\ln \Gamma_N(E, V)$ ,  $\ln \varphi_N(E, V)$ , and  $\ln D_N(E, V)$ ?
5. For which essential properties of the *statistical entropy* must evidence be provided, in order to be able to identify it with the entropy known from Thermodynamics?
6. In what way is the entropy of two systems in thermal contact additive? Which conditions are to be fulfilled?
7. How can one formulate the condition for thermal equilibrium in an isolated system by the energy-dependence of the entropy?
8. What is the connection between the *statistical temperature* and the phase volume  $\Gamma_N(E, V)$  of the micro-canonical ensemble?
9. Which connection exists between temperature, entropy and energy in an isolated system?
10. How does the Statistical Physics for isolated systems justify the *second law of thermodynamics*?
11. What is the connection between the chemical potential  $\mu$ , the entropy  $S$ , and the temperature  $T$ ?
12. How can the chemical potential  $\mu$  be derived from the phase volume  $\Gamma_N(E, V)$ ?
13. How does  $\mu$  appear in the equilibrium conditions of an isolated system?
14. Why is for Statistical Physics the pressure  $p$  a physical quantity, which is qualitatively different from the quantities  $\mu$  and  $T$ ?
15. How is the pressure of a gas determined by its Hamilton function?
16. What does one understand by an *external parameter* of the Hamilton function? Give examples!
17. What does one understand in Statistical Physics by a quasi-static change of state of an isolated system?
18. Formulate the general implementation concept of the Statistical Physics!
19. How does the *generalized equipartition theorem* read?
20. How much energy does each degree of freedom contribute, on average, to the *virial of forces*?
21. What is the assertion of the virial theorem?
22. What is expressed by *Gibb's paradox*?



23. What is to be understood by the *correct Boltzmann-counting*? Give reasons for it!
24. How does the phase volume  $\Gamma_N(E, V)$  of an  $N$ -particle gas look like, when the gas is composed by  $n_0$  different kinds of particles ( $\sum_{j=1}^{n_0} N_j = N$ )?

## To Section. 1.4

1. How do the canonical and the micro-canonical ensemble differ from one another?
2. To which physical situation does the canonical ensemble correspond?
3. How does the normalized density-distribution function  $\rho(\mathbf{q}, \mathbf{p})$  of the canonical ensemble read?
4. Is the canonical ensemble stationary?
5. How does one calculate the average of a classical observable  $F(\mathbf{q}, \mathbf{p})$  in the framework of the canonical ensemble?
6. How is the classical (canonical) partition function defined?
7. What is the connection between the partition function and the thermal de Broglie wavelength?
8. Express the partition function as an energy integral over the density of states  $D_N(E, V)$ !
9. How is the internal energy  $U$  related to the Hamilton function  $H$ ?
10. How can  $U$  be derived from the partition function?
11. Why is the free energy  $F$  for the canonical ensemble the central thermodynamic potential?
12. What is the relationship between free energy and canonical partition function?
13. What are the important requirements that must be fulfilled by the free energy, which is defined via the canonical ensemble, in order that it can be identified with the corresponding thermodynamic potential?
14. What is to be understood by *thermal stability*?
15. What has to be presumed for the distribution of the energies of the systems of a canonical ensemble around the average value  $U = \langle H \rangle$ , in order to guarantee the statistical equivalence with the micro-canonical ensemble?
16. What is the order of magnitude of the relative mean square deviation of the energy in the canonical ensemble?
17. Why can we not expect for systems of only few particles that canonical and micro-canonical ensemble yield identical results?
18. What must be shown in order to prove the equivalence of canonical and micro-canonical ensemble?

**To Section. 1.5**

1. What type of physical systems can be conveniently described by the grand-canonical ensemble?
2. How is the grand-canonical potential  $\Omega(T, V, \mu)$  defined?
3. What are the central thermodynamic functions of the micro-canonical, the canonical, and the grand-canonical ensemble? How are they labeled?
4. How is the grand-canonical partition function  $\Xi_\mu(T, V)$  related to the canonical partition function  $Z_N(T, V)$ ?
5. Which quantity is called *fugacity*?
6. How does the ensemble-average of an observable  $F_N(\mathbf{q}, \mathbf{p})$  read in the grand-canonical ensemble?
7. How can the average particle number  $\langle N \rangle$  be expressed by the grand-canonical partition function  $\Xi_\mu$ ?
8. How do, in the grand-canonical ensemble, the representations  $U(T, V, \mu)$  and  $U(T, V, z)$  of the internal energy differ?
9. What is the connection between the grand-canonical potential  $\Omega(T, V, \mu)$  and the grand-canonical partition function  $\Xi_\mu(T, V)$ ?
10. What is the decisive precondition for the *statistical equivalence* of canonical and grand-canonical ensemble?
11. What is the connection between the *grand-canonically calculated* free energy  $F(T, V, \langle N \rangle)$  and the grand-canonical partition function  $\Xi_\mu(T, V)$ ?
12. What is denoted as *mechanical stability condition*?
13. How does the relative mean square deviation of the particle number look like for the ideal gas?

# Chapter 2

## Quantum Statistics



### 2.1 Basic Principles

Our rather detailed considerations on Statistical Physics have so far been purely of *classical nature*. It goes without saying that we would not have any problem to uncover the limits of its validity, i.e., to expose inconsistencies with the experiment, as we have been with the Classical Mechanics. Ultimately, the correct description of nature needs the *superordinate* Quantum Mechanics. We therefore will have to rewrite the *Classical Statistical Physics* of the first chapter to a *Quantum Statistics*. It will turn out thereby that the basic concepts will remain the same, but they will have to be combined, though, with some typical quantum-mechanical aspects. Let us recall once more: **Classically** the complete description of a physical system is accomplished by the specification of the phase  $\pi = (\mathbf{q}, \mathbf{p})$ , which changes with time in the *phase space* according to Hamilton's equations of motion (1.13) and defines therewith the *phase trajectory* of the system. Statistical methods become necessary in the case of incomplete information about the initial conditions, which are indispensable for the solution of the equations of motion. Such an incomplete information is the normal case for macroscopic systems.

**Quantum-mechanically** one meets a completely different situation, which is characterized, in a certain sense, by a *twofold lack of knowledge*. There is at first the **specific quantum-mechanical indeterminism**. Even if the state of the system actually is known (*pure state*), the results of measurements are in general not precisely predictable. The measurement itself leads to an uncontrollable perturbation of the system. This uncertainty manifests itself in the *statistical interpretation* of the wave function (subsection 2.2.1, Vol. 6), and in the *uncertainty relation* ((1.5), (3.155), Vol. 6). Positions  $q_i$  and momenta  $p_i$  are no longer simultaneously precisely measurable. Therewith, terms like *phase space* and *phase trajectory* are automatically losing their sense in Quantum Mechanics; terms which are, on the other hand, of great importance in Classical Statistical Physics. The second uncertainty is then the **incomplete information**, which calls for macroscopic systems classically as well as quantum-mechanically for statistical concepts to get the solution of a problem.

This uncertainty is in principle treated in Quantum Statistics in the same manner as in Classical Statistics. The main task will therefore consist in an extension of the methods, which were developed in Chap. 1, by the above mentioned *typical quantum-mechanical aspect*.

### 2.1.1 Statistical Operator (Density Matrix)

Strictly speaking, we have already discussed the just formulated set of problems of the *twofold indeterminacy*, which is to be handled by *Quantum Statistics*, in the *Quantum Mechanics* (subsection 3.3.4, Vol. 6). The simultaneous carrying out of both the qualitatively drastically different average processes succeeds by the use of the *statistical operator*, sometimes also called the *density matrix*, an operator, whose manner of action we will recall with the following list. The presentation in the following will be brief and compact and details can be found in Vol. 6 of this **basic course in Theoretical Physics**. The *statistical operator* for Quantum Statistics, though, is of such a central importance that a certain repetition of the basic facts is surely justified.

Quantum Mechanics distinguishes two types of states for the physical systems, the *pure* and the *mixed state*.

#### 1) Pure State

This state is prepared by the measurement of a **complete** set of commutable observables, i.e., by a set of measuring processes which is sufficient for the unique identification of the state. To a pure state there can therefore always be ascribed a Hilbert vector  $|\psi\rangle$ . Nevertheless, even for a system in such a pure state, the results of measurements are normally not precisely predictable.

Let  $\hat{F}$  be an observable with the eigen-value equation:

$$\hat{F}|f_n\rangle = f_n|f_n\rangle ; \quad \langle f_n | f_m \rangle = \delta_{nm} .$$

The eigen-states  $\{|f_n\rangle\}$  shall represent a complete orthonormalized (CON) system. Each state  $|\psi\rangle$  can then be written, according to the expansion law ((3.27), Vol. 6), as linear combination of the  $|f_n\rangle$ :

$$|\psi\rangle = \sum_n c_n |f_n\rangle ; \quad c_n = \langle f_n | \psi \rangle .$$

(We disregard here, at first, the so-called *improper* Dirac states (subsection 3.2.4, Vol. 6), for which the sum would have to be replaced by an integral.) The square of the absolute value of the coefficient,  $|c_n|^2$ , represents the probability to obtain with a measurement, on the state  $|\psi\rangle$  of the system, of the observable  $\hat{F}$  the measuring

value  $f_n$ . It is a number in between 0 and 1, which expresses the *quantum-mechanical uncertainty* mentioned above. A precise statement is possible only if  $|\psi\rangle$  is prepared as eigen-state of  $\widehat{F}$ . It is therefore reasonable to introduce a **mean value** as the *average value* of many measurements performed on one and the same system under always the same conditions, or simultaneously on many congeneric systems. The latter strongly reminds of the concept of the *ensemble*, fundamental for the Statistics, which we encountered in this connection indeed already in Quantum Mechanics:

$$\begin{aligned} \langle \widehat{F} \rangle &= \sum_n f_n |c_n|^2 = \sum_n f_n \langle \psi | f_n \rangle \langle f_n | \psi \rangle \\ &= \sum_n \langle \psi | \widehat{F} | f_n \rangle \langle f_n | \psi \rangle = \langle \psi | \widehat{F} | \psi \rangle . \end{aligned} \quad (2.1)$$

In the last step we exploited the completeness relation.

## 2) Mixed State

If only an incomplete advance information about the system is present, i.e., if a complete set of commutable observables could not be measured, then one says that the system is in a *mixed state*. This situation is typical for macroscopic systems; but not only for these, when we, e.g., remember our standard example in Vol. 6, the *unpolarized electron beam*. To the mixed state **no** Hilbert vector can be ascribed. But characterizations of the following kind are thinkable:

**The system is with the probability  $p_m$  in the pure state  $|\psi_m\rangle$ ;**  
 **$m = 1, 2, \dots$ :**

$$0 \leq p_m \leq 1: \quad \sum_m p_m = 1 .$$

We do not know, because of our incomplete advance information, in which state the system really is, but we are able to cut down the possibilities a bit. Let  $|\psi_m\rangle$  be one of the *thinkable* states of the system, which we want to presume as orthonormalized:

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} . \quad (2.2)$$

The assumption of the orthogonality is convenient, but actually not necessary. We demonstrate in Exercise 2.1.2 that the assumption of the normalizability is in principle already sufficient. The main task will later consist in fixing the probability  $p_m$  with which the system occupies the state  $|\psi_m\rangle$ .

We now perform a measurement of the observable  $\widehat{F}$ . If the system were *without a doubt* in the state  $|\psi_m\rangle$ , we would obtain, according to (2.1) the average

$$\langle \psi_m | \widehat{F} | \psi_m \rangle .$$

Because of incomplete information we do not have this doubtlessness, but are forced to apply an additional statistical averaging:

$$\langle \hat{F} \rangle = \sum_m p_m \langle \psi_m | \hat{F} | \psi_m \rangle . \quad (2.3)$$

This average value now contains **two** different processes, where the quantum-mechanical one is of *intrinsic nature*, (2.1), and can therefore be by no means avoided. It comes into play by the states themselves, which are influenced by the respective measuring processes. Typical consequences are the known interference effects (section 2.1, Vol. 6). The statistical averaging ( $p_m$ ) is a result of the incomplete advance information, and therefore in principle removable. It is thus not of such a basic nature, and takes place via expectation values (numbers!), and does therefore not lead to any interference effects.

The following representation is equivalent to (2.3):

$$\langle \hat{F} \rangle = \sum_n f_n w_n .$$

$w_n$  is thereby the probability to find, with a measurement of  $\hat{F}$  on the system in the *mixed state*, the eigen-value  $f_n$ .  $w_{nm} = |\langle f_n | \psi_m \rangle|^2$  is the corresponding probability for the case that the system is definitely in the pure state  $|\psi_m\rangle$ . Then it obviously holds

$$w_n = \sum_m p_m w_{nm} , \quad (2.4)$$

which expresses once more the *twofold nature* of the Quantum Statistics. The central quantity of Quantum Statistics, which in a certain sense encompasses simultaneously both the averaging processes, is the **statistical operator**  $\hat{\rho}$ :

$$\hat{\rho} = \sum_m p_m |\psi_m\rangle \langle \psi_m| . \quad (2.5)$$

We compile its most important properties (see subsection 3.3.4, Vol. 6):

### 1. Mean values

$$\langle \hat{F} \rangle = \text{Tr}(\hat{\rho}\hat{F}) . \quad (2.6)$$

The term *trace* (Tr) we have got to know in subsection. 3.2.8 in Vol. 6 as the sum of the diagonal elements of a matrix. It has, amongst others, the useful property that it is independent of the CON-basis used. That can bring about computational advantages, because one can choose the basis according to expedience. We recall further useful properties of the trace in Exercise 2.1.1. Because of its fundamental

significance we will sketch once more the proof of the relation (2.6). Let  $\{|\varphi_i\rangle\}$  be a CON-system:

$$\begin{aligned} \langle \widehat{F} \rangle &= \sum_m p_m \langle \psi_m | \widehat{F} | \psi_m \rangle = \sum_{\substack{m \\ i,j}} p_m \langle \psi_m | \varphi_i \rangle \langle \varphi_i | \widehat{F} | \varphi_j \rangle \langle \varphi_j | \psi_m \rangle \\ &= \sum_{i,j} \left( \sum_m p_m \langle \varphi_j | \psi_m \rangle \langle \psi_m | \varphi_i \rangle \right) \langle \varphi_i | \widehat{F} | \varphi_j \rangle \\ &= \sum_{i,j} \widehat{\rho}_{ji} \widehat{F}_{ij} = \sum_j (\widehat{\rho} \widehat{F})_{jj} = \text{Tr}(\widehat{\rho} \widehat{F}) . \end{aligned}$$

2. **Hermiticity:**  $\widehat{\rho} = \widehat{\rho}^+$

This fact is immediately read off from the definition (2.5). The projection operator  $|\psi_m\rangle\langle\psi_m|$  is Hermitian ((3.84), Vol. 6), and  $p_m$  is real.

3. **Trace**

$$\text{Tr} \widehat{\rho} = 1 . \quad (2.7)$$

This follows directly from (2.6) for  $\widehat{F} = \mathbb{1}$ .

4.  **$\widehat{\rho}$  non-negative**

This means that the expectation value of the operator  $\widehat{\rho}$ , taken in any arbitrary state  $|\varphi\rangle$ , can not be negative:

$$\langle \varphi | \widehat{\rho} | \varphi \rangle = \sum_m p_m |\langle \varphi | \psi_m \rangle|^2 \geq 0 .$$

If  $|\varphi\rangle$  is normalized, this expectation value can also be interpreted as the probability to find the system, described by  $\widehat{\rho}$ , in the state  $|\varphi\rangle$ .

5. **Eigen-values**

$\widehat{\rho}$  as a Hermitian operator possesses real eigen-values, and eigen-states which are orthogonal to each other. Since we have presumed the  $|\psi_m\rangle$  as orthonormalized (2.2), they are already the eigen-states with the probabilities  $p_m$  as corresponding eigen-values. This statement is obviously no longer correct when the  $|\psi_m\rangle$  are normalized, but not orthogonal (Exercise 2.1.2).

6. **Pure state**

Even this special case can formally be treated by the use of a statistical operator. In the relation (2.5) there is then only one of the  $p_m$  equal to 1, while all the others are zero (complete information!).  $\widehat{\rho}$  is in this special case therefore identical to the projection operator on the pure state:

$$\widehat{\rho}_\psi \equiv P(\psi) = |\psi\rangle\langle\psi| . \quad (2.8)$$

All the general properties of the statistical operator of course remain valid. Let us check ( $\{|\varphi_n\rangle\}$ -CON-system):

$$\text{Tr}\hat{\rho}_\psi = \sum_n \langle \varphi_n | \hat{\rho}_\psi | \varphi_n \rangle = \sum_n \langle \psi | \varphi_n \rangle \langle \varphi_n | \psi \rangle = \langle \psi | \psi \rangle = 1 \iff (2.7) ,$$

$$\begin{aligned} \text{Tr}(\hat{\rho}_\psi \hat{F}) &= \sum_n \langle \varphi_n | \hat{\rho}_\psi \hat{F} | \varphi_n \rangle = \sum_n \langle \psi | \hat{F} | \varphi_n \rangle \langle \varphi_n | \psi \rangle \\ &= \langle \psi | \hat{F} | \psi \rangle \iff (2.1), (2.6) . \end{aligned}$$

## 7. Operator square

Because of the orthonormality of the *thinkable* states  $|\psi_m\rangle$  one obtains from the definition (2.5):

$$\hat{\rho}^2 = \sum_m p_m^2 |\psi_m\rangle \langle \psi_m| . \quad (2.9)$$

This means in particular:

$$\text{Tr}\hat{\rho}^2 = \sum_m p_m^2 . \quad (2.10)$$

Because of  $0 \leq p_m \leq 1$ :

$$\sum_m p_m^2 \leq \sum_m p_m = 1 .$$

The equality sign holds for pure states.

## 8. Time-evolution

We have derived the equation of motion of the statistical operator in the *Schrödinger picture* with equation (3.167) in Vol. 6:

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [H, \hat{\rho}]_- . \quad (2.11)$$

We will see in the next subsection that it can be interpreted as the quantum-mechanical analog of the classical *Liouville equation* (1.36).

Since all observable properties of a physical system can be determined by the use of the statistical operator, we can call, consequently, *two mixed states to be identical*, if the same statistical operator is ascribed to both.



### 2.1.2 Principle of Correspondence

We now look for an *assignment*, i.e., for a ‘*translation requirement*’ between Quantum Statistics and Classical Statistical Physics. For this purpose we have first to think about the fundamental concept of the *statistical ensemble*. This, however, does not mean a serious problem for us, because we can introduce this concept into Quantum Statistics in complete analogy to the *classical counterpart* (Sect. 1.2.2).

By a **statistical ensemble** one understands a set (‘*mixture*’) of (‘*thought*’, ‘*virtual*’) identical systems, which are all exact copies of the real system. About the latter only incomplete information is available, which is therefore in a *mixed* state. Each member of the ensemble occupies one of the *thinkable* states  $|\psi_m\rangle$  of the real system. It is an important fact that the ensemble takes up an **incoherent** amount of states. The systems of the ensemble do not interact with each other, the states do not interfere.

This definition is completely identical to the corresponding classical definition, which also implies that the statistical operator  $\hat{\rho}$  must be seen by direct analogy with the classical density-distribution function. That becomes particularly evident when we contrast the *ensemble averages*, the determination of which represents the predominant goal of Statistical Physics:

**Classical** ((1.26), (1.52), (1.134), (1.135)):

$$\langle F \rangle = \frac{1}{h^{3N} N!} \int \cdots \int d^{3N} q d^{3N} p \rho(\mathbf{q}, \mathbf{p}) F(\mathbf{q}, \mathbf{p}) ,$$

$$\mathbb{1} \stackrel{!}{=} \frac{1}{h^{3N} N!} \int \cdots \int d^{3N} q d^{3N} p \rho(\mathbf{q}, \mathbf{p}) .$$

**Quantum-mechanical:**

$$\langle \hat{F} \rangle = \text{Tr}(\hat{\rho} \hat{F}) ,$$

$$\mathbb{1} \stackrel{!}{=} \text{Tr} \hat{\rho} .$$

A further hint is given by the **equations of motion**:

**Classical:** (Liouville equation (1.36))

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} \quad (H: \text{Hamilton function}) .$$

**Quantum-mechanical:**

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}] \quad (\hat{H}: \text{Hamilton operator}) .$$

In order to be able to take over practically all the results of the Classical Statistical Physics from Chap. 1 for the Quantum Statistics, we *only* have to remember the **principle of correspondence** (section 3.5 (3.228), (3.229), Vol. 6). This suggests the following assignments (left: *classical*, right: *quantum-mechanical*):

- |   |        |   |
|---|--------|---|
| 1) phase space function<br>$F(\mathbf{q}, \mathbf{p})$  | $\iff$ | observable (operator)<br>$\widehat{F}$  |
| 2) density-distribution function<br>$\rho(\mathbf{q}, \mathbf{p})$  | $\iff$ | statistical operator<br>$\widehat{\rho}$  |
| 3) Poisson bracket<br>$\{F, G\} =$<br>$= \sum_j \left( \frac{\partial F}{\partial q_j} \frac{\partial G}{\partial p_j} - \frac{\partial G}{\partial q_j} \frac{\partial F}{\partial p_j} \right)$ | $\iff$ | commutator<br>$\frac{1}{i\hbar} [\widehat{F}, \widehat{G}]_-$<br>$= \frac{1}{i\hbar} (\widehat{F}\widehat{G} - \widehat{G}\widehat{F})$ |
| 4) phase-space integration  | $\iff$ | trace   |

$$\frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p \dots \quad \text{Tr}(\dots)$$

- |                      |        |  |
|----------------------|--------|--|
| 5) $\{\rho, H\} = 0$ | $\iff$ | <i>stationary ensemble</i><br>$[\widehat{\rho}, \widehat{H}]_- = 0.$ |
|----------------------|--------|--|
- (2.12)

Also in Quantum Statistics only *stationary* ensembles are interesting, because only these lead to time-independent ensemble-averages. It holds for not explicitly time-dependent observables ((3.211), Vol. 6):

$$i\hbar \frac{d}{dt} \langle \widehat{F} \rangle = \langle [\widehat{F}, \widehat{H}]_- \rangle.$$

We reformulate the right-hand side by exploiting the *cyclic invariance* of the trace (see Exercise 2.1.1):

$$\langle [\widehat{F}, \widehat{H}]_- \rangle = \text{Tr}(\widehat{\rho}(\widehat{F}\widehat{H} - \widehat{H}\widehat{F})) = \text{Tr}(\widehat{H}\widehat{\rho}\widehat{F} - \widehat{\rho}\widehat{H}\widehat{F}) = \text{Tr}([\widehat{H}, \widehat{\rho}]_- \widehat{F}).$$

Therewith it follows indeed:

$$\frac{d}{dt} \langle \widehat{F} \rangle = 0 \iff [\widehat{H}, \widehat{\rho}]_- = 0. \quad (2.13)$$

### 2.1.3 Exercises

#### Exercise 2.1.1

Let  $\widehat{F}$ ,  $\widehat{G}$ ,  $\widehat{H}$  be quantum-mechanical operators and  $\alpha$ ,  $\beta$  complex numbers. Prove the following useful properties of the *trace*:

1.  $\text{Tr}\widehat{F}^+ = (\text{Tr}\widehat{F})^*$ ,
2.  $\text{Tr}(\alpha\widehat{F} + \beta\widehat{G}) = \alpha\text{Tr}\widehat{F} + \beta\text{Tr}\widehat{G}$ ,
3.  $\text{Tr}(\widehat{F}^+\widehat{F}) \geq 0$ ,
4.  $\text{Tr}(\widehat{F}\widehat{G}\widehat{H}) = \text{Tr}(\widehat{H}\widehat{F}\widehat{G}) = \text{Tr}(\widehat{G}\widehat{H}\widehat{F})$  (*cyclic invariance of the trace*),
5.  $\text{Tr}(\widehat{U}^+\widehat{F}\widehat{U}) = \text{Tr}\widehat{F}$ ,  $\widehat{U}$ : unitary operator.

#### Exercise 2.1.2

Prove that the characteristic properties of the statistical operator,

$$\hat{\rho} = \sum_m p_m |\psi_m\rangle \langle \psi_m|,$$

remain valid even when the states  $|\psi_m\rangle$  are normalized, but **not** orthogonal.

#### Exercise 2.1.3

Is it possible that the statistical operator

$$\rho = \alpha \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 3 \\ 1 & 2 & 1 \end{pmatrix} \quad (\alpha: \text{real})$$

describes a pure state? If yes, what must be assumed for  $\alpha$ ?

## 2.2 Micro-Canonical Ensemble

We will now start to transfer the *statistical ensembles*, which we got to know in the *Classical Statistical Physics* of the first chapter, to Quantum Mechanics.

The task can be considered as done, when we succeed to formulate the *statistical operator* responsible for the respective ensemble. We begin also here with the *micro-canonical ensemble*, for which the statistical operator is easily derivable, if one accepts the validity of the *postulate of the same 'a-priori' probabilities* (Sect. 1.1.1). For the detailed discussion of the micro-canonical ensemble we will restrict ourselves only to facts, which are really new and hence are of quantum-mechanical nature. The further considerations, which proceed completely parallel to the *classical line* in Chap. 1, will only be briefly indicated. It is, however, recommendable to look up, in the case of need, the corresponding passages in Chap. 1. That also holds for the following two sections concerning the canonical ensemble (Sect. 2.3) and grand-canonical ensemble (Sect. 2.4), respectively.

After having developed the micro-canonical ensemble we will be able to comment on the *third law of Thermodynamics* (Sect. 2.2.2), which is of quantum-mechanical nature, and had therefore to be left open in Chap. 1.

### 2.2.1 Phase Volume

The characterizing viewpoint of the micro-canonical ensemble is, as in the Classical Statistical Physics, the fact that it shall describe an

**isolated system**

with a quasi-sharp energy between  $E$  and  $E + \Delta$ .  $\Delta$  is thereby a small *energy-tolerance* (Fig. 2.1). The exact energy constancy can **not** be expected for the here interesting macroscopic systems (see remarks in Sect. 1.1.1). The system, whose Hamilton operator is surely time-independent, shall of course be in its thermal equilibrium. The corresponding *ensemble* must therefore be characterized in any case by a **stationary** distribution. This means, according to (2.13), that the statistical operator  $\hat{\rho}$  commutes with the Hamilton operator. Quantum Mechanics tells us that in such a case  $\hat{\rho}$  and  $\hat{H}$  must have a common set of eigen-states. This fact will help us in the following derivation of  $\hat{\rho}$ .

*Conceivable* states of the system are such that their energies lie between  $E$  and  $E + \Delta$ . The energy representation will therefore be convenient:

$$\begin{aligned} \hat{H}|E_n\rangle &= E_n|E_n\rangle, \\ \langle E_n | E_m \rangle &= \delta_{nm}; \quad \langle E_n | \hat{H} | E_m \rangle = E_m \delta_{nm}. \end{aligned} \quad (2.14)$$

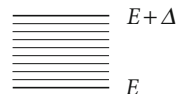
$\hat{\rho}$ , too, must be diagonal in the energy-representation:

$$\langle E_n | \hat{\rho} | E_m \rangle \sim \delta_{nm}.$$

For (quasi-)isolated systems the fundamental *postulate of the same 'a priori'-probabilities* (Sect. 1.1.1) holds. All states, which are compatible with the boundary conditions, should appear with the same probability. Then the following ansatz is obvious:

$$\begin{aligned} \hat{\rho}_{mce} &= \sum_m p_m^{mce} |E_m\rangle \langle E_m|, \\ p_m^{mce} &= \begin{cases} \text{const}, & \text{if } E < E_m < E + \Delta, \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \quad (2.15)$$

**Fig. 2.1** Energy tolerance of a (quasi-)isolated macroscopic system



The constant is easily derivable from the condition  $\text{Tr}\hat{\rho} = 1$ . At first we define:

$$\Gamma(E) = \text{Tr} \left( \sum_m^{E < E_m < E + \Delta} |E_m\rangle \langle E_m| \right). \quad (2.16)$$

This is the quantum-mechanical analog to the classical **phase volume** (1.44). We recognize its meaning, when we evaluate the trace in the energy representation:

$$\Gamma(E) = \sum_m^{E < E_m < E + \Delta} 1 = \begin{array}{l} \text{number of states with energies} \\ \text{between } E \text{ and } E + \Delta. \end{array}$$

In the concrete case,  $\Gamma(E)$  will of course also still depend on other parameters, as for instance on  $N$  and  $V$ . That we will label, in the case of need, by corresponding indexes.

It therefore follows from  $\text{Tr}\hat{\rho} = 1$  for the weights  $p_m$  of the micro-canonical ensemble according to (2.15):

$$p_m^{mce} = \frac{1}{\Gamma(E)} \quad \text{for all } m \text{ with } E < E_m < E + \Delta. \quad (2.17)$$

Mean values of observables  $\hat{F}$  are then calculated in the concept of the micro-canonical ensemble according to:

$$\langle \hat{F} \rangle = \frac{1}{\Gamma(E)} \text{Tr} \left( \sum_m^{E < E_m < E + \Delta} |E_m\rangle \langle E_m| \hat{F} \right). \quad (2.18)$$

If one applies the principle of correspondence of the last section to this, and compares it with the classical ensemble-average (1.52), then the full equivalence is easily recognizable. Note that in (2.18) the summation is over *states* and not over *energies*. In the case of degeneracy all the states are to be counted explicitly.

All the further considerations, in particular what concerns the connection to Thermodynamics, turn out to be exactly the same as in the Classical Statistical Physics (Sect. 1.3). The arguments can be taken over word-by-word. There is therefore no need to repeat them here in complete detail. As an example we mention the *internal energy*  $U$ , only:

$$\begin{aligned} U \equiv \langle \hat{H} \rangle &= \frac{1}{\Gamma(E)} \text{Tr} \left( \sum_m^{E < E_m < E + \Delta} |E_m\rangle \langle E_m| \hat{H} \right) \\ &= \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} E_m \approx E. \end{aligned} \quad (2.19)$$

This agrees with (1.57)!—The *entropy* represents also in the Quantum Statistics the central quantity of the micro-canonical ensemble, because its variables  $U = E, V, N$  are the *natural* variables of the entropy. Its definition reads, analogous to (1.71):

$$S = k_B \ln \Gamma(E) . \quad (2.20)$$

(More precisely:  $\Gamma(E) \rightarrow \Gamma_N(E, V)$  for an  $N$ -particle quantum system in the volume  $V$ ). By the way, with the definition (2.20) a *Gibb's paradox* (Sect. 1.3.7) is avoided in the Quantum Statistics. The correct counting of the states is already guaranteed by (2.16).—If one finally introduces via

$$D(E) = \lim_{\Delta \rightarrow 0} \frac{\Gamma(E)}{\Delta} \quad (2.21)$$

a *density of states*  $D(E)$ , then the representation

$$S = k_B \ln D(E) \quad (2.22)$$

is for macroscopic systems equivalent to (2.20). The proof corresponds to that for (1.74).—Sometimes the quantum-mechanical analog to the classical phase volume  $\varphi(E)$  (1.48),

$$\varphi(E) = \sum_m^{E_m \leq E} 1 , \quad (2.23)$$

can be useful. There exist, as in the Classical Statistical Physics, the connections:

$$\Gamma(E) = \varphi(E + \Delta) - \varphi(E); \quad D(E) = \frac{d}{dE} \varphi(E) . \quad (2.24)$$

$\varphi(E)$  is simply the number of eigen-states of the Hamilton operator with energies less than or equal to  $E$ .

### 2.2.2 Third Law of Thermodynamics

The first two laws of Thermodynamics could be explained within the framework of the Classical Statistical Physics. That we have demonstrated in the Sects. 1.3.3 and 1.3.5, and we combined them in form of the *basic relation of Thermodynamics* (1.103). The discussion of the third law of Thermodynamics we had to postpone, because it is of quantum-mechanical nature. It reads ((3.82), (3.83), Vol. 5):

*The entropy of a thermodynamic system at the absolute zero ( $T = 0$ ) is a universal constant, which can be chosen to be zero. This holds independently of the values of the other state variables.*

The practical consequences (e.g., the unattainability of the absolute zero) of the third law of Thermodynamics, which is also called *Nernst's heat theorem*, have been discussed in section 3.8 of Vol. 5. We can now try to even justify the law on the basis of the quantum-statistical formulations (2.20) and (2.22), respectively, of the entropy.

If the system possesses a discrete energy spectrum, then there is an energetically lowest state, the *ground state*. Exactly this state is taken by the system for  $T \rightarrow 0$ . If the ground state is  $g$ -fold degenerate, then it follows from (2.20) for the entropy at the absolute zero:

$$S(T = 0) = k_B \ln g . \quad (2.25)$$

In the case that there is no degeneracy ( $g = 1$ ) the third law of Thermodynamics can directly be read off from this formula because of  $\ln 1 = 0$ . However, a problem arises for  $g > 1$ , when the ground state is degenerate because of *internal symmetries* of the Hamilton operator.  $S$  would then not be equal to zero. To say it the other way round, since so far the *Nernst's heat theorem* has always proven to be correct, one might also conclude that such symmetries are *broken* and the degeneracy is lifted at  $T = 0$ , for instance due to phase transitions.

For systems with quasi-continuous spectra (e.g. macroscopic solids) one better investigates the entropy using the representation (2.22), according to which the  $T \rightarrow 0$ -behavior of the *density of states*  $D(E)$  becomes decisive. In all calculable (!) cases the density of states indeed appears for  $T \rightarrow 0$  in such a way that the third law of Thermodynamics is fulfilled. As an example, for the lattice dynamics of a solid at very low temperatures the *Debye theory* is applicable, by which one calculates a contribution to the heat capacity of the type  $C_V = \alpha T^3$  (see Exercise 2.3.12 and Sect. 3.3.7). The entropy thus vanishes at the absolute zero like  $T^3$ . Another example is Sommerfeld's theory of the electrons in a metallic solid (Sect. 3.2), which predicts a linear temperature-behavior of the heat capacity ( $C_V = \gamma T$ ), in accordance with the third law of Thermodynamics. The latter is, however, violated by the classical ideal gas, which, on the other hand, is not a realistic model system for  $T \rightarrow 0$  (phase transitions!).

We assert that even in the framework of Quantum Statistics, the third law of Thermodynamics is not generally and rigorously provable. It thus remains actually a theorem, based on empirical observation, and is strongly supported by quantum-statistically evaluable special cases and model systems

### 2.2.3 Exercises

#### Exercise 2.2.1

Express the probability  $p_m$  appearing in the general definition of the statistical operator

$$\hat{\rho} = \sum_m p_m |\psi_m\rangle \langle \psi_m|$$

for the micro-canonical ensemble by the entropy  $S$  and the free energy  $F = U - TS$ , respectively!

### Exercise 2.2.2

1. Let

$$\hat{\rho}(E) = \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} |E_m\rangle \langle E_m|$$

be the micro-canonical statistical operator in the energy-representation. Which form does  $\hat{\rho}$  get, when instead of the eigen-states  $|E_m\rangle$  of the Hamilton operator  $\hat{H}$  another CON-system is used for the representation? Does the quantum-mechanical *phase volume*  $\Gamma(E)$  thereby change?

2. Let  $\hat{A}$  be an observable, which does not commute with  $\hat{H}$ . For its eigen-states  $|a_n\rangle$  to the eigen-value  $a_n$  there exists an expansion in the  $|E_m\rangle$ . Calculate the micro-canonical average  $\langle \hat{A} \rangle$ !

### Exercise 2.2.3

Let a system of  $N$   $S = 1/2$ -spins, localized at lattice sites, be in a homogeneous magnetic field  $\mathbf{B}$ . To each spin there is ascribed a magnetic moment  $\mu_B$ . The energy of the system is then given by

$$E = -(N_\uparrow - N_\downarrow)\mu_B B = -M\mu_B B,$$

where  $N_\uparrow$  ( $N_\downarrow$ ) denote the numbers of spins parallel (antiparallel) to  $\mathbf{B}$ . Calculate with the micro-canonical ensemble as functions of  $N$  and  $M$

1. the entropy  $S$  of the system,
2. the temperature  $T$ ,
3. the internal energy  $U$ ,
4. the heat capacity  $C_V$ .

### Exercise 2.2.4

Consider a system of  $N$  distinguishable particles, whose energies are  $\varepsilon_r$  ( $r = 1, 2, 3, \dots$ ).

1. Calculate the entropy  $S(E)$  of the system. Assume for simplicity that all occupation numbers  $N_r$  of the levels  $\varepsilon_r$  allow for the application of the Stirling formula!
2. Calculate the equilibrium distribution  $\{N_r\}$  of the occupation numbers  $N_r$ , i.e., the most probable distribution under the boundary conditions:

$$\text{fixed } N = \sum_r N_r,$$

$$\text{fixed } E = \sum_r N_r \varepsilon_r.$$



Take these boundary conditions into consideration according to the method of the Lagrange multipliers (subsection 1.2.5, Vol. 2).

3. Discuss the physical meaning of the multipliers!

### Exercise 2.2.5

Calculate the expectation values  $\langle \hat{p}_x^2 \rangle$ ,  $\langle \hat{p}_y^2 \rangle$ ,  $\langle \hat{q}_x^2 \rangle$ ,  $\langle \hat{q}_y^2 \rangle$ ,  $\langle \hat{T} \rangle$  and  $\langle \hat{V} \rangle$  ( $\hat{T}(\hat{V})$ ): operator of the kinetic (potential) energy) via the micro-canonical ensemble for a two-dimensional, quantum-mechanical, harmonic oscillator of the mass  $m$  and the frequency  $\omega$ .

### Exercise 2.2.6

Consider a system of  $N$  harmonic oscillators, all with the same mass  $m$  and the same frequency  $\omega$ . Let it have the energy

$$E = \frac{1}{2}N\hbar\omega + N_0\hbar\omega \quad (N_0 \geq 0; \text{ integer}) .$$

1. Calculate the quantum-mechanical *phase volume*  $\Gamma_N(E)$ .
2. Calculate the entropy  $S$  and the temperature  $T$  as functions of the energy  $E$ .
3. Find the connection between the quantum number  $N_0$  and the temperature  $T$ .

## 2.3 Canonical Ensemble

The micro-canonical ensemble with its variables  $E, V, N$  is adapted to the description of isolated or quasi-isolated systems. This actually corresponds rather seldom to the experimental situation. Instead, the case, where the system is with fixed particle number  $N$  and with constant volume  $V$  in thermal contact with a heat bath of the temperature  $T$ , is surely more common. In Sect. 1.4, we have already got to know, in the framework of the Classical Statistical Physics, the *canonical ensemble* as such a statistical ensemble which belongs to the variables  $T, V, N$ . When deriving the concept of the *canonical ensemble* from that of the *micro-canonical ensemble* in Sect. 1.4.1 we actually did not apply any specific classical viewpoints. That means that we now can execute the corresponding *quantum-mechanical transition* in almost identical manner. This will be performed in Sect. 2.3.1, where, though, because of this reason not all details have to be presented with the same level of thoroughness as in Sect. 1.4.1. In fact we will deal with two further methods, which permit a *direct* access to the *canonical partition function*, without any reference to the *micro-canonical ensemble*. In particular, we will thereby get to know mathematical procedures, which have proved their worth for the solution of typical problems of Quantum Statistics.

### 2.3.1 Canonical Partition Function

The partition function, which we are going to derive in analogy to (1.136), turns out to be also in Quantum Statistics the central quantity, from which all important relations can be derived. Let us briefly sketch its determination in this subsection. For this purpose we consider, as for the *classical chain of conclusions* in Sect. 1.4.1, a reference system  $\Sigma_1$  as a very small, but nevertheless macroscopic part of a very large isolated system  $\Sigma$ , for which a micro-canonical ensemble can be defined. This total system or *superordinate system*  $\Sigma$  may be in thermal equilibrium, so that an entropy can be defined, and that everywhere in  $\Sigma$ , i.e., also in  $\Sigma_1$ , the same temperature  $T$  is set up. The *complementary system*  $\Sigma_2$  ( $\Sigma = \Sigma_1 \cup \Sigma_2$ ) represents for the essentially smaller  $\Sigma_1$  a *heat bath* of the temperature  $T$ . For installing the *thermal equilibrium*  $\Sigma_1$  and  $\Sigma_2$  must of course exchange energy, i.e. they must interact. As already assumed several times (see reasoning of (1.82)), however, the contact can be considered as to be so weak that one can refrain from an explicit taking into account of the interaction energy in the following considerations.

The *canonical ensemble* shall consist of systems, which are physically equivalent to  $\Sigma_1$ , where each system occupies a state  $|\psi_m\rangle$ , which is *conceivable for*  $\Sigma_1$ . For the derivation of the statistical operator  $\hat{\rho}$  we need, according to (2.5), the probability  $p_m$ , with which  $\Sigma_1$  is now indeed in the state  $|\psi_m\rangle$ . As to  $|\psi_m\rangle$ , it shall be an eigen-state of the Hamilton operator  $\hat{H}$  with the eigen-value  $E_m$ . The total system is isolated and has the energy  $E$ . It must therefore hold

$$E = E_m + E_2 ,$$

where  $E_2$  is the energy of the *complementary system*  $\Sigma_2$ . The number of states of the total system with the energy  $E$  is given by

$$\Gamma(E) = \sum_{E_1} \Gamma_1(E_1) \Gamma_2(E - E_1); ,$$

where the sum runs over **all** energies  $E_1$  of the small subsystem  $\Sigma_1$ . When, however,  $\Sigma_1$  is in a well-defined state  $|\psi_m\rangle$  with  $E_1 = E_m$ , then there remain for the total system only  $\Gamma_2(E - E_m)$  possibilities. According to the *postulate of the same 'a priori'-probabilities* (Sect. 1.1.1) all these possibilities appear with the same probability. The more states of the total system are coming into question for a certain  $\Sigma_1$ -state  $|\psi_m\rangle$ , the more probable it is then that  $\Sigma_1$  is indeed in just this state  $|\psi_m\rangle$ :

$$p_m \sim \Gamma_2(E - E_m) .$$

This explanatory statement corresponds exactly in every detail to that which we have applied in the classical case for (1.133).—Because of the chosen differences in the order of magnitudes between  $\Sigma_1$ , on the one hand, and  $\Sigma$ ,  $\Sigma_2$ , on the other hand, we can assume that  $E_m \ll E$ , so that a Taylor expansion can be justified. One can easily convince oneself that such an expansion is not so reasonably done directly for

the *phase volume*  $\Gamma_2$ , but rather for its logarithm:

$$\begin{aligned} \ln \Gamma_2(E - E_m) &= \ln \Gamma_2(E) - E_m \left( \frac{\partial}{\partial E_2} \ln \Gamma_2(E_2) \right)_{E_2=E} + \dots \\ &\approx \ln \Gamma_2(E) - \frac{E_m}{k_B T} + \dots \end{aligned}$$

On the right-hand side,  $T$  should actually be the temperature, which  $\Sigma_2$  takes in the thermal equilibrium at the energy  $E$  and not at the energy  $E - E_m$ . Because of  $E - E_m \approx E$ , however, this temperature will hardly differ from the temperature  $T$  of the isolated total system. The same simplification we used, by the way, also for the classical derivation! The first summand in the above expression is a constant for  $\Sigma_1$ . It thus holds:

$$p_m \sim \Gamma_2(E - E_m) \sim \exp(-\beta E_m).$$

That, in turn, means for the **statistical operator**:

$$\hat{\rho} \sim \sum_m e^{-\beta E_m} |E_m\rangle \langle E_m| = e^{-\beta \hat{H}} \sum_m |E_m\rangle \langle E_m|.$$

On the right-hand side we have the identity for the states of the  $\Sigma_1$ -Hilbert space. The proportionality constant is fixed by the normalization condition (2.7):

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr} e^{-\beta \hat{H}}}. \quad (2.26)$$

$\hat{\rho}$  is therewith completely determined for the canonical ensemble. In order to recognize the full equivalence, one should compare this expression with the classical canonical density-distribution function  $\rho(\mathbf{q}, \mathbf{p})$  in (1.134) taking thereby into consideration the principle of correspondence from Sect. 2.1.2.

Obviously,  $\hat{\rho}$  commutes with the Hamilton operator  $\hat{H}$  describing therewith a *stationary ensemble*. The denominator in (2.26) represents the extraordinarily important

**partition function (sum of states) of the canonical ensemble**

$$Z(T) = \text{Tr} e^{-\beta \hat{H}}. \quad (2.27)$$

If the system is an  $N$ -particle system in the volume  $V$ , then we will later write, as in the classical case,  $Z_N(T, V)$ . Furthermore, we will predominantly use the notion ‘partition function’ even if ‘sum of states’ would actually be more appropriate. Equation (2.27) is the representation-independent formulation of the partition function. For practical purposes the energy-representation turns out to be the most important one:

$$Z(T) = \sum_n e^{-\beta E_n}. \quad (2.28)$$

The evaluation of the trace in (2.27) in the CON-system of the energy-eigen states  $|E_n\rangle$  makes clear that it is summed in (2.28) over all **states**. The exponential functions  $e^{-\beta E_n}$ , which correspond to degenerate states, have to be counted as often as the degree of degeneracy is.

With (2.26) one finds for the expectation value of an arbitrary observable  $\widehat{F}$  in the *canonical ensemble* an expression equivalent to (1.135):

$$\langle \widehat{F} \rangle = \text{Tr}(\widehat{\rho}\widehat{F}) = \frac{\text{Tr}(e^{-\beta\widehat{H}}\widehat{F})}{\text{Tr}e^{-\beta\widehat{H}}} . \quad (2.29)$$

We have therewith all the means to create the connection to Thermodynamics, and also to demonstrate the equivalence of the micro-canonical and the canonical ensemble. That we will not do here in all the details, though, because the derivations and justifications are **exactly** the same as the *classical ones* in the Sects. 1.4.2 and 1.4.4. So one gets directly from (2.29) the representation of the **internal energy** ( $N$ -particle system in the volume  $V$ ):

$$U = \langle \widehat{H} \rangle = -\frac{\partial}{\partial\beta} \ln Z_N(T, V) . \quad (2.30)$$

The important fluctuation formula (1.149) holds classically as well as quantum-mechanically (see Exercise 2.3.1), one has to, of course, only replace for the Quantum Statistics the Hamilton function by the Hamilton operator:

$$\sqrt{\frac{\langle \widehat{H}^2 \rangle - \langle \widehat{H} \rangle^2}{\langle \widehat{H} \rangle^2}} = \frac{\sqrt{C_V k_B T^2}}{U} \sim \frac{1}{\sqrt{N}} . \quad (2.31)$$

By this formula it is confirmed that in the case of macroscopic systems *almost all* members of the canonical ensemble have the same energy  $E = \langle \widehat{H} \rangle$ . That we have already realized in Sect. 1.4 as the decisive precondition for the canonical ensemble to be *statistically equivalent* to a micro-canonical ensemble of the energy  $E = U = \langle \widehat{H} \rangle$ . The variables of the canonical ensemble,  $(T, V, N)$ , are the natural variables of the **free energy**,

$$F(T, V, N) = -k_B T \ln Z_N(T, V) , \quad (2.32)$$

whose connection with the partition function is found as in Sect. 1.4.2. For *pressure* and *entropy* the formulas (1.142) and (1.146), respectively, remain valid if one interprets there  $Z_N(T, V)$  as the quantum-mechanical partition function. The equivalence of *micro-canonically* and *canonically* introduced quantities such as entropy and temperature is proven, without any change, as in Sect. 1.4.4.

If the system to be investigated is composed of two non-interacting or only very weakly interacting partial systems  $\Sigma_a$  and  $\Sigma_b$ , then the partition function will factorize, since the eigen-states of the total system can be written as direct products of the individual eigen-states and the eigen-energies as the sum of one energy from

$\Sigma_a$  and one from  $\Sigma_b$ :

$$Z(T) = \sum_{n_a} \sum_{n_b} e^{-\beta(E_{n_a} + E_{n_b})} = Z_a(T)Z_b(T) . \quad (2.33)$$

That demonstrates the additivity of the free energy:

$$F(T) = F_a(T) + F_b(T) . \quad (2.34)$$

### 2.3.2 Saddle-Point Method

In the preceding subsection we have derived the canonical partition function, actually, from the micro-canonical ensemble. There exists a more direct way, which will be introduced in Sect. 2.3.3 as **Darwin-Fowler method**. This method uses a procedure, which plays an important role also in other contexts of Statistical Physics. It shall therefore be developed here, at first irrespectively of its actual subject matter, as a general method of solution for Classical Statistical Physics as well as for Quantum Statistics. It refers to the so-called *saddle-point method*.

In Statistical Physics one has to deal very often with integrals of the type

$$I_M = \int_C \exp(Mg(z))dz , \quad (2.35)$$

where  $M$  is a very large number ( $M \rightarrow \infty$ ), and where

$$g(z) = u(x, y) + iv(x, y) \quad (z = x + iy)$$

represents an analytic function in a region which contains the path  $C$ . Let the first derivative of  $g(z)$  vanish at the point  $z = z_0$  so that real and imaginary parts of  $g(z)$  adopt there extremal values:

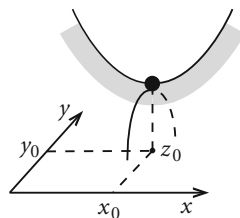
$$\left. \frac{dg(z)}{dz} \right|_{z=z_0=x_0+iy_0} = 0 . \quad (2.36)$$

For the following it will become a decisive fact that the path  $C$  can be arbitrarily shifted and deformed within the region of analyticity, without changing thereby the value of the integral  $I_M$ . We thus can also lay the path through  $z_0$ .

Real and imaginary parts of a differentiable complex function obey the two-dimensional Laplace equation, i.e., the *Cauchy-Riemann differential equations* (Exercise 2.3.18):

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0 ; \quad \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = 0 .$$

**Fig. 2.2** Representation of a saddle point



If one combines these equations with the extremal condition (2.36),

$$\left. \frac{\partial u}{\partial x} \right|_{z_0} = \left. \frac{\partial u}{\partial y} \right|_{z_0} = \left. \frac{\partial v}{\partial x} \right|_{z_0} = \left. \frac{\partial v}{\partial y} \right|_{z_0} = 0,$$

then one realizes that real and imaginary parts of the function  $g(z)$  possess at  $z_0$  a **saddle point** (Fig. 2.2). Because of

$$\left. \frac{\partial^2(u, v)}{\partial x^2} \right|_{z_0} = - \left. \frac{\partial^2(u, v)}{\partial y^2} \right|_{z_0},$$

the extremum of  $u$  and  $v$ , respectively, is at  $z_0$  in  $x$ -direction a minimum and in  $y$ -direction a maximum or vice versa.—Of course, not only  $g(z)$  has a saddle point at  $z_0$ , but also the total integrand in (2.35):

$$J(z) \equiv \exp(Mg(z)).$$

Because of

$$J''(z = z_0) = Mg''(z_0)J(z_0),$$

for  $M \rightarrow \infty$ , at the saddle point  $z_0$  an extremely sharp minimum encounters an extremely sharp maximum. For large  $M$  that allows for special approximations.

We choose the path  $C$  such that the real part  $u(x, y)$  of  $g(z)$  has a maximum at  $z_0$ , while the imaginary part  $v(x, y)$  is practically constant in the close neighborhood of  $z_0$ , so that not all too strong oscillations of  $J(z)$  are to be feared. For large  $M$  an extremely sharp maximum of the magnitude of the integrand in (2.35) will be the consequence. When no further point on  $C$  exhibits a similarly pronounced maximum, then only the immediate neighborhood of  $z_0$  will essentially contribute to the integral. We therefore expand  $g(z)$  up to the second order around  $z_0$ ,

$$g(z) \approx g(z_0) + \frac{1}{2}g''(z_0)(z - z_0)^2,$$

and insert this into (2.35):

$$I_M \approx \exp(Mg(z_0)) \int_C \exp\left(\frac{1}{2}Mg''(z_0)(z - z_0)^2\right) z.$$

The path  $C$  is chosen such that at least in the immediate neighborhood of  $z_0$  the term

$$t = \sqrt{-g''(z_0)}(z - z_0)$$

is **real**. (If, for instance,  $z_0 = x_0$  and  $g''(x_0) > 0$  both are real, then the path  $C$  would be chosen parallel to the imaginary axis through  $x_0$  (Exercise 2.3.19)). It follows:

$$I_M \approx \frac{\exp(Mg(z_0))}{\sqrt{-g''(z_0)}} \int_{\dots}^{\dots} \exp\left(-\frac{1}{2}Mt^2\right) dt .$$

Because of the rapidly decreasing integrand we can push, in a further harmless step of approximation, the bounds of integration to  $\pm\infty$ . The integral then simply takes the value  $\sqrt{2\pi/M}$ :

$$I_M \approx \sqrt{\frac{2\pi}{-Mg''(z_0)}} e^{Mg(z_0)} . \quad (2.37)$$

This very useful estimation of the integral is the more precise the larger  $M$  is. Of course, this presumes  $g''(z_0) \neq 0$ .

Very often one needs in Statistical Physics not so much  $I_M$ , but rather the logarithm of  $I_M$ . Then (2.37) can for large  $M$  further be simplified, because the root only provides a contribution of the order  $\mathcal{O}(\ln M)$ :

$$\ln I_M \approx Mg(z_0) .$$

### 2.3.3 Darwin-Fowler Method

Because of its fundamental importance for Quantum Statistics, the *canonical partition function* (2.28) will be derived in this subsection in a somewhat more direct manner than in Sect. 2.4.1. For this purpose we use a procedure given by Darwin and Fowler (RH. Fowler, *Statistical Mechanics*, Cambridge University Press, Cambridge 1966). This procedure applies, in particular, the just presented *saddle-point method*. The following line of thought, however, will not lead to new results, but will only confirm the considerations of Sect. 2.4.1.

We start with the assumption that for the macroscopic system, in which we are interested, there are available the energy levels

$$E_0 < E_1 < E_2 < \dots < E_m < \dots , .$$

Because of the always free choice of the energy zero, we can assume that all the energies are positive. Furthermore, we choose the energy unit such that the  $E_j$  are

**relatively prime, integral numbers.** That can always be achieved and somewhat simplifies the following considerations. It will of course be again important to find out, with which probabilities the system will occupy the respective energy states at the temperature  $T$ , in order to fix therewith the statistical operator (2.5).

For this purpose we think of an ensemble of  $M$  systems, which are all physically completely identical to the actually to be investigated real system, and which are distributed in a certain manner over the *conceivable* energy levels  $E_0, E_1, \dots, E_m, \dots$ . Let the systems be completely equivalent, but nevertheless distinguishable, i.e., somehow indexable. One could for instance imagine a certain fixed spatial arrangement. Between the systems, there exists a certain *thermal contact*, which, however, can be assumed, as done already several times before, as so *weak* that the interactions between the systems remain negligible. We can then consider the entirety of the systems as a huge isolated *superordinate system*, whose *particles* are, in a certain sense, represented by the single systems, which are distributed with the *occupation numbers*

$$\begin{aligned}\{n_m\} &= n_0, n_1, \dots, n_m, \dots \\ n_m &= 0, 1, 2, 3, \dots\end{aligned}$$

over the available energy levels. The *superordinate system* defines a fixed energy  $\hat{E}$  and a constant *particle number*  $M$  (number of the systems in the ensemble), for which it must hold:

$$\hat{E} = \sum_m n_m E_m ; \quad M = \sum_m n_m . \quad (2.38)$$

All distributions  $\{n_m\}$ , which are compatible with these boundary conditions are '*a priori*' of equal probability. *Thermal equilibrium* of the superordinate system is therefore defined by the *most probable* distribution  $\{n_m\}$ , i.e., by the sequence of occupation numbers, to which the maximal number of possibilities of realization is ascribed. The individual systems are all physically equivalent and indexable. The number of possibilities of realization for a special distribution  $\{n_m\}$  then obviously amounts to:

$$W(\{n_m\}) = \frac{M!}{n_0! n_1! \dots n_m! \dots} . \quad (2.39)$$

The total number of states, which are available for the *superordinate system*, i.e., its quantum-mechanical phase volume, is given by

$$\Gamma_M(\hat{E}) = \sum_{\{n_m\}}^{(2.38)} W(\{n_m\}) . \quad (2.40)$$



It is summed over all distributions  $\{n_m\}$ , which are compatible with the boundary conditions (2.38). In the thermal equilibrium in the isolated *superordinate system* there will be the same temperature  $T$  everywhere:

$$\frac{1}{T} = k_B \frac{\partial}{\partial \widehat{E}} \ln \Gamma_M(\widehat{E}) . \quad (2.41)$$

All the individual systems thus possess the same temperature, and of course, trivially, the same volume and the same particle number. But these are just the boundary conditions of a **canonical ensemble**.

The number  $W(\{n_m\})$  in (2.40) is proportional to the probability, to find indeed the sequence  $\{n_m\}$ , which is compatible with the boundary conditions (2.38). It therefore holds for the **mean value**  $\langle n_j \rangle$  of a certain occupation number:

$$\langle n_j \rangle = \frac{\sum_{\{n_m\}} n_j W(\{n_m\})}{\sum_{\{n_m\}} W(\{n_m\})} . \quad (2.42)$$

A primary concern in the following will consist in the explicit calculation of these mean values. That is to say, if we then are still able to show that the *relative mean square deviation*

$$(\overline{\langle n_j \rangle})_r = \sqrt{\frac{\langle n_j^2 \rangle - \langle n_j \rangle^2}{\langle n_j \rangle^2}}$$

tends to zero for  $M \rightarrow \infty$ , this will mean that the scattering of the  $n_j$ -values around  $\langle n_j \rangle$  vanishes. The average configuration  $\{\langle n_m \rangle\}$  is in such a case identical to the *most probable one*, thus being identical to the configuration which defines the *thermal equilibrium*. For *almost all* states of the *superordinate system* the occupation number  $n_j$  then has the value  $\langle n_j \rangle$ . On the other hand, this can also be interpreted in such a way that

$$p_j = \lim_{M \rightarrow \infty} \frac{\langle n_j \rangle}{M} \quad (2.43)$$

represents the probability that the actually interesting system under consideration is in the *conceivable* energy-eigen state  $|E_j\rangle$ . That, in turn, is exactly the quantity, which we need for the construction of the statistical operator  $\hat{\rho}$  of the respective ensemble.

It is recommendable to calculate, at first, the phase volume  $\Gamma_M(\widehat{E})$ . For that we define the *auxiliary function*

$$Q_M(z) = \sum_{E=0}^{\infty} z^E \Gamma_M(E) . \quad (2.44)$$

Since all the  $E_m$  are integers,  $E = \sum_j n_j E_j$  is also an integer. We insert (2.39) and (2.40) into (2.44):

$$Q_M(z) = \sum_{E=0}^{\infty} z^E \sum_{\{n_m\}}^{(2.38)} W(\{n_m\}) = \sum_{E=0}^{\infty} \sum_{\{n_m\}}^{(2.38)} \frac{M!}{n_0! n_1! \dots} z^{n_0 E_0 + n_1 E_1 + \dots} .$$

Since the  $E$ -sum runs through **all** non-negative integers, and the sum over  $\{n_m\}$  comprises of **all** the sequences of occupation numbers, which are compatible with the boundary conditions (2.38),  $Q_M(z)$  can be expressed as follows:

$$Q_M(z) = \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \dots \sum_{n_m=0}^{\infty} \dots \frac{M!}{n_0! n_1! \dots} (z^{E_0})^{n_0} (z^{E_1})^{n_1} \dots (z^{E_m})^{n_m} \dots$$

$$\left( \sum_j n_j = M \right) .$$

Except for the boundary condition  $\sum_j n_j = M$  the summations over the occupation numbers run independently of each other. With the multinomial theorem it eventually follows:

$$Q_M(z) = (z^{E_0} + z^{E_1} + \dots + z^{E_m} + \dots)^M = [q(z)]^M , \quad (2.45)$$

$$q(z) = \sum_j z^{E_j} . \quad (2.46)$$

According to our ansatz (2.44),  $\Gamma_M(\widehat{E})$  is the coefficient of  $z^{\widehat{E}}$  in the expansion of  $Q_M$  in powers of  $z$ . In the *Laurent expansion* ((4.320), Vol. 3) of the function

$$\frac{Q_M(z)}{z^{\widehat{E}+1}}$$

$\Gamma_M(\widehat{E})$  thus represents the *residue*. According to *Cauchy's residue theorem* ((4.424), Vol. 3) it then holds,

$$\Gamma_M(\widehat{E}) = \frac{1}{2\pi i} \oint_C dz \frac{[q(z)]^M}{z^{\widehat{E}+1}} , \quad (2.47)$$

where  $C$  is a closed path in the complex plane (e.g. a circle) around the singularity  $z = 0$ . With

$$g(z) = \ln q(z) - \frac{1}{M}(\widehat{E} + 1) \ln z \quad (2.48)$$

$\Gamma_M(\widehat{E})$  has now exactly the structure of (2.35):

$$\Gamma_M(\widehat{E}) = \frac{1}{2\pi i} \oint_C \exp(Mg(z)) dz . \quad (2.49)$$

We write, as in the last subsection, for abbreviation

$$J(z) \equiv \exp(Mg(z)) \quad (2.50)$$

and investigate at first the function  $g(z)$ . On the positive-real axis,  $q(x)$  (2.46) is a monotonously increasing function of  $x$  with a radius of convergence  $R$  ( $0 < R \leq +\infty$ ). We thus have:

$$q(z = x \rightarrow R) = +\infty .$$

In the case of a *finite* radius of convergence  $R$  it follows from that immediately with (2.48):

$$g(z = x \rightarrow R) = +\infty .$$

But this holds also for  $R \rightarrow +\infty$ , which one realizes straightaway, when one represents (2.48) as follows:

$$g(x) = \ln \sum_j x^{E_j} - \ln x^{\frac{1}{M}(\widehat{E}+1)} .$$

Except for the trivial special case that all the systems are in the same energy state, there exists at least one  $E_j$  with  $E_j > \frac{1}{M}\widehat{E}$ . Hence,  $g(x)$  diverges in either case for  $x \rightarrow R \leq +\infty$ .

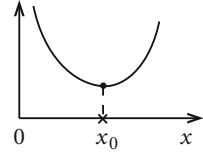
For  $x \rightarrow 0$  we estimate, with (2.46) and (2.48), as follows:

$$q(x \rightarrow 0) \approx x^{E_0} \quad \curvearrowright \quad g(x \rightarrow 0) \approx \ln x^{E_0} - \frac{1}{M}(\widehat{E} + 1) \ln x \approx \left( E_0 - \frac{1}{M}\widehat{E} \right) \ln x .$$

For  $x \rightarrow 0$  it holds  $\ln x \rightarrow -\infty$ . If we exclude that all the systems are in the lowest energy state  $E_0$ , so that  $n_0 < M$ , then  $(E_0 - \frac{1}{M}\widehat{E}) < 0$  and hence

$$g(x \rightarrow 0) = +\infty .$$

**Fig. 2.3** Qualitative behavior of the function  $g(z)$  (2.48) on the real axis



Along the real axis,  $g(z)$  therefore shows the behavior, schematically plotted in Fig. 2.3, with a minimum at  $x_0$  ( $0 < x_0 < R$ ). It thus holds:

$$\left. \frac{dg(z)}{dz} \right|_{z=x_0} = 0 \quad \text{and} \quad \left. \frac{\partial^2 g(z)}{\partial x^2} \right|_{z=x_0} > 0 .$$

Except at  $z = 0$ ,  $g(z)$  is analytic in the whole complex plane, in particular at the point  $z = x_0$ . The *Cauchy-Riemann differential equations* (see Sect. 2.4.2) are therefore valid. That has the consequence:

$$\left. \frac{\partial^2 g(z)}{\partial y^2} \right|_{z=x_0} < 0 .$$

$g(z)$  thus exhibits a minimum along a path on the real axis at  $z = x_0$ , and has there, along a path parallel to the imaginary axis ( $y$ -axis) through  $z = x_0$ , a maximum.  $z = x_0$  therefore represents a saddle point for  $g(z)$ .

When we again assume that not all the systems occupy the same state, then there is at least one  $E_j > \frac{1}{M}\widehat{E}$ , and at least one  $E_i < \frac{1}{M}\widehat{E}$ . Since, in addition,  $x_0$  is positive (greater or less than 1), it can be concluded:

$$q(x_0) = \sum_j x_0^{E_j} \geq x_0^{\frac{1}{M}\widehat{E}} \quad \curvearrowright \quad g(x_0) \geq 0 .$$

These properties transfer to the integrand  $J(z)$  (2.50). Because of

$$\begin{aligned} \frac{d}{dz} J(z) &= M g'(z) J(z) \\ \frac{d^2}{dz^2} J(z) &= M g''(z) J(z) + M^2 (g'(z))^2 J(z) \end{aligned}$$

we have:

$$\begin{aligned} J(x_0) &\geq 0 \quad \left. \frac{d}{dz} J(z) \right|_{z=x_0} = 0 \\ \left. \frac{\partial^2 J(z)}{\partial x^2} \right|_{z=x_0} &= M \left. \frac{\partial^2 g(z)}{\partial x^2} \right|_{z=x_0} J(x_0) \xrightarrow{M \rightarrow +\infty} +\infty \\ \left. \frac{\partial^2 J(z)}{\partial y^2} \right|_{z=x_0} &= M \left. \frac{\partial^2 g(z)}{\partial y^2} \right|_{z=x_0} J(x_0) \xrightarrow{M \rightarrow +\infty} -\infty \end{aligned} \quad (2.51)$$

At the saddle point, an extremely sharp minimum thus encounters a very steep maximum for  $J(z)$  (see Fig. 2.2). The preconditions for the saddle-point method, developed in Sect. 2.4.2, are obviously fulfilled. The saddle point itself results from the extremum condition for  $g(z)$ :

$$g'(z)|_{z=x_0} = \frac{q'(x_0)}{q(x_0)} - \frac{1}{M} (\widehat{E} + 1) \frac{1}{z_0} \stackrel{!}{=} 0 .$$

In the bracket, we can surely neglect the 1 in relation to the *macroscopic* integer  $\widehat{E}$ , to find then an implicit conditional equation for  $x_0$ :

$$\widehat{E} = M \frac{\sum_j E_j x_0^{E_j}}{\sum_j x_0^{E_j}} . \tag{2.52}$$

In order to finally be able to perform the saddle-point method, we still have now to fix the (closed) path  $C$  in (2.49). This must take course in the region, in which the integrand  $J(z)$  is analytic. Furthermore, the path should run through the saddle point  $z = x_0$ , but, on the other hand, should not contain any other point, which provides a comparably large contribution to the integral as the saddle point. We consider the path  $C$  therefore as a circle around  $z = 0$  with the radius  $x_0$ :

$$C = \{z = x_0 e^{i\varphi}; 0 \leq \varphi < 2\pi\} .$$

$C$  therefore passes through the **saddle point**  $z = x_0$  parallel to the imaginary axis. On  $C$  there appears at  $x_0$  then a sharp maximum (!) of the integrand in (2.49). Are there further maxima of the integrand on  $C$ ? There we have:

$$|e^{Mg(z)}| \stackrel{(C)}{=} \frac{1}{x_0^{\widehat{E}}} \left| \sum_j (x_0 e^{i\varphi})^{E_j} \right|^M .$$

This expression is maximal, exactly when all summands on the right-hand side are positive-real! That means:

$$\varphi \cdot E_j \stackrel{!}{=} 2\pi \alpha_j \quad \alpha_j \in \mathbb{Z} .$$

One possibility is  $\varphi = 0 \Leftrightarrow \alpha_j \equiv 0$ . This corresponds indeed to the discussed saddle point  $z = x_0$ . For other points of the circle,  $\varphi \neq 0$ , so that the above condition must be fulfilled by

$$E_j = \frac{2\pi}{\varphi} \alpha_j .$$

Since the  $E_j$  are, according to the prerequisites, relative prime, this condition then requires  $\varphi = 2\pi$ , which, however, is equivalent to  $\varphi = 0$ . There is therefore for the integrand in (2.49) on  $C$  only one maximum at  $\varphi = 0$ , i.e., at  $z = x_0$ . The preconditions for the applicability of the *saddle-point method* are thus all fulfilled. Formula (2.37) can therefore be directly used to solve (2.49):

$$\Gamma_M(\widehat{E}) \approx \frac{1}{2\pi i} \sqrt{\frac{2\pi}{-Mg''(x_0)}} e^{Mg(x_0)} = \sqrt{\frac{1}{2\pi Mg''(x_0)}} e^{Mg(x_0)}. \quad (2.53)$$

One finds with (2.48):

$$\begin{aligned} g''(z)|_{z=x_0} &= \frac{q''(x_0)}{q(x_0)} - \left( \frac{q'(x_0)}{q(x_0)} \right)^2 + \frac{\widehat{E}}{Mx_0^2} \\ &= \frac{\sum_j E_j (E_j - 1) x_0^{E_j - 2}}{\sum_j x_0^{E_j}} - \frac{\widehat{E}/M (\widehat{E}/M - 1)}{x_0^2} \\ &\stackrel{(2.50)}{=} x_0^{-2} \frac{\sum_j \left[ E_j^2 - (\widehat{E}/M)^2 \right] x_0^{E_j}}{\sum_j x_0^{E_j}}. \end{aligned}$$

$g''(x_0)$  will turn out to be, except for the factor  $x_0^{-2}$ , the relative mean square deviation of the energy of a **single** system of the ensemble. In

$$\ln \Gamma_M(\widehat{E}) = -\frac{1}{2} \ln 2\pi Mg''(x_0) + Mg(x_0)$$

one can therefore neglect for  $M \rightarrow \infty$  the first summand compared to the second term:

$$\ln \Gamma_M(\widehat{E}) \approx Mg(x_0). \quad (2.54)$$

Insertion into (2.41) allows for the determination of  $x_0$ :

$$\frac{1}{T} = k_B \frac{\partial}{\partial \widehat{E}} Mg(x_0) \stackrel{(2.48)}{\approx} -k_B \ln x_0.$$

This means:

$$x_0 = e^{-\beta}; \quad \beta = \frac{1}{k_B T}. \quad (2.55)$$

We can now go over to the initially formulated task, namely to the calculation of the average occupation number  $\langle n_j \rangle$ . For this purpose we apply a ‘*computational trick*’. We integrate into the probabilities  $W(\{n_m\})$  ‘*artificially*’ factors  $\{\alpha_m\}$ , which at the end of the calculation are set to 1. That means, we now write instead of (2.39):

$$W_\alpha(\{n_m\}) = \frac{M!}{n_0! n_1! \dots} \alpha_0^{n_0} \alpha_1^{n_1} \dots$$

This transfers via (2.40) to the phase volume,

$$\Gamma_M(\widehat{E}) \longrightarrow \Gamma_M^\alpha(\widehat{E}),$$

and via (2.45) to

$$q(z) \longrightarrow q_\alpha(z) = \sum_j \alpha_j z^{E_j}.$$

We can now write for (2.42):

$$\begin{aligned} \langle n_j \rangle &= \left( \alpha_j \frac{\partial}{\partial \alpha_j} \ln \Gamma_M^\alpha(\widehat{E}) \right)_{\{\alpha_i\}=1} \stackrel{(2.52)}{=} \left( M \frac{\partial}{\partial \alpha_j} \ln q_\alpha(x_0) \right)_{\{\alpha_i\}=1} \\ &= \left( M \frac{x_0^{E_j}}{q_\alpha(x_0)} \right)_{\{\alpha_i\}=1}. \end{aligned}$$

With (2.55) it follows therewith for the average occupation number:

$$\langle n_j \rangle = M \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}. \quad (2.56)$$

We now check the mean square deviation of the occupation number:

$$\begin{aligned} \langle n_j^2 \rangle &= \frac{\sum_{\{n_m\}} n_j^2 W(\{n_m\})}{\sum_{\{n_m\}} W(\{n_m\})} = \left[ \frac{1}{\Gamma_M^\alpha} \alpha_j \frac{\partial}{\partial \alpha_j} \left( \alpha_j \frac{\partial}{\partial \alpha_j} \Gamma_M^\alpha \right) \right]_{\{\alpha_i\}=1} \\ &= \left[ \alpha_j \frac{\partial}{\partial \alpha_j} \left( \frac{1}{\Gamma_M^\alpha} \alpha_j \frac{\partial}{\partial \alpha_j} \Gamma_M^\alpha \right) \right]_{\{\alpha_i\}=1} + \left[ \alpha_j^2 \left( \frac{1}{\Gamma_M^\alpha} \frac{\partial}{\partial \alpha_j} \Gamma_M^\alpha \right)^2 \right]_{\{\alpha_i\}=1}. \end{aligned}$$

From this expression we get by manifold application of the formula before Eq. (2.56):

$$\begin{aligned}
 \langle n_j^2 \rangle - \langle n_j \rangle^2 &= \left[ \frac{\partial}{\partial \alpha_j} \left( \alpha_j \frac{\partial}{\partial \alpha_j} \ln \Gamma_M^\alpha \right) \right]_{\{\alpha_i\}=1} \\
 &= \langle n_j \rangle + \left[ \alpha_j \frac{\partial^2}{\partial \alpha_j^2} \ln \Gamma_M^\alpha \right]_{\{\alpha_i\}=1} \\
 &= \langle n_j \rangle + \left[ \alpha_j \frac{\partial}{\partial \alpha_j} \left( M \frac{x_0^{E_j}}{q_\alpha(x_0)} \right) \right]_{\{\alpha_i\}=1} \\
 &= \langle n_j \rangle + M \left[ -\frac{x_0^{E_j}}{q_\alpha^2(x_0)} x_0^{E_j} \right]_{\{\alpha_i\}=1} \\
 &= \langle n_j \rangle - M \frac{\langle n_j \rangle^2}{M^2} \\
 \leadsto \frac{\langle n_j^2 \rangle - \langle n_j \rangle^2}{\langle n_j \rangle^2} &= \frac{1}{\langle n_j \rangle} - \frac{1}{M} \stackrel{(2.56)}{=} \mathcal{O} \left( \frac{1}{M} \right) .
 \end{aligned}$$

The *relative mean square deviation* can therefore be estimated to

$$(\overline{\Delta n_j})_r \approx \mathcal{O} \left( \frac{1}{\sqrt{M}} \right) \xrightarrow{M \rightarrow \infty} 0 .$$

In the limit  $M \rightarrow \infty$ , there thus belong to *almost all* states of the *superordinate system* occupation numbers  $n_j$ , which practically agree with their mean values  $\langle n_j \rangle$ . The sequence of the  $\langle n_j \rangle$  determines the *thermal equilibrium*. The probability  $p_j$ , to find the *real* single system in the energy state  $|E_j\rangle$ , is according to (2.43) and (2.56) given by

$$p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} . \tag{2.57}$$

But this is exactly the same result as the one we have already derived for the canonical ensemble in another way in Sect. 2.2.1. The statistical operator  $\hat{\rho}$  is therewith confirmed in the form (2.26), and all the further formulas are replicated. So we have, e.g., for the **internal energy**

$$U = \sum_j E_j p_j = -\frac{\partial}{\partial \beta} \ln Z , \tag{2.58}$$



if we define the **partition function**  $Z$  as in (2.28). The **entropy** is found with (2.48), (2.50) and (2.54) to be:

$$S = \frac{1}{M} k_B \ln \Gamma_M(\widehat{E}) = k_B g(x_0) \approx k_B \ln \sum_j e^{-\beta E_j} + k_B \beta U . \quad (2.59)$$

From this it follows for the **free energy**

$$F = U - TS = -k_B T \ln Z ,$$

the well-known result (2.32) of the canonical ensemble.

### 2.3.4 The Method of Lagrange Multipliers

The Darwin-Fowler method of the last subsection suggests, from the vanishing of the relative mean square deviation in the limit  $M \rightarrow \infty$ , that the sequence  $\{\langle n_m \rangle\}$  of the average values of the *occupation numbers*  $n_m$  represents the *most probable* distribution of the  $M$  individual systems over the energy levels  $E_0, E_1, \dots, E_m, \dots$ , and therewith defines the *thermal equilibrium*. This means for the isolated *superordinate system*, which is composed by the  $M$  individual systems, that the number of possibilities of realization  $W(\{n_m\})$ , defined in (2.39), exhibits a sharp maximum at  $\{\langle n_m \rangle\}$ . Out of all the states of the *superordinate system*, which are compatible with the boundary conditions (2.38), the overwhelming majority corresponds to the distribution  $\{\langle n_m \rangle\}$ . The *canonical ensemble* is therewith uniquely defined, and we can draw, by the means of it, the known conclusions with respect to the thermodynamic properties of the actual system of interest.

Following these considerations, we could have also used from the beginning, for the derivation of the *canonical partition function*, our previous knowledge about macroscopic (*asymptotically large*,  $M \rightarrow \infty$ ) systems, which we got in several parts of Chap. 1 (e.g., Sects. 1.1.2, 1.3.1). According to this precognition, the distribution function (2.39) possesses such a pronounced maximum that, for instance, for the calculation of the equilibrium temperature  $T$  of the *superordinate system* according to (2.41), the full phase volume  $\Gamma_M(\widehat{E})$  actually could have been reduced to this maximal term only:

$$\frac{1}{T} = k_B \frac{\partial}{\partial E} \ln \Gamma_M(\widehat{E}) \approx k_B \frac{\partial}{\partial E} \ln W_{\max} . \quad (2.60)$$

We want to show in this subsection that the distribution  $\{n_m^{(0)}\}$ , which makes  $W(\{n_m\})$  maximal, and which determines therewith the equilibrium properties of the *superordinate system*, is indeed identical to the sequence  $\{\langle n_m \rangle\}$  of the average occupation numbers. The determination of  $W_{\max}$  leads to the same *canonical*

partition function  $Z$  as that, which was found by the use of the procedure presented in the Sects. 2.2.1 and 2.2.3.

For fixing  $W_{\max}$  we use the **method of Lagrange multipliers** (subsections 1.2.5, 1.2.6, Vol. 2). Since, when seeking the maximum of the expression (2.39), the boundary conditions (2.38) must of course be fulfilled, it is not sufficient, simply to set the first variation of  $W(\{n_m\})$  with respect to the  $n_m$  equal to zero. Because of the boundary conditions the  $n_m$  can not be varied freely and independently of each other. The free variation is guaranteed only when the two constraints (2.38) are coupled to the quantity, which is to be varied, by two Lagrange multipliers  $\lambda_1$  and  $\lambda_2$  ((1.97), Vol. 2):

$$\delta \left( \ln W(\{n_m^{(0)}\}) - \lambda_1 \sum_m n_m^{(0)} E_m - \lambda_2 \sum_m n_m^{(0)} \right) = 0. \quad (2.61)$$

It proves to be convenient not to vary  $W$  but  $\ln W$ , because then one can make use of the helpful *Stirling formula* (1.8). It is clear that  $\ln W$  is maximal at the same point as  $W$ . We assume that the number of systems  $M$  is so large that the occupation numbers  $n_m$  by themselves allow for the application of the *Stirling formula*, and that they can be considered as practically continuous variables.

The variation is quickly done. With

$$\ln W(\{n_m\}) \stackrel{(2.39)}{\approx} M (\ln M - 1) - \sum_m n_m (\ln n_m - 1)$$

(2.61) becomes:

$$\sum_m (\ln n_m^{(0)} + \lambda_1 E_m + \lambda_2) \delta n_m^{(0)} = 0.$$

All the  $n_m^{(0)}$  are subject, after *coupling* to the boundary conditions, to *free* variations. We can, for instance, *single out* a special  $\delta n_m^{(0)}$  and set it unequal zero, while all the other  $\delta n_m^{(0)}$  are chosen to be zero. This means nothing but that already each term in the sum must vanish separately. This, in turn, immediately leads to the intermediate result:

$$n_m^{(0)} = \exp(-\lambda_1 E_m - \lambda_2). \quad (2.62)$$

The boundary conditions (2.38) yield two implicit conditional equations for the multipliers  $\lambda_1$  and  $\lambda_2$ :

$$M = e^{-\lambda_2} \sum_m e^{-\lambda_1 E_m}, \quad (2.63)$$

$$\widehat{E} = e^{-\lambda_2} \sum_m E_m e^{-\lambda_1 E_m}. \quad (2.64)$$

$\lambda_1$  and  $\lambda_2$  are thus fixed by the given quantities  $M$  and  $\widehat{E}$ . We can, however, also exploit the relation (2.62), therewith bringing into play the temperature  $T$  of the canonical ensemble:

$$\begin{aligned} \ln W_{\max} &\approx M \ln M - \sum_m n_m^{(0)} \ln n_m^{(0)} \\ &= M \ln M + \sum_m n_m^{(0)} (\lambda_1 E_m + \lambda_2) = M \ln M + \lambda_1 \widehat{E} + \lambda_2 M . \end{aligned}$$

It follows then with (2.60) and (2.63):

$$\lambda_1 = \frac{1}{k_B T} = \beta ; \quad e^{-\lambda_2} = \frac{M}{\sum_m e^{-\beta E_m}} .$$

When we insert these expressions into (2.60), then we realize that the occupation numbers  $n_m^{(0)}$ , which make  $W(\{n_m\})$  maximal, coincide indeed with the average values  $\langle n_m \rangle$ , which we have derived by the Darwin-Fowler method (2.56) in the last subsection:

$$n_m^{(0)} = M \frac{e^{-\beta E_m}}{\sum_m e^{-\beta E_m}} \equiv \langle n_m \rangle . \quad (2.65)$$

This means in particular that

$$p_m = \frac{n_m^{(0)}}{M} = \frac{e^{-\beta E_m}}{\sum_m e^{-\beta E_m}} \quad (2.66)$$

can be considered as the probability for the single system to be in the state  $|E_m\rangle$ , at thermal equilibrium. This is now the third time that we have derived just this result, which defines the canonical ensemble.

### 2.3.5 Exercises

#### Exercise 2.3.1

Let  $\widehat{H}$  be the Hamilton operator of a physical system of  $N$  particles in the volume  $V$ . Prove the fluctuation formula (2.31)

$$\sqrt{\frac{\langle \widehat{H}^2 \rangle - \langle \widehat{H} \rangle^2}{\langle \widehat{H} \rangle^2}} = \frac{\sqrt{C_V k_B T^2}}{U} ,$$

by a direct calculation of the expectation values  $\langle \widehat{H}^2 \rangle$  and  $\langle \widehat{H} \rangle$ .

**Exercise 2.3.2**

Consider the statistical operator  $\hat{\rho}$  of the linear harmonic oscillator (frequency  $\omega$ , mass  $m$ ) in the canonical ensemble.

1. Verify that the diagonal element of  $\hat{\rho}$  in the position representation,

$$\rho(q) \equiv \langle q | \hat{\rho} | q \rangle ,$$

fulfills the differential equation

$$\frac{d}{dq} \rho(q) = \left( -\frac{2m\omega}{\hbar} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \right) q \rho(q) .$$

2. Which meaning does  $\rho(q)$  have? Why should we have

$$\int_{-\infty}^{+\infty} dq \rho(q) = 1 ?$$

Solve therewith the differential equation from part 1.!

**Exercise 2.3.3**

Find the canonical partition function  $Z_2$  of the two-dimensional harmonic oscillator:

$$H = \frac{1}{2m} (p_x^2 + p_y^2) + \frac{1}{2} m \omega^2 (x^2 + y^2)$$

It should also be possible to understand the oscillator as the total system of two decoupled one-dimensional oscillators. Show that indeed:

$$Z_2 = (Z_1)^2 .$$

**Exercise 2.3.4**

An ideal gas of  $N$  *distinguishable* particles, all of the same mass  $m$ , is enclosed in a volume (cuboid)  $V = L_x \cdot L_y \cdot L_z$ . For the energy of a single particle we have

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} ,$$

where the components of the wave vector  $\mathbf{k}$  take discrete values due to '*periodic boundary conditions*':

$$k_i = \frac{2\pi}{L_i} n_i; \quad i = x, y, z. \quad n_x, n_y, n_z \text{ run through all the integers.}$$

1. Formulate the canonical partition function  $Z_N(T, V)$  of the ideal gas.
2. In the macroscopic system discrete sums can be replaced by integrals:

$$\sum_{n_i} \rightarrow \int_{-\infty}^{+\infty} dn_i .$$

Calculate therewith  $Z_N(T, V)$ !

3. Show that for the internal energy the classical result is valid:

$$U = \frac{3}{2} N k_B T$$

### Exercise 2.3.5

Calculate the canonical partition function of a system of  $N$  independent linear harmonic oscillators, all with the same frequency  $\omega$ .

### Exercise 2.3.6

For a physical system (gas!) the canonical partition function

$$Z_N(T, V) = \left( \gamma \cdot \frac{V}{N} T^3 \right)^N$$

is given ( $\gamma = \text{const}$ ).

1. Calculate the internal energy  $U(T, V, N)$  and the entropy  $S(T, V, N)$ .
2. Find reasons why the formula for the entropy can be correct only for temperatures  $T > T^*$  ( $T^* > 0$ ). Calculate  $T^*$ !
3. Choose an ansatz for the thermal equation of state by analogy with the ideal gas

$$pV = x \cdot U .$$

What is  $x$ ?

4. Calculate the chemical potential  $\mu$  as a function of the temperature  $T$ !

### Exercise 2.3.7

Graphite has a strongly anisotropic structure. Consider for the calculation of the heat capacity the following simplified model: Each of the  $N$  C-atoms oscillates harmonically in the three space directions  $x, y, z$  with the eigen-frequencies  $\omega_x, \omega_y, \omega_z$ . Calculate

1. the partition function  $Z$ ,
2. the internal energy  $U$ ,
3. the heat capacity  $C_V$ . Simplify the expression of  $C_V$  for the case

$$\hbar\omega_x = \hbar\omega_y \gg k_B T; \quad \hbar\omega_z \ll k_B T.$$

**Exercise 2.3.8**

Consider a linear chain of  $N$  magnetic moments. Each moment is due to a  $S = 1/2$ -spin and thus possesses only two possibilities of orientation (parallel or antiparallel to the  $z$ -direction):

$$S_i^z |\sigma_1 \sigma_2 \cdots \sigma_n\rangle = \sigma_i |\sigma_1 \sigma_2 \cdots \sigma_n\rangle; \quad \sigma_i = \pm \frac{1}{2}.$$

A spontaneous order of the moments (ferromagnet!) is possible only if there is an interaction between the spins (moments) (Ising model):

$$\hat{H} = - \sum_{i=1}^{N-1} J_i S_i^z S_{i+1}^z \quad (J_i: \text{interaction constant}).$$

1. How many different spin states  $|\sigma_1 \cdots \sigma_n\rangle$  do exist? Formulate the canonical partition function  $Z_N$  by means of the spin-values  $\sigma_i$ !
2. Enlarge the chain by one link ( $N \rightarrow N + 1$ ). Derive the recursion formula

$$Z_{N+1}(T) = 2Z_N(T) \cosh\left(\frac{1}{4}\beta J_N\right).$$

3. Explain why it holds for the single spin

$$Z_1(T) \equiv 2.$$

Calculate therewith  $Z_N(T)$ !

4. Calculate the ‘correlation function’

$$\langle S_i^z S_{i+1}^z \rangle !$$

**Exercise 2.3.9**

Consider the canonical ensemble of a system of  $N$  noninteracting spatially fixed, i.e., distinguishable spins  $S = 1/2$ , which are in a homogeneous external magnetic field  $\mathbf{B} = B\mathbf{e}_z$ . The Hamilton operator is then given by

$$\hat{H} = - \sum_{i=1}^n \hat{\mu}_i \cdot \mathbf{B} = -2\mu_B B \sum_{i=1}^n \hat{S}_i^z$$

( $\mu_B$ : Bohr magneton). The eigen-states

$$\hat{H} |\sigma_1 \sigma_2 \cdots \sigma_N\rangle = -2\mu_B B \sum_{i=1}^n \hat{S}_i^z |\sigma_1 \sigma_2 \cdots \sigma_N\rangle,$$

fulfill:

$$\widehat{S}_i^z |\sigma_1 \sigma_2 \cdots \sigma_N\rangle = \sigma_i |\sigma_1 \sigma_2 \cdots \sigma_N\rangle; \quad \sigma_i \in \left\{ -\frac{1}{2}, +\frac{1}{2} \right\}.$$

Determine therewith

1. the possible energy-eigen values and their degrees of degeneracy,
2. the partition function,
3. the free energy and the internal energy,
4. the entropy,
5. the heat capacity  $C_B$ ,
6. the average magnetic total moment:

$$M = \left\langle 2\mu_B \sum_{i=1}^N \widehat{S}_i^z \right\rangle.$$

7. Discuss the result for high and low temperatures, i.e.,  $\beta\mu_B B \ll 1$  and  $\beta\mu_B B \gg 1$ , and compare it with the *classical* result from Exercise 1.4.6.
8. Does the system obey the third law of Thermodynamics?

### Exercise 2.3.10

Consider, as in the preceding exercise, a system of noninteracting spatially fixed magnetic moments  $\mu_i$  in a homogeneous magnetic field  $\mathbf{B} = B\mathbf{e}_z$ . However, let the moments  $\hat{\mu}_i$  now be caused by an arbitrary angular momentum  $\hat{\mathbf{J}}_i$ . Assume that the quantum numbers of the angular momentum  $J_i \equiv J$  are for all moments the same. The system can then be described by the following Hamilton operator (*Langevin paramagnetism*):

$$\widehat{H} = - \sum_{i=1}^n \hat{\mu}_i \cdot \mathbf{B} = -g_J \mu_B \sum_{i=1}^N \hat{\mathbf{J}}_i \cdot \mathbf{B}$$

( $g_J$ : Landéfactor).

1. Calculate the canonical partition function.
2. Show that we now have for the average value of the magnetic total moment

$$M = M_0 B_J(\beta g_J \mu_B B),$$

where

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right)$$

represents the so-called *Brillouin function* and

$$M_0 = N g_J J \mu_B$$

the *saturation moment*.

3. Discuss  $M$  for  $J = 1/2$ ,  $J \rightarrow \infty$ ,  $\beta\mu_B B \gg 1$ ,  $\beta\mu_B B \ll 1$ .

### Exercise 2.3.11

After transformation to the so-called *normal coordinates* ((2.152), Vol. 9) one can approximately express the Hamilton function of a solid of  $N$  atoms by

$$H(\mathbf{q}, \mathbf{p}) = \sum_{j=1}^{3N} \left( \frac{p_j^2}{2m} + \frac{1}{2} m \omega_j^2 q_j^2 \right);$$

i.e., by a system of  $3N$  uncoupled, linear harmonic oscillators.

1. Calculate with the classical *equipartition theorem* the internal energy and the heat capacity of the solid.
2. Derive with the Hamilton *operator*, which corresponds to the function  $H(\mathbf{q}, \mathbf{p})$ , ( $\hat{q}_j, \hat{p}_j$ : now observables), quantum-mechanically the canonical partition function, and from that once more the heat capacity. For this purpose use the so-called *Einstein-assumption*  $\omega_j \equiv \omega_E \forall j$ .
3. Discuss the result of part 2. for  $T \gg \Theta_E$  and  $T \ll \Theta_E$ , respectively, where  $\Theta_E = \hbar\omega_E/k_B$  is the so-called *Einstein-temperature*. Compare it with the classical result from part 1. and check the third law of Thermodynamics. What can be said about the validity of the classical equipartition theorem?

### Exercise 2.3.12

Consider, as in Exercise 2.3.11, the *normal oscillations* of a solid. Calculate again the heat capacity, but now not in the framework of the *Einstein model* ( $\omega_j = \omega_E \forall j$ ), but by the use of the *Debye model*, which distributes the frequencies of the uncoupled oscillators according to the density of states

$$D(\omega) = \begin{cases} \frac{9N}{\omega_D^3} \omega^2 & \text{for } \omega \leq \omega_D, \\ 0 & \text{otherwise.} \end{cases}$$

$D(\omega)d\omega$  thus is the number of oscillator frequencies between  $\omega$  and  $\omega + d\omega$ . The *Debye frequency*  $\omega_D$  is fixed by the condition

$$\int_0^{\infty} D(\omega)d\omega = 3N \quad (\text{total number of the eigen-oscillations of the crystal}),$$

where  $N$  is the number of lattice sites.



Discuss the heat capacity at high and low temperatures, check the validity of the third law of Thermodynamics, and check the validity of the classical *Dulong-Petit law* ( $C^{\text{class}} = 3Nk_B$ ).

Useful formula:

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4}{15} \pi^4 .$$

### Exercise 2.3.13

Molecular hydrogen ( $\text{H}_2$ ) appears as *ortho-hydrogen* with parallel nuclear spins of the H-atoms and as *para-hydrogen* with antiparallel nuclear spins. Both types can be, under certain conditions, at equilibrium to each other.

In a most simple model for  $\text{H}_2$  only the rotational energy is to be taken into consideration

$$\hat{H} = \frac{1}{2J} \hat{\mathbf{L}}^2 \quad (\text{dumbbell model}),$$

$J$  = moment of inertia,

$$\hat{\mathbf{L}}: \text{operator of the angular momentum; } \hat{\mathbf{L}}^2 |l\rangle = \hbar^2 l(l+1) |l\rangle,$$

ortho- $\text{H}_2$ : *l* odd,

para- $\text{H}_2$ : *l* even.

1. Calculate the partition functions, the internal energy, and the heat capacities for the different components.
2. Discuss the results for high and low temperatures.
3. Calculate the partition function, the internal energy, and the heat capacity for the ortho-para mixture at thermal equilibrium. How does the equilibrium-ratio

$$\alpha(T) = \frac{Z_{\text{ortho}}(T)}{Z_{\text{para}}(T)}$$

depend on temperature? Discuss again the limiting cases of high and low temperatures! Is the third law of Thermodynamics fulfilled?

### Exercise 2.3.14

Let a system of  $N$  particles be at the temperature  $T$  in the volume  $V$ , and let  $Z_N(T, V)$  be the canonical partition function. Prove the following relation:

$$N \left( \frac{\partial \ln Z_N}{\partial N} \right)_{T,V} + V \left( \frac{\partial \ln Z_N}{\partial V} \right)_{T,N} = \ln Z_N .$$

**Exercise 2.3.15**

Derive by the use of the saddle-point method from the *Gamma function*

$$\Gamma(N + 1) = \int_0^{\infty} e^{-x} x^N dx = N!$$

the useful *Stirling formula*

$$N! \approx \sqrt{2\pi N} N^N e^{-N} .$$

**Exercise 2.3.16**

Let  $\hat{H}$  be the Hamilton operator of a physical system with a discrete eigen-value spectrum:

$$\begin{aligned} \hat{H}|E_n\rangle &= E_n|E_n\rangle , \\ \langle E_n | E_m \rangle &= \delta_{nm} . \end{aligned}$$

1. Introduce *average values* by

$$\langle E \rangle = \sum_n d_n E_n ; \quad \langle F(E) \rangle = \sum_n d_n F(E_n) ,$$

where the coefficients  $d_n$  fulfill

$$d_n \geq 0; \quad \sum_n d_n = 1 ,$$

but being otherwise completely arbitrary. Show that then it holds for each *convex* function  $F(E)$  ( $F''(E) \geq 0$ ):

$$\langle F(E) \rangle \geq F(\langle E \rangle) .$$

2. Let  $\{|\varphi_n\rangle\}$  now be an arbitrary orthonormal, but not necessarily complete set of quantum-mechanical states. By using 1., show that for the *free energy*  $\mathbf{F}$  of the systems the inequality

$$F \leq -k_B T \ln \left[ \sum_n \exp(-\beta \langle \varphi_n | \hat{H} | \varphi_n \rangle) \right]$$

is valid, which enables a *variational procedure* for the determination of  $F$ . When does the equality sign hold?

**Exercise 2.3.17**

In connection with the solution of the quantum-mechanical eigen-value problem of a particle in the homogeneous force field (electric field, gravitational field close to the earth surface) one encounters the Airy-function:

$$Ai(\eta) = \frac{1}{\pi} \int_0^{\infty} ds \cos\left(\frac{s^3}{3} + s\eta\right).$$

For large  $\eta$  we have the asymptotic formula:

$$Ai(\eta) \approx \frac{1}{2\sqrt{\pi}} \eta^{-1/4} \exp\left(-\frac{2}{3}\eta^{3/2}\right).$$

1. Justify this formula by means of the saddle-point method!
2. Why is the saddle-point method applicable only with respect to the saddle point in the upper complex half plane?

**Exercise 2.3.18**

Let the function

$$g(z) = u(x, y) + i v(x, y)$$

be analytic in the neighborhood of  $z = x + iy$ .

1. Show that for  $u(x, y)$  and for  $v(x, y)$  the Cauchy-Riemann differential equations must be valid.
2. Let  $g(z)$  have at  $z = z_0 = x_0 + iy_0$  an extremal value. Show that then it must hold

$$\left. \frac{\partial u}{\partial x} \right|_{z_0} = \left. \frac{\partial u}{\partial y} \right|_{z_0} = \left. \frac{\partial v}{\partial x} \right|_{z_0} = \left. \frac{\partial v}{\partial y} \right|_{z_0} = 0!$$

**Exercise 2.3.19**

For the derivation of the 'saddle-point formula' (2.37) it had to be assumed that, at least in the immediate neighborhood of the saddle point  $z_0$ , on the integration path  $C$  the quantity

$$t = \sqrt{-g''(z_0)} (z - z_0)$$

is real. The notation is the same here as in the main text.

1. Show that this assumption can always be fulfilled!
2. What holds for the special cases

(a)

$$z_0 = x_0 \in \mathbb{R}; \quad g''(z_0) > 0$$

(b)

$$z_0 = i\eta, \quad \eta \in \mathbb{R}; \quad g''(z_0) < 0?$$

## 2.4 Grand-Canonical Ensemble

In connection with the quantum-mechanical formulation of the *canonical ensemble* in the Sect. 2.2.1 we recognized that all important quantities, and the relations between them, could directly be transferred, with the aid of the *principle of correspondence* (Sect. 2.1.2), from Classical Statistical Physics to Quantum Statistics. For the argumentation in Sect. 2.2 we could very often refer to the considerations in Sect. 1.4. So that we could spare, for instance, the explicit proof of the quantum-mechanical equivalence of the *micro-canonical ensemble* and the *canonical ensemble*, because the proof follows word-by-word the classical line of thought. The situation is completely analogous for the *grand-canonical ensemble*. When deriving it in Sect. 1.5.1 classically from the *micro-canonical ensemble*, we applied hardly any specifically classical argumentation, so that the quantum-mechanical reasoning of the grand-canonical ensemble is almost superimposable with the classical reasoning. We can therefore restrict our review on the partition function to the bare necessary, i.e., to those details, which are of typical quantum-mechanical nature and therefore do not appear in the classical representation.

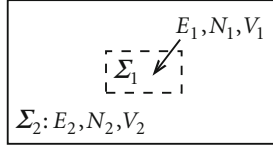
### 2.4.1 Grand-Canonical Partition Function

The grand-canonical ensemble shall describe, also in Quantum Statistics, situations, in which the physical system under investigation exhibits besides *thermal contact* also *particle exchange contact* with its surroundings. By thermal contact with a *heat bath* its temperature  $T$  is definitely given as in the canonical ensemble, while for this purpose the energy may fluctuate. The new feature is the *particle exchange contact* with a *particle reservoir*, which takes care for a definite chemical potential  $\mu$ , whereas the number  $N$  of particles is variable.

$(T, V, \mu)$ : **state variables of the grand-canonical ensemble.**

The corresponding thermodynamic potential, introduced in (1.154) is the **grand-canonical potential**

$$\begin{aligned} \Omega(T, V, \mu) &= F - G = F - \mu\langle N \rangle = -pV, \\ d\Omega &= -SdT - pdV - \langle N \rangle d\mu. \end{aligned}$$



**Fig. 2.4** Small system  $\Sigma_1$  with walls permeable for particles in the heat bath of an isolated superordinate system  $\Sigma = \Sigma_1 \cup \Sigma_2$ . Schematic representation for the interpretation of the grand-canonical ensemble

We imagine the reference system  $\Sigma_1$ , which is to be investigated, as a small, but nevertheless macroscopic part of an **isolated superordinate system**  $\Sigma = \Sigma_1 \cup \Sigma_2$ . It is delimited against the very much larger *complementary system*  $\Sigma_2$  by *walls*, which are permeable for energy and particles (Fig. 2.4). The volumes  $V_1$  and  $V_2$  are fixed. For the isolated *superordinate system*  $\Sigma$  with the total volume  $V = V_1 + V_2$  a micro-canonical ensemble can be defined, and therewith an entropy. In the *thermal equilibrium*, the same temperature  $T$  and the same chemical potential  $\mu$  are established at all points of  $\Sigma$ , and therewith also in  $\Sigma_1$ . The necessary interaction between  $\Sigma_1$  and  $\Sigma_2$  may again be negligibly weak. For the *equilibrium values* of the energy and the particle number it must be assumed in any case that

$$\hat{E}_1 \ll \hat{E}_2; \quad \hat{N}_1 \ll \hat{N}_2 .$$

The *grand-canonical ensemble* shall consist of systems, which are physically equivalent to  $\Sigma_1$ , where each of them is in one of the states, which are *conceivable* for  $\Sigma_1$ . As such states we take the common eigen-states  $|E_m(N_1)\rangle$  of the Hamilton operator  $\hat{H}_1$  and the particle number operator  $\hat{N}_1$ :

$$\begin{aligned} \hat{H}_1 |E_m(N_1)\rangle &= E_m(N_1) |E_m(N_1)\rangle , \\ \hat{N}_1 |E_m(N_1)\rangle &= N_1 |E_m(N_1)\rangle . \end{aligned} \quad (2.67)$$

We thus presume that  $\hat{H}_1$  and  $\hat{N}_1$  commute. Let  $E$  and  $N$  be the fixed values for the energy and the particle number of the *superordinate system*  $\Sigma$ :

$$E = E_2(N_2) + E_m(N_1) ; \quad N = N_1 + N_2 . \quad (2.68)$$

(We disregard here the small *micro-canonical energy-uncertainty*  $\Delta$  with respect to  $\Sigma$ .)  $E_2(N_2)$  is the energy of the *complementary system*  $\Sigma_2$ . For the **statistical operator**  $\hat{\rho}$  of the grand-canonical ensemble the following ansatz suggests itself, because of (2.5):

$$\hat{\rho} = \sum_{N_1} \sum_m p_m(N_1) |E_m(N_1)\rangle \langle E_m(N_1)| \quad (2.69)$$

The remaining task consists in finding the probability  $p_m(N_1)$ , with which  $\Sigma_1$  is really in the state  $|E_m(N_1)\rangle$ . The total number of states (*phase volume*), which are at the disposal of the *superordinate system*, amounts to:

$$\Gamma_N(E, V) = \sum_{N_1} \sum_m \Gamma_{N_1}^{(1)}(E_m(N_1), V_1) \Gamma_{N-N_1}^{(2)}(E - E_m(N_1), V_2) .$$

If we fix the  $\Sigma_1$ -state  $|E_m(N_1)\rangle$  then there remain still

$$\Gamma_{N-N_1}^{(2)}(E - E_m(N_1), V_2)$$

possible states for  $\Sigma_2$ , and therewith also for  $\Sigma$ . All these states appear '*a priori*' with the same probability. The more of such states exist, the larger is the probability that  $\Sigma_1$  is indeed in the state  $|E_m(N_1)\rangle$ . We can therefore assume

$$p_m(N_1) \sim \Gamma_{N-N_1}^{(2)}(E - E_m(N_1), V_2) .$$

Because of the different orders of magnitude of  $\Sigma_1$  and  $\Sigma$ , at least for the interesting constellations near the equilibrium,  $E_m \ll E$  and  $N_1 \ll N$  can be presumed. A Taylor expansion is therefore obvious, which we perform for the logarithm of the phase volume, and which we terminate after the linear term:

$$\begin{aligned} \ln \Gamma_{N-N_1}^{(2)}(E - E_m(N_1), V_2) &\approx \frac{1}{k_B} S_2(E, N, V_2) - \frac{E_m(N_1)}{k_B} \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (E, N, V_2) \\ &\quad - \frac{N_1}{k_B} \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} (E, N, V_2) . \end{aligned}$$

The first summand is for  $\Sigma_1$  a constant, and therefore here uninteresting. For the two others we have:

$$\begin{aligned} \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (E, N, V_2) &\approx \left( \frac{\partial S_2}{\partial E_2} \right)_{N_2, V_2} (\widehat{E}_2, \widehat{N}_2, V_2) = \frac{1}{T} , \\ \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} (E, N, V_2) &\approx \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} (\widehat{E}_2, \widehat{N}_2, V_2) = -\frac{\mu}{T} . \end{aligned}$$

It remains therewith:

$$p_m(N_1) \sim \Gamma_{N-N_1}^{(2)}(E - E_m(N_1), V_2) \sim e^{-\beta(E_m(N_1) - \mu N_1)} . \quad (2.70)$$

This result we use in (2.69) for the statistical operator:

$$\begin{aligned} \hat{\rho} &\sim \sum_{N_1} \sum_m e^{-\beta(E_m(N_1) - \mu N_1)} |E_m(N_1)\rangle \langle E_m(N_1)| \\ &= e^{-\beta(\widehat{H}_1 - \mu \widehat{N}_1)} \sum_{N_1} \sum_m |E_m(N_1)\rangle \langle E_m(N_1)| . \end{aligned}$$

On the right-hand side there appears the identity of the  $\Sigma_1$ -Hilbert space. The not yet determined proportionality constant follows by the normalization condition (2.7). From now on the index 1 can be dropped because the *complementary system*  $\Sigma_2$  no longer plays any role in the following considerations.

### Statistical operator of the grand-canonical ensemble

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\text{Tr}e^{-\beta(\hat{H}-\mu\hat{N})}}. \quad (2.71)$$

$\hat{\rho}$  commutes with  $\hat{H}$ , and thus describes a *stationary ensemble*. The denominator is the *representation-independent* formulation of the

### partition function of the grand-canonical ensemble

$$\Xi_\mu(T, V) = \text{Tr}e^{-\beta(\hat{H}-\mu\hat{N})}. \quad (2.72)$$

The energy-particle representation

$$\Xi_\mu(T, V) = \sum_{N=0}^{\infty} \sum_m \exp[-\beta(E_m(N) - \mu N)], \quad (2.73)$$

$$\Xi_z(T, V) = \sum_{N=0}^{\infty} z^N Z_N(T, V) \quad (2.74)$$

reveals the equivalence to the *classical* result (1.159), if one takes into consideration the *principle of correspondence* (2.12).  $Z_N(T, V)$  is the *canonical partition function* of the  $N$ -particle system (2.28), and

$$z = e^{\beta\mu}$$

is the *fugacity* (1.160). One should notice that, because of the variable particle number, there does not exist a direct classical analog to  $\hat{\rho}$ . The classical density-distribution function (1.164) can be defined only for fixed  $N$ , since different  $N$  lead to different phase spaces.

With (2.71) the average value of an arbitrary observable  $\hat{F}$  is calculated as follows:

$$\langle \hat{F} \rangle = \text{Tr}(\hat{\rho}\hat{F}) = \frac{\text{Tr}(e^{-\beta(\hat{H}-\mu\hat{N})}\hat{F})}{\text{Tr}e^{-\beta(\hat{H}-\mu\hat{N})}}. \quad (2.75)$$

This means in the energy-particle number representation:

$$\langle \hat{F} \rangle = \frac{1}{\Xi_\mu} \sum_{N=0}^{\infty} \sum_m e^{-\beta(E_m(N)-\mu N)} F_{mm}(N), \quad (2.76)$$

$$F_{mm}(N) = \langle E_m(N) | \hat{F} | E_m(N) \rangle. \quad (2.77)$$

If  $\langle \widehat{F}_N \rangle_{ce}$  is the corresponding average value of the canonical  $N$ -particle ensemble then one has as a third alternative:

$$\langle \widehat{F} \rangle = \frac{\sum_{N=0}^{\infty} z^N Z_N(T, V) \langle \widehat{F}_N \rangle_{ce}}{\sum_{N=0}^{\infty} z^N Z_N(T, V)} . \quad (2.78)$$

We have now gathered all that we need to be able to create the connection of the grand-canonical ensemble to Thermodynamics. We are here, however, content, more or less, with a compilation of the important formulas only. Their derivations are, namely, **exactly** the same as those in Sect. 1.5.2 for the *classical* case.

One finds the average particle number, because of  $\langle \widehat{N} \rangle_{ce} = N$ , most directly with (2.78):

$$\langle \widehat{N} \rangle = \frac{1}{\beta} \left( \frac{\partial}{\partial \mu} \ln \Xi_{\mu}(T, V) \right)_{T, V} \quad (2.79)$$

$$= z \left( \frac{\partial}{\partial z} \ln \Xi_z(T, V) \right)_{T, V} . \quad (2.80)$$

One has to distinguish  $\Xi_{\mu}$  (2.73) and  $\Xi_z$  (2.74)! (2.79) can in principle be used to represent the chemical potential  $\mu$  as function of  $T, V$  and  $\langle N \rangle$ . With (2.80) one easily realizes that, as in the classical case (1.167),

$$w_N(T, V) = \frac{z^N Z_N(T, V)}{\Xi_z(T, V)} \quad (2.81)$$

can be interpreted as the probability to find the system at the temperature  $T$  with  $N$  particles in the volume  $V$ . The equivalence of the canonical and the grand-canonical ensemble is certainly guaranteed only if the distribution  $w_N$  has an extremely sharp maximum at  $N = \langle \widehat{N} \rangle$ . That this is indeed the case one recognizes by the *fluctuation formula*

$$(\overline{\Delta N})_r = \sqrt{\frac{\kappa_T}{\beta_V}} = \sqrt{\frac{\kappa_T}{\kappa_T^{(0)}}} \frac{1}{\sqrt{\langle \widehat{N} \rangle}} , \quad (2.82)$$

the proof of which was done with Eq. (1.200) in Sect. 1.5.3. In the case of *macroscopic* particle numbers the relative fluctuation practically vanishes, i.e., *almost all* systems of the ensemble possess the same particle number  $\langle \widehat{N} \rangle$ . To a good approximation, one can then apply instead of (2.72) also

$$\Xi_z(T, V) \approx z^{\langle \widehat{N} \rangle} Z_{\langle \widehat{N} \rangle}(T, V) . \quad (2.83)$$



For the **internal energy** it holds as in (1.173) and (1.174):

$$U = - \left( \frac{\partial}{\partial \beta} \ln \Xi_{\mu}(T, V) \right)_{\mu, V} + \mu \langle N \rangle \quad (2.84)$$

$$= - \left( \frac{\partial}{\partial \beta} \ln \Xi_z(T, V) \right)_{z, V} . \quad (2.85)$$

The meaning, which the entropy has in the *micro-canonical ensemble*, and the free energy in the *canonical ensemble*, is taken over in the *grand-canonical ensemble* by the **grand-canonical potential**:

$$\Omega(T, V, \mu) = -k_B T \ln \Xi_{\mu}(T, V) = -pV , \quad (2.86)$$

$$\Xi_{\mu}(T, V) = \exp \left( -\beta \Omega(T, V, \mu) \right) . \quad (2.87)$$

We have developed in this subsection the concept of the grand-canonical ensemble out of that of the micro-canonical ensemble. There are further possibilities. One possibility is to derive the partition function  $\Xi_{\mu}(T, V)$  also with the *method of Lagrange multipliers*, which we have used in subsection 2.3.4 for the determination of the canonical partition function  $Z_N(T, V)$ . The corresponding explicit derivation will be performed as Exercise 2.4.1.

## 2.4.2 Exercises

### Exercise 2.4.1

Consider a system of  $M$  physically equivalent systems. Each of them has a thermal contact to a heat bath of the temperature  $T$  and has a *particle exchange contact* to a *particle reservoir*. Let  $|E_m(N)\rangle$  be simultaneous an eigen-state of the Hamilton operator  $\hat{H}$  and the particle number operator  $\hat{N}$  of the single system. We understand the entirety of the systems as an isolated *superordinate system* of the energy  $E_r$  and the particle number  $N_r$ . The *occupation numbers*  $n_m(N)$  indicate the number of single systems in the states  $|E_m(N)\rangle$ . Let these be for  $M \rightarrow \infty$  so large that, when needed, the Stirling formula can be applied.

1. Find the number of possibilities of realization

$$W(\{n_m(N)\})$$

for a certain distribution  $\{n_m(N)\}$  of the  $M$  systems over the available states  $|E_m(N)\rangle$ . Formulate the boundary conditions.

2. Determine, using the *method of Lagrange multipliers* (subsection 2.3.4), the distribution  $\{n_m^{(0)}\}$ , which makes, under the given boundary conditions,  $W$  maximal.

3. Fix the Lagrange multipliers of part 2. by the fact that the maximum of  $W$  is extremely sharp, so that for the phase volume of the *superordinate system* it holds approximately

$$\ln \Gamma_N(E_t) \approx \ln W_{\max} .$$

4. Verify with the results of part 1. and part 3. the representation (2.71) of the grand-canonical statistical operator  $\hat{\rho}$ .

### Exercise 2.4.2

Show that the canonical partition function  $Z_N$  can be expressed as follows by the grand-canonical partition function  $\Xi_z$ :

$$Z_N = \frac{1}{2\pi i} \oint_C \frac{\Xi_z}{z^{N+1}} dz,$$

$C$ : closed path in the complex plane around  $z = 0$ .

### Exercise 2.4.3

Evaluate the integral in Exercise 2.4.2 by using the saddle-point method. Show that the saddle-point condition requires

$$N = \langle \hat{N} \rangle \quad (\hat{N} : \text{operator of the particle number}) ,$$

and that the saddle-point approximation leads to

$$F = \Omega + \mu \langle \hat{N} \rangle .$$

$F$  is thereby the free energy, and  $\Omega$  is the grand-canonical potential.

### Exercise 2.4.4

Prove the following inequality:

$$\frac{\partial}{\partial z} \left( z \frac{\partial}{\partial z} \ln \Xi_z \right) \geq 0 .$$

## 2.5 Extremal Properties of the Thermodynamic Potentials

Important equilibrium properties of thermodynamic systems are due to the tendency of their potentials to achieve extremal values. For all (irreversible) processes, which are possible under certain boundary conditions, the potential with the corresponding natural variables can only increase or only decrease (section 3.7, Vol. 5). This we have already discussed in Sect. 1.3.3 for the entropy of the micro-canonical ensemble. We will now formulate the extremal properties on a more general basis.

### 2.5.1 Entropy and Statistical Operator

We show at first that for all the three ensembles (micro-canonical, canonical, grand-canonical) the following important connection exists between the entropy  $S$  and the statistical operator  $\hat{\rho}$ :

$$S = -k_B \text{Tr}(\hat{\rho} \ln \hat{\rho}) = -k_B \langle \ln \hat{\rho} \rangle . \quad (2.88)$$

The entropy is thus essentially equal to the expectation value of the logarithm of the statistical operator, whose eigen-values are probabilities (property 5 in Sect. 2.1.1), and therewith numerical values between 0 and 1. The logarithm will therefore be negative, and hence the entropy is surely positive. We will prove (2.88) separately for the three ensembles, where we begin with the *micro-canonical ensemble*. Starting point is (2.15):

$$\hat{\rho}_{mce} = \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} |E_m\rangle \langle E_m| \quad (2.89)$$

With the eigen-value equation

$$\hat{\rho}_{mce} |E_m\rangle = \begin{cases} \frac{1}{\Gamma(E)} |E_m\rangle , & \text{if } E < E_m < E + \Delta , \\ 0 & \text{otherwise} \end{cases} \quad (2.90)$$

and the hermiticity of the statistical operator ( $\hat{\rho}_{mce} = \hat{\rho}_{mce}^+$ ) we have:

$$\begin{aligned} \text{Tr}(\hat{\rho}_{mce} \ln \hat{\rho}_{mce}) &= \sum_i \langle E_i | \hat{\rho}_{mce} \ln \hat{\rho}_{mce} | E_i \rangle \\ &= \sum_i^{E < E_i < E + \Delta} \frac{1}{\Gamma(E)} \ln \frac{1}{\Gamma(E)} \langle E_i | E_i \rangle \\ &= -\ln \Gamma(E) . \end{aligned}$$

With (2.20) it already follows therewith the assertion:

$$S \equiv k_B \ln \Gamma(E) = -k_B \text{Tr}(\hat{\rho}_{mce} \ln \hat{\rho}_{mce}) . \quad (2.91)$$

The proof of (2.88) for the *canonical ensemble* is equally simple. Starting point is here (2.26):

$$\hat{\rho}_{ce} = \frac{1}{Z} e^{-\beta \hat{H}} . \quad (2.92)$$

$Z$  is the canonical partition function. According to (2.32) it has the following connection to the free energy:

$$Z = e^{-\beta F} . \quad (2.93)$$

This yields with (2.92)

$$\hat{\rho}_{ce} = e^{\beta(F-\hat{H})} . \quad (2.94)$$

Therewith we get the expectation value

$$-k_B \langle \ln \hat{\rho}_{ce} \rangle = -k_B \beta (F - \langle \hat{H} \rangle) = -\frac{1}{T}(F - U) = -\frac{1}{T}(-TS) = S ,$$

which verifies (2.88) also for the canonical ensemble.

Finally what remains is the relation of the *grand-canonical ensemble* with the statistical operator (2.71)

$$\hat{\rho}_{gce} = \frac{1}{\Xi} e^{-\beta(\hat{H}-\mu\hat{N})} , \quad (2.95)$$

for which the partition function  $\Xi$  can directly be expressed by the grand-canonical potential  $\Omega = F - G = F - \mu \langle \hat{N} \rangle$  (2.87):

$$\Xi = e^{-\beta\Omega} . \quad (2.96)$$

It therefore holds

$$\hat{\rho}_{gce} = e^{\beta(\Omega-\hat{H}+\mu\hat{N})} . \quad (2.97)$$

We average the logarithm of  $\hat{\rho}_{gce}$ :

$$\begin{aligned} -k_B \langle \ln \hat{\rho}_{gce} \rangle &= -\frac{1}{T}(\Omega - \langle \hat{H} \rangle + \mu \langle \hat{N} \rangle) \\ &= -\frac{1}{T}(F - U) = S . \end{aligned}$$

That proves, also in this case, Eq. (2.88).

### 2.5.2 Boltzmann's $H$ -Function

The now to be introduced function  $H$  ( $H$ : Greek capital letter) looks at first rather abstract, but can be exploited to a very large extent. Let:

$\hat{\rho}$  : statistical operator in the equilibrium  
(mixed state),

$\hat{\rho}'$  : statistical operator in any  
non-equilibrium state.

We assume that both operators are normalized as follows:

$$\text{Tr}\hat{\rho} = \text{Tr}\hat{\rho}' = 1 . \quad (2.98)$$

As statistical operators,  $\hat{\rho}$  and  $\hat{\rho}'$  are both Hermitian with the eigen-value equations:

$$\hat{\rho}|\rho_n\rangle = \rho_n|\rho_n\rangle ; \quad \hat{\rho}'|\rho'_n\rangle = \rho'_n|\rho'_n\rangle . \quad (2.99)$$

We define therewith the  
 **$H$ -function**

$$H = \text{Tr}[\hat{\rho}'(\ln \hat{\rho} - \ln \hat{\rho}')] . \quad (2.100)$$

For later applications, the fact will turn out to be useful that  $H$  has an upper bound, which we now want to fix by some simple estimations:

$$\begin{aligned} H &= \sum_m (\langle \rho'_m | \hat{\rho}' \ln \hat{\rho} | \rho'_m \rangle - \langle \rho'_m | \hat{\rho}' \ln \hat{\rho}' | \rho'_m \rangle) \\ &= \sum_m \rho'_m (\langle \rho'_m | \ln \hat{\rho} | \rho'_m \rangle - \ln \rho'_m \langle \rho'_m | \rho'_m \rangle) . \end{aligned}$$

Here we have at first utilized the hermiticity of  $\hat{\rho}'$ . The completeness of the eigenstates  $|\rho_m\rangle$  allows for further rearrangements:

$$\begin{aligned} H &= \sum_{m,n} \rho'_m (\langle \rho'_m | \ln \hat{\rho} | \rho_n \rangle \langle \rho_n | \rho'_m \rangle - \ln \rho'_m |\langle \rho'_m | \rho_n \rangle|^2) \\ &= \sum_{m,n} \rho'_m \ln \frac{\rho_n}{\rho'_m} |\langle \rho'_m | \rho_n \rangle|^2 . \end{aligned}$$

For an estimation one considers the function

$$f(x) = x - 1 - \ln x \quad \text{for } x > 0$$

This function has a minimum at  $x = 1$  ( $f(1) = 0, f'(1) = 0, f'' = 1/x^2 > 0$ ), so that it holds:

$$f(x) \geq 0 \Leftrightarrow x - 1 \geq \ln x \quad \text{for } x > 0$$

The eigen-values  $\rho_n, \rho'_m$  are, as probability quantities, positive-semidefinite so that the inequality

$$\ln \frac{\rho_n}{\rho'_m} \leq \frac{\rho_n}{\rho'_m} - 1$$

can be exploited for an estimation of  $H$ :

$$\begin{aligned} H &\leq \sum_{n,m} \rho'_m \left( \frac{\rho_n}{\rho'_m} - 1 \right) |\langle \rho'_m | \rho_n \rangle|^2 \\ &= \sum_{n,m} (\rho_n \langle \rho_n | \rho'_m \rangle \langle \rho'_m | \rho_n \rangle - \rho'_m \langle \rho'_m | \rho_n \rangle \langle \rho_n | \rho'_m \rangle) \\ &= \sum_n \langle \rho_n | \hat{\rho} | \rho_n \rangle - \sum_m \langle \rho'_m | \hat{\rho}' | \rho'_m \rangle \\ &= \text{Tr} \hat{\rho} - \text{Tr} \hat{\rho}' = 0 . \end{aligned}$$

It holds therewith for arbitrary mixed non-equilibrium states, which are characterized by the statistical operator  $\hat{\rho}'$ :

$$\text{Tr}[\hat{\rho}'(\ln \hat{\rho} - \ln \hat{\rho}')] \leq 0 . \quad (2.101)$$

This extremal condition of the  $H$ -function shall be utilized in the following to come to concrete physical statements.

### 2.5.3 Entropy

Starting point is (2.88) as representation of the entropy:

$$\begin{aligned} S &= -k_B \text{Tr}(\hat{\rho} \ln \hat{\rho}) , \\ S' &= -k_B \text{Tr}(\hat{\rho}' \ln \hat{\rho}') . \end{aligned}$$

The Boltzmann's  $H$ -function can therewith be written as follows:

$$k_B H = S' + k_B \text{Tr}(\hat{\rho}' \ln \hat{\rho}) . \quad (2.102)$$

We consider at first the second term on the right-hand side of this equation:

$$\begin{aligned} k_B \text{Tr}(\hat{\rho}' \ln \hat{\rho}) &= k_B \sum_n \langle \rho_n | \hat{\rho}' \ln \hat{\rho} | \rho_n \rangle \\ &= k_B \sum_n \ln \rho_n \langle \rho_n | \hat{\rho}' | \rho_n \rangle . \end{aligned} \quad (2.103)$$

The entropy is the central thermodynamic potential of the micro-canonical ensemble, for which it holds because of (2.90)

$$\begin{aligned} k_B \text{Tr}(\hat{\rho}' \ln \hat{\rho}) &= k_B \ln \frac{1}{\Gamma(E)} \sum_n \langle \rho_n | \hat{\rho}' | \rho_n \rangle \\ &= -k_B \ln \Gamma(E) \text{Tr} \hat{\rho}' = -S , \end{aligned}$$

so that we have:

$$k_B H = S' - S \leq 0 .$$

This means

$$S' \leq S . \quad (2.104)$$

In the equilibrium the entropy is therefore never smaller than it would be in any other non-equilibrium state. All processes, which can take place in an isolated system, and which lead (irreversibly) to equilibrium, let the entropy increase or at least not decrease. This is nothing else but the **‘second law of Thermodynamics’**:

$$dS \geq 0 . \quad (2.105)$$

### 2.5.4 Free Energy

We use again the  $H$ -function in the formulation (2.102), and the intermediate result (2.103), into which we insert the eigen-values of the statistical operator of the canonical ensemble

$$\rho_n = \frac{1}{Z} e^{-\beta E_n} ; . \quad (2.106)$$

Because of (2.92) the eigen-states of  $\hat{\rho}_{ce}$  are simultaneously those of the Hamilton operator  $\hat{H}$ :

$$\begin{aligned}
 k_B \text{Tr}(\hat{\rho}' \ln \hat{\rho}) &= k_B \sum_n (-\ln Z - \beta E_n) \langle \rho_n | \hat{\rho}' | \rho_n \rangle \\
 &= -k_B \ln Z \text{Tr} \hat{\rho}' - \frac{1}{T} \sum_n E_n \langle \rho_n | \hat{\rho}' | \rho_n \rangle \\
 &= -k_B \ln Z - \frac{1}{T} \sum_n \langle \rho_n | \hat{\rho}' \hat{H} | \rho_n \rangle \\
 &= -k_B \ln Z - \frac{1}{T} \text{Tr}(\hat{\rho}' \hat{H}) = -k_B \ln Z - \frac{1}{T} U' \\
 &= \frac{1}{T} (F - U') .
 \end{aligned}$$

$U'$  is the internal energy of the non-equilibrium state. The temperature  $T$  is as natural variable of the canonical ensemble the same for both states which are to be compared. Equations (2.100), (2.101), and (2.102) then lead to the estimation:

$$k_B H = S' - \frac{1}{T} U' + \frac{1}{T} F = \frac{1}{T} (F - F') \leq 0 .$$

This means:

$$F \leq F' \iff dF \leq 0 . \quad (2.107)$$

For all processes, which are still possible in a system with  $T = \text{const}$ ,  $V = \text{const}$ ,  $N = \text{const}$ , the free energy can never increase. The free energy is minimal at equilibrium ((3.73), Vol. 5).

### 2.5.5 Grand-Canonical Potential

Also in this case we start with (2.102) and (2.103), being interested in such processes, which can take place in systems with

$$T = \text{const} , \quad V = \text{const} , \quad \mu = \text{const} .$$

The eigen-values of the statistical operator of the grand-canonical ensemble,

$$\rho_n(N) = \frac{1}{\Xi} e^{-\beta (E_n(N) - \mu N)} , \quad (2.108)$$



as well as the eigen-states  $|\rho_n\rangle$ , which are, because of (2.95), also eigen-states of the Hamilton operator  $\widehat{H}$  and of the particle-number operator  $\widehat{N}$ , help with the following rearrangement:

$$\begin{aligned}
 k_B \text{Tr}(\hat{\rho}' \ln \hat{\rho}) &= k_B \sum_n \sum_N (-\ln \Xi - \beta(E_n(N) - \mu N)) \langle \rho_n(N) | \hat{\rho}' | \rho_n(N) \rangle \\
 &= -k_B \ln \Xi, \text{Tr} \hat{\rho}' - \frac{1}{T} \sum_n \sum_N (E_n(N) - \mu N) \langle \rho_n(N) | \hat{\rho}' | \rho_n(N) \rangle \\
 &= -k_B \ln \Xi - \frac{1}{T} \sum_n \sum_N \langle \rho_n(N) | \hat{\rho}' (\widehat{H} - \mu \widehat{N}) | \rho_n(N) \rangle \\
 &= -k_B \ln \Xi - \frac{1}{T} \text{Tr}(\hat{\rho}' (\widehat{H} - \mu \widehat{N})) \\
 &= \frac{\Omega}{T} - \frac{1}{T} (U' - \mu \langle \widehat{N} \rangle') = \frac{\Omega}{T} - \frac{1}{T} (F' + TS' - G') \\
 &= \frac{1}{T} (\Omega - \Omega') - S'.
 \end{aligned}$$

Chemical potential  $\mu$  and temperature  $T$  are same in both the states which are to be compared. This means according to (2.102)

$$k_B H = S' + \frac{1}{T} (\Omega - \Omega') - S' \stackrel{!}{\leq} 0,$$

where (2.101) causes the inequality. We are left with the important statement:

$$\Omega \leq \Omega' \iff d\Omega \leq 0. \quad (2.109)$$

In all processes, which are possible at constant temperature  $T$ , constant volume  $V$  and constant chemical potential  $\mu$ , the grand-canonical potential does not increase.  $\Omega$  is thus minimal at equilibrium.

## 2.6 Approximation Methods

Only very few problems of Quantum Mechanics and Quantum Statistics are mathematically rigorously tractable. Approximation methods have to be developed, and, above all, must be tolerated. We will find in this section at first a perturbational approximation of the canonical partition function and the free energy, in order to discuss at the end a variational procedure for the same quantities.

### 2.6.1 Thermodynamic Interaction Representation

Let the Hamilton operator be decomposable into a ‘free part’  $H_0$ , whose eigen-value problem can be considered as solved, and an ‘interaction part’  $H_1$ , which prevents the exact solution of the full problem:

$$H = H_0 + H_1 . \quad (2.110)$$

We are seeking something like an ‘interaction representation’ (subsection 3.4.4, Vol. 6) of the statistical operator. We introduce

$$x = e^{-\beta H} = x(\beta) \quad (2.111)$$

with the differential equation:

$$\frac{\partial}{\partial \beta} x = -(H_0 + H_1)x , \quad (2.112)$$

which we try to solve by the ansatz

$$x(\beta) = e^{-\beta H_0} y(\beta); \quad (y(0) = 1) : \quad (2.113)$$

$$\begin{aligned} \frac{\partial x}{\partial \beta} &= e^{-\beta H_0} \left( -H_0 y + \frac{\partial y}{\partial \beta} \right) \\ &= -H_0 x + e^{-\beta H_0} \frac{\partial y}{\partial \beta} = -H_0 e^{-\beta H} + e^{-\beta H_0} \frac{\partial y}{\partial \beta} \\ &\stackrel{!}{=} -(H_0 + H_1) e^{-\beta H} . \end{aligned}$$

It remains the intermediate result:

$$e^{-\beta H_0} \frac{\partial y}{\partial \beta} = -H_1 e^{-\beta H} , \quad (2.114)$$

which in the form

$$\begin{aligned} \frac{\partial y}{\partial \beta} &= -(e^{\beta H_0} H_1 e^{-\beta H_0})(e^{\beta H_0} e^{-\beta H}) \\ &= -(e^{\beta H_0} H_1 e^{-\beta H_0})y(\beta) \end{aligned}$$

suggests the introduction of a ‘**modified**’ interaction representation:

$$\bar{A}(x) = e^{xH_0} A e^{-xH_0} \quad (2.115)$$

(see (3.201), Vol. 6 for  $x \leftrightarrow i/\hbar t$ ). We get therewith from (2.114):

$$\frac{\partial y}{\partial \beta} = -\bar{H}_1(\beta)y(\beta) . \quad (2.116)$$

The formal solution ( $y(0) = 1$ ),

$$y(\beta) = 1 - \int_0^\beta dx \bar{H}_1(x)y(x),$$

yields an integral equation, which obviously can be solved by iteration:

$$y(\beta) = 1 + \sum_{n=1}^{\infty} (-1)^n y^{(n)}(\beta) , \quad (2.117)$$

$$y^{(n)}(\beta) = \int_0^\beta dx_1 \int_0^{x_1} dx_2 \cdots \int_0^{x_{n-1}} dx_n \bar{H}_1(x_1)\bar{H}_1(x_2)\cdots\bar{H}_1(x_n)$$

$$\beta \geq x_1 \geq x_2 \geq \cdots \geq x_n \geq 0 . \quad (2.118)$$

A more compact representation succeeds with the following analog to the Dyson's time ordering operator ((3.173), Vol. 6):

$$T(A(x_1)B(x_2)) = \begin{cases} A(x_1)B(x_2) & , \text{ if } x_1 > x_2 \\ B(x_2)A(x_1) & , \text{ if } x_2 > x_1 \end{cases} \quad (2.119)$$

The same considerations as those in Vol. 6, which there have led to Eq. (3.176), yield here:

$$y^{(n)}(\beta) = \frac{1}{n!} \int_0^\beta \cdots \int_0^\beta dx_1 \cdots dx_n T(\bar{H}_1(x_1)\cdots\bar{H}_1(x_n)) .$$

Inserting this into (2.117), one finds as first important result the **'thermodynamic interaction representation' of the unnormalized statistical operator**

$$e^{-\beta H} = e^{-\beta H_0} y(\beta) = e^{-\beta H_0} T \exp \left( - \int_0^\beta dx \bar{H}_1(x) \right) . \quad (2.120)$$

For the special case that  $H_0$  and  $H_1$  commute, we have  $\bar{H}_1(x) \equiv H_1$ . The right-hand side of (2.120) therewith simplifies to  $e^{-\beta H_0} e^{-\beta H_1}$ .

We will use the result (2.120) in the next subsection for an approximate determination of the canonical partition function and the free energy.

## 2.6.2 Perturbation Theory of Second Order

We start with the canonical partition function, where we presume that the ‘unperturbed’ problem, given by  $H_0$ , is solved:

$$H_0|n\rangle = \varepsilon_n|n\rangle . \quad (2.121)$$

The eigen-states  $|n\rangle$  build a complete orthonormal system, so that the partition function can be represented as follows:

$$Z = \sum_n \langle n | e^{-\beta H} | n \rangle . \quad (2.122)$$

We expand  $e^{-\beta H}$  according to (2.120) up to the second order of the *perturbation*  $H_1$ :

$$\begin{aligned} Z &\approx \sum_n e^{-\beta \varepsilon_n} - \sum_n \langle n | e^{-\beta H_0} \int_0^\beta dx_1 \bar{H}_1(x_1) | n \rangle \\ &\quad + \sum_n \langle n | e^{-\beta H_0} \int_0^\beta dx_1 \int_0^{x_1} dx_2 \bar{H}_1(x_1) \bar{H}_1(x_2) | n \rangle \\ &= \sum_n e^{-\beta \varepsilon_n} \left( 1 - \int_0^\beta dx_1 \langle n | \bar{H}_1(x_1) | n \rangle \right. \\ &\quad \left. + \int_0^\beta dx_1 \int_0^{x_1} dx_2 \langle n | \bar{H}_1(x_1) \bar{H}_1(x_2) | n \rangle \right) . \end{aligned}$$

The modified interaction representation (2.115) leads to

$$\langle n | \bar{H}_1(x) | m \rangle = e^{x(\varepsilon_n - \varepsilon_m)} \langle n | H_1 | m \rangle .$$

This also means

$$\int_0^y dx e^{x(\varepsilon_n - \varepsilon_m)} \langle n | H_1 | m \rangle = \begin{cases} y \langle n | H_1 | m \rangle & \text{for } n = m, \\ \frac{\langle n | H_1 | m \rangle}{\varepsilon_n - \varepsilon_m} (e^{y(\varepsilon_n - \varepsilon_m)} - 1) & \text{for } n \neq m. \end{cases}$$

In second order it must be calculated:

$$\begin{aligned} & \int_0^\beta dx_1 \int_0^{x_1} dx_2 \langle n | \bar{H}_1(x_1) \bar{H}_1(x_2) | n \rangle \\ &= \sum_m \int_0^\beta dx_1 \int_0^{x_1} dx_2 \langle n | \bar{H}_1(x_1) | m \rangle \langle m | \bar{H}_1(x_2) | n \rangle \\ &= \int_0^\beta dx_1 x_1 |\langle n | H_1 | n \rangle|^2 \\ & \quad + \sum_m^{\neq n} \int_0^\beta dx_1 \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_m - \varepsilon_n} e^{x_1(\varepsilon_n - \varepsilon_m)} (e^{x_1(\varepsilon_m - \varepsilon_n)} - 1) \\ &= \frac{\beta^2}{2} |\langle n | H_1 | n \rangle|^2 \\ & \quad + \sum_m^{\neq n} \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_m - \varepsilon_n} \left[ \beta - \frac{1}{\varepsilon_n - \varepsilon_m} (e^{\beta(\varepsilon_n - \varepsilon_m)} - 1) \right]. \end{aligned}$$

Inserted into the expansion of the partition function the last term

$$A = \sum_{n,m}^{\neq} \frac{|\langle n | H_1 | m \rangle|^2}{(\varepsilon_n - \varepsilon_m)^2} (e^{-\beta\varepsilon_m} - e^{-\beta\varepsilon_n}).$$

vanishes because one recognizes, when interchanging the summation indexes ( $n \leftrightarrow m$ ), that  $A$  is equal to  $-A$  and therewith equal to zero. The canonical partition function in second order perturbation theory thus reads

$$\begin{aligned} Z \approx \sum_n e^{-\beta\varepsilon_n} \left( 1 - \beta \langle n | H_1 | n \rangle + \frac{1}{2} \beta^2 |\langle n | H_1 | n \rangle|^2 \right. \\ \left. - \beta \sum_m^{\neq n} \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_n - \varepsilon_m} \right) \quad (2.123) \end{aligned}$$

All the terms on the right-hand side are calculated with eigen-values and eigen-states of the 'free' system. The expression (2.123) can further be rearranged a bit. With the eigen-values  $\rho_n^{(0)}$  of the 'free' statistical operator,

$$\rho_n^{(0)} = \frac{1}{Z_0} e^{-\beta \varepsilon_n}; \quad Z_0 = \sum_n e^{-\beta \varepsilon_n}, \quad (2.124)$$

one finds, for instance,

$$e^{-\beta \varepsilon_n} = Z_0 \rho_n^{(0)}; \quad \sum_n \rho_n^{(0)} = 1,$$

so that (2.123) can also be read as follows:

$$Z \approx Z_0 \left( 1 - \beta \sum_n \langle n | H_1 | n \rangle \rho_n^{(0)} + \frac{1}{2} \beta^2 \sum_n |\langle n | H_1 | n \rangle|^2 \rho_n^{(0)} - \beta \sum_{n,m}^{n \neq m} \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_n - \varepsilon_m} \rho_n^{(0)} \right). \quad (2.125)$$

Therewith we now calculate the free energy

$$F = -k_B T \ln Z = F_0 + F^*, \quad (2.126)$$

$$F_0 = -k_B T \ln Z_0.$$

$F^*$  is determined by the bracket in (2.125). The correction terms, caused by the 'perturbation'  $H_1$ , are to be considered as small, so that the series expansion of the logarithm,

$$\ln(1+x) \approx x - \frac{1}{2} x^2,$$

allows for the following consistent estimation up to quadratic terms of the perturbation  $H_1$ :

$$F^* \approx \sum_n \langle n | H_1 | n \rangle \rho_n^{(0)} - \frac{1}{2} \beta \sum_n |\langle n | H_1 | n \rangle|^2 \rho_n^{(0)} + \sum_{n,m}^{n \neq m} \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_n - \varepsilon_m} \rho_n^{(0)} + \frac{1}{2} \beta \left( \sum_n \langle n | H_1 | n \rangle \rho_n^{(0)} \right)^2.$$

The first and the fourth summand contain the mean value of the ‘*perturbation*’ in the ‘*unperturbed*’ system:

$$\langle H_1 \rangle^{(0)} = \text{Tr}(\hat{\rho}_0 H_1) = \sum_n \langle n | H_1 | n \rangle \rho_n^{(0)}. \quad (2.127)$$

The second and the third summand can be combined by the following considerations:

$$\begin{aligned} \sum_{n,m}^{n \neq m} \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_n - \varepsilon_m} \rho_n^{(0)} &= \frac{1}{2} \sum_{n,m}^{n \neq m} \frac{|\langle n | H_1 | m \rangle|^2}{\varepsilon_n - \varepsilon_m} (\rho_n^{(0)} - \rho_m^{(0)}); \\ \lim_{n \rightarrow m} \frac{\rho_n^{(0)} - \rho_m^{(0)}}{\varepsilon_n - \varepsilon_m} &= \rho_n^{(0)} \lim_{n \rightarrow m} \frac{1 - e^{-\beta(\varepsilon_m - \varepsilon_n)}}{\varepsilon_n - \varepsilon_m} = -\beta \rho_n^{(0)}. \end{aligned}$$

We have therewith found in second order perturbation theory the following expression for the free energy:

$$F \approx F_0 + \langle H_1 \rangle^{(0)} + \frac{1}{2} \beta \left( \langle H_1 \rangle^{(0)} \right)^2 + \frac{1}{2} \sum_{n,m} |\langle n | H_1 | m \rangle|^2 \frac{\rho_n^{(0)} - \rho_m^{(0)}}{\varepsilon_n - \varepsilon_m} \quad (2.128)$$

If one can restrict oneself for practical applications to corrections of first order, then it remains to be calculated, besides  $F_0$ , only the ‘*unperturbed*’ average  $\langle H_1 \rangle^{(0)}$  of the ‘*perturbation*’.

### 2.6.3 Variational Procedure

We finally discuss a further approximation procedure, which plays an important role for the quantum-statistical calculation of thermodynamic functions. It concerns a variational method for the canonical partition function and the free energy, respectively. Let  $H^*$  be a Hermitian ‘*test-Hamilton operator*’, the eigen-value problem of which can be considered as solved:

$$H^* |\eta_n\rangle = \eta_n |\eta_n\rangle. \quad (2.129)$$

With this test-operator and its eigen-values, the corresponding partition function  $Z^*$  and the statistical weights  $p_m^*$  can formally be defined:

$$Z^* = \sum_m e^{-\beta \eta_m}; \quad p_m^* = \frac{1}{Z^*} e^{-\beta \eta_m}; \quad \sum_m p_m^* = 1. \quad (2.130)$$

The  $|\eta_m\rangle$  can be expanded using the complete set of the ‘true’ eigen-states of the ‘real’ Hamilton operator:

$$|\eta_m\rangle = \sum_n |E_n\rangle \langle E_n | \eta_m \rangle . \quad (2.131)$$

We assume thereby that the  $|\eta_m\rangle$  are normalized:

$$\sum_n |\langle E_n | \eta_m \rangle|^2 = 1 . \quad (2.132)$$

Together with (2.130) this also means:

$$\sum_{n,m} p_m^* |\langle E_n | \eta_m \rangle|^2 = 1 . \quad (2.133)$$

We fix the averaging process with respect to the ‘test-system’ as follows:

$$\begin{aligned} \langle H - H^* \rangle^* &= \sum_m p_m^* \langle \eta_m | (H - H^*) | \eta_m \rangle \\ &= \sum_{m,n} p_m^* \langle \eta_m | (H - H^*) | E_n \rangle \langle E_n | \eta_m \rangle . \end{aligned}$$

With the hermiticity of  $H^*$  it remains:

$$\langle H - H^* \rangle^* = \sum_{m,n} (E_n - \eta_m) p_m^* |\langle \eta_m | E_n \rangle|^2 . \quad (2.134)$$

Analogously one finds:

$$\begin{aligned} \langle e^{-\beta H} e^{\beta H^*} \rangle^* &= \sum_m p_m^* \langle \eta_m | e^{-\beta H} e^{\beta H^*} | \eta_m \rangle \\ &= \sum_{m,n} p_m^* \langle \eta_m | e^{-\beta H} | E_n \rangle \langle E_n | e^{\beta H^*} | \eta_m \rangle \\ &= \sum_{m,n} e^{-\beta (E_n - \eta_m)} p_m^* |\langle \eta_m | E_n \rangle|^2 . \end{aligned} \quad (2.135)$$

Thereby it is **not** presumed that the operators  $H$  and  $H^*$  commute. We now exploit the Taylor-series expansion (Lagrange-remainder term):

$$\begin{aligned} f(x) &= f(x_0) + (x - x_0)f'(x_0) + \frac{1}{2}(x - x_0)^2 f''(x_0 + \alpha (x - x_0)) ; \\ &0 \leq \alpha \leq 1 . \end{aligned}$$



If in addition  $f(x)$  is convex, i.e. it holds  $f''(x) \geq 0$ , then it can be estimated:

$$f(x) \geq f(x_0) + (x - x_0)f'(x_0) .$$

The tangent at a convex curve lies always below the curve.  $e^{-\beta E}$  is, as function of  $E$ , convex, so that it can be concluded: ( $x \leftrightarrow E_n - \eta_m$ ,  $x_0 \leftrightarrow \langle H - H^* \rangle^*$ ):

$$e^{-\beta(E_n - \eta_m)} \geq e^{-\beta \langle H - H^* \rangle^*} + (E_n - \eta_m - \langle H - H^* \rangle^*) (-\beta e^{-\beta \langle H - H^* \rangle^*}) .$$

We multiply this inequality by  $p_m^* |\langle \eta_m | E_n \rangle|^2 \geq 0$ , and sum over all  $n$  and  $m$ . The comparison with (2.133) and (2.134) then yields:

$$\langle e^{-\beta H} e^{\beta H^*} \rangle^* \geq e^{-\beta \langle H - H^* \rangle^*} . \quad (2.136)$$

The normalization (2.133) has thereby been used. We are now able to formulate an upper bound for the free energy:

$$\begin{aligned} Z &= \text{Tr} e^{-\beta H} = \text{Tr}(e^{-\beta H} e^{\beta(H^* - H^*)}) = \text{Tr}(e^{-\beta H^*} e^{-\beta H} e^{\beta H^*}) \\ &= Z^* \text{Tr}(\hat{\rho}^* e^{-\beta H} e^{\beta H^*}) = Z^* \langle e^{-\beta H} e^{\beta H^*} \rangle^* . \end{aligned}$$

Note that  $H$  and  $H^*$  need not necessarily commute. The second step therefore uses the ‘*cyclic invariance of the trace*’. With (2.136) the above, still exact relation for  $\text{Tr} e^{-\beta H}$  leads to an estimation for the canonical partition function:

$$Z \geq Z^* \exp(-\beta \langle H - H^* \rangle^*) . \quad (2.137)$$

This result can immediately be transferred to the free energy:

$$\ln Z \geq \ln Z^* - \beta \langle H - H^* \rangle^* \implies -k_B T \ln Z \leq -k_B T \ln Z^* + \langle H - H^* \rangle^* .$$

If now

$$F^* = -k_B T \ln Z^* \quad (2.138)$$

is the free energy of the test-system, then it follows eventually:

$$F \leq F^* + \langle H - H^* \rangle^* . \quad (2.139)$$

If the Hamilton operator can be decomposed as in (2.110) ( $H = H_0 + H_1$ ), and if  $H^*$  is identified with  $H_0$ , then (2.139) corresponds as equation to the perturbational result of first order, derived with Eq. (2.128). The worth of the inequality (2.139) lies, however, in the fact that one can implement into the test-Hamilton operator  $H^*$  some ‘*free variational parameters*  $\alpha_i$ ’, by which one can look for a minimal  $F^* + \langle H - H^* \rangle^*$ , for which of course (2.139) remains valid:

$$\frac{\partial}{\partial \alpha_i} (F^* + \langle H - H^* \rangle^*) \stackrel{!}{=} 0 . \quad (2.140)$$

In this way one gets *optimal parameters*  $\alpha_i$ , which yield a *minimal* upper bound for the 'true' free energy. So one can approach very closely the exact result by a '*convenient choice*' of the test-operator.

## 2.6.4 Exercises

### Exercise 2.6.1

The Hamilton operator of the linear harmonic oscillator is given in the form:

$$H = H_0 + H_1$$

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2, \quad H_1 = \alpha \frac{1}{2}m\omega^2 q^2; \quad |\alpha| < 1$$

1. Calculate the free energy in perturbation theory of the first order!
2. Compare the result with the exact solution!

### Exercise 2.6.2

The Hamilton operator of the anharmonic oscillator is given as

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 + \alpha \frac{m^2 \omega^2}{\hbar} q^4; \quad \alpha > 0$$

1. Calculate with

$$H^* = \frac{p^2}{2m} + \frac{1}{2}m\omega^* q^2$$

as test-Hamilton operator an upper bound for the free energy of the anharmonic oscillator (variational procedure).

2. Derive a conditional equation for the '*optimal*' variational parameters  $\omega^*$ . Discuss the resulting transcendental conditional equation for the special case  $T = 0!$

### Exercise 2.6.3

Let  $A$  and  $B$  be two operators, which do not necessarily commute, and let  $x$  be a real parameter. Show that

$$\frac{d}{dx} \text{Tr}(e^{xA+B}) = \text{Tr}(Ae^{xA+B})$$

is valid even if  $[A, B]_- \neq 0$ .

## 2.7 Self-Examination Questions

### To Section 2.1

1. What is the fundamental difference between the concepts of the Classical Statistical Physics and the Quantum Statistics?
2. Why does Quantum Mechanics not know a *phase space*?
3. What does one understand by a *mixed state*?
4. One says that Quantum Statistics deals with two different types of averaging processes. Characterize them!
5. How is the statistical operator  $\hat{\rho}$  defined?
6. How does one calculate, by the use of  $\hat{\rho}$ , averages of observables?
7. Which properties of  $\hat{\rho}$  do you know?
8. Which special form does  $\hat{\rho}$  take for a pure state?
9. How does the equation of motion of the statistical operator read?
10. What does Quantum Statistics understand by a *statistical ensemble*? Are there essential differences to the classical concept?
11. When is a quantum-statistical ensemble stationary?

### To Section 2.2

1. What is the quantum-statistical analog to the classical phase volume?
2. Write down the statistical operator in the micro-canonical ensemble!
3. How are averages of observables calculated in the micro-canonical ensemble?
4. Does the Quantum Statistics know a *Gibb's paradox*? Explain!
5. What is the meaning of the *quantum-statistical phase volume*  $\Gamma(E)$ ?
6. How does the entropy read at  $T = 0$  for a system with a discrete energy spectrum?
7. Is it possible to prove the third law of Thermodynamics in a strict mathematical sense? Explain!
8. Does the classical ideal gas fulfill the third law of Thermodynamics?

### To Section 2.3

1. Write down the statistical operator in the canonical ensemble? Why does it concern a stationary ensemble?
2. What is the relation between the canonical partition function and the statistical operator  $\hat{\rho}$ ?
3. How does the expectation value  $\langle \hat{F} \rangle$  of an observable  $\hat{F}$  look like in the canonical ensemble?

4. Which type of integral can be successfully treated, under which preconditions, by the saddle-point method?
5. What is the basic idea of the Darwin-Fowler method for the calculation of the canonical partition function?
6. Does the Darwin-Fowler method also work in Classical Statistical Physics?
7. How is the Darwin-Fowler method influenced by the postulate of the equal 'a-priori'-probabilities?
8. How can the canonical partition function be derived by the *method of Lagrange multipliers*?
9. How do the average ( $\langle n_m \rangle$ ) and the most probable ( $n_m^{(0)}$ ) occupation numbers, by which the systems of a canonical ensemble populate the given energy levels  $E_m$ ,  $m = 0, 1, 2, \dots$ , depend on the temperature?

### To Section 2.4

1. In which way does the *postulate of the equal 'a-priori'-probabilities* enter the derivation of the statistical operator of the grand-canonical ensemble?
2. How does the statistical operator  $\hat{\rho}$  of the grand-canonical ensemble read?
3. How does one recognize that  $\hat{\rho}$  describes a *stationary* ensemble?
4. Is there a direct classical analog to  $\hat{\rho}$  in the grand-canonical ensemble?
5. How does the representation-independent formulation of the grand-canonical partition function  $\Xi_\mu(T, V)$  look like?
6. Which form does  $\Xi_\mu(T, V)$  exhibit in the energy-particle representation?
7. Which difference exists between  $\Xi_\mu(T, V)$  and  $\Xi_z(T, V)$ ?
8. How does one calculate in the quantum-mechanical grand-canonical ensemble the average of an observable  $\hat{F}$ ?
9. How can the mean value of the particle number operator be expressed by  $\Xi_\mu(T, V)$  and by  $\Xi_z(T, V)$ , respectively?
10. Which formula guarantees for macroscopic systems the equivalence of canonical and grand-canonical ensemble?

### To Section 2.5

1. Which general relation, valid for all the three ensembles, exists between the statistical operator  $\hat{\rho}$  and the entropy  $S$ ?
2. How can the statistical operator of the canonical ensemble be represented by the free energy  $F$  and by the Hamilton operator  $\hat{H}$ ?
3. How can the statistical operator of the grand-canonical ensemble be expressed by the grand-canonical potential  $\Omega$ , the Hamilton operator  $\hat{H}$  and the particle number operator  $\hat{N}$ ?

4. How is the Boltzmann's  $H$ -function defined? In which respect can this function be useful for practical applications?
5. Which extremal properties are fulfilled by the  $H$ -function?
6. In which way does the Boltzmann's  $H$ -function lead to an extremal property of the entropy?
7. What holds for the free energy in the case of (irreversible) processes, which are still possible to take place in a system at constant  $T, V, N$ ?

## To Section 2.6

1. How does the '*thermodynamic interaction representation*' for the term  $e^{-\beta\hat{H}}$  read, if  $\hat{H}$  can be decomposed as  $\hat{H}_0 + \hat{H}_1$ ?
2. How does  $e^{-\beta\hat{H}}$  present itself, when  $\hat{H}_0$  and  $\hat{H}_1$  commute?
3. How can one develop with the '*interaction representation*' for  $e^{-\beta\hat{H}}$  a perturbation theory for the canonical partition function and the free energy?
4. How does the canonical partition function look like up to the first order in the perturbation?
5. How does the free energy present itself in first order of the perturbation theory?
6. How can one determine the free energy by means of a variational procedure?
7. Which relation can be recognized between the perturbation theory and the variational procedure?

## Chapter 3

# Quantum Gases



We have got to know the basic concepts of Classical Statistical Physics and Quantum Statistics in the first two chapters. This and the following chapter deal with some characteristic applications of these concepts and with very special, complementary problems. Let us start with the important *quantum gases*.

The treatment of many-particle systems almost always requires *model assumptions* and special *approximate techniques of solution* (see Vol. 9). Only for very few, generally strongly idealized systems can the partition function be exactly calculated. The problems, which prevent a rigorous evaluation, are always to be ascribed to particle interactions. Therefore, the most drastic model assumption is to completely neglect, at first, all particle interactions (*free system, ideal gas*). This, on the one hand, normally excludes from the beginning a quantitative comparison of the theoretical results with experimental data, but, on the other hand, helps to become familiar with the fundamental concepts of the theory by an exactly calculable example. However, the treatment of the *free systems* need not necessarily be exclusively justified by *didactic points of view*. There are important physical border zones, in which real systems can be *reasonably* substituted by the corresponding ideal ones. In this sense, the so-called *Sommerfeld-model* of non-interacting electrons (*ideal Fermi gas* (see Sect. 3.2)) could provide, some decades ago, seminal contributions to the understanding of the conduction electrons of a metal. Something similar holds for the *phonon-picture* of the crystal lattice, which quantum-statistically is to be treated as *ideal Bose gas* (see Sect. 3.3). Thus, there are sufficiently many reasons to deal at this stage with the **ideal quantum gases**.

We have already treated the **classical** ideal gas in Sect. 1.3.7 in the framework of the micro-canonical ensemble. Quantum-mechanically we expect, according to the extensive investigations in chapter 8 of Vol. 7, the *statistical properties* of systems of *distinguishable* and those of *indistinguishable* particles to be significantly different from each other. In the case of distinguishable particles, classical and quantum-mechanical considerations come in the usual way to possibly deviating results, caused, however, alone by the fact that Classical Mechanics represents only a limiting case of the superordinate Quantum Mechanics. In contrast, we expect really

novel phenomena from the **quantum gases of indistinguishable particles**, which shall therefore be exclusively the topic of this section. For this purpose, however, we should recall at first some of the facts, which we have worked out for systems of identical particles in the framework of Quantum Mechanics (see chapter 8, Vol. 7), when we reflected on the special regularities for the description of such systems.

## 3.1 Basics

### 3.1.1 Identical Particles

Particles are denoted as *identical* if they coincide in **all** their *particle properties* (mass, charge, spin, magnetic moment,...). According to the *principle of indistinguishability* (see subsection 8.2.1, Vol. 7) such particles in Quantum Mechanics are by no measurement individually identifiable. In particular, they are not *indexable*. Even Classical Mechanics *knows* identical particles, which are, however, always distinguishable. When we have been able to measure their momenta and their positions at a single point of time  $t_0$ , then we can exactly follow up their paths for all times due to the Hamilton's equations of motion. The *classical particle* describes in the phase space a well-defined individual *trajectory*. This concept loses its sense in Quantum Mechanics. The indistinguishability of identical *quantum-mechanical particles* has far-reaching consequences, which we have discussed and reasoned in detail in chapter 8 of Vol. 7. We restrict ourselves here to a compact compilation of the fundamental facts.

The corresponding one-particle problem is presumed to be solved:

$$\widehat{H}_1^{(i)} |\varphi_{\alpha_i}^{(i)}\rangle = \varepsilon_{\alpha_i} |\varphi_{\alpha_i}^{(i)}\rangle. \quad (3.1)$$

The eigen-states  $|\varphi_{\alpha_i}^{(i)}\rangle$  of the one-particle Hamilton operator  $\widehat{H}_1^{(i)}$  shall represent a complete orthonormal system.  $\alpha_i$  is a set of quantum numbers, being complete for the characterization of the state (e.g.  $\alpha_i \leftrightarrow (n, l, m_l, m_s), (k_x, k_y, k_z, m_s)$ ). The upper index  $i$  formally indexes the particles. (3.1) is therefore the eigen-value equation of the Hamilton operator  $\widehat{H}_1^{(i)}$  of the  $i$ -th particle. The indexing is, even for systems of identical particles, unavoidable because of computational reasons, e.g. for the discrimination of the integration and summation variables, although actually physically unreasonable and obviously contradicting the *principle of indistinguishability*. One has therefore to make sure that this '*forbidden indexing*' does not have any physical consequences, i.e., physically relevant quantities (measurands) should not be affected by this indexing. This fact alone leads to a series of very special properties of the systems of identical particles.

In the case of  $N$  **distinguishable** particles the indexing is of course not only reasonable but also allowed. The states of such systems are then all direct products

of the one-particle states,

$$|\varphi_N\rangle \equiv |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle \equiv |\varphi_{\alpha_1}^{(1)}\rangle |\varphi_{\alpha_2}^{(2)}\rangle \cdots |\varphi_{\alpha_N}^{(N)}\rangle, \quad (3.2)$$

or linear combinations of them. If the  $|\varphi_{\alpha_i}\rangle$  build a basis in the one-particle Hilbert space, then the product states (3.2) form a basis of the  $N$ -particle space. On the other hand, the  $N$ -particle state  $|\varphi_N\rangle$  possesses the same *statistical interpretation* (see chapter 2, Vol. 6) as the one-particle state. Systems of distinguishable particles thus do not bring about any *new physics*.

In the case of **identical** particles the *principle of indistinguishability* brings about special symmetry properties. Each interchange of two particle numbers in (3.2) must lead at most to a change of the sign of the  $N$ -particle state. This requires a proper (anti)symmetrization of the state product:

$$|\varphi_N^{(\pm)}\rangle \equiv |\varphi_{\alpha_1} \cdots \varphi_{\alpha_N}\rangle^{(\pm)} \equiv \frac{1}{N!} \sum_{\mathcal{P}} (\pm)^p \mathcal{P}(|\varphi_{\alpha_1}^{(1)}\rangle |\varphi_{\alpha_2}^{(2)}\rangle \cdots |\varphi_{\alpha_N}^{(N)}\rangle). \quad (3.3)$$

It is summed over all permutations of the  $N$ -tuple  $(1, 2, \dots, N)$  of the upper particle indexes. The exponent  $p$  is the number of pairwise interchanges (transpositions), which build up the permutation  $\mathcal{P}$ . The states of a given system of identical particles are **all** symmetric of the type  $|\varphi_N^{(+)}\rangle$ , or **all** antisymmetric of the type  $|\varphi_N^{(-)}\rangle$ . The symmetry character is temporally unchangeable and can by no means, by no operation, be altered. States with different symmetry character are orthogonal to each other. They are elements of two different Hilbert spaces (see subsection 8.2.3, Vol. 7). The **spin-statistics theorem**, proven quantum-field theoretically by W. Pauli, explains which particle type is to be ascribed to which Hilbert space:

$H_N^{(+)}$ : Space of the symmetric states  $|\varphi_N^{(+)}\rangle$ . Identical particles of **integer** spin ( $S = 0, 1, 2, \dots$ ). Name:

**bosons.**

Examples: photons ( $S = 1$ ), phonons ( $S = 1$ ), magnons ( $S = 1$ ),  $\alpha$ -particles ( $S = 0$ ),...

$H_N^{(-)}$ : Space of the antisymmetric states  $|\varphi_N^{(-)}\rangle$ . Identical particles of **half-integer** spin ( $S = \frac{1}{2}, \frac{3}{2}, \dots$ ). Name:

**fermions.**

Examples: electrons, protons, neutrons ( $S = 1/2$ ).

One recognizes a specialty of the fermion systems with (3.3). Their states can be written as determinants (*Slater determinant*):

$$|\varphi_N^{(-)}\rangle = \frac{1}{N!} \begin{vmatrix} |\varphi_{\alpha_1}^{(1)}\rangle & |\varphi_{\alpha_1}^{(2)}\rangle & \cdots & |\varphi_{\alpha_1}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\varphi_{\alpha_N}^{(1)}\rangle & |\varphi_{\alpha_N}^{(2)}\rangle & \cdots & |\varphi_{\alpha_N}^{(N)}\rangle \end{vmatrix}. \quad (3.4)$$



This determinant is zero as soon as two rows are same. That is the case when there are two identical sets of quantum numbers  $\alpha_i = \alpha_j$ . This statement represents the fundamental **Pauli principle**:

*Two identical fermions can never have all their quantum numbers  
same!*

Such a restriction does not exist for bosons.

An especially elegant and transparent representation lends itself in the case of a **discrete** one-particle basis  $\{|\varphi_{\alpha_i}\rangle\}$ . It is obvious that the  $N$ -particle states are completely determined by listing the **occupation numbers**  $n_{\alpha_i}$ , i.e., the frequencies with which the  $|\varphi_{\alpha_i}\rangle$  appear in  $|\varphi_N^{(\pm)}\rangle$ . However, one has to obey certain rules:

$$|N; n_{\alpha_1} \cdots n_{\alpha_i} \cdots\rangle^{(\pm)} \equiv c_{\pm} \sum_{\mathcal{P}} (\pm)^p \mathcal{P} \left\{ \underbrace{|\varphi_{\alpha_1}^{(1)}\rangle |\varphi_{\alpha_1}^{(2)}\rangle}_{n_{\alpha_1}} \cdots \underbrace{|\varphi_{\alpha_i}^{(p)}\rangle |\varphi_{\alpha_i}^{(p+1)}\rangle}_{n_{\alpha_i}} \cdots \right\}. \quad (3.5)$$

In these **Fock states**, **all** the occupation numbers of the complete one-particle basis  $\{|\varphi_{\alpha_i}\rangle\}$  must be indicated. One-particle states, which do not explicitly appear in  $|\varphi_N^{(\pm)}\rangle$  are marked by  $n_{\alpha} = 0$ . The declaration of the total particle number  $N$  in the state symbol is because of  $N = \sum_i n_{\alpha_i}$  actually superfluous, being, however, sometimes rather helpful.

The factor

$$c_{\pm} = \left( N! \prod_i n_{\alpha_i}! \right)^{-1/2}$$

takes care for a proper normalization of the orthogonal Fock states:

$$\langle N; \dots n_{\alpha_i} \dots | \widehat{N}; \dots \widehat{n}_{\alpha_i} \dots \rangle^{(\pm)} = \delta_{N\widehat{N}} \prod_i \delta_{n_{\alpha_i} \widehat{n}_{\alpha_i}}.$$

It holds for the occupation numbers:

$$\begin{aligned} n_{\alpha_i} = 0 \text{ or } 1 &\iff \text{fermions} \\ n_{\alpha_i} = 0, 1, 2, \dots &\iff \text{bosons.} \end{aligned}$$

The Fock states (3.5) build for the  $H_N^{(\pm)}$  a complete orthonormal basis.

Many-body problems are nowadays mostly treated in the formalism of *second quantization*, which we introduced and extensively discussed in section 8.2 of Vol. 7. Characteristic is the introduction of a *creation operator*  $a_{\alpha_i}^+$ , which *creates* the one-particle state  $|\varphi_{\alpha_i}\rangle$  out of the *vacuum state*  $|0\rangle$ :

$$|\varphi_{\alpha_i}\rangle = a_{\alpha_i}^+ |0\rangle.$$

Its adjoint operator  $a_{\alpha_i}$  has the opposite effect. It is therefore called *annihilation operator*:

$$a_{\alpha_i}|\varphi_{\alpha_i}\rangle = |0\rangle ; \quad a_{\alpha_i}|0\rangle = 0 .$$

Taking into consideration symmetry and normalization we find for the actions on a general  $N$ -particle Fock state:

### Bosons

$$\begin{aligned} a_{\alpha_r}^+|N; \dots n_{\alpha_r} \dots\rangle^{(+)} &= \sqrt{n_{\alpha_r}+1}|N+1; \dots n_{\alpha_r}+1 \dots\rangle^{(+)} , \\ a_{\alpha_r}|N; \dots n_{\alpha_r} \dots\rangle^{(+)} &= \sqrt{n_{\alpha_r}}|N-1; \dots n_{\alpha_r}-1 \dots\rangle^{(+)} , \\ n_{\alpha_r} &= 0, 1, 2, \dots \end{aligned} \quad (3.6)$$

### Fermions

$$\begin{aligned} a_{\alpha_r}^+|N; \dots n_{\alpha_r} \dots\rangle^{(-)} &= (-1)^{N_r} \delta_{n_{\alpha_r},0} |N+1; \dots n_{\alpha_r}+1 \dots\rangle^{(-)} , \\ a_{\alpha_r}|N; \dots n_{\alpha_r} \dots\rangle^{(-)} &= (-1)^{N_r} \delta_{n_{\alpha_r},1} |N-1; \dots n_{\alpha_r}-1 \dots\rangle^{(-)} , \\ n_{\alpha_r} &= 0, 1; \quad N_r = \sum_{j=1}^{r-1} n_{\alpha_j} . \end{aligned} \quad (3.7)$$

Each Fock state can be *created* out of the vacuum state  $|0\rangle$  by a repeated application of suitable creation operators:

$$|N; \dots n_{\alpha_r} \dots\rangle^{(\pm)} = \prod_j \frac{(a_{\alpha_j}^+)^{n_j}}{\sqrt{n_j!}} (\pm)^{N_j} |0\rangle . \quad (3.8)$$

By the introduction of the operators  $a$  and  $a^+$  we get rid of the nasty (anti)symmetrization of the  $N$ -particle state. The full *symmetry problem* is now covered by three

### fundamental commutation relations:

$$[a_{\alpha_r}, a_{\alpha_s}]_{\pm} = [a_{\alpha_r}^+, a_{\alpha_s}^+]_{\pm} = 0; \quad [a_{\alpha_r}, a_{\alpha_s}^+]_{\pm} = \delta_{rs} . \quad (3.9)$$

For fermions it holds the anticommutator  $[\dots]_{+}$ , and for bosons the commutator  $[\dots]_{-}$ .

In order to really be able to apply the formalism of the second quantization, of course one has to not only represent states, but also observables in terms of creation and annihilation operators (see subsection. 8.3.2, Vol. 7). The observables  $\widehat{F}_N$  of the  $N$ -particle systems, which are of relevance here, consist of one- and two-particle

parts:

$$\widehat{F}_N = \sum_{i=1}^N \widehat{F}_1^{(i)} + \frac{1}{2} \sum_{\substack{i \neq j \\ i,j}} F_2^{(i,j)} .$$

For the one-particle part one finds ((8.113), Vol. 7):

$$\sum_{i=1}^N \widehat{F}_1^{(i)} \longrightarrow \sum_{\alpha, \beta} (F_1)_{\alpha, \beta} a_{\alpha}^{\dagger} a_{\beta} ; \quad (F_1)_{\alpha, \beta} = \langle \varphi_{\alpha}^{(1)} | \widehat{F}_1^{(1)} | \varphi_{\beta}^{(1)} \rangle . \quad (3.10)$$

With a given basis  $\{|\varphi_{\alpha}\rangle\}$  the matrix element  $\langle \varphi_{\alpha}^{(1)} | \widehat{F}_1^{(1)} | \varphi_{\beta}^{(1)} \rangle$  is in general easily calculable. This holds also for the matrix element needed for the two-particle part ((8.114), Vol. 7):

$$\frac{1}{2} \sum_{\substack{i \neq j \\ i,j}} \widehat{F}_2^{(i,j)} \longrightarrow \frac{1}{2} \sum_{\substack{\alpha \beta \\ \gamma \delta}} (F_2)_{\alpha \beta}^{\gamma \delta} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma} \quad (3.11)$$

$$(F_2)_{\alpha \beta}^{\gamma \delta} = \langle \varphi_{\alpha}^{(1)} | \langle \varphi_{\beta}^{(2)} | \widehat{F}_2^{(1,2)} | \varphi_{\gamma}^{(1)} \rangle | \varphi_{\delta}^{(2)} \rangle .$$

Let us finally recall a few special operators, as for instance the **occupation number operator**:

$$\hat{n}_{\alpha_r} = a_{\alpha_r}^{\dagger} a_{\alpha_r} . \quad (3.12)$$

One easily verifies with (3.6) and (3.7), respectively, that the Fock states (3.5) are eigen-states of  $\hat{n}_{\alpha_r}$  with the *occupation number*  $n_{\alpha_r}$  as eigen-value:

$$\hat{n}_{\alpha_r} |N; \dots n_{\alpha_r} \dots\rangle^{(\pm)} = n_{\alpha_r} |N; \dots n_{\alpha_r} \dots\rangle^{(\pm)} . \quad (3.13)$$

The **particle number operator**

$$\widehat{N} = \sum_r \hat{n}_{\alpha_r} = \sum_r a_{\alpha_r}^{\dagger} a_{\alpha_r} \quad (3.14)$$

obviously has the same eigen-states with the *particle number*  $N = \sum_r n_{\alpha_r}$  as eigen-value.

The **ideal quantum gases**, which we will be mainly interested in the following subsections, are characterized by the absence of interactions between the particles. Their Hamilton operator,

$$\widehat{H} = \sum_{i=1}^N \widehat{H}_1^{(i)} ; \quad \widehat{H}_1^{(i)} = \frac{1}{2m} \hat{\mathbf{p}}_i^2 + V(\hat{\mathbf{r}}_i) , \quad (3.15)$$

thus consists only of one-particle operators. That is, on the one hand, the kinetic energy, on the other hand, possibly in addition, the interaction of the particle with an *external* potential  $V$  (electric field, magnetic field, periodic lattice potential, ...). These special operators are written in second quantization, when one uses the eigenstates  $|\varepsilon_r\rangle$  of  $\hat{H}_1$  as one-particle basis:

$$\hat{H} = \sum_r \varepsilon_r a_{\alpha_r}^+ a_{\alpha_r} = \sum_r \varepsilon_r \hat{n}_{\alpha_r} \quad (3.16)$$

$$\varepsilon_r \delta_{rs} = \langle \varepsilon_r | \hat{H}_1 | \varepsilon_s \rangle .$$

The Fock states (3.5) are eigen-states also of  $\hat{H}$ :

$$\hat{H}|N; \dots n_{\alpha_r} \dots\rangle^{(\pm)} = \left( \sum_r \varepsilon_r n_{\alpha_r} \right) |N; \dots n_{\alpha_r} \dots\rangle^{(\pm)} \quad (3.17)$$

### 3.1.2 Partition Functions of the Ideal Quantum Gases

The most direct access to the statistical treatment of the ideal quantum gases is provided by the **grand-canonical partition function**:

$$\Xi_{\mu}(T, V) = \text{Tr} e^{-\beta(\hat{H} - \mu\hat{N})} .$$

$\hat{H}$  is here the Hamilton operator (3.16) and  $\hat{N}$  the particle number operator (3.14). For the evaluation of the trace it is recommendable to use the Fock states (3.13), because these are eigen-states simultaneously of  $\hat{H}$  and  $\hat{N}$ :

$$\begin{aligned} \Xi_{\mu}^{(\pm)}(T, V) &= \sum_{N=0}^{\infty} \sum_{\{n_r\}}^{\sum_r n_r = N} \exp \left[ -\beta \sum_r n_r (\varepsilon_r - \mu) \right] \\ &= \sum_{N=0}^{\infty} \sum_{\{n_r\}}^{\sum_r n_r = N} \prod_r \exp \left[ -\beta n_r (\varepsilon_r - \mu) \right] . \end{aligned} \quad (3.18)$$

The sign (+) holds for bosons, the sign (−) for fermions. Moreover, we have written, for simplicity,  $n_r$  instead of  $n_{\alpha_r}$ . The sum over  $\{n_r\}$  concerns all combinations of occupation numbers, which are possible for a given total number  $N$ . This restriction of the summation is, however, set aside by the sum over all total particle numbers  $N$ :

$$\sum_{N=0}^{\infty} \sum_{\{n_r\}}^{\sum_r n_r = N} \dots \iff \sum_{n_1} \sum_{n_2} \dots \sum_{n_r} \dots .$$

The *combination of sums* in (3.18) can be replaced by independent summations over the individual occupation numbers. To verify that, one can check the fact that indeed each term on the left-hand side appears also on the right-hand side, and vice versa. By the way, the possibility, to modify the summation processes, required for the partition function, in the indicated manner, is the reason why the grand-canonical treatment of the quantum gases is essentially easier than the canonical one. The canonical partition function  $Z_N(T, V)$  can not be evaluated in closed form, because of the fixed particle number.—We write for (3.18):

$$\begin{aligned}\Xi_{\mu}^{(\pm)}(T, V) &= \left( \sum_{n_1} e^{-\beta n_1 (\varepsilon_1 - \mu)} \right) \left( \sum_{n_2} e^{-\beta n_2 (\varepsilon_2 - \mu)} \right) \dots \left( \sum_{n_r} e^{-\beta n_r (\varepsilon_r - \mu)} \right) \dots \\ &= \prod_r \left( \sum_{n_r} e^{-\beta n_r (\varepsilon_r - \mu)} \right).\end{aligned}$$

For **bosons**,  $n_r$  runs through all non-negative integers. The bracket thus represents just the geometric series:

$$\Xi_{\mu}^{(+)}(T, V) = \prod_r \left[ \frac{1}{1 - e^{-\beta (\varepsilon_r - \mu)}} \right]. \quad (3.19)$$

For **fermions**, on the other hand, the sum over  $n_r$  contains, because of  $n_r = 0, 1$ , only two terms:

$$\Xi_{\mu}^{(-)}(T, V) = \prod_r \left[ 1 + e^{-\beta (\varepsilon_r - \mu)} \right]. \quad (3.20)$$

From the equations for the partition functions of the ideal Bose gas and the ideal Fermi gas all the desired thermodynamic statements can be derived. So it follows with (2.86) for the total *grand-canonical potential*:

$$\begin{aligned}\Omega^{(+)}(T, V, \mu) &= -k_B T \ln \Xi_{\mu}^{(+)}(T, V) \\ &= k_B T \sum_r \ln \left[ 1 - e^{-\beta (\varepsilon_r - \mu)} \right],\end{aligned} \quad (3.21)$$

$$\begin{aligned}\Omega^{(-)}(T, V, \mu) &= -k_B T \ln \Xi_{\mu}^{(-)}(T, V) \\ &= -k_B T \sum_r \ln \left[ 1 + e^{-\beta (\varepsilon_r - \mu)} \right].\end{aligned} \quad (3.22)$$

The volume-dependence, by the way, is *hidden* in the one-particle energies  $\varepsilon_r$ . When the particles of the ideal gas are confined to a finite volume  $V$ , then this means quantum-mechanically that they move in a *potential well* with infinitely high walls. In this sense the energies  $\varepsilon_r$  become dependent on the spatial dimensions of the *well* (see, e.g., exercise 4.2.1, Vol. 6).

To come with (3.21) and (3.22) to the *thermal equations of state* of the ideal Fermi and Bose gases, the chemical potential  $\mu$  has to be still replaced by the expectation value of the particle number. We use (2.79):

$$\langle \widehat{N} \rangle^{(+)} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi_{\mu}^{(+)}(T, V) = \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1}, \quad (3.23)$$

$$\langle \widehat{N} \rangle^{(-)} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Xi_{\mu}^{(-)}(T, V) = \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1}. \quad (3.24)$$

At least in principle, these equations can be solved for  $\mu$ :

$$\mu = \mu(T, V, \langle \widehat{N} \rangle^{(\pm)}). \quad (3.25)$$

When one inserts the result into (3.21) and (3.22), one obtains the **thermal equations of state** of the ideal quantum gases:

$$pV = k_B T \ln \Xi_{\mu(T, V, \langle \widehat{N} \rangle^{(\pm)})}^{(\pm)}(T, V). \quad (3.26)$$

The internal energy is calculated with (2.84):

$$U^{(+)} = -\frac{\partial}{\partial \beta} \ln \Xi_{\mu}^{(+)}(T, V) + \mu \langle \widehat{N} \rangle^{(+)} \stackrel{(3.21)}{=} \sum_r \frac{\varepsilon_r - \mu}{e^{\beta(\varepsilon_r - \mu)} - 1} + \mu \langle \widehat{N} \rangle^{(+)}.$$

From that it follows with (3.23):

$$U^{(+)} = \sum_r \frac{\varepsilon_r}{e^{\beta(\varepsilon_r - \mu)} - 1}. \quad (3.27)$$

Analogously one finds for fermions:

$$U^{(-)} = \sum_r \frac{\varepsilon_r}{e^{\beta(\varepsilon_r - \mu)} + 1}. \quad (3.28)$$

When we insert (3.25) for  $\mu$  into  $U^{(\pm)}$ , then we have found the **caloric equations of state** of the ideal quantum gases.

A revealing quantity, which will keep us occupied in the next sections also, is the **average occupation number**  $\langle \hat{n}_r \rangle^{(\pm)}$  of the  $r$ -th one-particle state. For its calculation one advisably starts at (3.18):

$$\begin{aligned} \langle \hat{n}_r \rangle^{(\pm)} &= \frac{1}{\Xi_\mu^{(\pm)}} \sum_N \sum_{\{n_p\}}^{\sum_p n_p = N} n_r \exp \left[ -\beta \sum_p n_p (\varepsilon_p - \mu) \right] \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_r} \ln \Xi_\mu^{(\pm)}(T, V) . \end{aligned}$$

This yields with (3.21) for bosons the

**Bose-Einstein distribution function**

$$\langle \hat{n}_r \rangle^{(+)} = \frac{1}{\exp[\beta (\varepsilon_r - \mu)] - 1} \quad (3.29)$$

and for fermions with (3.22) the

**Fermi-Dirac distribution function**

$$\langle \hat{n}_r \rangle^{(-)} = \frac{1}{\exp[\beta (\varepsilon_r - \mu)] + 1} . \quad (3.30)$$

For fermions the chemical potential  $\mu$  can adopt in principle any arbitrary value. It is always:

$$0 \leq \langle \hat{n}_r \rangle^{(-)} \leq 1 . \quad (3.31)$$

Some peculiarities appear in the case of bosons, which we will still refer to in detail later, but which we will already foreshadow a bit at this stage. At first one recognizes that  $\mu$  must in any case be smaller than the lowest one-particle energy  $\varepsilon_0$ , because otherwise some of the occupation numbers would be negative.  $\mu$  must even be truly smaller than  $\varepsilon_0$ , because  $\varepsilon_0 = \mu$  would let  $\langle \hat{n}_0 \rangle$  diverge. That, however, creates problems when  $T \rightarrow 0$ , since then **all** occupation numbers would be zero and therewith also the total number  $N$  of the bosons.

In principle, the theory does not exclude such a situation, since the grand-canonical systems are coupled to particle reservoirs which permit particle fluctuations and do not necessarily forbid  $N = 0$ . But how are we have to understand the limiting case  $T \rightarrow 0$ , when the particle number  $N$  is strictly pre-given? We get rid of the dilemma obviously only by the assumption that for  $T \rightarrow 0$  the chemical potential  $\mu$  of the ideal Bose gas *tends to*  $\varepsilon_0$ , and that in such a way that at  $T = 0$  the lowest one-particle state is *macroscopically* occupied:

$$\langle \hat{n}_0 \rangle^{(+)}(T = 0) = N . \quad (3.32)$$

This phenomenon is known as **Bose-Einstein condensation**. We will dedicate to it, in view of its importance, the Sect. 3.3.3.

By comparison of (3.29) and (3.30) with (3.23) and (3.24), on the one hand, and with (3.27) and (3.28), on the other hand, one finds the following physically plausible connections between the average occupation numbers and the average number operator and the internal energy, respectively:

$$\langle \widehat{N} \rangle^{(\pm)} = \sum_r \langle \hat{n}_r \rangle^{(\pm)}, \quad (3.33)$$

$$U^{(\pm)} = \sum_r \varepsilon_r \langle \hat{n}_r \rangle^{(\pm)}. \quad (3.34)$$

For large one-particle energies,  $\varepsilon_r - \mu \gg k_B T$ , Bose-Einstein- and Fermi-Dirac distribution function turn into the classical *Maxwell-Boltzmann distribution function*:

$$\langle \hat{n}_r \rangle^{(\pm)} \sim e^{-\beta \varepsilon_r} \quad (\varepsilon_r - \mu \gg k_B T). \quad (3.35)$$

In the *classical limit* the differences between bosons and fermions are washed out.

It is now recommendable to perform the further detailed discussions separately for the ‘*Fermi-case*’ and the ‘*Bose-case*’.

### 3.1.3 Exercises

#### Exercise 3.1.1

1. Express the *average occupation number*  $\langle \hat{n}_r \rangle$  of the ideal quantum gases by the **canonical** partition function  $Z_N(T, V)$ .
2. Calculate approximately with the *Darwin-Fowler method (saddle-point method)*

$$\ln Z_N(T, V).$$

3. Fix the physical meaning of the *saddle point* by the thermodynamic relation

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} \quad (\mu: \text{chemical potential, } F: \text{free energy})$$

and determine the explicit temperature-dependences of the average occupation numbers  $\langle \hat{n}_r \rangle$ . Compare the results with the *grand-canonical expressions* (3.29) and (3.30).



**Exercise 3.1.2**

$S = 1/2$ -fermions occupy at the temperature  $T$  a **finite** number of one-particle energy levels  $\varepsilon_r$ ,  $r = 1, 2, \dots, M$ .

1. How large can be, at most, the expectation value of the particle number  $\langle \hat{N} \rangle$ ?
2. Formulate the grand-canonical partition function.
3. Show by the use of the relation

$$F = -k_B T \ln \Xi_\mu + \mu \langle \hat{N} \rangle,$$

that the thermodynamic properties of this system come out in the same way when one distributes  $(2M - \langle \hat{N} \rangle)$  'holes' with the chemical potential  $-\mu$  over the energy levels  $-\varepsilon_r$ .

**Exercise 3.1.3**

For the quantum gases calculate the relative mean square deviation of the one-particle occupation numbers:

$$(\Delta \bar{n}_r)^2 = \frac{\langle \hat{n}_r^2 \rangle - \langle \hat{n}_r \rangle^2}{\langle \hat{n}_r \rangle^2}.$$

**Exercise 3.1.4**

Are the following particles fermions or bosons:

$$\text{H}_2\text{-molecule}, \quad {}^4\text{He}^+\text{-ion}, \quad {}^6\text{Li}^+\text{-ion}, \quad {}^3\text{He-atom?}$$

**Exercise 3.1.5**

Let the one-particle energies of an ideal quantum gas in the volume  $V_d$  be given by

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}.$$

Due to periodic boundary conditions the wave vectors  $\mathbf{k}$  are discrete. The grid volume in the  $\mathbf{k}$ -space, which contains just one allowed  $\mathbf{k}$ -state, is given by

$$\Delta_d k = \frac{(2\pi)^d}{V_d}.$$

$d$ : dimension of the space,  $V_d$ : volume of the ideal quantum gas. Calculate for arbitrary dimensions  $d$  the density of states  $D(E)$ :

$$D(E) dE = \frac{2S + 1}{\Delta_d k} \int_{E \leq \varepsilon(\mathbf{k}) \leq E + dE} d^d k.$$

Give the density of states explicitly for  $d = 1, 2, 3!$

**Exercise 3.1.6**

Consider a system of  $N$  electrons (wave vector  $\mathbf{k}$ , spin projection  $\sigma = \uparrow, \downarrow$ ). Use for their description the simultaneous eigen-states

$$|\mathbf{k}\sigma\rangle = |\mathbf{k}\rangle|\sigma\rangle$$

of the wave-vector operator  $\hat{\mathbf{k}}$ ,

$$\hat{\mathbf{k}}|\mathbf{k}\rangle = \mathbf{k}|\mathbf{k}\rangle$$

and the electron-spin operator  $\sigma_z$ :

$$\begin{aligned}\sigma_z|\sigma\rangle &= (\delta_{\sigma\uparrow} - \delta_{\sigma\downarrow}) \frac{\hbar}{2}|\sigma\rangle \\ |\uparrow\rangle &= \begin{pmatrix} 1 \\ 0 \end{pmatrix}; |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ \sigma_z &= \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\end{aligned}$$

Formulate therewith in second quantization:

1. the operator of the total momentum

$$\mathbf{P} = \sum_{i=1}^N \mathbf{p}_i,$$

2. the operator of the  $x$ -component of the total spin

$$S^x = \sum_{i=1}^N \sigma_{ix}.$$

3. Calculate with the results from 1. and 2. the commutator

$$[S^x, \mathbf{P}]_-.$$

**3.2 Ideal Fermi Gas**

In this section we will be concerned with the rigorously calculable case of the *ideal Fermi gas*, whose properties are strongly influenced by the action of the **Pauli principle**. That particularly holds for the so-called **degenerate Fermi gas**, which

is defined by

$$\mu \gg k_{\text{B}}T \iff \beta\mu \gg 1 . \quad (3.36)$$

In this limit, quantum-mechanical elements especially strongly stand out, so that the *degenerate Fermi gas* has little in common with the *classical ideal gas*. At first, we will try to become familiar with the general properties, in order to then discuss concrete applications, in particular with respect to the important case of the *metal electrons*. For simplicity, and because there are no mix-ups to be feared, we will suppress in this section the index  $(-)$  at the functions and the quantities, which refer to Fermi systems. We will re-introduce it, as soon as a delimitation towards the corresponding quantities of the Bose systems becomes necessary.

### 3.2.1 Equations of State

The grand-canonical potential provides the access to the *thermal equation of state*. In the evaluation of the relation (3.22), we have to think about the summation  $\Sigma_r$  over the one-particle states. We remember that it is to sum over *states* and not over *energies*. The eigen-functions of non-interacting particles are plane waves. A complete set of quantum numbers thus consists of, for instance, the three Cartesian components of the wave vector  $\mathbf{k}$  and the spin projection  $m_S$  of the fermion spin  $\mathbf{S}$ . Over these quantum numbers it must be summed in (3.22):

$$r \equiv (\mathbf{k}, m_S) .$$

Since the Hamilton operator (3.16) does not contain any spin part, the eigen-states will be *spin-degenerate*, i.e., they will be independent of  $m_S$  ( $m_S = -S, -S + 1, \dots, S$ ):

$$\sum_r \dots \implies (2S + 1) \sum_{\mathbf{k}} \dots$$

The fermions are in a container of finite volume  $V$ , which we can imagine, without restricting the general validity of our considerations, as a cuboid with the edge lengths  $L_x, L_y, L_z$ . The boundary condition, that at the walls the wave function must vanish, leads to *discrete* wave vectors  $k$ . The same could be achieved by *boundary conditions* ((2.77), Vol. 7), which are a bit more convenient to work with, and the application of which is likewise allowed, at least for the asymptotically large system:

$$k_{x,y,z} = \frac{2\pi}{L_{x,y,z}} n_{x,y,z} ; \quad n_{x,y,z} \in \mathbf{Z} .$$

To each state there is thus assigned in the  $k$ -space an average

$$\text{grid volume } \Delta k = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V}.$$

In the so-called *thermodynamic limit* ( $V \rightarrow \infty$ ,  $N \rightarrow \infty$  with  $n = N/V = \text{const}$ , see Sect. 4.5) the possible  $\mathbf{k}$ -values lie quasi-densely ( $\Delta k \rightarrow 0$ ). One can therefore replace the sums by integrals:

$$\begin{aligned} \sum_r \dots &\rightarrow (2S+1) \frac{1}{\Delta k} \int d^3 k \dots = (2S+1) \frac{V}{(2\pi)^3} \int d^3 k \dots \\ &= (2S+1) \frac{V}{h^3} \int d^3 p \dots \end{aligned} \quad (3.37)$$

The last expression explains, by the way, the appearance of the factor  $1/h^{3N}$  in the *correct Boltzmann counting* (1.45) of the Classical Statistical Physics. The grand-canonical potential (3.22) can now be calculated with (3.37). For the concrete evaluation, though, we still have to fix the one-particle energies  $\varepsilon_r$ . We choose the simplest case (no external potential!):

$$\varepsilon_r \implies \varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}. \quad (3.38)$$

Therewith (3.22) and (3.26), respectively, reads:

$$-\beta \Omega(T, V, \mu) = (2S+1) \frac{V}{(2\pi)^3} 4\pi \int_0^\infty dk k^2 \ln \left[ 1 + z \exp \left( -\beta \frac{\hbar^2 k^2}{2m} \right) \right].$$

We substitute

$$x = \hbar k \sqrt{\frac{\beta}{2m}} \implies k^2 dk = \left( \frac{2m}{\beta \hbar^2} \right)^{3/2} x^2 dx$$

and have then to evaluate:

$$-\beta \Omega(T, V, \mu) = (2S+1) \frac{4V}{\sqrt{\pi}} \left( \frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \int_0^\infty dx x^2 \ln (1 + z e^{-x^2}).$$

We remember the definition (1.137) of the *thermal de Broglie wavelength*

$$\lambda = \sqrt{\frac{2\pi\beta\hbar^2}{m}}$$

and write therewith:

$$-\beta \Omega(T, V, \mu) = \frac{2S+1}{\lambda^3} \frac{4V}{\sqrt{\pi}} \int_0^{\infty} dx x^2 \ln(1 + ze^{-x^2}).$$

With the series expansion of the logarithm,

$$\ln(1+y) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{y^n}{n}; \quad |y| \leq 1, \quad (3.39)$$

the integral can be further evaluated:

$$\begin{aligned} \int_0^{\infty} dx x^2 \ln(1 + ze^{-x^2}) &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n} \int_0^{\infty} dx x^2 e^{-nx^2} \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n} \left( -\frac{d}{dn} \int_0^{\infty} dx e^{-nx^2} \right) \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n} \left( -\frac{d}{dn} \frac{1}{2} \sqrt{\pi} \frac{1}{\sqrt{n}} \right) \\ &= \frac{\sqrt{\pi}}{4} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{5/2}}. \end{aligned}$$

One defines:

$$f_{5/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx x^2 \ln(1 + ze^{-x^2}) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{5/2}}, \quad (3.40)$$

where the power of  $n$  explains the index  $5/2$ . This holds analogously for

$$f_{3/2}(z) = z \frac{d}{dz} f_{5/2}(z) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{z^n}{n^{3/2}}. \quad (3.41)$$

With (3.40), the grand-canonical potential of the ideal Fermi gas is determined, by which all the other thermodynamical quantities become derivable:

$$\beta \Omega(T, V, z) = -\frac{2S+1}{\lambda^3} V f_{5/2}(z). \quad (3.42)$$

It follows immediately, because of  $\Omega = -pV$ :

$$\beta p = \frac{2S+1}{\lambda^3(T)} f_{5/2}(z). \quad (3.43)$$

In order to come eventually to the *thermal equation of state*, the fugacity  $z$  on the right-hand side still has to be replaced by the *particle density*  $n = \langle \widehat{N} \rangle / V$ . Thereby (2.78) helps:

$$\langle \widehat{N} \rangle = z \left( \frac{\partial}{\partial z} \ln \Xi_z \right)_{T,V} = Vz \left( \frac{\partial}{\partial z} \beta p \right)_{T,V}.$$

It results with (3.41):

$$n = \frac{\langle \widehat{N} \rangle}{V} = \frac{2S+1}{\lambda^3(T)} f_{3/2}(z). \quad (3.44)$$

From the two Eqs. (3.43) and (3.44),  $z$  can, at least in principle, be eliminated, and one obtains therewith the **thermal equation of state** of the ideal Fermi gas.

For the *caloric equation of state* we need the internal energy. A possible representation is (3.28). In the case here it is, however, more reasonable to start once again at (2.84):

$$U = -\frac{\partial}{\partial \beta} \ln \Xi_\mu + \mu \langle \widehat{N} \rangle.$$

We rewrite the second summand with the aid of (3.44):

$$\begin{aligned} \mu \langle \widehat{N} \rangle &= \mu V \frac{2S+1}{\lambda^3} z \frac{d}{dz} f_{5/2}(z) = V \frac{2S+1}{\lambda^3} \frac{\partial}{\partial \beta} \left( \frac{\lambda^3}{V(2S+1)} \ln \Xi_\mu \right) \\ &= \frac{\partial}{\partial \beta} \ln \Xi_\mu + \frac{3}{2} \frac{1}{\beta} \ln \Xi_\mu = \frac{\partial}{\partial \beta} \ln \Xi_\mu + \frac{3}{2} pV. \end{aligned}$$

It follows:

$$U = \frac{3}{2} k_B T V \frac{2S+1}{\lambda^3} f_{5/2}(z) = \frac{3}{2} pV. \quad (3.45)$$

When we still replace, by the use of (3.44),  $z$  by a function of  $T$ ,  $V$  and  $\langle \widehat{N} \rangle$ , then we have the **caloric equation of state** of the ideal Fermi gas. The right-hand part of (3.45),  $U = 3/2 pV$ , is in this form also valid for the classical ideal gas. One should, however, not forget that for the one-particle energy the relation (3.38) was presumed. For *relativistic fermions*, for instance, with one-particle energies being different from (3.38), (3.45) gets modified (see Exercise 3.2.10)

### 3.2.2 Classical Limiting Case

For the limiting case

$$z \ll 1 \quad (3.46)$$

we want to calculate explicitly the equation of state of the ideal Fermi gas. Looking at the *average occupation number* (3.30),

$$\langle \hat{n}_r \rangle = \frac{1}{z^{-1} e^{\beta \varepsilon_r} + 1} \approx z e^{-\beta \varepsilon_r} ,$$

which in this case goes over into the classical *Maxwell-Boltzmann distribution*, one realizes that (3.46) represents indeed the *classical limiting case (non-degenerate Fermi gas)*.

As to the series expansions (3.40), (3.41) we can restrict ourselves to the first two terms:

$$f_{5/2}(z) \approx z - \frac{z^2}{2^{5/2}} ,$$

$$f_{3/2}(z) \approx z - \frac{z^2}{2^{3/2}} .$$

Therewith (3.43) and (3.44) simplify to:

$$\beta p \lambda^3 \approx (2S + 1) z (1 - 2^{-5/2} z) ,$$

$$n \lambda^3 \approx (2S + 1) z (1 - 2^{-3/2} z) .$$

Solving the equation for the particle density yields in the simplest approximation:

$$z^{(0)} \approx \frac{n \lambda^3}{2S + 1} .$$

By this it becomes clear that the condition (3.46) is equivalent to

$$n \lambda^3 \ll 1 . \quad (3.47)$$

The *classical limiting case* is thus given for **low particle density** and **small de Broglie wave length**. Small  $\lambda$ , on the other hand, means, because of  $\lambda \sim T^{-1/2}$ , high temperature.

If we execute the approximation one step further ( $(1 - x)^{-1} \approx 1 + x$ ;  $x \ll 1$ ),

$$z^{(1)} \approx z^{(0)} (1 + 2^{-3/2} z^{(1)}) = z^{(0)} (1 - z^{(0)} 2^{-3/2})^{-1} \approx z^{(0)} (1 + z^{(0)} 2^{-3/2}),$$

and insert this into the equation for the pressure,

$$\begin{aligned} \beta p \lambda^3 &\approx (2S + 1) \left[ z^{(0)} (1 + z^{(0)} 2^{-3/2}) - 2^{-5/2} (z^{(0)})^2 \right] \\ &= n \lambda^3 \left( 1 + 2^{-5/2} \frac{n \lambda^3}{2S + 1} \right), \end{aligned}$$

then it is left as thermal equation of state:

$$pV = \langle \widehat{N} \rangle k_B T \left( 1 + \frac{n \lambda^3}{4\sqrt{2}(2S + 1)} \right). \quad (3.48)$$

The first term corresponds to the equation of state of the classical ideal gas. The second summand represents a first quantum-mechanical correction. More refined approximations would follow an expansion up to higher powers of  $n \lambda^3$ .

In an analogous manner, all the other thermodynamic functions can be expressed by those of the classical ideal gas together with small *quantum corrections*.

### 3.2.3 Density of States, Fermi Function

In the last subsection we have treated the *classical limiting case* of low particle densities and high temperatures. For applications, particularly in solid state physics (metal electrons!), the opposite limiting case of the **degenerate Fermi gas**, on which we now will concentrate, is still more interesting. For its description the *density of states*  $D(E)$  (2.21) is a useful and important quantity, which we therefore will at first derive explicitly for the ideal Fermi gas.

$D(E)dE$  is the number of states with energies between  $E$  and  $E + dE$ , which we can easily count by means of the considerations on (3.37):

$$D(E)dE = \frac{2S + 1}{\Delta k} \int_{E \leq \varepsilon(\mathbf{k}) \leq E + dE} d^3 k. \quad (3.49)$$

It is integrated over a shell in the  $k$ -space, which contains all those states, whose energy values are between  $E$  and  $E + dE$ . We use for  $\varepsilon(\mathbf{k})$  the isotropic energy relation (3.38). Therefore, the spin-degeneracy  $(2S + 1)$  remains to be taken into



consideration. With the *phase volume*

$$\varphi(E) = \int_{\varepsilon(\mathbf{k}) \leq E} d^3k$$

and the relation  $\Delta k = (2\pi)^3/V$  for the *grid volume*, (3.49) can be written as follows:

$$D(E) = (2S + 1) \frac{V}{(2\pi)^3} \frac{d}{dE} \varphi(E) .$$

Because of the isotropic energy relation (3.38)  $\varphi(E)$  represents in the  $k$ -space a sphere of the volume

$$\varphi(E) = \frac{4\pi}{3} k^3 \Big|_{\varepsilon(\mathbf{k})=E} = \frac{4\pi}{3} \left( \frac{2mE}{\hbar^2} \right)^{3/2} .$$

Therewith it holds for the

**density of states of the ideal quantum gas:**

$$D(E) = \begin{cases} d\sqrt{E}, & \text{if } E \geq 0 , \\ 0 & \text{otherwise .} \end{cases} \quad (3.50)$$

$$d = (2S + 1) \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} . \quad (3.51)$$

Up to now we did not have to utilize special properties of the Fermi gas. (3.50) is therefore valid also for Bose systems, if their one-particle energies correspond to (3.38). A typical feature is the  $\sqrt{E}$ -dependence of the density of states.

$D(E)$  delivers information about the density of the available energy states. The next information we obviously need is, with which probability these states are actually occupied at the temperature  $T$ . That, however, we have already calculated with (3.30). The average occupation number  $\langle \hat{n}_r \rangle$  is a number in between 0 and 1, which is given by the **Fermi-Dirac distribution function**

$$f_-(E) = [e^{\beta(E-\mu)} + 1]^{-1} \quad (3.52)$$

$$\langle \hat{n}_r \rangle = f_-(E = \varepsilon_r) .$$

(In most cases  $f_-(E)$  is shortly referred to as *Fermi function*.) Therewith it is

$D(E)f_-(E)$  the density of the states, which are **occupied** at the temperature  $T$ .

For the internal energy  $U$  and the particle number  $\langle \hat{N} \rangle$  of the ideal Fermi gas there are obviously the following integrals to be calculated:

$$\langle \hat{N} \rangle = \int_{-\infty}^{+\infty} dE f_{-}(E) D(E) , \tag{3.53}$$

$$U = \int_{-\infty}^{+\infty} dE E f_{-}(E) D(E) . \tag{3.54}$$

Before we evaluate these functions, let us inspect the *Fermi function*  $f_{-}(E)$  in some more detail. When  $f_{-}(E)$  is the probability for the fact that a state of the energy  $E$  is **occupied** at the temperature  $T$ , then  $(1 - f_{-}(E))$  obviously represents the probability that just this state is **unoccupied**. Because of

$$f_{-}(\mu + \Delta) = \frac{1}{e^{\beta\Delta} + 1} = 1 - \frac{e^{\beta\Delta}}{e^{\beta\Delta} + 1} = 1 - \frac{1}{e^{-\beta\Delta} + 1} = 1 - f_{-}(\mu - \Delta) \tag{3.55}$$

the state with the energy  $E = \mu + \Delta$  is occupied with the same probability as the state with  $E = \mu - \Delta$  is unoccupied. In particular it holds for **all** temperatures:

$$f_{-}(E = \mu) = \frac{1}{2} . \tag{3.56}$$

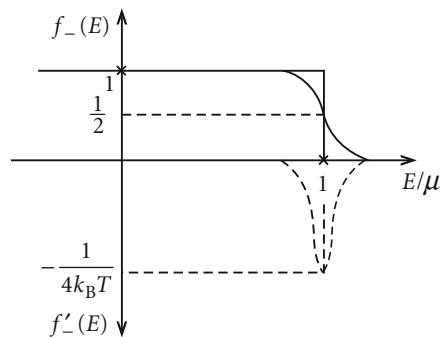
The chemical potential  $\mu$  by itself is temperature-dependent (see Sect. 3.2.5). —At  $T = 0$ , the Fermi function  $f_{-}(E)$  is a *step function* (Fig. 3.1):

$$f_{-}^{T=0}(E) = \Theta(\mu(T = 0) - E) . \tag{3.57}$$

One denotes

$$\mu(T = 0) = E_F \tag{3.58}$$

**Fig. 3.1** Fermi function as average occupation number of the ideal Fermi gas



as **Fermi energy**. At finite temperatures ( $T > 0$ ), the Fermi function *softens up* at the *Fermi edge* with a width of about  $4k_B T$  (Fig. 3.1), as one easily realizes by

$$f'_-(E) = \frac{d}{dE} f_-(E) = -\frac{\beta e^{\beta(E-\mu)}}{[e^{\beta(E-\mu)} + 1]^2} \xrightarrow{E \rightarrow \mu} -\frac{1}{4k_B T}. \quad (3.59)$$

This ‘*softening up*’ of the Fermi function is responsible for many electronic properties of the solid state which are of rather crucial importance, what we will demonstrate in the following subsections by some simple examples.—An *estimation for metal electrons* ( $S = 1/2$ ),

$$\begin{aligned} E_F &= 1 \dots 10 \text{ eV}, \\ k_B T [\text{eV}] &= \frac{T[\text{K}]}{11605}; \quad T_{rt} = 300 \text{ K} \\ \implies \frac{k_B T_{rt}}{E_F} &\lesssim \frac{1}{40}; \quad (z \gg 1), \end{aligned} \quad (3.60)$$

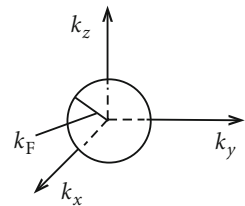
shows that at *normal* temperatures, e.g. room temperature  $T_{rt}$ , only a very small region around the Fermi edge will be *softened up*. Outside this *layer* it is

$$\frac{d}{dE} f_-(E) \approx -\beta e^{-\beta|E-\mu|} \approx 0.$$

The *physical background* of the behavior of the Fermi function can rather easily be understood. Because of the Pauli principle, two fermions can never occupy the same state. In the ground state of the system ( $T = 0$ ) the particles fill up the lowest energy levels up to a maximal energy  $E_F$ . If we further presume the isotropic one-particle energy relation (3.38), it means that in the  $k$ -space all states within a sphere (**Fermi sphere**) of the radius  $k_F$  (**Fermi wave vector**) (Fig. 3.2) are occupied, each by  $2S + 1$  fermions, which differ by the spin quantum number  $m_S$ . The quantities  $k_F$  and  $E_F$  obviously depend on the particle number  $N = \langle \hat{N} \rangle$ , and are easily determined if one assumes  $N$  as fixedly pre-given:

$$N \stackrel{!}{=} \frac{1}{\Delta k} \frac{4\pi}{3} k_F^3 (2S + 1) = \frac{V}{6\pi^2} k_F^3 (2S + 1).$$

**Fig. 3.2** Fermi sphere in the space of the wave vectors of the radius  $k_F$  (Fermi wave vector)



With the *particle density*  $n = \langle \hat{N} \rangle / V = N/V$  one finds:

$$k_F = \left( \frac{6\pi^2}{2S+1} n \right)^{1/3}, \quad (3.61)$$

$$E_F = \frac{\hbar^2}{2m} \left( \frac{6\pi^2}{2S+1} n \right)^{2/3}. \quad (3.62)$$

Furthermore, one calculates as *average energy per fermion* at  $T = 0$  (see Exercise 3.2.3):

$$\varepsilon = \frac{1}{N} U(T=0) = \frac{3}{5} E_F. \quad (3.63)$$

For comparative purposes, the definition of a *Fermi temperature*  $T_F$ ,

$$T_F = \frac{E_F}{k_B}, \quad (3.64)$$

appears sometimes to be rather reasonable. The following table contains some typical numerical values for conduction electrons of the simple metals.

	$n$ [ $\text{cm}^{-3}$ ]	$k_F$ [ $\text{cm}^{-1}$ ]	$E_F$ [eV]	$T_F$ [K]
<i>Li</i>	$4.6 \cdot 10^{22}$	$1.10 \cdot 10^8$	4.7	$5.5 \cdot 10^4$
<i>Na</i>	$2.5 \cdot 10^{22}$	$0.90 \cdot 10^8$	3.1	$3.7 \cdot 10^4$
<i>K</i>	$1.34 \cdot 10^{22}$	$0.73 \cdot 10^8$	2.1	$2.4 \cdot 10^4$
<i>Cu</i>	$8.50 \cdot 10^{22}$	$1.35 \cdot 10^8$	7.0	$8.2 \cdot 10^4$
<i>Ag</i>	$5.76 \cdot 10^{22}$	$1.19 \cdot 10^8$	5.5	$6.4 \cdot 10^4$
<i>Au</i>	$5.90 \cdot 10^{22}$	$1.20 \cdot 10^8$	5.5	$6.4 \cdot 10^4$

At finite temperatures the fermions will try to use the thermal energy for excitations into higher levels. Because of the Pauli principle, though, only those fermions will succeed to do that, which before the excitation have an energetic distance from the Fermi edge  $E_F$ , which is at most of the order of  $k_B T$ . For the others there are no free states available, which they can reach by exploiting the thermal energy. That explains the *softening up* of the Fermi function only in a *thin* layer around  $E_F$ .

### 3.2.4 Sommerfeld Expansion

When evaluating the thermodynamic properties of the *ideal Fermi gas* we meet, again and again, integrals of the type (3.53) for  $\langle \hat{N} \rangle$  or (3.54) for  $U$ . The Fermi

function  $f_-(E)$ , which essentially determines the temperature-dependences, raises thereby certain difficulties. For the *classical limiting case* ( $z \ll 1$ ) we could terminate the exact series expansions of the Sect. 3.2.1 after a few terms obtaining therewith the results of Sect. 3.2.2. Unfortunately, this works no longer for the *degenerate* Fermi gas ( $z \gg 1$ ). The integrals to be solved have all the structure:

$$I(T) = \int_{-\infty}^{+\infty} dE g(E) f_-(E) . \quad (3.65)$$

$f_-(E)$  is thereby the Fermi function which takes care for the fact that this integral deviates from its  $T = 0$ -value,

$$I(T = 0) = \int_{-\infty}^{E_F} dE g(E) , \quad (3.66)$$

by a contribution which is exclusively determined by the behavior of the function  $g(E)$  in the a few  $k_B T$  broad *Fermi layer* around  $E = \mu$ . If  $g(E)$  is there *well-behaved*, then series expansions become promising. An extraordinarily useful expansion, because it rapidly converges for the interesting systems, we will discuss, as an *insertion* in this subsection. It will be of great use for us in the following subsections when we discuss the *thermodynamics* of the Fermi gas. We will agree upon three preconditions for the function  $g(E)$ :

1.  $g(E) \xrightarrow{E \rightarrow -\infty} 0$ ,
2.  $g(E)$  remains finite for  $E \rightarrow +\infty$  or diverges at most with a finite power of  $E!$
3.  $g(E)$  is regular within the *Fermi layer*.

We define

$$p(E) = \int_{-\infty}^E dx g(x) \implies g(E) = \frac{d}{dE} p(E)$$

and obtain then by integration by parts:

$$\int_{-\infty}^{+\infty} dE g(E) f_-(E) = p(E) f_-(E) \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} dE p(E) \frac{\partial f_-(E)}{\partial E} .$$

The integrated part vanishes, because  $f_-(E)$  disappears for  $E \rightarrow +\infty$  more rapidly than any power of  $E$  diverges. At the lower bound,  $f_-(E) = 1$  and  $p(E) = 0$ . It thus remains as intermediate result for the integral in (3.65):

$$I(T) = - \int_{-\infty}^{+\infty} dE p(E) \frac{\partial f_-(E)}{\partial E} . \quad (3.67)$$

We know that the derivative of the Fermi function is distinctly different from zero only in the narrow *Fermi layer*. We therefore insert the Taylor expansion of  $p(E)$  around  $E = \mu$ ,

$$p(E) = p(\mu) + \sum_{n=1}^{\infty} \frac{(E - \mu)^n}{n!} \left( \frac{d^n}{dE^n} p(E) \right)_{E=\mu},$$

into (3.67). The first summand yields the following contribution to  $I(T)$ :

$$I_0(T, \mu) = -p(\mu) \int_{-\infty}^{+\infty} dE \frac{\partial f_-(E)}{\partial E} = p(\mu) = \int_{-\infty}^{\mu} dx g(x).$$

From the above sum only the even powers of  $(E - \mu)$  contribute to (3.67), because

$$\frac{\partial f_-(E)}{\partial E} = -\beta \frac{e^{\beta(E-\mu)}}{[e^{\beta(E-\mu)} + 1]^2} = \frac{-\beta}{4 \cosh^2((1/2)\beta(E-\mu))}$$

is an even function of  $(E - \mu)$ :

$$I(T) = I_0(T, \mu) + \beta \sum_{n=1}^{\infty} \frac{1}{(2n)!} \left( \frac{d^{2n-1}}{dE^{2n-1}} g(E) \right)_{E=\mu} I_{2n}(T, \mu). \quad (3.68)$$

We have defined here for abbreviation:

$$I_{2n}(T, \mu) = \int_{-\infty}^{+\infty} dE (E - \mu)^{2n} \frac{e^{\beta(E-\mu)}}{[e^{\beta(E-\mu)} + 1]^2}. \quad (3.69)$$

This can be further evaluated:

$$\begin{aligned} I_{2n}(T, \mu) &= \frac{1}{\beta^{2n+1}} \int_{-\infty}^{+\infty} dx x^{2n} \frac{e^x}{(e^x + 1)^2} = \frac{-2}{\beta^{2n+1}} \left( \frac{d}{d\alpha} \int_0^{\infty} dx \frac{x^{2n-1}}{e^{\alpha x} + 1} \right)_{\alpha=1} \\ &= \frac{-2}{\beta^{2n+1}} \left( \frac{d}{d\alpha} \alpha^{-2n} \int_0^{\infty} dy \frac{y^{2n-1}}{e^y + 1} \right)_{\alpha=1} = \frac{4n}{\beta^{2n+1}} \left( \int_0^{\infty} dy \frac{y^{2n-1}}{e^y + 1} \right). \end{aligned}$$

The integral in the bracket is a standard integral, well-known in mathematical physics (e.g. M. Abramowitz, I. A. Stegun: *Handbook of Mathematical Functions*,

p. 807, Dover, New York, 1972). It is a substantial part of *Riemann's*  $\zeta$ -function:

$$\zeta(n) = \sum_{p=1}^{\infty} \frac{1}{p^n} = \frac{1}{(1 - 2^{1-n})\Gamma(n)} \int_0^{\infty} dy \frac{y^{n-1}}{e^y + 1}, \quad (3.70)$$

which is available in tabulated form:

$$\zeta(2) = \frac{\pi^2}{6}; \quad \zeta(4) = \frac{\pi^4}{90}; \quad \zeta(6) = \frac{\pi^6}{945}; \quad \dots \quad (3.71)$$

$\Gamma(n)$  is the *Gamma function* with  $\Gamma(n) = (n-1)!$ , if  $n$  is a natural number. It remains therewith for the integral (3.69):

$$I_{2n}(T, \mu) = 2(1 - 2^{1-2n})\beta^{-(2n+1)}(2n)! \zeta(2n).$$

When we insert this into (3.68), then the integral (3.65) is represented by its **Sommerfeld expansion**

$$I(T) = \int_{-\infty}^{\mu} dE g(E) + 2 \sum_{n=1}^{\infty} (1 - 2^{1-2n}) \zeta(2n) (k_B T)^{2n} \left[ \frac{d^{2n-1} g(E)}{dE^{2n-1}} \right]_{E=\mu}. \quad (3.72)$$

That looks, though, rather complicated. The real value of this expansion therefore becomes noticeable above all in the case where a function can be approximately estimated

$$\left. \frac{d^n}{dE^n} g(E) \right|_{E=\mu} \approx \frac{g^{(n)}(\mu)}{\mu^n}.$$

The density of states  $D(E)$  of the ideal *degenerate* Fermi gas, for instance, belongs to this class of functions. In such cases the expansion converges extremely rapidly because the ratio of subsequent members of the series is of the order of magnitude  $(k_B T/\mu)^2$ . For the important example of application of the conduction electrons of simple metals (see the above table) the ratio is about  $10^{-4}$  at room temperature! In most of the cases of interest already the very first summands of the expansion (3.72) are therefore sufficient:

$$\begin{aligned} \int_{-\infty}^{+\infty} dE g(E) f_{-}(E) &= \int_{-\infty}^{\mu} dE g(E) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) \\ &+ \frac{7\pi^4}{360} (k_B T)^4 g'''(\mu) + \dots \end{aligned} \quad (3.73)$$

With this useful formula we will be able to derive in the next subsection statements about the thermodynamic properties of the ideal Fermi gas.

### 3.2.5 Thermodynamic Properties

We presume for the following an ideal Fermi gas with a **fixed** particle number  $\langle \hat{N} \rangle \equiv N$ . Via the particle number we want to investigate, at first, the temperature-dependence of the **chemical potential**  $\mu$ . According to formula (3.53),  $N$  is determined by the integral over the density of the occupied states (Fig. 3.3)

$$D(E)f_-(E) .$$

The temperature-dependence in (3.53) can of course be only of formal nature. The fermion number is the same for all temperatures. The density of states  $D(E)$  (3.50) fulfills all preconditions for the applicability of the *Sommerfeld expansion*. With (3.73) we then have:

$$N \approx \int_{-\infty}^{\mu} dE D(E) + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) + \dots$$

In the case of the *degenerate* Fermi gas, we can cut the expansion for all ‘reasonable’ temperatures already after the first correction term. We insert  $D(E)$  according to (3.50), where, however, it is advisable to use for the constant  $d$ , instead of (3.51), the equivalent expression (Exercise 3.2.3, part 4.):

$$d = \frac{3N}{2E_F^{3/2}} \tag{3.74}$$

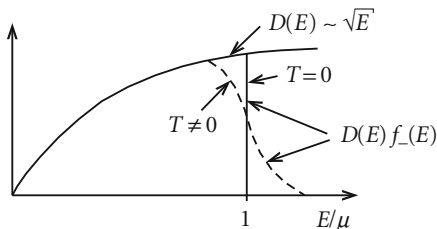
$N$  is then canceled out:

$$1 \approx \left( \frac{\mu}{E_F} \right)^{3/2} \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 \right] .$$

The second summand is for typical cases of the order of magnitude  $10^{-4}$ . With  $(1 + x)^{n/m} \approx 1 + \frac{n}{m}x$ , if  $x \ll 1$ , we thus obtain:

$$\mu(T) \approx E_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right] . \tag{3.75}$$

**Fig. 3.3** Density of states  $D(E)$  and density of the occupied states  $D(E)f_-(E)$  of the ideal Fermi gas as function of the reduced energy  $E/\mu$





Under normal conditions in *degenerate* Fermi gases, the temperature-dependence of the chemical potential is therefore almost negligible. As a rule,  $\mu(T)$  is well approximated by the *Fermi energy*  $E_F$ . It decreases only slightly with increasing temperature.

In the next step we calculate the internal energy of the ideal Fermi gas, for which it must be evaluated with (3.54) and (3.73):

$$\begin{aligned} U(T) &\approx \int_0^\mu dE E D(E) + \frac{\pi^2}{6} (k_B T)^2 (\mu D'(\mu) + D(\mu)) \\ &= \frac{2}{5} d \mu^{5/2} + \frac{\pi^2}{4} (k_B T)^2 d \mu^{1/2} \\ &= d \frac{2}{5} E_F^{5/2} \left[ \left( \frac{\mu}{E_F} \right)^{5/2} + \frac{5\pi^2}{8} \left( \frac{k_B T}{E_F} \right)^2 \left( \frac{\mu}{E_F} \right)^{1/2} \right]. \end{aligned}$$

In front of the bracket there stands the  $T = 0$ -value of the internal energy:

$$d \frac{2}{5} E_F^{5/2} \stackrel{(3.74)}{=} N \frac{3}{5} E_F \stackrel{(3.63)}{=} U(T = 0).$$

Furthermore, we can estimate with (3.75):

$$\left( \frac{\mu}{E_F} \right)^n \approx 1 - n \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2.$$

The internal energy of the ideal Fermi gas thus changes with the temperature as follows:

$$U(T) \approx U(0) \left[ 1 + \frac{5\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right]. \quad (3.76)$$

The result concerning the temperature-behavior of the **heat capacity**, following from (3.76), belongs to the most important successes of the ‘*early*’ Quantum Statistics. The classical metal physics was completely unable to understand, why, on the one hand, electrons ( $S = 1/2$ -fermions) participate in the electric conduction, as if they were quasi-freely movable, but, on the other hand, do not contribute in a significant manner to the heat capacity. From a classical point of view, according to the equipartition theorem (1.113),  $N$  quasi-free electrons should exhibit an internal energy of  $(3/2)Nk_B T$ . This means:

$$C_V^{cl} \approx \frac{3}{2} N k_B \quad (\text{Dulong-Petit}).$$

We know that this result is correct for  $T \rightarrow \infty$ . For moderate and low temperatures, on the other hand, it is observed:

$$C_V \leq 10^{-2} C_V^{cl}; \quad C_V = C_V(T) \xrightarrow{T \rightarrow 0} 0 .$$

The explanation is given by the **Pauli principle**, according to which with a heating of the metal from  $T = 0$  to  $T > 0$ , in contrast to the classical assumption, only very few electrons can indeed accept the thermal energy  $k_B T$ . Only for the electrons in the thin *Fermi layer* free states are *within reach*, on to which they can be excited by absorbing thermal energy. The number of these electrons can be estimated to be about  $N(k_B T/E_F)$ . The internal energy of the Fermi gas thus changes approximately by  $\Delta U(T) = N(k_B T/E_F)k_B T$ . The heat capacity can therewith be given as  $C_V \approx (Nk_B^2/E_F)T$ . These estimations are actually not so bad, as one recognizes when one differentiates (3.76) with respect to the temperature:

$$C_V = \gamma T , \tag{3.77}$$

$$\gamma = \frac{a}{E_F} = bD(E_F) , \tag{3.78}$$

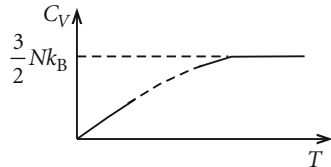
$$a = \frac{1}{2}N\pi^2 k_B^2 ; \quad b = \frac{1}{3}\pi^2 k_B^2 . \tag{3.79}$$

The Quantum Statistics is therefore able to reproduce and to explain the experimentally observed linear temperature-dependence of the heat capacity. The ideal Fermi gas therefore fulfills also the third law of Thermodynamics (Fig. 3.4). When comparing it with the *classical expectation*

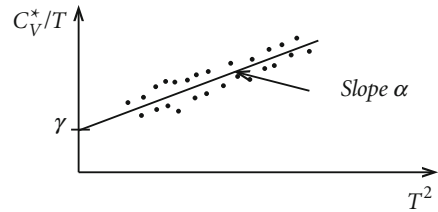
$$\frac{C_V}{C_V^{cl}} = \frac{\pi^2}{3} \left( \frac{k_B T}{E_F} \right)$$

for metals at room temperature this fraction is indeed of the order of magnitude  $10^{-2}$ . In a real metallic solid, besides the electrons, the *phonons* of the crystal lattice also contribute to the heat capacity. Phonons are bosons. We will therefore concentrate on them in Sect. 3.3. At low temperatures they yield a  $T^3$ -contribution to  $C_V$  (*Debye's  $T^3$ -law*, Exercise 2.3.12). It then holds in good approximation for a

**Fig. 3.4** Temperature behavior of the heat capacity of an ideal Fermi gas



**Fig. 3.5** Low-temperature behavior of the heat capacity of a metallic solid having regard to the contribution of phonons



solid at sufficiently low temperatures:

$$C_V^* = \gamma T + \alpha T^3 . \quad (3.80)$$

When one plots the experimental values of the heat capacity in the form of  $C_V^*/T$  as a function of  $T^2$ , it results, at least for the simple metals, a straight line (Fig. 3.5), whose axis intercept is equal to the *electronic*  $\gamma$ , and whose slope is equal to the *phononic*  $\alpha$ . The following table contains some measured values and the comparison to their theoretical values (3.78). Deviations are of course to be ascribed to the neglected electron-electron and to the electron-ion interactions.

	$\gamma$ [mJ mol <sup>-1</sup> K <sup>-2</sup> ]	$\gamma_{\text{ex}}/\gamma$
Na	1.38	1.22
K	2.08	1.23
Cu	0.695	1.38
Ag	0.646	1.01
Au	0.729	1.09

With (3.45) we have derived the relation, which is exact for the ideal Fermi gas:

$$U = \frac{3}{2}pV$$

Since we know  $U$ , (3.76), we can now explicitly write down the **thermal equation of state**:

$$pV = \frac{2}{5}NE_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right] . \quad (3.81)$$

$pV$  is therefore only very weakly temperature-dependent, since the fermions, because of the Pauli principle, react only very '*lazily*' on temperature variations. The Pauli principle is furthermore the only reason why the Fermi gas, in contrast to the classical ideal gas, exhibits a *zero-point pressure*:

$$p(T = 0) = \frac{2}{5} \frac{N}{V} E_F \stackrel{(3.62)}{=} \frac{2}{5} \frac{\hbar^2}{2m} \left( \frac{6\pi^2}{2S+1} \right)^{2/3} \left( \frac{N}{V} \right)^{5/3} . \quad (3.82)$$

The Pauli principle *permits* only  $(2S + 1)$  particles to have the momentum  $\mathbf{p} = 0$ . All the other fermions have even at  $T = 0$  finite momenta causing therewith the pressure (3.82), which is surely non-negligible, as it is documented by the numerical values in Exercise 3.2.3 (part 4.). When we think of the electrons of a metallic solid, the zero-point pressure must obviously be compensated by the here still neglected attractive forces of the positively charged ions, in order to prevent the electrons from leaving the solid.

Let us finally calculate the **entropy** of the ideal Fermi gas. For this purpose we use the thermodynamic relation (1.155):

$$\begin{aligned} S(T, V, \mu) &\stackrel{(3.22)}{=} - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} = \left( \frac{\partial}{\partial T} k_B T \ln \Xi_\mu(T, V) \right)_{V, \mu} \\ &\stackrel{(3.22)}{=} \left( \frac{\partial}{\partial T} k_B T \sum_r \ln (1 + e^{-\beta(\varepsilon_r - \mu)}) \right)_{V, \mu} \\ &= k_B \sum_r \ln (1 + e^{-\beta(\varepsilon_r - \mu)}) + \frac{1}{T} \sum_r \frac{e^{-\beta(\varepsilon_r - \mu)}}{1 + e^{-\beta(\varepsilon_r - \mu)}} (\varepsilon_r - \mu) . \end{aligned}$$

We can express the various terms by the average occupation numbers  $\langle \hat{n}_r \rangle$ :

$$\begin{aligned} \frac{e^{-\beta(\varepsilon_r - \mu)}}{1 + e^{-\beta(\varepsilon_r - \mu)}} &= \langle \hat{n}_r \rangle , \\ \frac{1}{1 + e^{-\beta(\varepsilon_r - \mu)}} &= 1 - \langle \hat{n}_r \rangle , \\ -\beta(\varepsilon_r - \mu) &= \ln \langle \hat{n}_r \rangle - \ln (1 - \langle \hat{n}_r \rangle) . \end{aligned}$$

It remains as entropy of the ideal Fermi gas:

$$\begin{aligned} S(T, V, \mu) &= -k_B \sum_r \ln (1 - \langle \hat{n}_r \rangle) - k_B \sum_r \langle \hat{n}_r \rangle (\ln \langle \hat{n}_r \rangle - \ln (1 - \langle \hat{n}_r \rangle)) \\ &= -k_B \sum_r \left[ (1 - \langle \hat{n}_r \rangle) \ln (1 - \langle \hat{n}_r \rangle) + \langle \hat{n}_r \rangle \ln \langle \hat{n}_r \rangle \right] . \end{aligned} \quad (3.83)$$

Since  $(1 - \langle \hat{n}_r \rangle)$  is the probability that the corresponding one-particle state is unoccupied, the first summand represents the contribution of the *holes* to the entropy, the second summand the contribution of the *particles*. Let us finally investigate the behavior for  $T \rightarrow 0$ :

$$\begin{aligned} \varepsilon_r > E_F : \langle \hat{n}_r \rangle &\xrightarrow{T \rightarrow 0} 0 ; & \ln(1 - \langle \hat{n}_r \rangle) &\xrightarrow{T \rightarrow 0} 0 , \\ \varepsilon_r < E_F : \langle \hat{n}_r \rangle &\xrightarrow{T \rightarrow 0} 1 ; & \ln \langle \hat{n}_r \rangle &\xrightarrow{T \rightarrow 0} 0 . \end{aligned}$$

Altogether we have found, as required by the third law of Thermodynamics:

$$S \xrightarrow{T \rightarrow 0} 0 .$$

### 3.2.6 Spin-Paramagnetism

The ideal quantum gases are characterized by the absence of interactions between the particles. They can, however, possibly be influenced by external (magnetic, electric) fields. We want to investigate in this and the following subsections some effects, which appear in an ideal Fermi gas due to the *switching on* of a magnetic field. These effects are detectable for the quasi-free conduction electrons ( $S = 1/2$ ) of the metals. We know from the *relativistic Dirac theory* (section 5.3, Vol. 7) that the electron possesses a permanent magnetic moment  $\mu_S$  which is related to its spin  $\mathbf{S}$  ((5.240), Vol.7):

$$\mu_S = -2 \frac{\mu_B}{\hbar} \mathbf{S} ; \quad \mu_B = \frac{e\hbar}{2m} .$$

This magnetic moment interacts with the external field  $\mathbf{B}_0$ , which we assume to be homogeneous:

$$\mathbf{B}_0 = B_0 \mathbf{e}_z .$$

(We denote magnetic moments of single particles by  $\mu$ , those of systems of particles by  $\mathbf{m}$ .) In the Hamilton operator an additional term of the form ((5.239), Vol. 7) appears:

$$H_m = - \sum_{i=1}^N \mu_S^{(i)} \mathbf{B}_0 = +2 \frac{\mu_B}{\hbar} B_0 \sum_{i=1}^N S_i^z .$$

In the formalism of second quantization the total Hamilton operator of the ideal Fermi gas then reads, when we here, at first, disregard the coupling of the magnetic field to the orbital motion of the electrons (Sect. 3.2.7):

$$H = \sum_{\mathbf{k}, \sigma} (\varepsilon(\mathbf{k}) + z_\sigma \mu_B B_0) a_{\mathbf{k}\sigma}^\dagger a_{\mathbf{k}\sigma} \quad (3.84)$$

$$(z_\uparrow = +1, z_\downarrow = -1) .$$

The one-particle energies of the electrons with a moment parallel to the field are shifted downwards by  $\mu_B B$ , while the energies of the electrons with an antiparallel moment increase by the same amount of energy. Note that the magnetic moment and the spin of the electron point into **opposite** directions. This is very often overlooked

in the literature. One therefore finds sometimes in the bracket of (3.84) a minus sign instead of the actually correct plus sign. This is for the following statements without any significance, strictly correct is, however, only the representation (3.84).

By **paramagnetism** one understands the reaction of the permanent magnetic moments on an external magnetic field

$$\mathbf{B}_0 = \mu_0 \mathbf{H}$$

( $\mathbf{B}_0$ : magnetic induction of the vacuum,  $\mathbf{H}$ : magnetic field,  $\mu_0$ : permeability of the vacuum). We now want to investigate the paramagnetism of the conduction electrons of a metal (*electron gas*). When the external field is switched off, the directions of the magnetic moments will be statistically distributed, so that the *total magnetization*  $M$  (total magnetic moment per volume) is zero.

In the field  $\mathbf{B}_0 \neq 0$  the magnetic moments try to orient themselves parallel to the field, because therewith the internal energy  $U = \langle \hat{H} \rangle$  decreases. This is opposed by the disordering tendency of the entropy. The at the finite temperature  $T$  resulting total magnetization therefore corresponds to an *optimal compromise*, which minimizes the *free energy*  $F = U - TS$ . From the **susceptibility**

$$\chi = \frac{1}{V} \left( \frac{\partial m}{\partial H} \right)_T = \left( \frac{\partial M}{\partial H} \right)_T \quad (3.85)$$

one should therefore expect that it is positive and strongly temperature-dependent. The experimental observation, which was for a long time absolutely unexplainable, does not, however, confirm this expectation. Compared to the susceptibility of **localized moments** (*Langevin paramagnetism*) the susceptibility of the conduction electrons is very small and almost temperature-**in**dependent. Besides the already mentioned interpretation of the linear low-temperature behavior of the heat capacity, a further great success of the 'early' Quantum Statistics consists in being able to explain this behavior of the susceptibility. The reason again is the *Pauli principle*. One speaks therefore also of **Pauli paramagnetism**. We will, at first, with a few simple considerations work out what is physically essential. A more precise derivation, being, though, mathematically much more demanding, will follow in the next subsections.

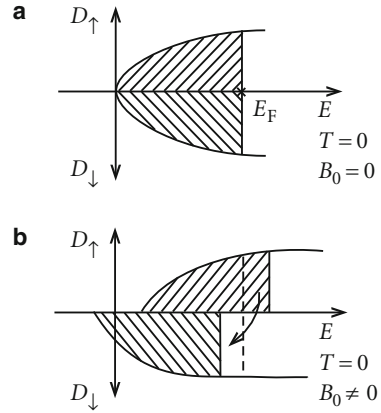
We decompose the density of states  $D(E)$  of the conduction electrons into two *spin parts*:

$$D(E) = D_{\uparrow}(E) + D_{\downarrow}(E) , \quad (3.86)$$

$D_{\uparrow}$  for electrons with field-parallel spin ( $m_S = +1/2$ ),  $D_{\downarrow}$  the one with field-antiparallel spin ( $m_S = -1/2$ ) (Fig. 3.6). When the field is switched off,  $B_0 = 0$ , the two parts are of course the same,

$$D_{\uparrow}(E) = D_{\downarrow}(E) = \frac{1}{2} D(E) ,$$

**Fig. 3.6** Spin-resolved density of states of the ideal Fermi gas as function of the energy, with magnetic field switched off (**a**) and in a homogeneous magnetic field (**b**). Hatched regions indicate the at  $T = 0$  K occupied states



so that the system contains the same number of  $\uparrow$ - and  $\downarrow$ -electrons. The resulting total magnetic moment,

$$m = \mu_B(N_{\downarrow} - N_{\uparrow}), \quad (3.87)$$

is therefore equal to zero.—When the field is switched on, the one-particle energies change,

$$\varepsilon(\mathbf{k}) \implies \eta_{\sigma}(\mathbf{k}) = \varepsilon(\mathbf{k}) + z_{\sigma} \mu_B B_0, \quad (3.88)$$

becoming in particular spin-dependent (Fig. 3.6). The densities of states  $D_{\uparrow}$  and  $D_{\downarrow}$  are rigidly shifted against each other (Exercise 3.2.12):

$$D_{\sigma}(E) = \frac{1}{2} D(E - z_{\sigma} \mu_B B_0). \quad (3.89)$$

For the build-up of a **common** chemical potential  $\mu$   $\uparrow$ -electrons will *spill* into the  $\downarrow$ -part (Fig. 3.6). For  $B_0 \neq 0$  we therefore expect  $N_{\downarrow} > N_{\uparrow}$  and thus a total moment  $m$  unequal zero. So the task is to determine the electron numbers  $N_{\uparrow, \downarrow}$ :

$$\begin{aligned} N_{\sigma} &= \int_{-\infty}^{+\infty} dE f_{-}(E) D_{\sigma}(E) = \frac{1}{2} \int_{z_{\sigma} \mu_B B_0}^{+\infty} dE f_{-}(E) D(E - z_{\sigma} \mu_B B_0) \\ &= \frac{1}{2} \int_0^{\infty} dy f_{-}(y + z_{\sigma} \mu_B B_0) D(y). \end{aligned}$$

We presume a *degenerate* electron gas. We can therefore assume that everywhere, where the Fermi function  $f_-$  remarkably deviates from its constant values 0 and 1, respectively,  $\mu_B B_0$  will be very small compared to  $y$ . One should note in this connection that

$$\mu_B = 0.579 \cdot 10^{-4} \frac{\text{eV}}{\text{T}} \quad (3.90)$$

Strong magnetic fields are of the order of magnitude of 10 tesla, i.e.,  $\mu_B B_0$  will hardly be larger than  $10^{-3}$  eV. So we can confidently terminate the Taylor expansion of  $f_-(y + z_\sigma \mu_B B_0)$  around  $f_-(y)$  after the linear term:

$$N_\sigma \approx \frac{1}{2} \int_0^\infty dy \left( f_-(y) + z_\sigma \mu_B B_0 \frac{\partial f_-}{\partial y} \right) D(y) .$$

One finds therewith for the magnetization

$$M = \frac{\mu_B}{V} (N_\downarrow - N_\uparrow) = -\frac{\mu_B^2}{V} B_0 \int_0^\infty dy \frac{\partial f_-}{\partial y} D(y) ,$$

and for the *Pauli susceptibility*  $\chi_p$ :

$$\chi_p = -\frac{1}{V} \mu_0 \mu_B^2 \int_0^\infty dy \frac{\partial f_-}{\partial y} D(y) . \quad (3.91)$$

This expression is brought, by integration by parts, where the integrated part vanishes, into a form,

$$\chi_p = \frac{1}{V} \mu_0 \mu_B^2 \int_0^\infty dy f_-(y) D'(y) ,$$

which permits the application of the *Sommerfeld expansion* (3.73):

$$\begin{aligned} \chi_p(T) &\approx \frac{1}{V} \mu_0 \mu_B^2 \left[ \int_0^\mu dy D'(y) + \frac{\pi^2}{6} (k_B T)^2 D''(\mu) \right] \\ &= \frac{1}{V} \mu_0 \mu_B^2 d \left[ \sqrt{\mu} - \frac{\pi^2}{24} (k_B T)^2 \mu^{-3/2} \right] . \end{aligned}$$



We finally still use (3.74) and (3.75):

$$\begin{aligned}\sqrt{\mu} &\approx \sqrt{E_F} \left( 1 - \frac{\pi^2}{24} \left( \frac{k_B T}{E_F} \right)^2 \right) \\ \chi_p(T) &= \frac{3N}{2V} \mu_0 \frac{\mu_B^2}{E_F} \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right].\end{aligned}\quad (3.92)$$

The susceptibility of the *Pauli paramagnetism* of the conduction electrons thus is, contrary to the *classical expectation*, only very weakly temperature-dependent, and is for *normal temperatures* very well approximated by its  $T = 0$ -value

$$\chi_p(0) = \frac{3N}{2V} \mu_0 \frac{\mu_B^2}{E_F} = \frac{1}{V} \mu_0 \mu_B^2 D(E_F). \quad (3.93)$$

The reason is given, as in the case of the heat capacity  $C_V$ , by the *Pauli principle*, which allows only for the electrons in the thin *Fermi layer* to absorb the thermal energy. The Pauli principle is also responsible for the tiny order of magnitude ( $\sim 10^{-6}$ ) of the susceptibility, because only those electrons can react on the field, which are not farther away from the Fermi edge than about  $\mu_B B_0$ .

### 3.2.7 Landau Levels

For the calculation of the *Pauli-spin paramagnetism* we got away with a rather rough simplification, which consisted in the assumption that the magnetic field couples only to the spin of the electron, but not to its orbital motion. Strictly speaking, this procedure is justified exclusively only by the result. The more thorough treatment of the problem, which will now be done, reveals that the *Pauli susceptibility*  $\chi_p$  is indeed an additive part of the complete result. The exact isothermal susceptibility of the **free electron gas** is composed, though, of three terms:

$$\chi_T = \left( \frac{\partial M}{\partial H} \right)_T = \chi_l + \chi_p + \chi_{\text{osc}}. \quad (3.94)$$

The coupling of the field with the spin leads, as explicitly shown in Sect. 3.2.6, to **paramagnetism**. The *Pauli susceptibility*  $\chi_p$  is positive. The coupling with the orbital motion yields **diamagnetism**. The so-called *Landau susceptibility*  $\chi_l$  is therefore negative. (as to the concepts of *dia-*, *paramagnetism* see subsection 3.4.2, Vol. 3.) However, the two phenomena cannot be completely separated. There appear interference terms, which, according to the strength of the magnetic field, show either paramagnetic or diamagnetic behavior.  $\chi_{\text{osc}}$  oscillates as function of the field  $\mathbf{B}_0 = \mu_0 H$ , and leads to the **de Haas-van Alphen effect**.

As Exercise 1.4.9 we have proven the **Bohr-van Leeuwen theorem**, whose statement is that *strictly classically* neither diamagnetism nor paramagnetism can really exist. With quantum-mechanical considerations, however, partly performed already as exercise 4.4.15 in Vol. 6, we can show that the magnetic field gives rise to a *quantization* of the orbital motion of the electrons, which, in the last analysis, explains the *diamagnetism*. The *orientation quantization* of the electron spin leads to *paramagnetism*.

We consider a *free electron gas* of  $N$  particles in the volume  $V = L_x L_y L_z$ , onto which a homogeneous magnetic field,  $\mathbf{B}_0 = B_0 \mathbf{e}_z = \mu_0 H \mathbf{e}_z$ , is switched on in the  $z$ -direction. We ask ourselves, which one-particle energies are available for the system. Since the electrons do not interact, we can restrict our considerations for the present to a single electron. Its energy-eigen states will separate into a space and a spin part. We look at first only to the orbital motion.

According to ((2.39), Vol. 2) the classical Hamilton function reads:

$$H = \frac{1}{2m} (\mathbf{p} + e\mathbf{A}(\mathbf{r}))^2 .$$

By the ansatz

$$\mathbf{A}(\mathbf{r}) = (0, B_0 x, 0)$$

for the *vector potential* the *Coulomb gauge*,

$$\operatorname{div} \mathbf{A} = 0 ,$$

is realized and

$$\operatorname{curl} \mathbf{A} = \mathbf{B}_0 = B_0 \mathbf{e}_z$$

is guaranteed. The transition to Quantum Mechanics takes place, as usual, by replacing the dynamical classical variables by quantum-mechanical operators (*observables*). In the Hamilton operator

$$\hat{H} = \frac{1}{2m} (\hat{\mathbf{p}} + e\hat{\mathbf{A}})^2 , \quad (3.95)$$

because of the Coulomb gauge, the operators of the momentum and the position-dependent vector potential do commute (proof?),

$$[\hat{\mathbf{p}}, \hat{\mathbf{A}}]_- = 0 , \quad (3.96)$$

so that  $\widehat{H}$  can be written as follows:

$$\begin{aligned}\widehat{H} &= \frac{1}{2m}(\widehat{\mathbf{p}}^2 + e^2\widehat{\mathbf{A}}^2 + 2e\widehat{\mathbf{A}} \cdot \widehat{\mathbf{p}}) \\ &= \frac{1}{2m}(\widehat{p}_x^2 + \widehat{p}_z^2 + (\widehat{p}_y^2 + e^2B_0^2\widehat{x}^2 + 2eB_0\widehat{x}\widehat{p}_y)) \\ &= \frac{1}{2m}(\widehat{p}_x^2 + \widehat{p}_z^2 + (\widehat{p}_y + eB_0\widehat{x})^2).\end{aligned}\quad (3.97)$$

For the solution of the time-independent Schrödinger equation we use the position representation and choose for the wave function the ansatz:

$$\psi(\mathbf{r}) = e^{ik_z z} e^{iky y} u(x).$$

We are then left with the eigen-value problem:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2m} (\hbar k_y + eB_0 x)^2 \right] u(x) = \left( E - \frac{\hbar^2 k_z^2}{2m} \right) u(x).$$

With the definition of the **cyclotron frequency**,

$$\omega_c = \frac{eB_0}{m} \iff \hbar\omega_c = 2\mu_B B_0, \quad (3.98)$$

and with the substitution,

$$q = x + \frac{\hbar k_y}{eB_0},$$

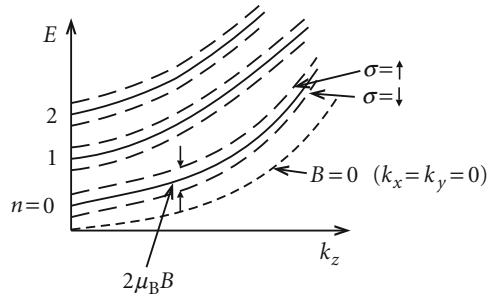
it results the **eigen-value equation of the linear harmonic oscillator**:

$$\begin{aligned}\left( -\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + \frac{1}{2} m \omega_c^2 q^2 \right) u(q) &= \widehat{E} u(q), \\ \widehat{E} &= E - \frac{\hbar^2 k_z^2}{2m}.\end{aligned}\quad (3.99)$$

The solution is known to us. The eigen-functions are the Hermite polynomials with the eigen-energies  $\widehat{E}_n = \hbar\omega_c (n + 1/2)$ ,  $n = 0, 1, 2, \dots$ . For the electron in the magnetic field there are at its disposal the *quantized* energies

$$\begin{aligned}E_n(k_z) &= \hbar\omega_c \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m} \\ n &= 0, 1, 2, \dots\end{aligned}\quad (3.100)$$

**Fig. 3.7** Landau levels of the ideal Fermi gas in the magnetic field as a function of the wave-vector component in field direction



These energies are denoted as **Landau levels**. The solution describes a quantized motion in the plane perpendicular to the field and a completely undisturbed motion in the direction parallel to the field. Taking account of the electron spin (Fig. 3.7) there still appears the additional term known from (3.88):

$$E_{n\sigma}(k_z) = \hbar\omega_c \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m} + z_\sigma \mu_B B_0 \quad (3.101)$$

$$n = 0, 1, 2, \dots$$

The space-part of the eigen-wave function has the structure

$$\psi(\mathbf{r}) = e^{ik_z z} e^{iky y} u_n(q) .$$

The eigen-energies  $E_{n\sigma}(k_z)$  are thus still degenerate with respect to  $k_y$ . The degree of degeneracy  $g_y$  can easily be calculated for periodic boundary conditions

$$k_{x,y,z} = \frac{2\pi}{L_{x,y,z}} n_{x,y,z} \quad n_{x,y,z} \in \mathbb{Z} .$$

We have only to divide the distance between the maximal and the minimal  $k_y$  by the raster  $2\pi/L_y$ :

$$g_y = \frac{L_y}{2\pi} (k_y^{\max} - k_y^{\min}) .$$

The particle is in a cuboid with the edge lengths  $L_x, L_y, L_z$ . This means in particular

$$-\frac{L_x}{2} \leq \pm x \leq +\frac{L_x}{2}$$

or

$$q - \frac{L_x}{2} \leq \frac{\hbar k_y}{eB_0} \leq q + \frac{L_x}{2} .$$

It is therefore  $k_y^{\max} - k_y^{\min} = \frac{1}{\hbar} L_x e B_0$ . **Each** Landau level is thus degenerate according to

$$g_y(B_0) = \frac{e L_x L_y}{2\pi \hbar} B_0 . \quad (3.102)$$

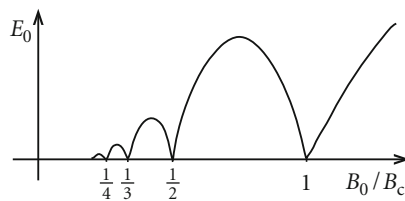
The degree of degeneracy is independent of the *Landau-quantum number*  $n$ , but is a linear function of the magnetic field. In order to understand the consequences, let us consider, for a moment, for simplicity a *two-dimensional system of  $N$  spin-less electrons*. Let the field be oriented in  $z$ -direction, and let the motion of the electrons be restricted to the  $xy$ -plane. For a very strong field it is  $g_y(B_0) > N$ . All the electrons find a place in the  $n = 0$ -Landau level. For a further rising strength of the field the total energy  $E_0$  will linearly increase because of  $\omega_c$ . With decreasing field, however, a critical value  $B_c$  is achieved at

$$N \stackrel{!}{=} g_y(B_c) ,$$

because then electrons will have to shift into the  $n = 1$ -level. As a consequence, the energy will at first increase with decreasing field. For  $B_0 < 1/2 B_c$  the  $n = 2$ -level will be populated, and so on. There result characteristic oscillations of the energy (Fig. 3.8), by which many other physical quantities are also influenced, as for instance the magnetization and the susceptibility. This we will investigate in detail in the next subsection. When the magnetic field is switched on, the number of states will of course not change. On the other hand, it holds the assignment:

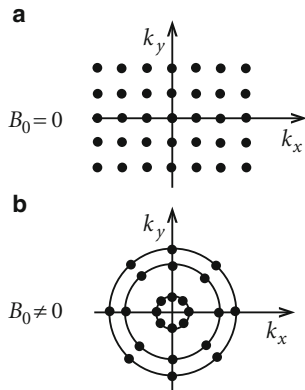
$$\frac{\hbar^2}{2m} (k_x^2 + k_y^2) \quad (B_0 = 0) \iff \hbar \omega_c \left( n + \frac{1}{2} \right) + z_\sigma \mu_B B_0 \quad (B_0 \neq 0) .$$

The  $k$ -values, which are without field regularly and rectangularly arranged in the (three-dimensional)  $\mathbf{k}$ -space (Fig. 3.9a), condense, when a field is applied, on cylinder surfaces (Fig. 3.9b), the axes of which coincide with the field direction. It



**Fig. 3.8** Oscillations of the ground-state energy of the ideal Fermi gas as function of the (normalized) magnetic field.  $B_c$  is the critical field, below which electrons become able for the first time to change from the  $n = 0$ -Landau level into the  $n = 1$ -level

**Fig. 3.9** Arrangement of the states of the free electron gas in the  $xy$ -plane of the  $\mathbf{k}$ -space, without field (a) and with field (b)



holds for the face surface of the cylinder:

$$S_{n\sigma} \equiv \pi(k_x^2 + k_y^2) = \pi(2n + 1 + z_\sigma) \frac{e}{\hbar} B_0. \tag{3.103}$$

The radius of the cylinder thus increases proportionally to  $\sqrt{B_0}$ . On the ring surface between two neighboring Landau-cylinders of the same spin there would be **without** field

$$2 \frac{S_{n+1\sigma} - S_{n\sigma}}{(4\pi^2/L_x L_y)} = \frac{L_x L_y}{\pi \hbar} e B_0 = 2g_y(B_0)$$

states (factor 2 because of spin degeneracy!). On a *Landau-circle* in the  $xy$ -plane there therefore lie just as many states as one finds, without field, in the corresponding ring-region. The area of a ring increases with the field to the same degree as the degree of degeneracy  $g_y$ .

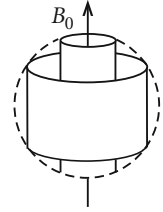
Somewhat more generally, we can write instead of (3.103)

$$S_{n\sigma} = 2\pi(n + \varphi_\sigma) \frac{e}{\hbar} B_0, \tag{3.104}$$

where in the case of free electrons  $\varphi_\sigma = 1/2(1 + z_\sigma)$ . If we leave  $\varphi_\sigma$  at first undetermined, then this formula for the front surface of the *Landau cylinder* possesses a larger region of application.—If with a field change each electron of the  $N$ -particle system remained in its Landau level, then the ground-state energy ( $T = 0$ ) would linearly increase with  $B_0$  because  $\hbar\omega_c \sim B_0$ .

Since the degree of degeneracy  $g_y(B_0)$  changes with  $B_0$ , in reality electrons can jump from outer to inner cylinders, and can shift on the cylinders themselves from larger to smaller  $|k_z|$ . By these processes the ground state energy is kept

**Fig. 3.10** Arrangement of the Landau cylinders within the Fermi sphere of the free electron gas



to its smallest possible value. When leaving the *Fermi sphere* (Fig. 3.10), the *Landau cylinder* empties. The  $n$ -th cylinder slips out of the *Fermi body* just when the front surface coincides with the Fermi body's maximal cross-section area  $A_0$  perpendicular to the field:

$$S_{n\sigma} = 2\pi (n + \varphi_\sigma) \frac{e}{\hbar} B_c^{(n)} \stackrel{!}{=} A_0 .$$

The next cylinder empties at the critical field  $B_c^{(n-1)}$ :

$$S_{n-1\sigma} = 2\pi (n - 1 + \varphi_\sigma) \frac{e}{\hbar} B_c^{(n-1)} \stackrel{!}{=} A_0 .$$

This leads to a period **independent** of the Landau-quantum number  $n$ :

$$\Delta \left( \frac{1}{B_0} \right) = \frac{1}{B_c^{(n)}} - \frac{1}{B_c^{(n-1)}} = \frac{e}{\hbar} \frac{2\pi}{A_0} . \quad (3.105)$$

Certain physical quantities, as for instance the susceptibility  $\chi_{osc}$ , exhibit as a function of the field an oscillating behavior with this period. The measurement of this period yields therewith  $A_0$ , the extremal cross-section area of the **Fermi body** perpendicular to the field. By variation of the field direction this can be used to gain a picture of the form of the Fermi surface. That explains the practical importance of the **de Haas-van Alphen effect** (Sect. 3.2.10).

In the special case of *free electrons*

$$A_0 = \pi k_F^2 = \pi \frac{E_F}{\mu_B} \frac{e}{\hbar}$$

and therewith:

$$\Delta \left( \frac{1}{B_0} \right) = \frac{2\mu_B}{E_F} . \quad (3.106)$$

### 3.2.8 Grand-Canonical Potential of Free Electrons in the Magnetic Field

With (3.101) and (3.102) we know the one-particle energies and their degrees of degeneracy for a system of  $N$  non-interacting electrons in the magnetic field  $H$  and  $B_0 = \mu_0 H$ , respectively. In principle, we are now prepared to calculate partition functions. Our actual goal is the derivation of the magnetization and the susceptibility, respectively. For this purpose we use the grand-canonical potential  $\Omega(T, B_0, \mu)$ , where we have to replace the *volume work*  $-pdV$  by the *magnetization work* in the expression (1.155) for the differential  $d\Omega$ . Unfortunately, the definition of the magnetization work is not completely unique (see subsection 1.5 in Vol. 5). The reason is that, in order to *magnetize* the system, an external magnetic field is mandatory, from which one does not know, whether or not it has to be incorporated into the thermodynamic energy balance (first law of Thermodynamics). Since  $B_0$  is only a *tool* for the realization of the magnetic moment  $m$ , it appears naturally to subtract again the pure field energy. That we did in the subsection 1.5 of Vol. 5, having found therewith as *magnetization work*:

$$\delta W_{(1)} = B_0 dm \quad ((1.37), \text{Vol. 5}) .$$

It is then

$$W_{(1)} = \int_0^{m_1} B_0 dm$$

the work, which is necessary to magnetize the system in the *zero-field* from 0 to  $m_1$  ( $B_0 = f(m, T)$ , see Fig. 3.11). In this formulation the analogy to the *volume work* is the most elegant one:

$$\begin{aligned} p &\longleftrightarrow B_0 \quad (\text{intensive}) , \\ V &\longleftrightarrow -m \quad (\text{extensive}) . \end{aligned}$$

There is an alternative definition:

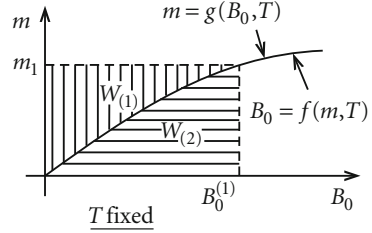
$$\delta W_{(2)} = -m dB_0 ,$$

where

$$W_{(2)} = - \int_0^{B_0^{(1)}} m dB_0$$



**Fig. 3.11** Illustration concerning the definition of the magnetization work



represents the work, which must be brought up to bring the system from the field-free space into the field  $B_0^{(1)}$ .  $W_{(1)}$  and  $W_{(2)}$  just differ by the potential energy  $-m_1 B_0^{(1)}$  of the magnetic moment  $m_1$  in the field  $B_0^{(1)}$  (see (3.52), Vol. 3). This potential energy is not accounted for in the definition of  $W_{(1)}$  (see rectangle in Fig. 3.11).

We have to of course apply here the definition, which is compatible with our definition of the *internal energy*  $U$  as expectation value  $\langle \hat{H} \rangle$  of the Hamilton operator. But that is  $W_{(2)}$ ,

$$W_{(2)} = \langle \hat{H}(B_0) - \hat{H}(0) \rangle ,$$

as it already became evident by the definition of the quantum-mechanical observable  $\hat{\mathbf{m}}$  as gradient of the Hamilton operator with respect to the field  $B_0$  (see subsection 5.2.1 and (5.125), Vol. 7). It holds therewith for the *grand-canonical potential* (the volume  $V$  is here not to be considered as thermodynamic variable!):

$$d\Omega = -SdT - m dB_0 - Nd\mu . \quad (3.107)$$

For the ensemble average of the magnetic moment it must therefore be calculated:

$$m = - \left( \frac{\partial \Omega}{\partial B_0} \right)_{T, \mu} . \quad (3.108)$$

This means, according to (3.22):

$$\begin{aligned} m &= k_B T \left( \frac{\partial}{\partial B_0} \ln \Xi_\mu(T, B_0) \right)_{T, \mu} \\ &= k_B T \left[ \frac{\partial}{\partial B_0} \sum_r \ln \left( 1 + e^{-\beta(\varepsilon_r - \mu)} \right) \right]_{T, \mu} . \end{aligned} \quad (3.109)$$

The  $\varepsilon_r$  correspond to the Landau levels  $E_{n\sigma}(k_z)$ . The scope of work is therewith clear. We have to at first determine the grand-canonical potential  $\Omega(T, B_0, \mu)$ .

We write:

$$\begin{aligned}\varphi_\sigma(E) &= \text{number of the } \sigma\text{-states with } E_{n\sigma} \leq E, \\ D_\sigma(E) &= \frac{d\varphi_\sigma}{dE}: \sigma\text{-density of states}.\end{aligned}$$

Because of the term  $\hbar^2 k_z^2/2m$  the Landau levels are arbitrarily densely arranged for the asymptotically large system (*thermodynamic limit*). Sums can therefore be represented by integrals:

$$\Omega(T, B_0, \mu) = -k_B T \sum_{\sigma} \int_{\dots}^{\infty} \ln(1 + e^{-\beta(E-\mu)}) D_\sigma(E) dE.$$

The lower bound of integration is given by  $\varphi_\sigma(E) = 0$ , but need not yet be explicitly specified here. With integration by parts it further follows:

$$\begin{aligned}\Omega(T, B_0, \mu) &= -k_B T \sum_{\sigma} \varphi_\sigma(E) \ln[1 + e^{-\beta(E-\mu)}] \Big|_{\dots}^{\infty} \\ &\quad - \sum_{\sigma} \int_{\dots}^{\infty} dE \varphi_\sigma(E) \frac{e^{-\beta(E-\mu)}}{1 + e^{-\beta(E-\mu)}}.\end{aligned}$$

The integrated part vanishes, at the lower bound because of  $\varphi_\sigma(E)$ , and at the upper bound because of the logarithm. In the integrand we recognize the Fermi function  $f_-(E)$ :

$$\Omega(T, B_0, \mu) = - \sum_{\sigma} \int_{\dots}^{\infty} dE \varphi_\sigma(E) f_-(E). \quad (3.110)$$

It remains as the main task, the determination of the *phase volume*  $\varphi_\sigma(E)$ . Let us at first think about how many energy-eigen values  $E_{n\sigma}(k_z) \leq E$  exist for a fixed Landau-quantum number  $n$ . Because of (3.101), these energies must fulfill:

$$k_z^2 \leq \frac{2m}{\hbar^2} \left[ E - \hbar\omega_c \left( n + \frac{1}{2} \right) - z_\sigma \mu_b B_0 \right]$$

( $m$  is here of course the electron mass, not to be confused with the magnetic moment (3.108).) Hence, there is a maximal and a minimal  $k_z$ . The difference, divided by the *raster*  $2\pi/L_z$  yields the number of energies:

$$\frac{k_z^{\max} - k_z^{\min}}{\frac{2\pi}{L_z}} = \frac{L_z}{\hbar\pi} \sqrt{2m \left[ E - \hbar\omega_c \left( n + \frac{1}{2} \right) - z_\sigma \mu_b B_0 \right]}.$$

For  $\varphi_\sigma(E)$  we have to count **all states**, i.e., we have to bring into play the degree of degeneracy (3.102):

$$\varphi_\sigma(E) = \frac{\sqrt{2mV}}{2\pi^2\hbar^2} eB_0 \sum_{n=0}^{n_0} \sqrt{E - \hbar\omega_c \left(n + \frac{1}{2}\right) - z_\sigma \mu_B B_0}. \quad (3.111)$$

The maximal quantum number  $n_0$  is the highest number, for which the radicand is still positive. We write for abbreviation:

$$\varepsilon = \frac{E}{\hbar\omega_c}; \quad \mu_0 = \frac{\mu}{\hbar\omega_c}; \quad b = \beta\hbar\omega_c, \quad \hat{f}_-(\varepsilon) = \left\{1 + \exp[b(\varepsilon - \mu_0)]\right\}^{-1}. \quad (3.112)$$

Therewith (3.110) reads:

$$\Omega(T, B_0, \mu) = -\frac{3}{2}\alpha \sum_{\sigma} \int_{-\infty}^{\infty} d\varepsilon \hat{f}_-(\varepsilon) \sum_{n=0}^{n_0} \sqrt{\varepsilon - n - \frac{1}{2}(1 + z_\sigma)} \quad (3.113)$$

$$\alpha = \frac{8}{3}V \frac{(\mu_B m B_0)^{5/2}}{m\pi^2\hbar^3}$$

After a further integration by parts the integrated term again vanishes:

$$\Omega(T, B_0, \mu) = \alpha \sum_{\sigma} \int_{-\infty}^{+\infty} d\eta \hat{f}'_-(\eta + \frac{1}{2}z_\sigma) \sum_{n=0}^{n_0} \left(\eta - n - \frac{1}{2}\right)^{3/2}. \quad (3.114)$$

We have substituted  $\eta = \varepsilon - 1/2z_\sigma$ , and we could choose the lower bound of integration to be  $-\infty$ , because of the  $\delta$ -function character of  $\hat{f}'_-$ .

In the next step we inspect the sum in the integrand of (3.114):

$$\Sigma(\eta) \equiv \sum_{n=0}^{n_0} \left(\eta - n - \frac{1}{2}\right)^{3/2}$$

$$= \int_0^\eta dx (\eta - x)^{3/2} \sum_{n=-\infty}^{+\infty} \delta\left[x - \left(n + \frac{1}{2}\right)\right].$$

Here we have exploited that it must be  $\eta \geq n + 1/2$  and  $n \leq n_0$ . The sum in the last row can be written as Fourier series (see Exercise 3.2.14):

$$\sum_{n=-\infty}^{+\infty} \delta\left[x - \left(n + \frac{1}{2}\right)\right] = \sum_{p=-\infty}^{+\infty} (-1)^p e^{i2p\pi x}.$$

Therewith we have:

$$\Sigma(\eta) = \sum_{p=-\infty}^{+\infty} (-1)^p I_p(\eta),$$

$$I_p(\eta) = \int_0^\eta dx (\eta - x)^{3/2} e^{i2p\pi x}.$$

The  $p = 0$ -term can of course be easily evaluated:

$$I_0(\eta) = \frac{2}{5} \eta^{5/2}.$$

For the  $p \neq 0$ -integrals the substitution  $u = \sqrt{\eta - x}$  is useful. One obtains then after twofold integration by parts:

$$I_{p \neq 0}(\eta) = \frac{i}{2p\pi} \eta^{3/2} + \frac{3}{8p^2\pi^2} \eta^{1/2} - \frac{3}{8p^2\pi^2} e^{i2p\pi\eta} \int_0^{\sqrt{\eta}} du e^{-i2p\pi u^2}.$$

When we insert this result into  $\Sigma(\eta)$ , then the first term vanishes after summation over  $p$ . For the second term we can apply

$$\sum_{p=-\infty}^{+\infty} \frac{(-1)^p}{p^2} = -\frac{\pi^2}{6} \quad (3.115)$$

getting therewith:

$$\Sigma(\eta) = \frac{2}{5} \eta^{5/2} - \frac{1}{16} \eta^{1/2} - \frac{3}{8\pi^2} \sum_{\substack{p=-\infty \\ (p \neq 0)}}^{+\infty} \frac{(-1)^p}{p^2} e^{i2p\pi\eta} \int_0^{\sqrt{\eta}} du e^{-i2p\pi u^2}. \quad (3.116)$$

We apply this result in the expression (3.114) of the grand-canonical potential. The first two terms can be easily evaluated. We therefore forestall them here:

$$\begin{aligned} \Omega_0 &= \alpha \sum_{\sigma} \int_{-\infty}^{+\infty} d\eta \hat{f}'_{-} \left( \eta + \frac{1}{2} z_{\sigma} \right) \left( \frac{2}{5} \eta^{5/2} - \frac{1}{16} \eta^{1/2} \right) \\ &= \alpha \sum_{\sigma} \int_{-\infty}^{+\infty} d\varepsilon \hat{f}'_{-}(\varepsilon) \left[ \frac{2}{5} \left( \varepsilon - \frac{1}{2} z_{\sigma} \right)^{5/2} - \frac{1}{16} \left( \varepsilon - \frac{1}{2} z_{\sigma} \right)^{1/2} \right]. \end{aligned}$$

The integrand is, because of  $\hat{f}'_-$ , essentially unequal zero only for  $\varepsilon \approx \mu_0$ . Furthermore, at normal metallic electron densities ( $\mu$ : some eV) and *normal* magnetic fields ( $\hbar\omega_c$ : some  $10^{-3}$  eV) it is to assume  $\mu_0 \gg 1$ . For this reason, we can expand the brackets as usual:

$$\begin{aligned} \left(\mu_0 - \frac{1}{2}z_\sigma\right)^n &= \mu_0^n \left(1 - \frac{1}{2}z_\sigma \frac{1}{\mu_0}\right)^n \\ &= \mu_0^n \left[1 - n\frac{z_\sigma}{2\mu_0} + \frac{n(n-1)}{2!} \left(\frac{z_\sigma}{2\mu_0}\right)^2 - \dots\right]. \end{aligned}$$

The linear terms drop out by the spin summation because of  $z_\sigma$ . It thus remains:

$$\Omega_0(T, B_0, \mu) \approx -\alpha \left[ \frac{4}{5}\mu_0^{5/2} + \frac{1}{8}\mu_0^{1/2} (3z_\sigma^2 - 1) \right]. \quad (3.117)$$

Thereby we have approximately taken

$$\hat{f}'_-(\varepsilon) \approx -\delta(\varepsilon - \mu_0). \quad (3.118)$$

The partial result (3.117) for the grand-canonical potential is responsible for the *Landau diamagnetism* and the *Pauli spin-paramagnetism*, while the still to be calculated oscillating remainder term in (3.116) leads to the *de Haas-van Alphen effect*. Intentionally, we have left the term  $(3z_\sigma^2 - 1)$  in (3.117) as it is, although it is of course equal to 2, in order to later be able to separate out the spin and the orbital contributions. All the contributions of the electron spin carry the sign factor  $z_\sigma$  ( $z_\uparrow = 1, z_\downarrow = -1$ ).

Before further evaluating (3.117) let us determine the contribution of the oscillating summands in (3.116) to the grand-canonical potential. This requires, though, a bit more effort.

The integral in (3.116) is of the type of an *error integral*:

$$I(\eta) = \int_0^{\sqrt{\eta}} du e^{-i2p\pi u^2} = \frac{1}{2\sqrt{2ip}} \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{2\pi ip\eta}} dx e^{-x^2}.$$

We need  $I(\eta)$  in the integrand of (3.114), which is, because of  $\hat{f}'_-$ , unequal zero only for  $\eta \approx \mu_0 \gg 1$ . For such values of  $\eta$ , one can expand the error function in a fast converging series (M. Abramowitz, T. A. Stegun: *Handbook of Mathematical Functions*, Dover, New York, 1972; formulas: 7.1.1, 7.1.2, 7.1.14): For our purposes here, we can even take it equal to 1:

$$I(\eta) \approx \frac{1}{2\sqrt{2ip}} = \frac{1}{2\sqrt{2|p|}} \exp\left(-i\frac{\pi}{4} \frac{p}{|p|}\right).$$

The third summand in (3.116) can therewith be approximated as follows:

$$\Sigma_{\text{osc}}(\eta) \approx -\frac{3}{8\sqrt{2}\pi^2} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{5/2}} \cos\left(2p\pi\eta - \frac{\pi}{4}\right).$$

This has to be inserted into (3.114). After having retracted there the substitution  $\eta = \varepsilon - (1/2)z_\sigma$ , and after having performed the spin summation, we have to calculate for the oscillatory part of the grand-canonical potential:

$$\begin{aligned} \Omega_{\text{osc}}(T, B_0, \mu) &= -\frac{3\alpha}{4\sqrt{2}\pi^2} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{5/2}} \cos(z_\sigma p\pi) \\ &\quad \cdot \int_{-\infty}^{+\infty} d\varepsilon \hat{f}'_-(\varepsilon) \cos\left(2p\pi\varepsilon - \frac{\pi}{4}\right). \end{aligned}$$

In the remaining integral, though, now we can not apply (3.118) for  $\hat{f}'_-$ , since, because of the cosine-function, in the interesting region of integration the integrand will very strongly oscillate. Fortunately, one can use the residue theorem to solve the integral even exactly. We perform the explicit derivation as Exercise 3.2.15, citing here only the result:

$$\int_{-\infty}^{+\infty} d\varepsilon \hat{f}'_-(\varepsilon) \cos\left(2p\pi\varepsilon - \frac{\pi}{4}\right) = -\frac{2\pi^2 p}{b} \frac{\cos(\pi/4 - 2p\pi\mu_0)}{\sinh(2\pi^2 p/b)}.$$

$\Omega_{\text{osc}}$  is therewith completely determined:

$$\Omega_{\text{osc}}(T, B_0, \mu) = \frac{3\alpha}{2\sqrt{2}b} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{3/2}} \cos(z_\sigma p\pi) \frac{\cos(\pi/4 - 2p\pi\mu_0)}{\sinh(2\pi^2 p/b)}. \quad (3.119)$$

Let us point out once more that the actually superfluous sign-factor  $z_\sigma$  ( $= \pm 1$ ) in the argument of the first cosine-function is retained only as an *indicator* for contributions of the electron spin. The remaining task now consists only in retracting the abbreviations (3.112), (3.113) in the partial results (3.117) and (3.119):

$$\Omega(T, B_0, \mu) = \Omega_0(T, B_0, \mu) + \Omega_{\text{osc}}(T, B_0, \mu), \quad (3.120)$$

$$\Omega_0(T, B_0, \mu) = -N \left(\frac{\mu}{E_F}\right)^{3/2} \left[ \frac{2}{5}\mu + \frac{(\mu_B B_0)^2}{4\mu} (3z_\sigma^2 - 1) \right], \quad (3.121)$$

$$\Omega_{\text{osc}}(T, B_0, \mu) = \frac{3}{2} k_B T N \left( \frac{\mu_B B_0}{E_F} \right)^{3/2} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{3/2}} \cos(z_\sigma p \pi) \cdot \frac{\cos[\pi/4 - p(\pi\mu/\mu_B B_0)]}{\sinh(p(\pi^2 k_B T / \mu_B B_0))}. \quad (3.122)$$

We have applied here (3.62) for  $E_F$ . The grand-canonical potential is therewith completely determined as a function of  $T$ ,  $B_0$ , and  $\mu$ . In the next step, by means of (3.94) and (3.108), the magnetization and the susceptibility of the free electron gas can be calculated. We realize that in spite of the very simple initial model (free (!) particles) the derivations require substantial effort.

### 3.2.9 Landau Diamagnetism

We had seen in Sect. 3.2.6 that the coupling of the electron spin to the homogeneous magnetic field leads to *paramagnetic effects*. Paramagnetism is characterized by a **positive** susceptibility. However, magnetic moments are also due to the *quantized* orbital motion. With the results of the last subsection we will now be able to show that these induced moments give rise to *diamagnetism*, i.e., they try to orient themselves antiparallel to the field, by which they are created (induced). Characteristic feature is thus a **negative** susceptibility.

For the calculation of the magnetization, according to formula (3.108), we have to differentiate the grand-canonical potential  $\Omega$  with respect to the field  $B_0$ ,

$$M(T, B_0) = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial B_0} \right)_{T, \mu},$$

where  $\mu$  must be expressed by  $T, B_0$  and by the (fixed) particle number  $N$ . Let us start with the last point. We determine the chemical potential from the thermodynamic relation

$$N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T, B_0}.$$

The partial differentiation of (3.120) is quickly done leading, with the abbreviations

$$\alpha(B_0) = \frac{(\mu_B B_0)^2}{8\mu^{1/2} E_F^{3/2}}; \quad \gamma(T, B_0) = \pi \left( \frac{k_B T}{E_F} \right) \left( \frac{\mu_B B_0}{E_F} \right)^{1/2}, \quad (3.123)$$

to the equation:

$$\left(\frac{\mu}{E_F}\right)^{3/2} = 1 - \alpha(B_0)(3z_\sigma^2 - 1) + \frac{3}{2}\gamma(T, B_0) \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p\pi) \frac{\sin(\pi/4 - p(\pi\mu/\mu_B B_0))}{\sinh(p\pi^2 k_B T/\mu_B B_0)}.$$

For a *degenerate electron gas* ( $E_F = 1 \dots 10 \text{ eV}$ ), the factors  $\alpha$  and  $\gamma$  are at *normal* temperatures and for *normal* fields very much smaller than 1, as can easily be realized because of

$$\mu_B = 0.579 \cdot 10^{-4} \frac{\text{eV}}{\text{T}}; \quad k_B \approx 0.862 \cdot 10^{-4} \frac{\text{eV}}{\text{K}}. \quad (3.124)$$

But this means that  $\mu$  differs only very slightly from  $E_F$ . We can therefore replace on the right-hand side of the above equation, as a well justifiable approximation, the chemical potential  $\mu$  by  $E_F$ , and can use the already several times applied approximation  $(1 - x)^n \approx 1 - nx$ :

$$\mu \approx E_F \left[ 1 - \frac{2}{3}\alpha(B_0)(3z_\sigma^2 - 1) + \gamma(T, B_0) \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p\pi) \frac{\sin(\pi/4 - p\pi E_F/\mu_B B_0)}{\sinh(p\pi^2 k_B T/\mu_B B_0)} \right]. \quad (3.125)$$

When comparing this expression with (3.75) with respect to the temperature-dependence, it must be taken into consideration that we have approximated at some points of the calculation (e.g. in (3.118)) the derivative of the Fermi function by a  $\delta$ -function. The finite width of  $f'_-$  around  $\mu$  takes care just for the correction term  $(\pi^2/12) \cdot (k_B T/E_F)^2$  in (3.75). For the *oscillating* third summand in the square bracket, though, the mentioned simplification was not used.

In any case we can read off from (3.125) that, for the calculation of the magnetization,  $\mu \approx E_F$  can be assumed with sufficient accuracy.—We now derive, at first, that contribution to the magnetization which results from the *non-oscillating* part of the grand-canonical potential (3.121):

$$M_0(T, B_0) = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial B_0} \right)_{T, \mu=E_F} = \frac{1}{2} \frac{N}{V} \frac{\mu_B^2}{E_F} (3z_\sigma^2 - 1) B_0. \quad (3.126)$$

The **susceptibility** of the conduction electrons, which in first approximation is neither temperature-dependent nor field-dependent,

$$\chi_0 = \mu_0 \left( \frac{\partial M}{\partial B_0} \right)_T = \frac{3}{2} \frac{N}{V} \mu_0 \frac{\mu_B^2}{E_F} \left( z_\sigma^2 - \frac{1}{3} \right), \quad (3.127)$$



obviously possesses a diamagnetic component as well as a paramagnetic one:

$$\chi_0 = \chi_p + \chi_L . \quad (3.128)$$

We remember that the *sign-factor*  $z_\sigma$  was left in the formulas only as an *indicator for spin parts*. (Of course:  $z_\sigma^2 = +1$ .) This spin part,

$$\chi_p = \frac{3N}{2V} \mu_0 \frac{\mu_B^2}{E_F} > 0 , \quad (3.129)$$

is called **Pauli spin-paramagnetism**, which we have derived already with (3.93) in Sect. 3.2.6 in a simpler and physically more transparent manner.

The second part,

$$\chi_L = -\frac{1}{2} \frac{N}{V} \mu_0 \frac{\mu_B^2}{E_F} < 0 , \quad (3.130)$$

is a diamagnetic component and is denoted as **Landau diamagnetism**. This arises by the ordering of the quantized orbital momenta, which are induced by the magnetic field. In the free electron gas it then holds:

$$\chi_L = -\frac{1}{3} \chi_p . \quad (3.131)$$

The free electron gas is of course a strongly *over-idealized* model of the conduction electrons. So the influence of the crystal lattice, for instance, is completely disregarded. For simple structures this influence can be brought into play in a first approximation by the concept of an *effective mass*  $m^*$  of the electron.  $m^*$  is thereby relevant only for the orbital motion of the electron, and not for the spin interaction with the external field (see Exercise 3.2.17). This means for the *Landau energies* (3.101):

$$E_{n\sigma}(k_z) = 2\mu_B^* B_0 \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m^*} + z_\sigma \mu_B B_0 , \quad (3.132)$$

$$\mu_B = \frac{e\hbar}{2m} ; \quad \mu_B^* = \frac{e\hbar}{2m^*} .$$

With this distinguishing of  $m$  and  $m^*$ , the results (3.121) and (3.122) for the grand-canonical potential change in such a way that everywhere in both the formulas  $\mu_B$  is to be replaced by  $\mu_B^*$ , and  $z_\sigma$  by  $m^*/m$ . As to the susceptibilities (3.129) and (3.130), the *Pauli component*  $\chi_p$  as the pure spin part remains unchanged, while in  $\chi_L$  there appears  $\mu_B^{*2}$  instead of  $\mu_B^2$ . In place of (3.131) it holds then for the ratio of the two components:

$$\chi_L = -\frac{1}{3} \left( \frac{m}{m^*} \right)^2 \chi_p . \quad (3.133)$$

For some metals  $m^*$  distinctly deviates from  $m$ , so that sometimes the diamagnetic Landau component even predominates. Normally, however,  $|\chi_L|$  and  $\chi_p$  are of the same order of magnitude. The measurement of the susceptibility of a metal always yields the **total** susceptibility, which is composed of  $\chi_L$ ,  $\chi_p$  and  $\chi_{\text{osc}}$  as well as of a contribution of the ion cores, which is denoted as *Larmor susceptibility*  $\chi_{\text{Larmor}}$ . A separate determination of  $\chi_L$  or  $\chi_p$  is therefore not at all a trivial task.

### 3.2.10 De Haas-Van Alphen Effect

By *de Haas-van Alphen effect* one understands the oscillations of the magnetic susceptibility as function of the external field  $B_0$ , or better  $1/B_0$ . One observes these oscillations also for other physical quantities such as the electrical and thermal conductivities, the magnetostriction, and the Hall effect. We have already discussed the physical origin of the oscillations in Sect. 3.2.7. Their manifestation in the susceptibility stems of course from the not yet evaluated part (3.122) of the grand-canonical potential. Three terms in (3.122) are field-dependent. The *magnetization*,

$$M_{\text{osc}}(T, B_0) = -\frac{1}{V} \left( \frac{\partial \Omega_{\text{osc}}}{\partial B_0} \right)_{T, \mu} = M_1 + M_2 + M_3, \quad (3.134)$$

is therefore composed, according to the product rule of differentiation, of three summands. As reasoned in the preceding subsection we can assume for the low-temperature region, which we are interested in here, that  $\mu \approx E_F$ . With the abbreviations

$$a(T, B_0) = \frac{3}{2} \left( \frac{k_B T}{E_F} \right) \left( \frac{\mu_B B_0}{E_F} \right)^{1/2}, \quad (3.135)$$

$$b(T, B_0) = \pi^2 \left( \frac{k_B T}{\mu_B B_0} \right), \quad (3.136)$$

$$c(B_0) = \pi \left( \frac{E_F}{\mu_B B_0} \right) \quad (3.137)$$

the three magnetization parts then read:

$$M_1 = -\frac{3}{2} a \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{3/2}} \cos(z_\sigma p \pi) \frac{\cos(\pi/4 - pc)}{\sinh(pb)}, \quad (3.138)$$

$$M_2 = ac \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p \pi) \frac{\sin(\pi/4 - pc)}{\sinh(pb)}, \quad (3.139)$$

$$M_3 = -ab \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p \pi) \frac{\cos(\pi/4 - pc)}{\sinh(pb)} \coth(pb). \quad (3.140)$$

One more differentiation then yields the susceptibility

$$\chi_{\text{osc}} = \mu_0 \left( \frac{\partial M_{\text{osc}}}{\partial B_0} \right)_T. \quad (3.141)$$

It results a rather involved expression (see Exercise 3.2.18). But let us assume here that the sums in (3.138) to (3.140) are all of the same order of magnitude, then the pre-factors determine their importance. But for a *degenerate* electron gas, at *normal* temperatures and for *normal* fields, these are of different orders of magnitude (3.124):

$$c(B_0) \gg b(T, B_0) \gg a(T, B_0).$$

When we differentiate the sine in  $M_2$  with respect to the field, there appears a contribution proportional to  $c^2$ . This term dominates under *normal circumstances*:

$$\begin{aligned} \chi_{\text{osc}} \approx \mu_0 \frac{N}{V} \frac{3}{2} \pi^2 \frac{k_B T}{B_0^2} \left( \frac{E_F}{\mu_B B_0} \right)^{1/2} \\ \cdot \sum_{p=1}^{\infty} (-1)^p p^{1/2} \cos(z_\sigma p \pi) \frac{\cos(\pi/4 - p\pi(E_F/\mu_B B_0))}{\sinh(p\pi^2(k_B T/\mu_B B_0))}. \end{aligned} \quad (3.142)$$

The factor  $\cos(z_\sigma p \pi)$  traces back to the spin of the electron. The other terms are all to be ascribed to the orbital motion. Orbital contributions and spin parts of the susceptibility thus do not behave simply additively. So they cannot be treated separately. That was what was meant in Sect. 3.2.6, when we remarked that the assumption that the magnetic field couples only to the electron spin, is justified *'only by the result'*. We could better demonstrate with this assumption the physical origin of the *Pauli spin-paramagnetism*, freed from all the *mathematical ballast*.

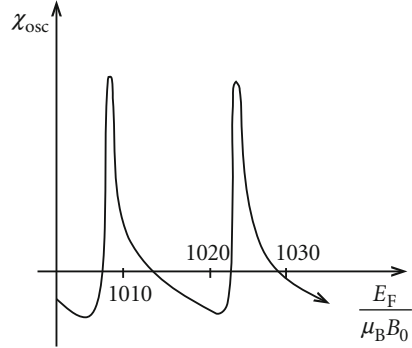
The signature of the de Haas-van Alphen effect is the  $\chi$ -oscillations with the period

$$\Delta \left( \frac{1}{B_0} \right) = p^{-1} \frac{2\mu_B}{E_F}, \quad (3.143)$$

which are caused by the cosine-term in  $\chi_{\text{osc}}$ . Figure 3.12 shows a typical example for  $T = 1$  K, and for an electron density  $r_s = 4$  ( $r_s$  is defined in Exercise 3.2.3). The period  $\Delta (1/B_0)$  is temperature-**independent**. The *basic oscillation (first harmonic)*  $p = 1$  agrees with (3.106). The oscillations are of course the better recognizable the larger the period  $\Delta$  is. That is the case for small  $E_F$ , i.e., according to (3.62), for as small an electron density as possible (as large as possible  $r_s$ ). Note, however, that at several points of the derivation of  $\chi_{\text{osc}}$  a *degenerate* electron gas was presumed.

The amplitudes of the oscillations are substantially influenced by the hyperbolic sine in the denominator of (3.142). It takes care for the fact that the amplitudes

**Fig. 3.12** Oscillations of the susceptibility of the free electron gas as function of the inverse magnetic field



decrease for very small fields as

$$\exp\left(-p\pi^2 \frac{k_B T}{\mu_B B_0}\right).$$

Furthermore, the hyperbolic sine is the reason that the sum in (3.142) converges very rapidly, so that one can restrict oneself very often to the  $p = 1$ -term, only.

### 3.2.11 Exercises

#### Exercise 3.2.1

Let the particle density  $n$  of an ideal Fermi gas be given. Show that for  $T \rightarrow +\infty$  the chemical potential  $\mu$  must tend to  $-\infty$ .

#### Exercise 3.2.2

When treating high-energy fermions relativistic effects are to be taken into consideration. The one-particle energies read in such a case:

$$\varepsilon(\mathbf{p}) = \sqrt{c^2 p^2 + m^2 c^4}.$$

Show that it holds for the average particle number  $\langle \hat{N} \rangle$ , and for the internal energy  $U$  of the ideal relativistic Fermi gas:

$$\langle \hat{N} \rangle = (2S + 1) \frac{m^3 c^3}{2\pi^2 \hbar^3} V \int_0^\infty \frac{\sinh^2 \alpha \cosh \alpha}{\exp(-\beta\mu + \beta mc^2 \cosh \alpha) + 1} d\alpha,$$

$$U = (2S + 1) \frac{m^4 c^5}{2\pi^2 \hbar^3} V \int_0^\infty \frac{\sinh^2 \alpha \cosh^2 \alpha}{\exp(-\beta\mu + \beta mc^2 \cosh \alpha) + 1} d\alpha.$$

(The chemical potential  $\mu$  contains the rest energy  $mc^2$ !) Evaluate the integrals for the case of low temperatures.

### Exercise 3.2.3

Consider a system of  $N$  noninteracting electrons in the volume  $V$ . ( $\varepsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m$ ).

1. Show that it holds for the internal energy

$$U(T = 0) = N \frac{3}{5} E_F .$$

2. Calculate the Fermi energy  $E_F$  for

$$N = 6 \cdot 10^{23} , \quad V = 25 \text{ cm}^3 , \quad m = 9.1 \cdot 10^{-28} \text{ g} .$$

3. Express the internal energy from part 1. by the dimensionless density parameter  $r_s$ :

$$\frac{V}{N} = \frac{4\pi}{3} (a_B r_s)^3 ; \quad a_B = \frac{4\pi \varepsilon_0 \hbar^2}{m e^2} \quad \text{Bohr radius} .$$

Use as energy unit:

$$1 \text{ ryd} = \frac{1}{4\pi \varepsilon_0} \frac{e^2}{2a_B} .$$

4. How is the constant  $d$  in the density of states (3.51) related to the Fermi energy  $E_F$ ?
5. Calculate the *zero-point pressure*  $p(T = 0)$  of the Fermi gas.

### Exercise 3.2.4

Consider a pure semiconductor with a band gap  $E_g$  between the valence band and the conduction band. Conduction electrons and holes behave both like free fermions with the effective masses  $m_e$  and  $m_h$ . Let the zero point of energy coincide with the upper edge of the at  $T = 0$  completely filled valence band. Assume for the following questions that the inequalities

$$E_g \gg k_B T ; \quad \mu \gg k_B T ; \quad E_g - \mu \gg k_B T$$

are valid, which is indeed the case for many semiconductors even at high temperatures (300 K).

1. Show that in the here considered region of '*intrinsic conduction*' the following relation is valid for the electron density  $n_e$  in the conduction band, and for the

hole density  $n_h$  in the valence band:

$$n_e = n_h = 2 \left( \frac{\sqrt{m_e m_h} k_B T}{2\pi \hbar^2} \right)^{3/2} \exp \left( -\frac{E_g}{2k_B T} \right) .$$

2. Show in addition that the chemical potential  $\mu$  is given by

$$\mu = \frac{1}{2} E_g + \frac{3}{4} k_B T \ln \frac{m_h}{m_e} .$$

### Exercise 3.2.5

Let a wide-gap semiconductor (band gap  $E_g$ ) be doped by impurity atoms (concentration  $n_i$ ), which lead to discrete energy levels at a distance  $\varepsilon_i$  below the lower conduction band edge, where we assume

$$E_g \gg \varepsilon_i .$$

The conduction electrons and the holes behave like free fermions with, what concerns the order of magnitude, similar effective masses  $m_e$  and  $m_h$ . We put the energy zero at the upper edge of the valence band. As to the temperature we presume

$$E_g \gg k_B T ,$$

which, in the case of wide-gap semiconductors, applies to low temperatures as well as even to room temperature. Furthermore, it shall be allowed to assume

$$A = \exp \frac{\mu - E_g}{k_B T} \ll 1 \quad \text{and} \quad \mu \simeq E_g .$$

1. Derive, under these conditions, the relation

$$2A \left( A \exp \frac{\varepsilon_i}{k_B T} + 1 \right) \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} = n_i ,$$

in which it is particularly taken into account that the valence band does not play any role as source for conduction electrons!

2. Show that one obtains, under the condition

$$A \exp \frac{\varepsilon_i}{k_B T} \gg 1 ,$$

for the density of conduction electrons  $n_e$  and for the chemical potential  $\mu$  the expressions

$$n_e = \sqrt{2n_D} \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/4} \exp \frac{-\varepsilon_i}{2k_B T}$$

and

$$\mu = E_g - \frac{\varepsilon_i}{2} + \frac{1}{2}k_B T \ln \frac{4\pi^3 \hbar^3 n_i}{(2\pi m_e k_B T)^{3/2}} .$$

Interpret this result!

3. Consider now the opposite limiting case,

$$A \exp \frac{\varepsilon_i}{k_B T} \ll 1 ,$$

and show that

$$n_e \approx n_i$$

and

$$\mu = E_g + k_B T \ln \frac{4\pi^3 \hbar^3 n_i}{(2\pi m_e k_B T)^{3/2}}$$

are valid. Interpret also this result!

4. Let the doped wide-gap semiconductor be characterized by the following material parameters:

$$E_g = 2 \text{ eV} , \quad \varepsilon_i = 0.02 \text{ eV} , \quad m_e = 10^{27} \text{ g} , \quad n_i = 10^{16} \text{ cm}^{-3} .$$

In connection with the low-temperature condition

$$A \exp \frac{\varepsilon_i}{k_B T} \gg 1$$

it is assumed  $T = 3 \text{ K}$ , and in connection with the condition

$$A \exp \frac{\varepsilon_i}{k_B T} \ll 1$$

it is assumed room temperature with  $T = 300 \text{ K}$ . Verify that by application of these numerical values all the above-mentioned conditions are fulfilled!

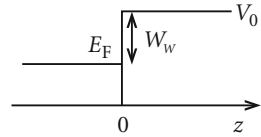
### Exercise 3.2.6

Calculate the low-temperature behavior of the chemical potential of a one-dimensional Fermi gas!

### Exercise 3.2.7

Derive the low-temperature behavior of the free energy of the (three-dimensional) ideal Fermi gas up to terms of the order of magnitude  $(k_B T/E_F)^2$ .

**Fig. 3.13** Illustration of the work function of a metal



### Exercise 3.2.8

The quasi-free conduction electrons have a lower potential energy within a metal than in the exterior space. Therefore they cannot leave the metal at  $T = 0$ . The energetic distance  $W_W$  between the outside potential  $V_0$  and the Fermi energy  $E_F$  inside the metal is called the *work function* (Fig. 3.13). At finite temperatures, though, some of the electrons, which occupy states of the high-energy tail of the Fermi-Dirac distribution function, will be able to leave the metal. Let the metal be in a closed container, where that part of the container, which is not filled by the metal, is vacuum at  $T = 0$ .

1. Find the density of states of the electrons in the exterior space. What are the average occupation numbers  $\langle \hat{n}_{\mathbf{k}\sigma}^{(ex)} \rangle$  there? ( $\sigma = \uparrow$  or  $\downarrow$  for the two possible spin projections.)
2. Determine the electron density  $n_{ex}$  outside the metal at the temperature  $T$  ( $\rightarrow$  *vapor pressure* of the metal electrons).
3. Assume that the metal occupies the half space  $z < 0$ . Calculate the density of the emission-current density:

$$j_z = \frac{-e}{V} \sum_{\mathbf{k}, \sigma}^{k_z \geq 0} \frac{\hbar k_z}{m} \langle \hat{n}_{\mathbf{k}\sigma}^{(ex)} \rangle .$$

It should result in the well-known *Richardson formula* ((1.47), Vol. 6).

### Exercise 3.2.9

Let  $N$  noninteracting spin- $\frac{1}{2}$  fermions be restricted in their motion to the surface of a sphere (radius  $R$ ).

1. How does the one-particle Hamilton operator read?
2. Let the ground-state energy

$$E^{(0)} = \frac{27\hbar^2}{mR^2}$$

be measured. Calculate the Fermi energy  $E_F = \mu(T = 0)$  and the particle number  $N$ .



**Exercise 3.2.10**

Consider a system of  $N$  noninteracting extremely relativistic fermions in the volume  $V$  with the one-particle energies:

$$\sqrt{c^2\mathbf{p}^2 + m^2c^4} \longrightarrow cp = c\hbar k = \varepsilon(k) .$$

1. Calculate the density of states  $D(E)$  of the Fermi gas!
2. Non-relativistically it holds (3.45) for the relation between pressure and internal energy. Show that in the case of extremely relativistic fermions it is found instead of that:

$$U = 3pV$$

3. Determine the *zero-point pressure*.

**Exercise 3.2.11**

Calculate for the extremely relativistic, *degenerate* Fermi gas the temperature-dependence

1. of the chemical potential  $\mu$ ,
2. of the internal energy  $U$ ,
3. and of the heat capacity.

Compare the results with the non-relativistic ones.

**Exercise 3.2.12**

Calculate the density of states of free fermions (spin  $S$ ) in the homogeneous magnetic field  $\mathbf{B} = B\mathbf{e}_z$  under the precondition that the field couples only to the spin.

**Exercise 3.2.13**

Calculate for a *degenerate* system of free electrons in the homogeneous magnetic field  $\mathbf{B}_0 = B_0\mathbf{e}_z$  the field- and temperature-dependences of the chemical potential  $\mu$  up to terms of the order  $(k_B T/E_F)^2$  and  $(\mu_B B_0/E_F)^2$ , respectively. Assume for simplicity that the field couples to the spin only.

**Exercise 3.2.14**

Show that

$$f(x) = \sum_{n=-\infty}^{+\infty} \delta \left[ x - \left( n + \frac{1}{2} \right) \right]$$

can be written as follows as a Fourier series:

$$f(x) = \sum_{p=-\infty}^{+\infty} (-1)^p e^{i2\pi px} .$$

**Exercise 3.2.15**

For the calculation of the oscillatory part of the grand-canonical potential of free electrons in the magnetic field one needs the integral (see (3.119)):

$$I_p = \int_{-\infty}^{+\infty} d\varepsilon \hat{f}'_-(\varepsilon) \cos\left(2\pi p\varepsilon - \frac{\pi}{4}\right),$$

where  $\hat{f}'_-$  is the derivative of the Fermi function:

$$\hat{f}'_-(\varepsilon) = \frac{d}{d\varepsilon} \left\{ 1 + \exp[b(\varepsilon - \mu_0)] \right\}^{-1}.$$

Calculate  $I_p$  by using the residue theorem.

**Exercise 3.2.16**

Consider a system of  $N$  noninteracting *spin-less* electrons in a homogeneous magnetic field  $\mathbf{B}_0 = B_0 \mathbf{e}_z$ .

1. Calculate the canonical partition function  $Z_1$  of a single electron.
2. Let the temperature be so high that approximately *Boltzmann Statistics* can be applied to the  $N$ -electron system. In particular, this means for the canonical partition function:

$$Z_N = \frac{Z_1^N}{N!}.$$

Calculate the average magnetic moment  $m$ .

**Exercise 3.2.17**

Calculate for a **non-degenerate** electron gas, to which, as in the preceding exercise, *Boltzmann Statistics* can be applied, the magnetic *zero-field susceptibility*:

$$\chi(T) = \frac{\mu_0}{V} \left( \frac{\partial m}{\partial B_0} \right)_T (B_0 \rightarrow 0).$$

For the separation of the orbital and the spin part, assume that the orbital motion of the electron takes place with an *effective mass*  $m^*$  different from the free electron mass  $m$ . (The latter is to be distinguished from the magnetic moment used above for the susceptibility.)

**Exercise 3.2.18**

Calculate explicitly the *oscillatory part* of the susceptibility of a free electron gas in the homogeneous magnetic field  $\mathbf{B}_0 = B_0 \mathbf{e}_z$ .

### 3.3 Ideal Bose Gas

After studying the properties of the *ideal Fermi gas* we will now investigate the properties of systems on  $N$  noninteracting bosons (spin  $S$ ) in the volume  $V$ . We learned in Sect. 3.1 that the canonical partition function of the  $N$ -particle system, in spite of the absence of interactions, does not simply factorize, as it would be the case in the classical *Boltzmann Statistics*. The symmetry condition for many-boson systems, due to the *principle of indistinguishability*, has very far-reaching consequences. This we will recognize already with the general equations of state in Sect. 3.3.1, which we discuss at first in complete analogy to the *ideal Fermi gas* (Sect. 3.2.1). With the investigation of the *classical limiting case*  $z \ll 1$  (Sect. 3.3.2) we will find correction terms with respect to the classical ideal gas equation, which have a formal similarity to those, which result in a real gas from the attractive interaction between the particles.—The most spectacular consequence of the quantum-mechanical symmetry condition is the *Bose-Einstein condensation* (Sect. 3.3.3), which exhibits all features of a phase transition of first order, and that too, in a system of **non**interacting particles.—As important examples of application of the theory of this chapter we will investigate the *photon gas* (Sect. 3.3.6) and the *phonon gas* (Sect. 3.3.7).

#### 3.3.1 Equations of State

Starting point for the derivation of the *thermal* and the *caloric* equation of state of the ideal Bose gas is the grand-canonical potential (3.21). (We omit the index (+) for the identification of bosonic quantities and functions, because in this section we will deal exclusively with Bose systems.) In the following it is thought of non-relativistic bosons with a spin  $S$  and the same isotropic one-particle energies

$$\varepsilon(\mathbf{k}) = \varepsilon(k) = \frac{\hbar^2 k^2}{2m}, \quad (3.144)$$

which we have used also for the ideal Fermi gas in Sect. 3.2. One should note, however, that some details of the upcoming results are influenced by this choice of  $\varepsilon(\mathbf{k})$ . For the photon gas as well as for the phonon gas we will have to replace (3.144) by other expressions.—The lowest one-particle energy (3.144) is zero. As already explained, subsequent to (3.31), the chemical potential has then to fulfill

$$-\infty < \mu < 0. \quad (3.145)$$

Let the Bose gas be in a cuboid of the volume  $V = L_x L_y L_z$  with *periodic boundary conditions* for the wave function. In the case of an asymptotically large system ( $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V \rightarrow n = \text{finite}$ ) we can then replace, as in (3.37), sums by

integrals. Furthermore, the ideal Bose gas possesses exactly the same *density of states* (3.50) as that of the ideal Fermi gas discussed in Sect. 3.2.

In connection with the replacement of sums by integrals, for instance in the grand-canonical potential, for the Bose gas there can arise a difficulty, namely then, when the chemical potential  $\mu$  approaches too closely the value 0. According to (3.29), under the precondition  $-\beta\mu \ll 1$ , it holds for the occupation of the energetically lowest one-particle level ( $\varepsilon(\mathbf{0}) = 0$ ):

$$\langle \hat{n}_{0m_s} \rangle = \frac{1}{e^{-\beta\mu} - 1} = \frac{1}{1 - \beta\mu + \dots - 1} \approx -\frac{1}{\beta\mu}.$$

$\langle \hat{n}_{0m_s} \rangle$  can thus adopt arbitrarily large macroscopic values. On the other hand, the density of states  $D(E) \sim \sqrt{E}$  vanishes at zero-energy. There obviously exists a serious source of error. For, if we replace for instance the sum  $\sum_r \dots$  by  $\int dE D(E) \dots$ , then the ground state gets the weight zero, i.e., it will be completely disregarded, although being possibly macroscopically occupied. Because of the *Pauli principle* ( $0 \leq \langle \hat{n}_r \rangle \leq 1$ ) such a problem does **not** appear in Fermi systems. We solve it for Bose systems in such a way that we separately extract the contributions of the ground state. This means for the grand-canonical potential (3.21):

$$\beta \Omega(T, V, z) = (2S + 1) \frac{V}{(2\pi)^3} 4\pi \int_0^\infty dk k^2 \ln(1 - ze^{-\beta \varepsilon(k)}) + (2S + 1) \ln(1 - z). \quad (3.146)$$

The factor  $(2S + 1)$  is due to the spin degeneracy.

Before we evaluate (3.146), we should assure ourselves that the *extraction* of the ground-state contribution is really sufficient. With periodic boundary conditions we get for the one-particle energies ( $L_x = L_y = L_z = L$ ):

$$\varepsilon(\mathbf{k}) \longrightarrow \frac{\hbar^2}{2m} \frac{4\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2); \quad n_{x,y,z} \in \mathbf{Z}.$$

In the asymptotically large system the lowest excited energy

$$\varepsilon_1 = \frac{\hbar^2}{2m} \frac{4\pi^2}{L^2} \quad (L^2 = V^{2/3})$$

approaches arbitrarily closely the ground-state energy zero. It is therefore not at all a matter of course that we have to *single out* in (3.146) only the ground-state contribution. We therefore check the contribution of the first excited state. In the here interesting region it is

$$\langle \hat{n}_{0m_s} \rangle \approx -\frac{1}{\beta\mu} = \gamma N,$$

where  $\gamma$  is a number of the order of magnitude 1. Furthermore it can also be estimated:

$$\begin{aligned}\langle \hat{n}_{1m_s} \rangle &= \frac{1}{e^{\beta(\varepsilon_1 - \mu)} - 1} \approx \frac{1}{\beta\varepsilon_1 - \beta\mu}, \\ \beta\varepsilon_1 &= \frac{\hbar^2}{2m}\beta \frac{4\pi^2}{V^{2/3}} = \left( \frac{\hbar^2}{2m} 4\pi^2 n^{2/3} \beta \right) \frac{1}{N^{2/3}} \\ &= (\pi\lambda^2 n^{2/3}) \frac{1}{N^{2/3}} \equiv \alpha \frac{1}{N^{2/3}}.\end{aligned}$$

By assumption the particle-number density  $n$  is finite. Quantum-phenomena become relevant when the de Broglie wavelength  $\lambda$  becomes of the order of magnitude of the average particle distance ( $\sim (V/N)^{1/3} = n^{-1/3}$ ). The number  $\alpha$  will therefore be in our case here also of the order 1. This means:

$$\frac{\langle \hat{n}_{1m_s} \rangle}{\langle \hat{n}_{0m_s} \rangle} \approx \frac{1}{\alpha\gamma N^{1/3} + 1} \approx N^{-1/3}. \quad (3.147)$$

We see that in the region, where the *extraction* of the two terms might be of importance for the grand-canonical potential (3.146),  $\langle \hat{n}_{1m_s} \rangle$  is smaller than  $\langle \hat{n}_{0m_s} \rangle$  by a huge factor ( $\sim 10^{-7}$ ). This term is therefore not at all of any weight. This holds even more for the higher excited states. This is an important point, to which we will come back once more in Sect. 3.3.3. Equation (3.146) is therefore the correct ansatz for the grand-canonical potential of the ideal Bose gas:

The further procedure now runs completely analogously to that for the Fermi gas in Sect. 3.2.1. With the substitution, already used there,

$$x = \hbar k \sqrt{\frac{\beta}{2m}},$$

and with the definition (1.137) of the *thermal de Broglie wavelength*  $\lambda$ , (3.146) becomes

$$\beta \Omega(T, V, z) = \frac{2S+1}{\lambda^3} \frac{4V}{\sqrt{\pi}} \int_0^\infty dx x^2 \ln(1 - ze^{-x^2}) + (2S+1) \ln(1-z).$$

With the series expansion of the logarithm,

$$\ln(1-y) = - \sum_{n=1}^{\infty} \frac{y^n}{n} \quad (|y| < 1),$$

we evaluate the remaining integral:

$$\int_0^{\infty} dx x^2 \ln(1 - ze^{-x^2}) = -\frac{\sqrt{\pi}}{4} \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}.$$

The calculation process is practically identical to that we performed subsequent to (3.39). We define:

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^{\infty} dx x^2 \ln(1 - ze^{-x^2}) = \sum_{n=1}^{\infty} \frac{z^n}{n^{5/2}}, \quad (3.148)$$

$$g_{3/2}(z) = z \frac{d}{dz} g_{5/2}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}} \quad (3.149)$$

(cf. (3.40), (3.41)). The grand-canonical potential therewith reads:

$$\beta \Omega(T, V, z) = -\frac{2S+1}{\lambda^3} V g_{5/2}(z) + (2S+1) \ln(1-z). \quad (3.150)$$

Except for the additive additional term, this is formally the same relation as that for fermions (3.42), only the function  $f_{5/2}(z)$  was replaced by  $g_{5/2}(z)$ . It follows immediately from (3.150) because of  $\Omega = -pV$ :

$$\beta p = \frac{2S+1}{\lambda^3} g_{5/2}(z) - \frac{2S+1}{V} \ln(1-z). \quad (3.151)$$

This is not the *thermal equation of motion* yet. The fugacity  $z$  has still to be expressed by the particle density  $n$ . For that we use (2.80):

$$n = \frac{\langle \hat{N} \rangle}{V} = z \left( \frac{\partial}{\partial z} \beta p \right)_{T,V} = \frac{2S+1}{\lambda^3} g_{3/2}(z) + \frac{2S+1}{V} \frac{z}{1-z}. \quad (3.152)$$

The combination of the two relations (3.151) and (3.152) leads to the **thermal equation of state**. The last summand in (3.152) represents the contribution of the ground state to the particle density,

$$\frac{1}{V} \langle \hat{n}_{0m_s} \rangle = \frac{1}{V} \frac{1}{z^{-1} - 1} = \frac{1}{V} \frac{z}{1-z} \equiv \frac{n_0}{2S+1} \quad (3.153)$$

$$(m_s = -S, -S+1, \dots, +S),$$

and can become, as mentioned, macroscopically large. This phenomenon is denoted as *Bose-Einstein condensation*, the in-depth investigation of which is the topic of Sect. 3.3.3.

We come to the *caloric equation of state* via the internal energy  $U$  (2.85):

$$U = - \left( \frac{\partial}{\partial \beta} \ln \Xi_z(T, V) \right)_{z, V} = \left( \frac{\partial}{\partial \beta} \beta \Omega(T, V, z) \right)_{z, V} .$$

The insertion of (3.150) yields:

$$U = \frac{3}{2} k_B T V \frac{2S+1}{\lambda^3} g_{5/2}(z) . \quad (3.154)$$

The internal energy of the ideal Bose gas has therewith formally the same structure as that of the ideal Fermi gas in (3.45). If we eliminate from the Eqs. (3.152) and (3.154) the fugacity  $z$ , then we have the **caloric equation of state** of the ideal Bose gas.

The combination of (3.151) with (3.154) yields for  $U$  and  $pV$  the connection,

$$U = \frac{3}{2} pV + \frac{3}{2} k_B T (2S+1) \ln(1-z) , \quad (3.155)$$

which differs by the second summand from the corresponding formula of the classical ideal gas and also from that of the ideal Fermi gas (3.45).

### 3.3.2 Classical Limiting Case

We will investigate, for the Bose gas also, at first the limiting case  $z \ll 1$ , for which, because of

$$\langle \hat{n}_r \rangle = \frac{1}{z^{-1} e^{\beta \varepsilon_r} - 1} \approx z e^{-\beta \varepsilon_r} \ll 1 ,$$

all levels are only very sparsely occupied. The probability of double occupations is almost zero. It is therefore not astonishing that in this limit the differences of Bose, Fermi, and Boltzmann Statistics are more or less *washed out*. The series expansions (3.148) and (3.149) can be restricted to the first two terms:

$$g_{5/2}(z) \approx z + \frac{z^2}{2^{5/2}} ; \quad g_{3/2}(z) \approx z + \frac{z^2}{2^{3/2}} .$$

It follows therewith in a very first approximation for the particle density (3.152):

$$n\lambda^3 \approx (2S+1) z^{(0)} \left( 1 + \frac{\lambda^3}{V} \right) ,$$

$$z^{(0)} \approx \frac{n\lambda^3}{(2S+1)(1 + \lambda^3/V)} .$$

As for the ideal Fermi gas (3.47), the *classical limiting case*  $z \ll 1$  thus comes up for

$$n\lambda^3 \ll 1,$$

i.e., for a **low particle density** and for a small de Broglie wave length, where the latter means **high temperature**. When, however,  $n\lambda^3 \ll 1$ , then it holds all the more:  $\lambda^3/V \ll 1$ . The *correction term* in (3.152) is then of course also negligible. It is clear that for  $z \ll 1$  the *extraction* of the ground-state contribution would actually not be necessary. We have motivated this *extraction* in the last subsection only for the problematic limit  $\mu \rightarrow 0$  and  $z \rightarrow 1$ , respectively, for which the ground state can be macroscopically occupied.—Hence we can write:

$$z^{(0)} \approx \frac{n\lambda^3}{2S+1}.$$

We had found the same result in Sect. 3.2.2 for fermions. In order to get the next higher correction, we use this result once more in the expression (3.152) for the particle density:

$$z^{(0)} \approx \frac{n\lambda^3}{2S+1} \approx z^{(1)} \left( 1 + \frac{z^{(1)}}{2^{3/2}} \right).$$

This leads to

$$z^{(1)} \approx z^{(0)} \left( 1 - \frac{z^{(0)}}{2^{3/2}} \right).$$

When we now insert this into the relation (3.151) for the pressure of the ideal Bose gas, we obtain an equation of state,

$$pV = \langle \widehat{N} \rangle k_B T \left[ 1 - \frac{n\lambda^3}{4\sqrt{2}(2S+1)} \right], \quad (3.156)$$

which differs from the analog (3.48) of the Fermi gas only by the sign before the *quantum correction*.—If one inspects for comparison the equation of state of (classical) **real** gases, by the inclusion of particle interactions one reaches formally similar corrections to the ideal gas equation (s. *van der Waals gas*, (1.14) in Vol. 5). One then recognizes that the symmetry conditions on  $N$ -particle states (3.3), due to the *principle of indistinguishability*, appear for the ideal Fermi gas like a repulsion, and for the ideal Bose gas like an attraction between the particles. Numerically, however, the *quantum corrections* in (3.48) and (3.156) are very much smaller than the usual correction terms which result from the real particle interactions.



### 3.3.3 Bose-Einstein Condensation

The region of high particle densities and low temperatures is much more interesting than the *classical limiting case*  $z \ll 1$  ( $n\lambda^3 \ll 1$ ), discussed in the preceding subsection, because there are serious discrepancies to the ideal Fermi gas and to the classical ideal gas. Under such boundary conditions, for which quantum-mechanical aspects are especially strongly effective, one speaks of a *degenerate Bose gas*.

In order that the Eq. (3.151) for the pressure of the ideal Bose gas can be understood as the *thermal equation of state*, by means of the relation (3.152) we have to eliminate the fugacity  $z$ , i.e., we have to find  $z$  as a function of the temperature  $T$  and the particle density  $n$ . The function  $g_{3/2}(z)$  will thereby play an important role, where, though, because of  $-\infty < \mu \leq 0$ , only the region  $0 < z < 1$  is interesting. The functions

$$g_\alpha(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\alpha} \quad (3.157)$$

are linked with each other by

$$g_{\alpha-1}(z) = z \frac{d}{dz} g_\alpha(z), \quad (3.158)$$

representing in the interval  $0 \leq z \leq 1$  positive, monotonously increasing functions of  $z$  (Fig. 3.14). For  $z = 1$  they are identical with the *Riemann's  $\zeta$ -function* (3.70):

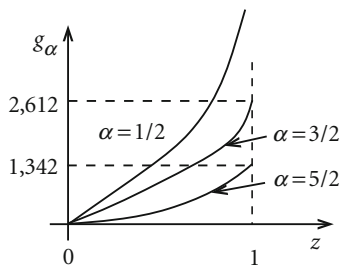
$$g_{5/2}(1) = \zeta\left(\frac{5}{2}\right) = 1.342; \quad g_{3/2}(1) = \zeta\left(\frac{3}{2}\right) = 2.612. \quad (3.159)$$

$g_{1/2}(z)$  diverges at  $z = 1$ . According to that,  $g_{3/2}(z)$  is finite at  $z = 1$ , but has a vertical tangent there.

We now write (3.152) in the form

$$n_0 = n - \frac{2S+1}{\lambda^3} g_{3/2}(z), \quad (3.160)$$

**Fig. 3.14** Qualitative behavior of the functions (3.157), important for the ideal Bose gas, as function of the fugacity  $z$



where, according to (3.153),  $n_0$  is the particle density of the  $(2S+1)$ -fold degenerate lowest one-particle energy level  $\varepsilon(\mathbf{k} = 0) = 0$ . Since  $g_{3/2}(z)$  is for  $0 < z \leq 1$  restricted to the numerical interval  $[0, 2.612]$ , such temperatures  $T$  and such particle densities  $n$  are conceivable for which

$$n > \frac{2S+1}{\lambda^3} g_{3/2}(1) .$$

But then  $n_0 > 0$ , i.e., a finite (*macroscopic*) part of the bosons occupies the ground-state level. According to our pre-considerations in Sect. 3.3.1, in such a case  $|\beta\mu|$  must be very close to zero. This phenomenon is called

### Bose-Einstein condensation

Strictly speaking, this *macroscopic* occupation of the ground state would not be noteworthy in particular, if it took place at temperatures, for which

$$k_B T < \varepsilon_1 - \varepsilon(\mathbf{k} = 0) = \varepsilon_1 ,$$

where  $\varepsilon_1$  is the first *excited* level. With the considerations subsequent to Eq. (3.146) this can be estimated for macroscopic systems to about  $T < 10^{-20}$  K. The states of a Bose system are not subject to any occupation restriction, as it is imposed on Fermi systems by the Pauli principle. At  $T = 0$ , **all** particles of the ideal Bose gas should indeed populate the lowest energy level. What is spectacular with the *Bose-Einstein condensation*, however, is the fact that the occupation of the ground state starts already at an essentially higher temperature.

The transition into the **region of condensation** is regulated by the condition

$$n\lambda^3 \stackrel{!}{=} (2S+1)g_{3/2}(1) . \quad (3.161)$$

At fixed particle density,

$$\lambda_c^3 = \frac{2S+1}{n} g_{3/2}(1) = \left( \frac{2\pi\hbar^2}{mk_B T_C} \right)^{3/2} ,$$

a **critical temperature**  $T_C$  is therewith defined

$$k_B T_C(n) = \frac{2\pi\hbar^2}{m} \left( \frac{n}{(2S+1)g_{3/2}(1)} \right)^{2/3} . \quad (3.162)$$

At fixed temperature  $T$  Eq. (3.161) determines a **critical particle density**  $n_C$ :

$$n_C(T) = \frac{2S+1}{\lambda^3} g_{3/2}(1) = (2S+1) \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} g_{3/2}(1) \quad (3.163)$$

Since  $n$  is inversely proportional to the third power of the average particle distance, it becomes clear from the last two relations that the *condensation* sets in when the

*thermal de Broglie wavelength*  $\lambda$  gets the order of magnitude of the average particle distance.

If one compares the critical temperature  $T_C$  of the ideal Bose gas with the *Fermi temperature*  $T_F$  of the ideal Fermi gas, defined in (3.64), then one finds for  $S = 1/2$ -fermions of the mass  $m_f$  and for  $S = 0$ -bosons of the mass  $m_b$  with equal particle densities:

$$\frac{T_F}{T_C} = \frac{1}{4\pi} (3\pi^2 g_{3/2}(1))^{2/3} \frac{m_b}{m_f} \approx 1.45 \frac{m_b}{m_f} .$$

In the case of equal masses the two temperatures are of the same order of magnitude. For the *prototypes*, however, conduction electrons and  ${}^4\text{He}$ -atoms, the mass ratio is  $m_b/m_f \approx 8 \cdot 10^3$ . Although Fermi temperatures in general amount to *some*  $10^4$  K, nevertheless  $T_C$  is always still to be found at *some Kelvin degrees*. If one takes the mass of the  ${}^4\text{He}$ -atom and the empirical density of liquid  ${}^4\text{He}$ , then it results from (3.162):

$$T_C \approx 3.13 \text{ K} \quad ({}^4\text{He}) . \quad (3.164)$$

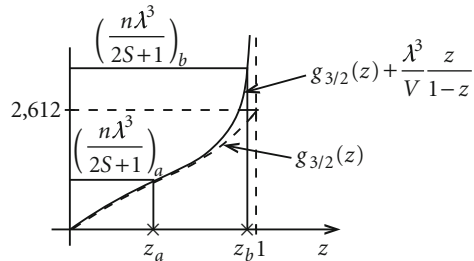
In any case  $T_C$  is still too large in order to be able to explain ‘*in a normal way*’ the transition of the bosons into the ground state. It rather exhibits the feature of a real **phase transition**, about which we will convince ourselves in the following.

At first we have to find an idea how the fugacity  $z$  looks like as a function of  $T$  and  $n$ . When one plots for fixed  $T$  and  $n$  the quantity  $g_{3/2}(z) + \lambda^3 z/[V(1-z)]$  as a function of  $z$  (Fig. 3.15), then the intersection point with the constant  $n\lambda^3/(2S+1)$  yields, according to (3.152), just the fugacity  $z$  belonging to the given  $T$  and  $n$ . This is schematically plotted in Fig. 3.15 for a large but finite volume  $V$ .

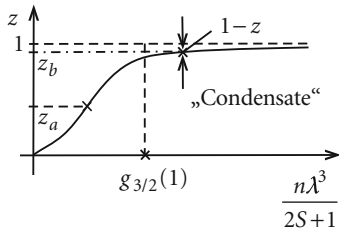
We are now able to provide *graphically* step by step  $z$  as function of  $T$  and  $n$ , but for fixed  $V$ . The solution  $z_b$  stems from the *region of condensation* (Fig. 3.16) because

$$\left( \frac{n\lambda^3}{2S+1} \right)_b > g_{3/2}(1) .$$

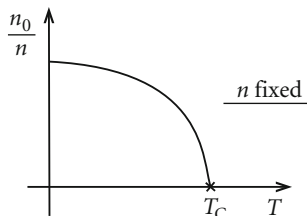
**Fig. 3.15** Graphical solution for the fugacity of the ideal Bose gas as a function of the temperature  $T$  and the particle density  $n$



**Fig. 3.16** Fugacity of the ideal Bose gas as a function of the temperature and the particle density



**Fig. 3.17** Occupation density of the ground-state level of the ideal Bose gas as a function of the temperature



If we now go to the *thermodynamic limit* ( $N \rightarrow \infty, V \rightarrow \infty, n \rightarrow \text{finite}$ ; see Sect. 4.5), then, in spite of  $V \rightarrow \infty$ , the *correction term*  $\lambda^3 z/[V(1-z)]$  must remain finite, in order to realize  $(n\lambda^3/(2S+1))_b$ . This means, on the other hand, that in the *region of condensation*  $(1-z)$  must during the limiting process  $V \rightarrow \infty$  behave like  $1/V$ . Thus we can write for very large  $V$  ( $V \rightarrow \infty$ ) approximately:

$$z = \begin{cases} \text{solution of: } \frac{n\lambda^3}{2S+1} = g_{3/2}(z), & \text{if } \frac{n\lambda^3}{2S+1} < g_{3/2}(1), \\ 1, & \text{if } \frac{n\lambda^3}{2S+1} \geq g_{3/2}(1). \end{cases} \quad (3.165)$$

Outside the *region of condensation* (upper row in (3.165)) the correction term  $\lambda^3 z/[V(1-z)]$  is unimportant because of  $V \rightarrow \infty$ . We can now use this result in (3.160) in order to get information about the occupation of the ground state (Fig. 3.17):

$$\frac{n_0}{n} \approx 0, \quad \text{if } \frac{n\lambda^3}{2S+1} < g_{3/2}(1), \quad (3.166)$$

$$\begin{aligned} \frac{n_0}{n} &\approx 1 - \frac{2S+1}{n\lambda^3} g_{3/2}(1) = 1 - \frac{\lambda_C^3}{\lambda^3} \\ &= 1 - \left(\frac{T}{T_C}\right)^{3/2}, \quad \text{if } \frac{n\lambda^3}{2S+1} \geq g_{3/2}(1). \end{aligned} \quad (3.167)$$

This behavior, however, strongly reminds of a **phase transition**, and that too remarkably in a system of particles, which do not interact with each other. One can assume for  $0 < T < T_C$  a mixture of two phases. One phase (*condensate*) is built up by the macroscopic part  $N_0$  of the altogether  $N$  bosons, which occupy the

lowest energy level  $\varepsilon(\mathbf{k} = 0) = 0$ :

$$N_0 = N \left[ 1 - \left( \frac{T}{T_C} \right)^{3/2} \right]. \quad (3.168)$$

The other phase, which we will denote as *gaseous*, is built up by the remaining particles, which are in excited ( $\mathbf{k} \neq 0$ )-levels:

$$N_1 = N - N_0 = N \left( \frac{T}{T_C} \right)^{3/2}. \quad (3.169)$$

The estimation (3.147) implies in addition that these  $N_1$  bosons are distributed *asymptotically thinly* over the excited states, i.e., the occupation number of a single level is practically zero. That holds at  $T > T_C$  also for the ( $\mathbf{k} = 0$ )-level (3.166). At  $T = 0$  **all** particles are in the energetically lowest state. Just this phenomenon (3.168) is called *Bose-Einstein condensation*. In the next subsection we will be able to further delve into the analogy to a phase transition.

### 3.3.4 Isotherms of the Ideal Bose Gas

The idea of the *phase mixture* in the *region of condensation* manifests a strong analogy to the gas-liquid phase transition. Furthermore, the abrupt change of  $n_0$  at  $T_C$  leads to discontinuities in the thermodynamic quantities. We will see that for this reason the thermodynamic potentials of the ideal Bose gas are represented above and below the transition point ( $T_C, n_C$ ) by two **different** analytical expressions. Even that is typical for a phase transition, as will be shown in Chap. 4.

We investigate the **thermal equation of state** of the ideal Bose gas for the asymptotically large system ( $N \rightarrow \infty, V \rightarrow \infty, n \rightarrow \text{finite}$ ). Starting point is Eq. (3.151), in which the second term on the right-hand side vanishes for  $V \rightarrow \infty$ :

$$\frac{2S+1}{V} \ln(1-z) \xrightarrow{V \rightarrow \infty} 0. \quad (3.170)$$

For  $z < 1$ , i.e.,  $n < n_C$ , it is trivial, but not at all for the *region of condensation*  $n \geq n_C$  because of  $z \rightarrow 1$ . However, we have realized in the last subsection, in connection with the *graphical solution* for  $z(T, n)$ , that in the *region of condensation*  $(1-z)$  behaves like  $1/V$ . The above expression therefore tends as  $\ln V/V$  for  $V \rightarrow \infty$  towards zero.

With (3.151) and (3.165) it thus holds for the pressure of the ideal Bose gas:

$$\beta p = \begin{cases} \frac{2S+1}{\lambda^3} g_{5/2}(z) & \text{for } n < n_C, \\ \frac{2S+1}{\lambda^3} g_{5/2}(1) & \text{for } n > n_C. \end{cases} \quad (3.171)$$

In the *region of condensation* the pressure is thus independent of the volume and the particle density, respectively, being a function of the temperature only. But that is not different from the phase transition between gas and liquid. We obtain the *phase boundary curve* in the  $(p - (1/n))$ -diagram by eliminating the temperature from the two *critical equations*:

$$p_C(T) = k_B T \frac{2S + 1}{\lambda^3} g_{5/2}(1), \quad (\text{vapor pressure}) \quad (3.172)$$

$$n_C(T) = \frac{2S + 1}{\lambda^3} g_{3/2}(1). \quad (3.173)$$

With

$$C_0 = \frac{2\pi\hbar^2}{m} \frac{(2S + 1)g_{5/2}(1)}{[(2S + 1)g_{3/2}(1)]^{5/3}} \quad (3.174)$$

we obviously have:

$$p_C = C_0 n_C^{5/3}. \quad (3.175)$$

The

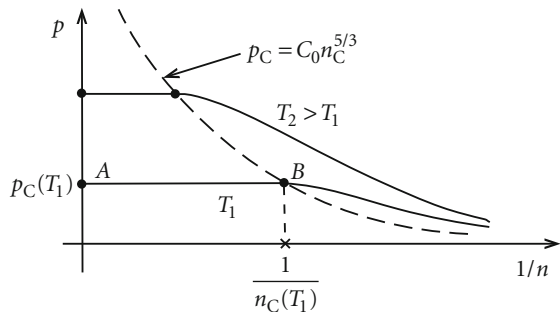
### isotherms of the ideal Bose gas

therefore indeed exhibit a strong similarity to those of the gas-liquid system (Fig. 3.18).

In the *two-phase region* between *A* and *B* there is a mixture of a *gaseous* phase of the composition *B* and a *condensate* of the composition *A* (Fig. 3.18). The *condensate* has the density  $\infty$  and the *specific volume* (volume per particle)  $v = 1/n = 0$ , respectively. The *gas* in the transition region has the density  $n_C$ .

In the region  $1/n > 1/n_C$  there is only *gas*. Since in the *gas-phase*, according to our *graphical solution* in the preceding subsection,  $z$  decreases at fixed temperature monotonously with decreasing particle density  $n$ , and the same does  $g_{5/2}(z)$ , it

**Fig. 3.18** Isotherms of the ideal Bose gas



results, according to (3.171), a continuous drop of the pressure with an increasing specific volume  $v = 1/n$ .

The *Bose-Einstein condensation* obviously exhibits the characteristic attributes of a phase transition of first order. It should therefore be also possible to find an analog to the **Clausius-Clapeyron equation** ((4.19), Vol. 5):

$$\frac{dp_C}{dT} = \frac{\Delta Q}{T\Delta v} . \quad (3.176)$$

When we differentiate the *vapor pressure* (3.172) with respect to the temperature, then it follows:

$$\frac{dp_C}{dT} = \frac{5}{2}k_B \frac{2S+1}{\lambda^3} g_{5/2}(1) \stackrel{(3.173)}{=} \frac{5}{2}k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} n_C .$$

It now holds for the difference of the specific volumes of the two co-existing phases:

$$\Delta v = v_C - 0 = v_C = \frac{1}{n_C} .$$

The *Clausius-Clapeyron equation* (3.176) is therewith formally fulfilled, when we define as *latent heat* per particle:

$$\Delta Q = \frac{5}{2}k_B T \frac{g_{5/2}(1)}{g_{3/2}(1)} . \quad (3.177)$$

The analogy of the Bose-Einstein condensation to a phase transition of first order becomes complete, when we also succeed to express the latent heat by the entropy difference  $\Delta S$  of the co-existing phases in the form  $N\Delta Q = T\Delta S$ . For this purpose we investigate in the next subsection the thermodynamic potentials of the ideal Bose gas.

### 3.3.5 Thermodynamic Potentials

We begin with the **internal energy**  $U$ , which we want to find for the ideal Bose gas in the *thermodynamic limit* ( $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $n \rightarrow \text{finite}$ ). Since  $U$ , as also all the other thermodynamic potentials, is an extensive state quantity, the calculation makes of course sense only for the *internal energy per particle*. Let the particle number be fixed ( $N \equiv \langle \hat{N} \rangle$ ). Because of

$$\frac{U}{N} = \frac{1}{n} \frac{U}{V}$$

the second term in (3.155) vanishes for  $V \rightarrow \infty$ , as has been proven in connection with (3.170). So, for the calculation of the internal energy, we can directly apply the result (3.171) for the pressure  $p$ :

$$\frac{1}{N}U = \frac{1}{n} \frac{3}{2} p = \begin{cases} \frac{3}{2} \frac{k_B T}{n \lambda^3} (2S+1) g_{5/2}(z) & \text{for } n < n_C, \\ \frac{3}{2} \frac{k_B T}{n \lambda^3} (2S+1) g_{5/2}(1) & \text{for } n > n_C. \end{cases} \quad (3.178)$$

The fugacity  $z$  on the right-hand side is fixed by (3.165) as function of  $T$  and  $n$ . This holds for all the subsequent expressions.

For the **free energy** we have to calculate

$$\frac{1}{N}F = -k_B T \frac{1}{N} \ln \Xi + \mu = -\frac{pV}{N} + k_B T \ln z,$$

which, however, can be immediately achieved with (3.171):

$$\frac{1}{N}F = -k_B T \begin{cases} \frac{2S+1}{n \lambda^3} g_{5/2}(z) - \ln z & \text{for } n < n_C, \\ \frac{2S+1}{n \lambda^3} g_{5/2}(1) & \text{for } n > n_C. \end{cases} \quad (3.179)$$

With regard to the *Clausius-Clapeyron equation* (3.176) or the *latent heat* (3.177) of the Bose-Einstein condensation, the **entropy** is of special interest. It follows with

$$\frac{\widehat{S}}{Nk_B} = \frac{U - F}{Nk_B T}$$

from the above results for  $U$  and  $F$ :

$$\frac{\widehat{S}}{Nk_B} = \begin{cases} \frac{5}{2} \frac{2S+1}{n \lambda^3} g_{5/2}(z) - \ln z & \text{for } n < n_C, \\ \frac{5}{2} \frac{2S+1}{n \lambda^3} g_{5/2}(1) & \text{for } n > n_C. \end{cases} \quad (3.180)$$

In the *two-phase region*,  $\lambda^{-3}$  gives rise to a temperature-dependence of the form:

$$\frac{\widehat{S}}{Nk_B} \sim T^{3/2} \quad (n > n_C). \quad (3.181)$$

In particular, the third law of Thermodynamics is therewith fulfilled. At  $T = 0$  only the *condensate* is present. Obviously this does not have any entropy. We thus can assume that at **each** temperature  $0 \leq T \leq T_C$  the entropy stems exclusively from the *gas phase*. For the entropy difference this has the consequence:

$$\frac{1}{N} \Delta S = \frac{1}{N} S(T, n_C) = \frac{5}{2} k_B \frac{2S+1}{n_C \lambda^3} g_{5/2}(1) \stackrel{(3.173)}{=} \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \quad (3.182)$$



The comparison with (3.177) then yields

$$N\Delta Q = T\Delta S, \quad (3.183)$$

and confirms therewith our classification of the Bose-Einstein condensation as phase transition of first order.

Eventually, we also calculate the **heat capacity**  $C_V$ . For that we have to differentiate the entropy with respect to the temperature. This is no problem in the *region of condensation*  $n > n_C$ , because, according to (3.180), the temperature-dependence arises only from the de Broglie wavelength  $\lambda$ :

$$\frac{C_V}{Nk_B} = \frac{T}{Nk_B} \left( \frac{\partial \widehat{S}}{\partial T} \right)_V = \frac{15}{4} \frac{2S+1}{n\lambda^3} g_{5/2}(1) \quad (n > n_C). \quad (3.184)$$

The heat capacity thus behaves as  $T^{3/2}$  (Fig. 3.19). For  $n < n_C$ , though, we have to take into consideration that the fugacity  $z$  is also temperature-dependent. With

$$\widehat{S} = \widehat{S}(T, V, z(T, V))$$

it follows:

$$\left( \frac{\partial \widehat{S}}{\partial T} \right)_V = \left( \frac{\partial \widehat{S}}{\partial T} \right)_{V,z} + \left( \frac{\partial \widehat{S}}{\partial z} \right)_{T,V} \left( \frac{\partial z}{\partial T} \right)_V.$$

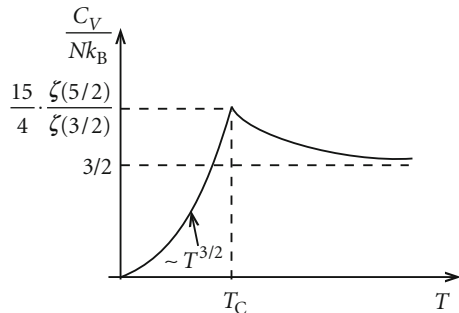
Because of (3.165) we can write instead of (3.180):

$$\frac{\widehat{S}}{Nk_B} = \frac{5}{2} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z \quad (n < n_C). \quad (3.185)$$

We have therewith:

$$\frac{C_V}{Nk_B} = \frac{T}{Nk_B} \left( \frac{\partial \widehat{S}}{\partial z} \right)_{T,V} \left( \frac{\partial z}{\partial T} \right)_V.$$

**Fig. 3.19** Temperature-behavior of the heat capacity of the ideal Bose gas



In (3.165),

$$n\lambda^3 = (2S + 1)g_{3/2}(z) ,$$

we differentiate both sides with respect to the temperature,

$$-\frac{3n\lambda^3}{2T} = (2S + 1) \left( \frac{d}{dz} g_{3/2}(z) \right) \left( \frac{\partial z}{\partial T} \right)_V ,$$

and we obtain then with (3.158):

$$\left( \frac{\partial z}{\partial T} \right)_V = -\frac{3z}{2T} \frac{g_{3/2}(z)}{g_{1/2}(z)} .$$

Again with (3.158), it results from (3.185):

$$\frac{1}{k_B N} \left( \frac{\partial \widehat{S}}{\partial z} \right)_{T,V} = \frac{1}{z} \left[ -\frac{5}{2} \frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^2(z)} + \frac{3}{2} \right] .$$

The heat capacity per particle therewith reads:

$$\frac{C_V}{Nk_B} = \frac{15}{4} \frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \quad (n < n_C) . \quad (3.186)$$

The fugacity on the right-hand side is again to be understood as solution  $z(T, n)$  of (3.165). For a given  $n$  we have to equate  $T \rightarrow T_C$  with  $z \rightarrow 1$ . For  $z \rightarrow 1$  the second summand in (3.186) becomes zero because of the divergence of  $g_{1/2}$ . Therefore at the critical temperature  $T_C$  we get:

$$\left( \frac{C_V}{Nk_B} \right)_{T_C} = \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} . \quad (3.187)$$

It will be shown in the solution of Exercise 3.3.1 that for  $T \rightarrow \infty$  the chemical potential tends to  $-\infty$ , and that, too, so strongly that it even holds:  $\beta\mu \rightarrow -\infty$ . Hence, the fugacity  $z$  tends to zero for  $T \rightarrow \infty$ . In the functions  $g_\alpha(z)$  ( $\alpha = 1/2, 3/2, 5/2, \dots$ ), defined in (3.157), the first summand then dominates:

$$\frac{g_\alpha(z)}{g_\beta(z)} \xrightarrow{z \rightarrow 0} \frac{z}{z} = 1 .$$

According to (3.186) we get therewith, as not unexpected, for  $T \rightarrow \infty$  the classical limiting case of the heat capacity:

$$\left( \frac{C_V}{Nk_B} \right)_{T \rightarrow \infty} = \frac{3}{2} . \quad (3.188)$$

With (3.184), (3.187), and (3.188) we now know already quite precisely the qualitative temperature-behavior of the heat capacity (Fig. 3.19).

At the end, one is of course confronted with the question, whether the spectacular Bose-Einstein condensation of the ideal Bose gas can also be experimentally detected. At first, the assumption of a noninteracting system is of course such a strong idealization that a quantitative agreement of theory and experiment cannot be expected, in particular, if one takes into consideration that for  $T \rightarrow 0$  no system will exist in the gaseous state. The only system, which might behave, at least approximately, for low temperatures like an ideal Bose gas, would be liquid  $^4\text{He}$ . This indeed shows a phase transition at 2.18 K, which is called  $\lambda$ -transition, because the temperature-behavior of the heat capacity near  $T_C$  bears a resemblance to the Greek letter  $\lambda$ . Strictly speaking,  $C_V$  exhibits there a logarithmic divergence. Is this transition a Bose-Einstein condensation modified by particle interactions? A positive answer is supported by the estimation (3.164) for  $T_C$ , which comes with 3.13 K very close to the experimental value. A further support is due to the fact that the so-called *two-phase theory* of  $^4\text{He}$  for  $T < T_C$  describes the phenomena rather well. This theory assumes the co-existence of two phases, a *superfluid* phase, which may correspond to the *Bose-Einstein condensate* (atoms in the ground-state), and a *normal* phase, which may be ascribed to the atoms in the excited states. Furthermore, it was a strong argument for a long time for the interpretation of the  $\lambda$ -transition as a Bose-Einstein condensation that superfluidity was observed only for  $^4\text{He}$ , but not for the Fermi system  $^3\text{He}$ . In the meantime, though, one knows that at very low temperatures  $^3\text{He}$  also becomes *superfluid*. Furthermore, the  $\lambda$ -transition is **not** a phase transition of **first** order, so that it is at least not a case of a *pure* Bose-Einstein condensation. The problem must be seen as up to now not completely solved. On the other hand, there does exist a first experimental realization of the Bose-Einstein condensation, seen in 1995 by E.A. Cornell, C.E. Wiemann, and W. Ketterle, who received the Nobel prize for their work (Phys. Rev. Lett. **75**, 3969 (1995)).

### 3.3.6 Photons

For the treatment of the ideal Bose gas we have so far always assumed that the particle number  $N$  can be arbitrarily given, independent of the variables *temperature* and *volume*. In the grand-canonical ensemble the particle number is regulated by the chemical potential  $\mu$  (*Lagrange multiplier!*). But this is not guaranteed for some important Bose systems, in which, in an unrestricted manner, particles can be created and annihilated, respectively. To this class of systems there belong the *photons* of the electromagnetic radiation, the *phonons* of the crystal lattice, and the *magnons* of the ferromagnet. We discuss the photons in this subsection, the phonons in the next subsection, while the magnons are intensively investigated in section 2.4 of Vol. 9. All these systems have in common that at the equilibrium the number of

bosons will adjust itself so that the free energy  $F(T, V, N)$  becomes minimal:

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} \stackrel{!}{=} 0.$$

The left-hand side, however, represents nothing else but the definition of the chemical potential  $\mu$ . Thus it holds likewise for photons, phonons, and magnons:

$$\mu = 0. \quad (3.189)$$

Let us now concentrate ourselves at first on the photon gas.

In the introductory section 1.2 of Vol. 6 we had denoted Planck's treatment of the *heat radiation* as the *hour of birth* of the *Quantum Mechanics*. The topic thereby was the spectral energy distribution of the electromagnetic radiation inside a hollow (box) of the volume  $V$ , whose walls are kept at the fixed temperature  $T$ . The atoms of the walls of the hollow emit and absorb electromagnetic radiation, so that a thermal equilibrium is installed between the electromagnetic field inside the hollow and its walls. Planck's groundbreaking idea consisted in the assumption that the electromagnetic energy is **not** unrestrictedly divisible, but rather is composed of a certain number of finitely big parts (*quanta*). This picture led to the term of the **photon**.

Classically, the radiation field inside the box (vacuum!) is determined by the *homogeneous wave equation* ((4.128), Vol. 3)

$$\Delta\psi = \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2},$$

where  $\psi$  can be any component of the electric field  $\mathbf{E}$ , of the magnetic induction  $\mathbf{B}$  or of the vector potential  $\mathbf{A}$  as well as the electrostatic potential  $\varphi$ . If one expands the solution in plane waves,

$$\psi(\mathbf{r}, t) \longrightarrow \psi(\mathbf{k}, t)e^{i\mathbf{k}\mathbf{r}},$$

then the wave equation turns into the equation of motion

$$\ddot{\psi}(\mathbf{k}, t) + (k^2 c^2)\psi(\mathbf{k}, t) = 0$$

of a linear harmonic oscillator with the frequency  $\omega = c|\mathbf{k}|$ . One can therefore write the Hamilton function of the electromagnetic field as a sum of such linear electromagnetic oscillators. After quantization the radiation field is therewith equivalent to a gathering of *quantum-mechanical* harmonic oscillators with a typically **discrete** eigen-value spectrum (section 4.4, Vol. 6):

$$E_n(\mathbf{k}) = \hbar c|\mathbf{k}| \left(n + \frac{1}{2}\right) \quad n = 0, 1, 2, \dots \quad (3.190)$$

The picture is now that the oscillator energy  $E_n(\mathbf{k})$  is caused by  $n$  **photons**, where each of them contributes the

$$\text{energy: } E = \hbar\omega = \hbar c|\mathbf{k}| = cp. \quad (3.191)$$

It follows then from the relativistic particle-energy relation ((2.63), Vol. 4) that the

$$\text{mass of the photon: } m = 0 \quad (3.192)$$

It moves with the *velocity of light*  $v = c$  and the momentum  $\hbar k = E/c$ . *Radiation* results from transitions between the oscillator levels, i.e., in the final analysis from changes in the numbers of photons. Photons are thereby *created* and *annihilated*. In this sense the introductory remarks before (3.189) are to be understood. The *zero-point energy* ( $n = 0$  in (3.190)) obviously does not play a role in the *photon picture* of the electromagnetic radiation, whose exact description, by the way, must be performed in the framework of the *Quantum-Electrodynamics*. For our purposes here, however, the above simple considerations completely suffice. Advanced relativistic considerations show that the

$$\text{photon spin: } S = 1, \quad (3.193)$$

as the spin of a particle with the rest mass zero, can only have two directional possibilities, namely parallel or antiparallel, but not perpendicular to the direction of the momentum  $\hbar\mathbf{k}$ . This corresponds to **two** independent directions of polarization of the electromagnetic wave. A given spin state can be identified, respectively, as a right-circularly polarized and as left-circularly polarized electromagnetic wave ((4.150), Vol. 3).—The assignment *photon*  $\longleftrightarrow$  *electromagnetic field* represents an important realization of the *particle-wave dualism* of the Quantum Theory.

Let the hollow, which is filled by *heat radiation*, be sufficiently large so that we can assume that the thermodynamic properties of the radiation field are not influenced by the actual shape of the hollow. Hence, we can exploit ‘*convenient*’ boundary conditions. In this sense, let the hollow be a cuboid with the edge length  $L$  ( $V = L^3$ ). *Periodic boundary conditions* then lead to the discretization of the wave numbers which was already utilized several times:

$$\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z); \quad n_{x,y,z} \in \mathbb{Z}.$$

In the *grid volume*

$$\Delta k = \frac{(2\pi)^3}{V}$$

of the  $k$ -space there is then exactly one  $k$ -state, which is twofold degenerate, though, because of the two independent directions of the polarization. Because of

the isotropic energy relation (3.191), the *phase volume*  $\varphi(E)$  can be very easily calculated:

$$\frac{2}{\Delta k} \varphi(E) = 2 \frac{(4\pi/3)k^3}{\Delta k} \Big|_{k=E/\hbar c} = \frac{V}{3\pi^2} k^3 \Big|_{k=E/\hbar c} = \frac{V}{3\pi^2(\hbar c)^3} E^3 .$$

Differentiation with respect to  $E$  yields the *density of states*  $D(E)$ :

$$D(E) = \begin{cases} \frac{V}{\pi^2(\hbar c)^3} E^2 & \text{for } E \geq 0 , \\ 0 & \text{for } E < 0 . \end{cases} \quad (3.194)$$

According to (3.191) there are only positive photon energies. The energy-dependence of the density of states is here different from that in (3.50). The only reason for that is the different  $k$ -dependence of the one-particle energy in (3.38) and (3.191).

In the next step we determine the **grand-canonical potential** of the photon gas. According to (3.21) it is to be calculated:

$$\begin{aligned} \Omega(T, V) &= 2k_B T \sum_{\mathbf{k}} \ln [1 - \exp(-\beta \hbar c k)] \\ &= \frac{2k_B T}{\Delta k} \int d^3 k \ln [1 - \exp(-\beta \hbar c k)] = k_B T \frac{V}{\pi^2} J(\beta) . \end{aligned}$$

The factor 2 is due to the two degenerate spin-polarization directions. The remaining integral  $J(\beta)$  we rearrange at first by an integration by parts:

$$\begin{aligned} J(\beta) &= \int_0^\infty dk k^2 \ln [1 - \exp(-\beta \hbar c k)] \\ &= \frac{1}{3} k^3 \ln [1 - \exp(-\beta \hbar c k)] \Big|_0^\infty - \frac{1}{3} \int_0^\infty dk k^3 \frac{\beta \hbar c \exp(-\beta \hbar c k)}{1 - \exp(-\beta \hbar c k)} . \end{aligned}$$

The integrated part vanishes (why?), and it remains with the substitution  $y = \beta \hbar c k$ :

$$J(\beta) = -\frac{1}{3(\beta \hbar c)^3} \int_0^\infty dy \frac{y^3}{e^y - 1} .$$

This integral is of the type, which is investigated in Exercise 3.3.3:

$$\int_0^\infty x \frac{x^{\alpha-1}}{e^x - 1} = \Gamma(\alpha) \zeta(\alpha) \quad (3.195)$$

( $\Gamma(\alpha)$ ): Gamma function;  $\zeta(\alpha)$ : Riemann's  $\zeta$ -function.) With  $\zeta(4) = \pi^4/90$  it thus follows for  $J(\beta)$ :

$$J(\beta) = -\frac{\pi^4}{45(\beta\hbar c)^3}.$$

This leads to the following temperature- and volume-dependence of the grand-canonical potential:

$$\Omega(T, V) = -\frac{\pi^2 V}{45(\hbar c)^3} (k_B T)^4. \quad (3.196)$$

The **pressure of the photon gas** (*radiation pressure*)  $p = -(1/V)\Omega$  is therewith only a function of the temperature:

$$p = \frac{1}{3}\alpha T^4 = p(T). \quad (3.197)$$

Here we have introduced for abbreviation the *Stefan-Boltzmann constant*

$$\alpha = \frac{\pi^2 k_B^4}{15(\hbar c)^3} \approx 7.578 \cdot 10^{-16} \frac{\text{J}}{\text{m}^3 \text{K}^4}. \quad (3.198)$$

Because of  $\mu = 0$  and because of the *Gibbs-Duhem relation*  $G = \mu N$ , the grand-canonical potential  $\Omega$  is for the photon gas identical to the free energy  $F$ . For the **entropy** we have:

$$S(T, V) = -\left(\frac{\partial \Omega}{\partial T}\right)_V = \frac{4}{3}\alpha VT^3. \quad (3.199)$$

We determine the **average number of photons**, which are present at equilibrium at the temperature  $T$ , via (3.23) by means of the density of states (3.194):

$$\langle \hat{N} \rangle = \int_{-\infty}^{+\infty} dE D(E) f_+(E).$$

$f_+(E)$  is the *Bose function* (see (3.29)), the counterpart of the *Fermi function* (3.52):

$$f_+(E) = \frac{1}{e^{\beta(E-\mu)} - 1}. \quad (3.200)$$

With (3.194) as well as  $\mu = 0$  we again obtain an integral of the type (3.195):

$$\begin{aligned} \langle \widehat{N} \rangle &= \frac{V}{\pi^2 (\hbar c)^3} \int_0^{+\infty} dE \frac{E^2}{e^{\beta E} - 1} = \frac{V}{\pi^2 (\beta \hbar c)^3} \int_0^{+\infty} dx \frac{x^2}{e^x - 1} \\ &= \frac{V}{\pi^2} \left( \frac{k_B T}{\hbar c} \right)^3 \Gamma(3) \zeta(3) . \end{aligned} \quad (3.201)$$

When one inserts the constants ( $\zeta(3) = 1.202$ ), one gets:

$$\langle \widehat{N} \rangle \approx 2.032 \cdot 10^7 \cdot VT^3 \text{ [K}^3 \text{ m}^3 \text{]} . \quad (3.202)$$

The average number of photons thus becomes zero for  $T \rightarrow 0$ .

The **internal energy** can be calculated quite analogously to (3.201):

$$\begin{aligned} U(T, V) &= \int_{-\infty}^{+\infty} dE E D(E) f_+(E) = \frac{V (k_B T)^4}{\pi^2 (\hbar c)^3} \int_0^{+\infty} dx \frac{x^3}{e^x - 1} \\ &= \frac{V (k_B T)^4}{\pi^2 (\hbar c)^3} \Gamma(4) \zeta(4) . \end{aligned}$$

The  $T^4$ -dependence is known as **Stefan-Boltzmann law** ((1.12), Vol. 6),

$$U(T, V) = \alpha VT^4 , \quad (3.203)$$

which can be derived also classically ((2.64), Vol. 5), where, though, the coefficient  $\alpha$  remains undetermined. With (3.196) and (3.199) we can test:

$$U = F + TS \stackrel{!}{=} \Omega + TS .$$

The **energy density** of the photon gas is, as the pressure, a pure function of the temperature:

$$\varepsilon = \frac{U}{V} = \alpha T^4 = \varepsilon(T) . \quad (3.204)$$

With (3.197) it results a simple relation between pressure and energy density,

$$p(T) = \frac{1}{3} \varepsilon(T) , \quad (3.205)$$



to which we have connected in Vol. 5 a series of thermodynamic considerations and evaluations (section 2.8, Vol. 5). We note in passing that the coefficient 1/3 does not contradict our previous result (3.155), but is explained by the different one-particle energies ( $\varepsilon(\mathbf{k}) \sim k$  for (3.205);  $\varepsilon(\mathbf{k}) \sim k^2$  for (3.155)).

If one finally defines via

$$U = V \int_0^{\infty} \hat{\varepsilon}(\omega, T) d\omega$$

the **spectral energy density**  $\hat{\varepsilon}(\omega, T)$  of the electromagnetic radiation in the hollow, then the comparison with the above expression for  $U$ ,

$$\hat{\varepsilon}(\omega, T) d\omega = \frac{1}{V} \hbar^2 \omega d\omega D(E = \hbar\omega) f_+(E = \hbar\omega) ,$$

leads to the famous **Planck's radiation formula**:

$$\hat{\varepsilon}(\omega, T) d\omega = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{d\omega}{\exp(\beta \hbar \omega) - 1} . \quad (3.206)$$

This turns for low frequencies,

$$\hbar \omega \ll k_B T ,$$

because of

$$[\exp(\beta \hbar \omega) - 1]^{-1} \approx \frac{k_B T}{\hbar \omega}$$

into the *classical Rayleigh-Jeans formula* ((1.20), Vol. 6),

$$\hat{\varepsilon}(\omega, T) d\omega \approx \frac{\omega^2}{\pi^2 c^3} k_B T d\omega , \quad (3.207)$$

and for high frequencies,

$$\hbar \omega \gg k_B T ,$$

into the *Wien's formula* ((1.14), Vol. 6):

$$\hat{\varepsilon}(\omega, T) d\omega \approx \frac{\hbar \omega^3}{\pi^2 c^3} \exp(-\beta \hbar \omega) d\omega . \quad (3.208)$$

### 3.3.7 Phonons

The  $N$  atoms of a crystalline solid execute oscillations around their *equilibrium positions*  $\mathbf{R}_i$  ( $i = 1, 2, \dots, N$ ), which, for their part, are defined by the minimal potential energy of the system. These oscillations, which are ultimately caused by the restoring *bonding forces* between the atoms, are significantly involved in the thermodynamic properties of the solid. As collective oscillations of the lattice elements (*lattice vibrations*) they are *quantized* just as the electromagnetic waves. The quantization unit is called **phonon**. Although the solid does not have the slightest similarity to a *gas* in the conventional sense, it can nevertheless be shown by suitable transformations, as for the electromagnetic waves, that the thermodynamic properties of the crystal lattice are equivalent, to a good (low-temperature) approximation, to those of an ideal Bose gas. Here we will not only hint at these transformations, but rather perform them explicitly. It is clear that these transformations by themselves are not of decisive importance for the ‘*genuine*’ *Statistical Physics*. So they could also be skipped, if one accepts, without further justification, Eq. (3.235) as the model-Hamilton operator of the lattice dynamics.

**(A) Model-Hamilton Operator** Let the solid consist of only a single type of atoms, so that the lattice elements (atoms) build a so-called *Bravais lattice*. We define

$\{\mathbf{R}_i\}$  : equilibrium positions of the  $N$  atoms,

$\mathbf{X}_i(t)$  : momentary position of the  $i$ -th atom,

$\mathbf{u}_i(t) = \mathbf{X}_i(t) - \mathbf{R}_i$  : displacement of the  $i$ -th atom out of its rest position.

For the *kinetic energy* of the lattice ions we have:

$$T = \frac{1}{2}M \sum_{i,\alpha} \dot{u}_{i,\alpha}^2(t); \quad \alpha = x, y, z. \quad (3.209)$$

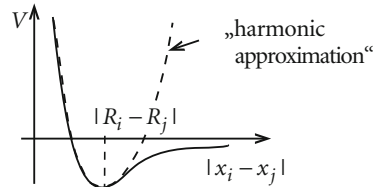
The *potential energy* is a function of the instantaneous atom positions  $V(\{\mathbf{X}_i\})$ . The minimum  $V_0 = V(\{\mathbf{R}_i\})$  defines the *bonding energy*. We expand  $V$  around  $V_0$ :

$$V(\{\mathbf{X}_i\}) = V_0 + \sum_{i\alpha} \varphi_{i\alpha} u_{i\alpha} + \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} \varphi_{i\alpha}^{j\beta} u_{i\alpha} u_{j\beta} + \mathcal{O}(u^3). \quad (3.210)$$

At not too high temperatures, the atoms will be only slightly displaced from their equilibrium positions. The expansion can then be terminated after the first non-trivial term, which is, because of

$$\varphi_{i\alpha} = \left. \frac{\partial V}{\partial X_{i\alpha}} \right|_{\{\mathbf{R}_i\}} = 0 \quad (3.211)$$

**Fig. 3.20** Illustration of the harmonic approximation for the pair potential between the lattice elements of a solid



(*equilibrium condition!*), the quadratic term. One speaks in this case of the **harmonic approximation**. The higher summands of the expansion in (3.210) are denoted as *anharmonic terms*. The *harmonic approximation* corresponds to a replacement of the interaction potential by an (*oscillator-*)parabola, which near the minimum of the potential certainly represents a good approximation (Fig. 3.20). The  $3N \times 3N$ -matrix of the atomic constants,

$$\varphi_{i\alpha}^{j\beta} \equiv \left. \frac{\partial^2 V}{\partial X_{j\beta} \partial X_{i\alpha}} \right|_{\{\mathbf{R}_i\}}, \quad (3.212)$$

determines in the framework of the *harmonic approximation* the physical properties of the crystal lattice. Thereby it means

$$-\varphi_{i\alpha}^{j\beta} \cdot u_{j\beta}$$

the force in  $\alpha$ -direction, which acts on the  $i$ -th atom (ion), if the  $j$ -th atom (ion) is displaced in  $\beta$ -direction by  $u_{j\beta}$ , while all the other particles are kept fixed in their equilibrium positions.—By reason of the neglect of *higher* terms in (3.210) it results a **linear** force law:

$$M\ddot{u}_{i\alpha} = -\frac{\partial V}{\partial u_{i\alpha}} = -\sum_{j\beta} \varphi_{i\alpha}^{j\beta} u_{j\beta}. \quad (3.213)$$

When we shift the crystal as a whole, i.e., each atom by the same amount  $\Delta \mathbf{x}$ , then there will not be any action of force, and we have therefore according to (3.213):

$$\sum_{j\beta} \varphi_{i\alpha}^{j\beta} = 0$$

A further obvious symmetry relation of the force matrix is

$$\varphi_{i\alpha}^{j\beta} = \varphi_{j\beta}^{i\alpha},$$

and in the case of translational symmetry it holds in addition:

$$\varphi_{i\alpha}^{j\beta} = \varphi_{i-j\alpha}^{0\beta}.$$

If we presume such a translational symmetry, then the following ansatz for the solution of the equation of motion (3.213) would be appropriate:

$$u_{i\alpha} = \sum_{\mathbf{q}} c_{\alpha}(\mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{R}_i - \omega t)}. \quad (3.214)$$

With the orthogonality relation

$$\delta_{ij} = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}$$

the system of the  $3N$  equations of motion (3.213) is reduced to the *eigen-value equation*

$$\omega^2 c_{\alpha}(\mathbf{q}) = \sum_{\beta} K_{\alpha\beta}(\mathbf{q}) c_{\beta}(\mathbf{q}) \quad (3.215)$$

of the transformed  $3 \times 3$ -force matrix:

$$K_{\alpha\beta}(\mathbf{q}) \equiv \frac{1}{MN} \sum_{i,j} \varphi_{i\alpha}^{j\beta} e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}. \quad (3.216)$$

This matrix is real and symmetric, and possesses therefore real eigen-values  $\omega^2$ . The *eigen-frequencies*

$$\omega = \omega_r(\mathbf{q}); \quad r = 1, 2, 3 \quad (3.217)$$

are thus also real or purely imaginary, where of course only the (positive) real frequencies are physically interesting. One denotes  $\omega_r(\mathbf{q})$  as *dispersion branch*.

As a side remark, we mention that for a *more complicated* solid with  $p$  atoms in the elementary cell, there are  $3p$  dispersion branches. Three of them are called *acoustic branches*, being characterized by  $\omega(\mathbf{q} = 0) = 0$ , while for the other  $3(p - 1)$  so-called *optical branches*  $\omega(\mathbf{q} = 0) \neq 0$ . For our purposes here, though, the restriction to  $p = 1$  suffices, which excludes optical branches.

A further side note concerns the *reciprocal lattice vector*  $\mathbf{G}$ , which is defined by

$$e^{i\mathbf{G}\cdot\mathbf{R}_i} = 1 \quad \forall i.$$

The force matrix (3.216) therefore does not change if one adds to the wave vector  $\mathbf{q}$  an arbitrary reciprocal lattice vector. This has the consequence

$$\omega_r(\mathbf{q} + \mathbf{G}) = \omega_r(\mathbf{q}) \quad \forall i$$

and allows for the restriction of the wave vectors to the *first Brillouin zone*. The reader, who is not familiar with terms like *reciprocal lattice vectors*, *Brillouin zone*, . . . , may be referred to the textbook literature on solid state physics. On the other hand, these terms are not of importance in the context of the here interesting *Statistical Physics*. We will therefore presume in the following that all wave vectors belong to the first Brillouin zone.

The *eigen-functions*, which belong to the *eigen-frequencies* (3.217),

$$c_\alpha(\mathbf{q}) \longrightarrow \varepsilon_{r\alpha}(\mathbf{q})$$

will always permit an orthonormalization:

$$\sum_\alpha \varepsilon_{r\alpha}^*(\mathbf{q}) \varepsilon_{r'\alpha}(\mathbf{q}) = \delta_{rr'} . \quad (3.218)$$

The general solution of the equation of motion (3.213) will be a linear combination of the special solutions  $\varepsilon_{r\alpha}(\mathbf{q})$ :

$$u_{i\alpha}(t) = \frac{1}{\sqrt{N}} \sum_{r=1}^3 \sum_{\mathbf{q}} Q_r(\mathbf{q}, t) \varepsilon_{r\alpha}(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_i} . \quad (3.219)$$

We have the time-factor  $e^{-i\omega_r t}$  incorporated into the so-called **normal coordinates**  $Q_r(\mathbf{q}, t)$ . For these one finds with (3.218) and with

$$\frac{1}{N} \sum_i e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}_i} = \delta_{\mathbf{q}\mathbf{q}'}$$

after the reversal of (3.219):

$$Q_r(\mathbf{q}, t) = \frac{1}{\sqrt{N}} \sum_{i,\alpha} u_{i\alpha}(t) \varepsilon_{r\alpha}^*(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}_i} . \quad (3.220)$$

One recognizes with (3.213) to (3.216) that the normal coordinates fulfill the **equation of motion of the harmonic oscillator**:

$$\ddot{Q}_r(\mathbf{q}, t) + \omega_r^2(\mathbf{q}) Q_r(\mathbf{q}, t) = 0 . \quad (3.221)$$

From the fact that the displacements  $u_{i\alpha}(t)$  must be real, we can further conclude

$$Q_r^*(\mathbf{q}, t) = Q_r(-\mathbf{q}, t); \quad \varepsilon_{r\alpha}^*(\mathbf{q}) = \varepsilon_{r\alpha}(-\mathbf{q}) , \quad (3.222)$$

so that the kinetic energy and the potential energy of the lattice take, written in normal coordinates, the following simple forms (explicit derivation as Exercise 3.3.13):

$$T = \frac{1}{2}M \sum_{\mathbf{q},r} \dot{Q}_r^*(\mathbf{q},t) \dot{Q}_r(\mathbf{q},t), \quad (3.223)$$

$$V = \frac{1}{2}M \sum_{\mathbf{q},r} \omega_r^2(\mathbf{q}) Q_r(\mathbf{q},t) Q_r^*(\mathbf{q},t) + V_0. \quad (3.224)$$

The *Lagrangian function*  $L = T - V$  provides the *generalized momentum*  $P_r(\mathbf{q},t)$ , which is *canonically conjugate* to  $Q_r(\mathbf{q},t)$  ((1.52), Vol. 2):

$$P_r(\mathbf{q},t) = \frac{\partial L}{\partial \dot{Q}_r} = M \dot{Q}_r^*(\mathbf{q},t). \quad (3.225)$$

Note that, because of (3.222), the term  $\dot{Q}_r$  appears twice in the sum in (3.223), which compensates for the factor 1/2.

The **Hamilton function** of the crystal lattice

$$H = \sum_{\mathbf{q},r} \left[ \frac{1}{2m} P_r(\mathbf{q},t) P_r^*(\mathbf{q},t) + \frac{1}{2} M \omega_r^2(\mathbf{q}) Q_r(\mathbf{q},t) Q_r^*(\mathbf{q},t) \right] \quad (3.226)$$

remarkably decomposes, in the framework of the *harmonic approximation*, into a sum of Hamilton functions of  $3N$  **independent linear harmonic oscillators**. From now on, the unimportant constant  $V_0$  is set to zero.

In the next step we have to convert, according to the *principle of correspondence* (section 3.5, Vol. 6), the classical dynamical variables to quantum-mechanical observables (operators):

$$\begin{aligned} \text{displacement } u_{i\alpha} &\longrightarrow \hat{u}_{i\alpha}, \\ \text{mechanical momentum } M\dot{u}_{i\alpha} &\longrightarrow \hat{p}_{i\alpha}. \end{aligned}$$

The following commutator relations hold for the observables of position and momentum:

$$[\hat{u}_{i\alpha}, \hat{u}_{j\beta}]_- = [\hat{p}_{i\alpha}, \hat{p}_{j\beta}]_- = 0, \quad [\hat{p}_{i\alpha}, \hat{u}_{j\beta}]_- = \frac{\hbar}{i} \delta_{ij} \delta_{\alpha\beta}. \quad (3.227)$$

We show in Exercise 3.3.14, how these relations transfer to the *quantized* normal coordinates and their canonically conjugate momenta:

$$[\hat{Q}_r(\mathbf{q}), \hat{Q}_{r'}(\mathbf{q})]_- = [\hat{P}_r(\mathbf{q}), \hat{P}_{r'}(\mathbf{q})]_- = 0, \quad [\hat{P}_r(\mathbf{q}), \hat{Q}_{r'}(\mathbf{q})]_- = \frac{\hbar}{i} \delta_{rr'} \delta_{\mathbf{q}\mathbf{q}'}. \quad (3.228)$$

The further procedure is now carried out as for the *harmonic oscillator* in section 4.4 of Vol. 6. We define *creation and annihilation operators*  $b_{\mathbf{q}r}^+, b_{\mathbf{q}r}$  ((4.127), (4.128), Vol.6):

$$\widehat{Q}_r(\mathbf{q}) = \sqrt{\frac{\hbar}{2\omega_r(\mathbf{q})M}} (b_{\mathbf{q}r} + b_{-\mathbf{q}r}^+) = \widehat{Q}_r^+(-\mathbf{q}), \quad (3.229)$$

$$\widehat{P}_r(\mathbf{q}) = -i\sqrt{\frac{1}{2}M\hbar\omega_r(\mathbf{q})} (b_{\mathbf{q}r} - b_{-\mathbf{q}r}^+) = \widehat{P}_r^+(-\mathbf{q}). \quad (3.230)$$

The reversal reads:

$$b_{\mathbf{q}r} = \frac{1}{\sqrt{2\hbar}} \left( \sqrt{M\omega_r(\mathbf{q})} \widehat{Q}_r(\mathbf{q}) + \frac{i}{\sqrt{M\omega_r(\mathbf{q})}} \widehat{P}_r(\mathbf{q}) \right), \quad (3.231)$$

$$b_{\mathbf{q}r}^+ = \frac{1}{\sqrt{2\hbar}} \left( \sqrt{M\omega_r(\mathbf{q})} \widehat{Q}_r(-\mathbf{q}) - \frac{i}{\sqrt{M\omega_r(\mathbf{q})}} \widehat{P}_r(-\mathbf{q}) \right). \quad (3.232)$$

One recognizes, by means of (3.228), that these are Bose operators:

$$[b_{\mathbf{q}r}, b_{\mathbf{q}'r'}]_- = [b_{\mathbf{q}r}^+, b_{\mathbf{q}'r'}^+]_- = 0, \quad (3.233)$$

$$[b_{\mathbf{q}r}, b_{\mathbf{q}'r'}^+]_- = \delta_{\mathbf{q}\mathbf{q}'} \delta_{rr'}. \quad (3.234)$$

The **Hamilton operator**, which results from (3.226) and (3.229) to (3.234),

$$H = \sum_{\mathbf{q},r} \hbar\omega_r(\mathbf{q}) \left( b_{\mathbf{q}r}^+ b_{\mathbf{q}r} + \frac{1}{2} \right), \quad (3.235)$$

corresponds to the operator of  $3N$  uncoupled linear harmonic oscillators. The interpretation is very similar to that we used for the photon gas (Sect. 3.3.6):

$b_{\mathbf{q}r}^+$  : creation operator of a *phonon*,

$b_{\mathbf{q}r}$  : annihilation operator of a *phonon*,

$\hbar\omega_r(\mathbf{q})$  : energy of a *phonon*.

Phonons are bosons! The physics of the lattice vibrations is, in the framework of the *harmonic approximation*, equivalent to the physics of an ideal Bose gas. It is determined by the distribution  $\{n_{\mathbf{q}r}\}$  of the phonon-occupation numbers. *Phonons* can in principle be created in arbitrary quantities. Therefore their chemical potential is also zero, as that of the *photons* (see (3.189)).

We still want to add a remark on the time-dependence of the *quantized normal coordinates*

$$\widehat{Q}_r(\mathbf{q}, t) = \widehat{Q}_r(\mathbf{q}) e^{-i\omega_r(\mathbf{q})t}.$$

This time-dependence transfers to  $b_{\mathbf{q}r}$ :

$$b_{\mathbf{q}r}(t) = b_{\mathbf{q}r} e^{-i\omega_r(\mathbf{q})t} . \quad (3.236)$$

That is now tantamount to the *Heisenberg representation* ((3.193), Vol.6),

$$b_{\mathbf{q}r}(t) = \exp\left(\frac{i}{\hbar}Ht\right) b_{\mathbf{q}r} \exp\left(-\frac{i}{\hbar}Ht\right) ,$$

and also to the resulting equation of motion:

$$i\hbar \frac{\partial}{\partial t} b_{\mathbf{q}r}(t) = [b_{\mathbf{q}r}, H]_-(t) \stackrel{(3.235)}{=} \hbar\omega_r(\mathbf{q}) b_{\mathbf{q}r}(t) .$$

Integration yields indeed with  $b_{\mathbf{q}r}(0) = b_{\mathbf{q}r}$  the Eq. (3.236). The transformation of the *lattice dynamics* to the free *phonon gas* thus seems to be consistent in every respect.

**(B) Phonon Statistics** We will now deal with the thermodynamic properties of the *phonon gas*. We have seen that the vibrational state of a crystal lattice is fixed by the phonon distribution over the dispersion branches  $\hbar\omega_r(\mathbf{q})$ . The spectrum of these dispersion branches ultimately depends of course on the special lattice structure, being therefore differing from solid to solid. When we intend to calculate, as, e.g., for the photon gas in the last subsection, the *grand-canonical potential* according to (3.21)

$$\Omega(T, V) = k_B T \sum_{\mathbf{q}, r} \ln \left[ 1 - \exp(-\beta \hbar\omega_r(\mathbf{q})) \right] = k_B T \int \mathbb{E} D(E) \ln(1 - e^{-\beta E}) , \quad (3.237)$$

then we obviously have to know the *density of states*  $D(E)$  of the phonon gas, which, like the one-particle energies  $\hbar\omega_r(\mathbf{q})$ , will be different for different lattice types. In order to get general statements, only those are interesting for us, we will have to accept some simplifications.

The harmonic approximation is basically a low-temperature approximation. On the other hand, at low temperatures the thermal excitations of oscillations of low frequencies are the most important ones. This corresponds to **long-wave** eigenoscillations (*acoustic waves*). For these waves the atomic structure of the solid is not so decisive, so that approximations appear reasonable. The solid can be considered as an elastic continuum. In the expression

$$D_r(E) dE = \frac{1}{\Delta^3 q} \int_{\substack{\text{shell} \\ (\hbar\omega_r, \hbar\omega_r + dE)}} d^3 q \quad (3.238)$$



for the density of states, with respect to the  $r$ -th dispersion branch,  $\Delta^3 q$  is the *grid (raster) volume* ( $\Delta^3 q = (2\pi)^3/V$ ) of the  $\mathbf{q}$ -space, caused by the *boundary conditions* which were already used several times. Exactly one state is located in this grid volume. When we denote by

$$\mathbf{v}_g^{(r)}(E) = \frac{1}{\hbar} \nabla_{\mathbf{q}} E \quad (E = \hbar\omega_r(\mathbf{q}))$$

the *group velocity* ((2.44), Vol. 6), then it holds for the distance  $dE$  of the two surfaces  $E = \text{const}$  and  $E + dE = \text{const}$  in the  $\mathbf{q}$ -space:

$$dE = |d\mathbf{q} \cdot \nabla_{\mathbf{q}} E| = dq_{\perp} |\nabla_{\mathbf{q}} E| = \hbar v_g^{(r)}(E) dq_{\perp} .$$

If  $df_E$  denotes an element of the surface  $E = \text{const}$ , then it follows for the volume-element of the shell, over which the integration is performed in (3.238):

$$d^3 q = df_E dq_{\perp} = \frac{1}{\hbar v_g^{(r)}(E)} df_E dE .$$

The following representation results for the density of states, as an alternative to (3.238):

$$D_r(E) = \frac{V}{(2\pi)^3} \int_{E=\text{const}} \frac{f_E}{\hbar v_g^{(r)}(E)} . \quad (3.239)$$

The

### Debye model

uses two simplifying assumptions:

1. The wave vector summation over the first Brillouin zone is replaced by a corresponding one over a sphere of the same volume. *The same volume* means that the sphere contains the same number of states as the Brillouin zone. The latter incorporates exactly  $N$  states, where  $N$  is the number of atoms, by which the solid is composed.
2. The group velocities (*sound velocities*) are assumed to be isotropic,

$$\mathbf{v}_g^{(r)}(E = \hbar\omega_r(\mathbf{q})) = v_g^{(r)} \frac{\mathbf{q}}{q} ,$$

what is equivalent to

$$\hbar\omega_r(\mathbf{q}) = \hbar v_g^{(r)} q . \quad (3.240)$$

With these two assumptions, (3.239) can easily be evaluated:

$$D_r(E) = \frac{V}{(2\pi)^3} \frac{1}{\hbar v_g^{(r)}} 4\pi q^2(E) = \frac{V}{2\pi^2} \frac{1}{(\hbar v_g^{(r)})^3} E^2 .$$

The three possibilities  $r = 1, 2, 3$  correspond to the three independent polarization directions of the lattice waves which one usually chooses as longitudinal and transversal to the direction  $\mathbf{q}/q$  of the wave propagation. The two transversal dispersions are in general degenerate:

$$v_g^{(r)} \rightarrow \begin{cases} v_l: & r = 1 , \\ v_t: & r = 2, 3 . \end{cases}$$

For each dispersion branch,  $\mathbf{q}$  runs through the  $N$  states of the first Brillouin zone. Therefore there are a total of  $3N$  states. Because of  $D_r(E) \sim E^2$ , there must thus exist an upper energy limit  $E_D = \hbar\omega_D$ . With the abbreviation

$$\frac{3}{\hat{v}^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3} \quad (3.241)$$

the following condition is to be fulfilled,

$$3N = \int_0^{\hbar\omega_D} (D_l(E) + 2D_t(E)) dE = \frac{3V}{2\pi^2 \hbar^3 \hat{v}^3} \frac{1}{3} (\hbar\omega_D)^3 ,$$

which fixes the *limiting frequency*  $\omega_D$ :

### Debye frequency

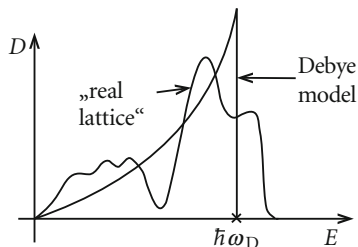
$$\omega_D = \left( 6\pi^2 \hat{v}^3 \frac{N}{V} \right)^{1/3} . \quad (3.242)$$

In the framework of the *Debye model*, the density of states of the phonon gas can therewith finally be written as follows (Fig. 3.21):

$$D(E) = \begin{cases} \frac{9N}{\hbar^3 \omega_D^3} E^2 & \text{for } 0 \leq E \leq \hbar\omega_D , \\ 0 & \text{otherwise .} \end{cases} \quad (3.243)$$

The only lattice-specific quantity is the Debye frequency  $\omega_D$ . The Debye model is therewith surely too simple to reproduce every detail of the physical properties of a particular solid. The quantum-statistical evaluation of the Debye model features, however, some spectacular successes with respect to general solid state

**Fig. 3.21** Comparison of the density of states of a real solid with that of the simplifying Debye model



properties. The *classical equipartition theorem* (1.113), e.g., argues for the averages of the kinetic and the potential energy of a system described by the Hamilton function (3.226):

$$\langle T \rangle = \langle V \rangle = \frac{3}{2} N k_B T .$$

This means an *internal energy*  $U = 3Nk_B T$  and therewith a temperature-independent heat capacity:

$$C_V^{\text{cl}} = 3Nk_B .$$

This agrees indeed at high temperatures with the experimental observation, being, however, in blatant contradiction to it at low temperatures. It is an outstanding success of the Quantum Statistics, similarly to the interpretation of the linear low-temperature behavior of the electronic contribution to the heat capacity ((3.77):  $C_V = \gamma T$ ), to be able to explain, via the picture of a gas of phonons, the  $T^3$ -part of the heat capacity of the crystal lattice. That shall be reproduced in the following.

We use (3.237) for the calculation of the grand-canonical potential  $\Omega(T, V)$  of the phonon gas, which, because of  $\mu = 0$ , is identical with the free energy  $F(T, V)$ . Insertion of the *Debye density of states* (3.243) leads at first to:

$$\begin{aligned} \Omega(T, V) &= \frac{9N}{(\hbar\omega_D)^3} k_B T \int_0^{\hbar\omega_D} dE E^2 \ln(1 - e^{-\beta E}) \\ &= \frac{9N}{(\hbar\omega_D)^3} (k_B T)^4 \int_0^{\beta\hbar\omega_D} dx x^2 \ln(1 - e^{-x}) . \end{aligned}$$

For abbreviation one defines the **Debye temperature**  $T_D$ :

$$k_B T_D \equiv \hbar\omega_D . \quad (3.244)$$

In  $\Omega(T, V)$ , as well as in the other still to be discussed thermodynamic potentials, there appear two typical integrals,

$$\widehat{D}(y) = \int_0^y dx \frac{x^3}{e^x - 1}, \quad (3.245)$$

$$J(y) = \int_0^y dx x^2 \ln(1 - e^{-x}) = \frac{1}{3} \left[ y^3 \ln(1 - e^{-y}) - \widehat{D}(y) \right], \quad (3.246)$$

which cannot be integrated in a closed form, but which can further be estimated in the limits  $y \gg 1$  and  $y \ll 1$ :

$$y \gg 1: \quad \widehat{D}(y) \approx \int_0^\infty dx \frac{x^3}{e^x - 1} \stackrel{(3.195)}{=} \Gamma(4)\zeta(4) = \frac{\pi^4}{15}, \quad (3.247)$$

$$\begin{aligned} y \ll 1: \quad \widehat{D}(y) &\approx \int_0^y dx \frac{x^2}{1 + (1/2)x + (1/6)x^2} \\ &\approx \int_0^y dx x^2 \left[ 1 - \left( \frac{1}{2}x + \frac{1}{6}x^2 \right) + \left( \frac{1}{2}x + \frac{1}{6}x^2 \right)^2 \right] \\ &\approx \frac{1}{3}y^3 - \frac{1}{8}y^4 + \frac{1}{60}y^5 + \mathcal{O}(y^6). \end{aligned} \quad (3.248)$$

The **grand-canonical potential** of the phonon gas therefore has the following form:

$$\Omega(T, V) = \frac{9N}{(\hbar\omega_D)^3} (k_B T)^4 J\left(\frac{T_D}{T}\right). \quad (3.249)$$

From this we obtain the **entropy** by differentiation with respect to the temperature:

$$S(T, V) = - \left( \frac{\partial \Omega}{\partial T} \right)_V = - \frac{9Nk_B}{(\hbar\omega_D)^3} (k_B T)^3 \left[ J\left(\frac{T_D}{T}\right) - \widehat{D}\left(\frac{T_D}{T}\right) \right]. \quad (3.250)$$

Here we have used:

$$\frac{d}{dy} J(y) = \frac{1}{y} \left( 3J(y) + \widehat{D}(y) \right).$$

Without the (unimportant) zero-point energy of the  $3N$  independent oscillators of the model-Hamilton operator (3.235) one finds as **internal energy** of the phonon

gas:

$$U(T, V) = F + TS = \Omega + TS = \frac{9N}{(\hbar\omega_D)^3} (k_B T)^4 \widehat{D}\left(\frac{T_D}{T}\right). \quad (3.251)$$

What now remains is the **heat capacity**, which we have already discussed once as Exercise 2.3.13 on the basis of the *canonical ensemble*. With the following relation, which one easily verifies, e.g., by means of integration by parts,

$$4\widehat{D}(y) - y \frac{d}{dy} \widehat{D}(y) = \int_0^y dx \frac{x^4 e^x}{(e^x - 1)^2}$$

one finds via (3.250):

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = 9Nk_B \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}. \quad (3.252)$$

It appears to be reasonable, to investigate the internal energy and the heat capacity in the limiting regions of very high and very low temperatures. We begin with the low-temperature region:

$$T \ll T_D: \quad \widehat{D}\left(\frac{T_D}{T}\right) \approx \widehat{D}(\infty) \stackrel{(3.247)}{=} \frac{\pi^4}{15}.$$

It follows for the internal energy in this limit:

$$U(T, V) \approx \frac{3}{5} \pi^4 Nk_B T \left( \frac{T}{T_D} \right)^3. \quad (3.253)$$

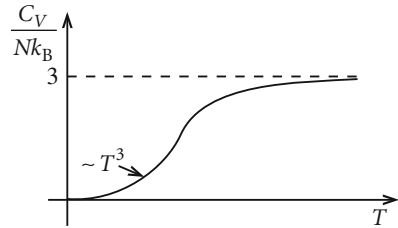
We have derived therewith for the heat capacity the famous, but *classically not understandable*

**Debye's  $T^3$ -law:**

$$C_V = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{T_D} \right)^3. \quad (3.254)$$

As already mentioned, this result must be considered as a spectacular success of the Quantum Statistics, because it describes essentially correctly the low-temperature behavior (Fig. 3.22). Minor deviations from the experimental data are to be ascribed to the actually rather crudely approximated density of states (3.243). In particular, the third law of Thermodynamics is fulfilled.

**Fig. 3.22** Schematic temperature behavior of the heat capacity of the free phonon gas



For the limiting case of high temperatures  $T \gg T_D$  we can use the expansion (3.248):

$$\widehat{D}\left(\frac{T_D}{T}\right) \approx \frac{1}{3}\left(\frac{T_D}{T}\right)^3 - \frac{1}{8}\left(\frac{T_D}{T}\right)^4 + \frac{1}{60}\left(\frac{T_D}{T}\right)^5.$$

Inserted into (3.251) it then results the following expression for the internal energy,

$$U(T, V) \approx 3Nk_B T \left[ 1 - \frac{3}{8} \frac{T_D}{T} + \frac{1}{20} \left(\frac{T_D}{T}\right)^2 \right], \quad (3.255)$$

and for the heat capacity:

$$C_V = 3Nk_B \left[ 1 - \frac{1}{20} \left(\frac{T_D}{T}\right)^2 + \dots \right]. \quad (3.256)$$

For sufficiently high temperatures the classical result  $C_V^{\text{cl}} = 3Nk_B$  is reproduced (Fig. 3.22). On the other hand, for high temperatures the *harmonic approximation* (3.210), which forms the basis of the results of this subsection, becomes more than questionable. The amplitudes of the oscillations of the atoms around their equilibrium positions grow very large. The solid expands, in order to finally even melt. The picture of the *free* phonon gas breaks down. A first potential improvement might consist in the introduction of *interactions* between the phonons, which, however, would in general have the consequence that the model is no longer rigorously solvable. Here we will not further follow this train of thought.

### 3.3.8 Exercises

#### Exercise 3.3.1

Let the particle density  $n$  of an ideal Bose gas be given. Show that for  $T \rightarrow +\infty$  the chemical potential  $\mu$  must tend to  $-\infty$ .

**Exercise 3.3.2**

Calculate the entropy  $S$  of an ideal Bose gas. Express  $S(T, V, \mu)$  by the average occupation number  $\langle \hat{n}_r \rangle$ . Check the behavior of the entropy for  $T \rightarrow 0$ , and that for the case of a fixed number  $N$  of bosons as well as for the case  $N(T) \xrightarrow{T \rightarrow 0} 0$  (magnons, phonons, photons). Compare the result with that of the ideal Fermi gas.

**Exercise 3.3.3**

When treating the ideal Bose gas one frequently has to work with the functions

$$g_\alpha(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\alpha} .$$

Verify the following representation,

$$g_\alpha(z) = \frac{1}{\Gamma(\alpha)} \int_0^{\infty} \frac{x^{\alpha-1}}{z^{-1}e^x - 1} dx ,$$

where  $\Gamma(\alpha)$  is the *Gamma-Funktion*,

$$\Gamma(\alpha) = \int_0^{\infty} t^{\alpha-1} e^{-t} dt .$$

**Exercise 3.3.4**

Show that for a  $d$ -dimensional quantum gas with one-particle energies  $\varepsilon(\mathbf{k}) = \hbar^2 k^2 / 2m$  the following relation exists between pressure  $p$ , volume  $V$ , and internal energy  $U$ :

$$pV = \frac{2}{d} U$$

The relation is valid for bosons as well as for fermions, where, however, the bosons do not be in the condensate ( $z < 1$ ). Hint: Use the  $d$ -dimensional density of states from Exercise 3.1.5.

**Exercise 3.3.5**

Consider an ideal quantum gas of bosons of the mass zero:

$$\varepsilon(\mathbf{k}) \longrightarrow \hbar c k .$$

1. Calculate the grand-canonical potential

$$\Omega = \Omega(T, V, z) .$$

- Determine the pressure  $p$ , the particle density  $n$ , and the internal energy  $U$  as functions of  $T$ ,  $V$  and  $z$ .
- Show that it holds in the *thermodynamic limit* ( $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $n \rightarrow \text{finite}$ )

$$U = 3pV.$$

- Determine the critical temperature  $T_C$  and the critical density  $n_C$  of the Bose-Einstein condensation.
- How does the number  $N_0$  of bosons in the ground state depend on the temperature in the *region of condensation* ( $z = 1$ )?
- Derive the *phase-boundary curve*  $p_C = f(n_C)$  of the  $p$ -( $1/n$ )-diagram.

### Exercise 3.3.6

Consider a **two**-dimensional ideal Bose gas (particle number  $N$ , 'volume'  $V = L^2$ ) with one-particle energies

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

- Calculate the grand-canonical potential.
- Represent the particle density  $n$  as a function of  $T$ ,  $V$  and  $z$ .
- Give reasons why a Bose-Einstein condensation can not take place.

### Exercise 3.3.7

For a two-dimensional ideal Bose gas with a **constant particle number** and with one-particle energies  $\varepsilon(\mathbf{k}) = \hbar^2 k^2 / 2m$  calculate the chemical potential  $\mu$  as a function of the particle density  $n$  and the temperature  $T$ !

### Exercise 3.3.8

Consider a **non**-degenerate ideal Bose gas (*classical limit*,  $z \ll 1$ ) with the one-particle energies

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}.$$

and with fixed particle number  $N$ . Show that the thermal equation of state can be written as *virial expansion* (cf. (3.156)):

$$pV = Nk_B T \left( 1 - \frac{1}{2^{5/2}} z^{(0)} + \left( \frac{1}{8} - \frac{2}{3^{5/2}} \right) (z^{(0)})^2 + \dots \right),$$

$$z^{(0)} = \frac{n\lambda^3}{2S + 1}$$

### Exercise 3.3.9

For a non-degenerate ideal Bose gas of  $N$  particles, each of the mass zero (see Exercise 3.3.5), in the volume  $V$  write the thermal equation of state as a *virial*



expansion with respect to the particle density

$$pV = Nk_B T (1 + \gamma_1 z^{(0)} + \gamma_2 (z^{(0)})^2 + \dots) ,$$

$$z^{(0)} = \frac{\pi^2 (\beta \hbar c)^3}{2S + 1} n .$$

Determine the coefficients  $\gamma_1$  and  $\gamma_2$ .

### Exercise 3.3.10

Consider a **two**-dimensional ideal quantum gas of bosons of the mass zero:

$$\varepsilon(\mathbf{k}) = \hbar c k .$$

1. Calculate the grand-canonical potential  $\Omega(T, V, z)$ .
2. Represent the particle density as a function of  $T, V$  and  $z$ .
3. Investigate, whether a Bose-Einstein condensation can exist. Compare it with part 3. of Exercise 3.3.6.

### Exercise 3.3.11

Electromagnetic waves within a big box of the volume  $V$  are at the temperature  $T$  at thermal equilibrium with the walls. In one of the box walls there is a hole of the area  $dS$ , which may be so small that the equilibrium inside is not disturbed. Calculate the spectral intensity  $I_\lambda(T, \vartheta)$ , i.e., the energy which per time unit and per area unit is transported out of the box with wavelengths between  $\lambda$  and  $\lambda + d\lambda$  into the solid angle  $d\Omega$ , which builds an angle  $\vartheta$  with the surface normal of  $dS$  (Fig. 3.23).

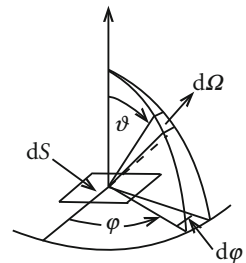
### Exercise 3.3.12

1. Show that the spectral energy density  $\hat{\varepsilon}(\omega, T)$  of the electromagnetic hollow-radiation exhibits a maximum, which is determined by the transcendental equation

$$(3 - x)e^x = 3$$

with  $x = \beta \hbar \omega$ .

**Fig. 3.23** Solid-angle dependence of the spectral intensity of electromagnetic radiation



2. How are the frequencies  $\omega_1$  and  $\omega_2$  related to each other, for which the spectral energy densities of two different hollows of the temperatures  $T_1$  and  $T_2$  become maximal (*Wien's displacement law*)?

**Exercise 3.3.13**

Show that the kinetic energy and the potential energy of a crystal lattice can be expressed as follows by *normal coordinates*  $Q_r(\mathbf{q}, t)$ :

$$T = \frac{1}{2}M \sum_{\mathbf{q}, r} \dot{Q}_r^*(\mathbf{q}, t) \dot{Q}_r(\mathbf{q}, t) ,$$

$$V = V_0 + \frac{1}{2}M \sum_{\mathbf{q}, r} \omega_r^2(\mathbf{q}) Q_r(\mathbf{q}, t) Q_r^*(\mathbf{q}, t) .$$

Use the transformation formulas (3.219) and (3.220).

**Exercise 3.3.14**

Prove the fundamental commutator relations of the normal coordinates  $\widehat{Q}_r(\mathbf{q}, t)$  and their canonically conjugate momenta  $\widehat{P}_r(\mathbf{q}, t)$ :

$$[\widehat{Q}_r(\mathbf{q}, t), \widehat{Q}_{r'}(\mathbf{q}, t)]_- = [\widehat{P}_r(\mathbf{q}, t), \widehat{P}_{r'}(\mathbf{q}, t)]_- = 0 ,$$

$$[\widehat{P}_r(\mathbf{q}, t), \widehat{Q}_{r'}(\mathbf{q}, t)]_- = \frac{\hbar}{i} \delta_{rr'} \delta_{\mathbf{q}\mathbf{q}'} .$$

**Exercise 3.3.15**

For the heat capacity  $C_V$  of the lattice vibrations in good approximation for low temperatures the *Debye's  $T^3$ -law* (3.254) holds. Calculate in the framework of the Debye model (3.243) the leading temperature corrections for the internal energy  $U(T, V)$  and also for the heat capacity  $C_V$ !

**Exercise 3.3.16**

Calculate for the Debye model the average phonon number  $\langle N_p \rangle$  at the temperature  $T > 0$ . Evaluate the analytic result for low and for high temperatures!

## 3.4 Self-Examination Questions

### To Section 3.1

1. What are identical particles?
2. What does the *principle of indistinguishability* imply?
3. How does a general  $N$ -particle state look like in the case of identical particles?
4. What is implied by the spin-statistics theorem?
5. What are *bosons*, what are *fermions*?

6. How does one recognize the *Pauli principle* in the *Slater determinant*, which is valid for fermions?
7. What does one understand by a *Fock state*?
8. Which occupation numbers  $n_\alpha$  of the one-particle states  $|\varphi_\alpha\rangle$  are available for bosons, and which ones for fermions?
9. How do the *fundamental commutation rules* between creation and annihilation operators read for bosons and for fermions, respectively?
10. How are the *occupation number operator* and the *particle number operator* defined?
11. How does the Hamilton operator of the ideal quantum gases read in second quantization. Which are its eigen-states?
12. Why are the grand-canonical partition functions of bosons and fermions different?
13. How do the *average occupation numbers*  $\langle \hat{n}_r \rangle^{(\pm)}$  of the one-particle states look like for bosons and fermions?
14. Which values can the chemical potential  $\mu$  take in the case of fermions, and which in the case of bosons?
15. What are the problems that arise at  $T = 0$  for the average bosonic occupation number?
16. How does the internal energy of the ideal Bose (Fermi) gas depend on the average occupation number?

## To Section 3.2

1. According to which rule and under which preconditions can sums over one-particle energies ( $\sum_r \dots$ ) be converted into integrals?
2. How are the functions  $f_{5/2}(z)$ ,  $f_{3/2}(z)$  defined? What is the relation between them?
3. By which relations for the pressure  $p$  and the particle density  $n$  is the thermal equation of state of the ideal Fermi gas fixed?
4. How does the caloric equation of state of the ideal Fermi gas read?
5. Which connection exists between  $U$  and  $pV$ ? How does the corresponding relation look like for the classical ideal gas?
6. What does one understand by, respectively, a *degenerate* and a *non-degenerate* Fermi gas?
7. When is the *classical limiting case* realized?
8. How does the thermal equation of state of the ideal Fermi gas read in the classical limit?
9. Which characteristic energy-dependence does the density of states  $D(E)$  of the ideal quantum gases exhibit ( $\varepsilon(k) \sim k^2$ )?
10. What is the probability that a state of the energy  $E$  is occupied at the temperature  $T$  in an ideal Fermi gas?

11. Which quantity specifies the density of those states which are occupied by an ideal Fermi gas at the temperature  $T$ ?
12. Which shape does the Fermi-Dirac function  $f_-(E)$  at  $T = 0$  have? What happens at  $T > 0$ ?
13. What is the relation between the Fermi energy  $E_F$  and the chemical potential  $\mu$ ?
14. How are the Fermi wavevector  $k_F$  and the Fermi energy  $E_F$  with the particle density  $n$  related to each other?
15. What is the order of magnitude of the Fermi temperature of simple metals?
16. Which types of integrals can be conveniently evaluated by the Sommerfeld expansion?
17. Of which form and of which order of magnitude is the first temperature correction for the chemical potential  $\mu$  of an ideal Fermi gas (metal electrons!) compared to the  $T = 0$ -value  $E_F$ ?
18. How does the internal energy of the Fermi gas change with the temperature?
19. What is the characteristic temperature behavior of the heat capacity  $C_V$ ? How can this be physically interpreted?
20. How is the coefficient  $\gamma$  of the heat capacity  $C_V$  related to the density of states of the Fermi gas?
21. How can the *zero-point pressure* of the ideal Fermi gas be explained?
22. What is the form of the entropy of the Fermi gas? Of which kind is the contribution of the *holes* (unoccupied one-particle states), and of which kind is the contribution of the *particles*?
23. Why should the susceptibility of a system of particles with permanent magnetic moments actually exhibit a distinct temperature-dependence? What is observed in this respect for quasi-free conduction electrons?
24. How does the density of states of the ideal Fermi gas change in the magnetic field, if it couples only to the spin?
25. What is the order of magnitude of the energy  $\mu_B B$ , when the field  $B$  amounts to about 10 Tesla?
26. How does the *Pauli susceptibility*  $\chi_p(T = 0)$  depend on the density of states  $D(E_F)$  at the Fermi edge?
27. Why is  $\chi_p(T)$  only very weakly temperature-dependent and relatively very small?
28. Of which three parts is the isothermal susceptibility of the free electron gas composed?
29. How is the *cyclotron frequency*  $\omega_c$  defined?
30. Which well-known eigen-value equation can the time-independent Schrödinger equation of an electron in the homogeneous magnetic field be traced back to?
31. What is a *Landau level*?
32. Which *quantization* does the motion of an electron experience in the homogeneous magnetic field?
33. Which typical dependence does the degree of degeneracy of the Landau levels exhibit? Does it depend on the *Landau-quantum number*  $n$ ?

34. How do the states order within the Fermi sphere after switching on a homogeneous magnetic field in  $z$ -direction?
35. Which measuring possibility is given by the *de Haas-van Alphen effect*?
36. For the *magnetization work* of a thermodynamic system one writes sometimes  $B_0 dm$  and sometimes  $-mdB_0$ . Can you comment on this seeming discrepancy?
37. Which thermodynamic connection exists between *magnetization* and *grand-canonical potential*?
38. How does *Landau diamagnetism* arise?
39. In which relation do the susceptibilities of the Pauli paramagnetism and the Landau diamagnetism stand to each other?
40. What is the distinguishing mark of the *de Haas-van Alphen effect*?
41. Which characteristic dependencies show the period and the amplitude of the oscillation of the isothermal susceptibility of the free electron gas?

### To Section 3.3

1. Which range of values is available for the chemical potential of the ideal Bose gas, if the lowest one-particle energy coincides with the energy-zero?
2. Which difficulty can arise for the ideal Bose gas, when one wants to replace for macroscopic systems sums by integrals in the thermodynamic relations? How is the problem solved? Why did we not meet this problem for the ideal Fermi gas?
3. In what respect does the grand-canonical potential of the ideal Bose gas differ from that of the ideal Fermi gas?
4. How are the functions  $g_{5/2}(z)$ ,  $g_{3/2}(z)$  defined?
5. What is the relation between the occupation of the lowest energy level and the Bose-Einstein condensation?
6. What is the relation between  $U$  and  $pV$  for the ideal Bose gas? Is it formally identical to that of the classical ideal gas and that of the ideal Fermi gas, respectively?
7. What is the explanation for the fact that for  $z \ll 1$  the differences between Bose, Fermi, and classical Boltzmann Statistics become unimportant?
8. For which particle densities and temperatures is the *classical limiting case* of the ideal Bose gas realized?
9. How does the thermal equation of state of the ideal Bose gas read in the *classical limit*? How does it differ from that of the ideal Fermi gas?
10. When does one speak of a *degenerate* Bose gas?
11. Which condition determines the beginning of the Bose-Einstein condensation?
12. Which value does the fugacity  $z$  take in the *region of condensation* for  $V \rightarrow \infty$ ?
13. Which temperature-dependence does the number  $N$  of bosons, which are condensed in the lowest energy level, show?
14. One says that below the critical temperature  $T_C$  the ideal Bose gas presents itself as a mixture of two phases. What does that mean?

15. Which qualitative behavior do the isotherms of the  $p$ - $(1/n)$ -diagram exhibit for the ideal Bose gas?
16. How does the pressure of the ideal Bose gas depend in the *region of condensation* on the particle density?
17. Which *densities* do the *condensate* and the *gaseous phase* possess in the *region of condensation*, where they are at equilibrium with each other?
18. How does the entropy behave at the absolute zero? Is the third law of Thermodynamics violated as in the case of the classical ideal gas?
19. What is the qualitative behavior of the heat capacity of the ideal Bose gas as a function of the temperature?
20. Which value does the heat capacity take at the critical temperature  $T_C$ ? How does it behave for  $T \rightarrow \infty$ ?
21. How does the chemical potential  $\mu$  behave for  $T \rightarrow \infty$ ? Towards which limiting value does the fugacity tend for  $T \rightarrow \infty$ ?
22. Why is the chemical potential  $\mu$  of photons, phonons, and magnons equal to zero?
23. Which characteristic properties does the photon possess?
24. Which possibilities of orientation does the photon spin possess?
25. Which energy-dependence does the density of states of the photon gas have?
26. Which temperature-dependence does the pressure of the photon gas have?
27. How does the average photon number depend on the temperature? What happens for  $T \rightarrow 0$ ?
28. What does the Stefan-Boltzmann law tell us for the photon gas?
29. What is the relation between pressure and energy density of the electromagnetic radiation?
30. Which physical quantity does Planck's radiation formula refer to?
31. What does one understand by the *harmonic approximation* in connection with the lattice vibrations of a solid?
32. What are *dispersion branches*?
33. Which structure has the (classical) Hamilton function of the crystal lattice in the harmonic approximation after transformation to *normal coordinates*?
34. What is a phonon?
35. How can one recognize that phonons are bosons?
36. How is the vibration state of a crystal lattice fixed?
37. For which temperature region does the *harmonic approximation* represent a reliable approach?
38. At which simplifying assumptions does the Debye model start?
39. By what is the *Debye frequency*  $\omega_D$  determined?
40. What an energy-dependence does the density of states of the phonon gas have in the Debye model?
41. What has *classically* to be expected as heat capacity of the phonon gas?
42. What does one understand by the *Debye temperature*  $T_D$ ?
43. Which temperature-dependencies do appear for the internal energy of the phonon gas in the regions  $T \gg T_D$  and  $T \ll T_D$ ?

44. How does the heat capacity of the phonon gas behave for low temperatures? Is the third law of Thermodynamics fulfilled?
45. Which value does the heat capacity take for very high temperatures?

# Chapter 4

## Phase Transitions



The question regarding the reasons and the mechanisms of the *phase transitions* is one of the oldest problems of physics. Since the commencement of the study of natural philosophy, scientists have been thinking about why the four different elements *fire, water, earth, air* do exist and under which conditions these *manifestations of matter* can convert into each other. We have dealt with the theory of phase transitions, which is still highly topical and represents an important region of application of *Statistical Physics*, in Vol. 5 of this basic course in Theoretical Physics, as far as it was possible to do within the framework of the classical phenomenological Thermodynamics. In Sect. 4.1, we will gather once more in a very short and compact form the most important results and concepts, and we will formulate some amendments which will be important for the following, in order to then look in Sect. 4.2 more closely to the *critical phenomena*, which are observed in connection with the so-called *second-order phase transition*.

Perhaps one can denote as the *hour of birth* of the modern era theory of phase transitions the publication of the dissertation thesis of J.D. van der Waals (1873), which comprises a first qualitative interpretation of this phenomenon for the example of the real gas. P. Weiss (1907) succeeded already before the development of the Quantum Theory in a *modeling* of the phase transition of a ferromagnet, although in the case of ferromagnetism, it is actually a purely quantum-mechanical phenomenon (*Bohr-van Leeuwen theorem*, Exercise 1.4.9, part 2.). The *Weiss-ferromagnet* turns out to be thermodynamically equivalent to the *van der Waals-gas*, both of which belong to the so-called **classical theories** of phase transition. To this class it also belongs the *Ornstein-Zernike theory*, by which one can understand the phenomenon of the *critical opalescence* in the light scattering, as well as the general *Landau theory*. These *classical theories* are all discussed in Sect. 4.3.

The first non-trivial model of a ferromagnet with the inclusion of microscopic interactions is ascribed to E. Ising, and is consequently named after him. It is defined



by the Hamilton function,

$$\tilde{H} = -J \sum_{i,j} S_i S_j - \mu B_0 \sum_i S_i \quad (B_0 = \mu_0 H ; \quad H: \text{magnetic field}) , \quad (4.1)$$

for which we use here, in order to distinguish it from the magnetic field  $H$ , as an exception the notation  $\tilde{H}$ .  $\tilde{H}$  is the model-Hamiltonian of a system of magnetic moments  $\mu_i$ , which reside at certain lattice sites of a solid and interact with each other. These moments are simulated by classical one-dimensional *spins*  $S_i$  ( $\mu_i = \mu S_i$ ) with two possibilities of orientation which are antiparallel to each other ( $S_i = \pm 1 \quad \forall i$ ). The interaction is mediated by  $J$  and takes place only between adjacent spins. Probably there does not exist any other theoretical model, which has been investigated in the past so intensively as this **Ising model**. Ising by himself got as doctoral candidate the task to find out, whether, due to the microscopic interaction  $J$ , a *spontaneous* order of the spins, i.e., an order which is not enforced by an external magnetic field  $H$ , can be explained, since it is typical for ferromagnets. Ising rigorously solved the one-dimensional ( $d = 1$ -)model (Z. Phys. **31**, 253 (1925)), but did **not** find a phase transition, as it was actually suggested by the Weiss theory, which predicts such a phase transition for each lattice dimension  $d$ . On the other hand, he could not solve the  $d = 2$ -model. The fact that the two-dimensional Ising model, in contrast to the one-dimensional model, exhibits indeed a phase transition, has been demonstrated only very much later, namely by R. Peierls (1936: existence proof of a phase transition for  $d \geq 2$ ), by H. A. Kramers and G. H. Wannier (1941:  $T_C$ -determination for the  $d = 2$ -model) as well as, in particular, by L. Onsager (1944: free energy of the  $d = 2$ -model, 1948: magnetization curve, critical exponent  $\beta = 1/8$ ) and by C. N. Yang (1952: first published derivation of the spontaneous magnetization in the  $d = 2$ -model). The complete analytical solution of the three-dimensional model is even today still lacking. However, the known approximations in the meantime are so convincing that one does not expect any substantial additional information from the still pending analytically exact solution. The Ising model, which is so important for the theory of phase transitions, will be investigated in Sect. 4.4.

At different stages of the preceding sections we realized already the meaning of the **thermodynamic limit**. We have, e.g., learned that it can be expected that the micro-canonical, canonical, and grand-canonical ensembles come to physically equivalent statements only for the *asymptotically large* system. On the other hand, it is of course not at all trivial that the relevant quantities, such as the canonical or the grand-canonical partition function do actually exist in the limit  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ . In Sect. 4.5 the consequences of the thermodynamic limit will therefore be discussed in detail. This becomes important particularly for the microscopically correct description of the phase transition, developed by T. D. Lee and C. N. Yang (1952), with which we will deal at the end in Sect. 4.6. The phase transition *gives itself away* by certain *irregularities*, i.e., by non-analyticities, in the thermodynamic potentials at the transition points, which, in turn, are mathematically detectable only for the infinitely large system.

## 4.1 Concepts

At first we want to collect, in concise form, some results, which we have already derived in the framework of the phenomenological Thermodynamics (Vol. 5).

### 4.1.1 Phases

Of fundamental importance is the term *phase*, by which one denotes a possible *form of the state* of a macroscopic system at thermal equilibrium. One and the same *matter* can exist in quite different phases, depending on the external conditions. The phases distinguish from each other by the fact that certain macroscopic observables adopt quite different values for them. Distinguishing marks are for instance:

1. *density*: gas, liquid, solid;
2. *magnetization*: paramagnet, ferromagnet, antiferromagnet;
3. *electric dipole moment*: paraelectric, ferroelectric;
4. *electrical conductivity*: insulator, metal, superconductor;
5. *crystal structure*: e.g.  $\alpha$  – Fe (body-centered cubic (bcc)),  $\gamma$  – Fe (face-centered cubic (fcc)).

In many systems there exist for certain variables, as the temperature  $T$ , the pressure  $p$ , the magnetic field  $\mathbf{H}$ , ... the so-called **critical regions**, in which changes of these variables induce transitions from one phase to the other. We will think about these transitions in the following.

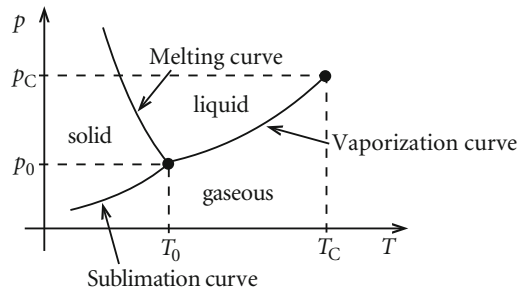
Let us recall at first the general case of a system, which is composed of  $\alpha$  *components* ( $j = 1, 2, \dots, \alpha$ ), where each of them can exist in  $\pi$  *phases* ( $v = 1, 2, \dots, \pi$ ). As to the different components one can for instance think of different particle types. If the system is *isolated*, then, as we know, all the still possible processes will run in such a way that the entropy thereby can never decrease. At the equilibrium we have  $dS = 0$ . From this fact we were able to derive in subsection 4.1.1 (Vol. 5) that all co-existing phases have the same temperature  $T$  and the same pressure  $p$ , as well as the same chemical potential  $\mu_j$ .

If it is, on the other hand, a *closed* system ( $N = \text{const}$ ) with  $T = \text{const}$  and  $p = \text{const}$ , then the free enthalpy  $G$  becomes minimal at the equilibrium,  $dG = 0$ . From that one can conclude that all phases of a certain component must possess the same chemical potential ( $\mu_{jv} \equiv \mu_j \quad \forall v$ ; (4.11), Vol. 5). A further important implication concerns the number  $f$  of the degrees of freedom, i.e., the number of independent variables which fulfills the **Gibbs phase rule** ((4.15), Vol. 5),

$$f = 2 + \alpha - \pi . \tag{4.2}$$

One should realize once more the meaning of this rule by the well-known example of the  $\text{H}_2\text{O}$ -phase diagram ( $\alpha = 1$ ) (Fig. 4.1).

**Fig. 4.1** Phase diagram of the  $\text{H}_2\text{O}$



At the *triple point*  $(p_0, T_0)$  three phases ( $\pi = 3$ ) are at equilibrium with each other. This means  $f = 0$ . For the triple point there does not exist, of course, an independently adjustable variable. On the vaporization (sublimation, melting) curve there are two phases at equilibrium ( $\pi = 2$ ) so that  $f = 1$ . One variable is thus still freely selectable, e.g. the temperature. All the other quantities are then fixed.

On the vaporization curve the free enthalpies of the liquid ( $G_l$ ) and the vapor (gas) ( $G_g$ ) are the same. They thus change along the curve in an identical manner:  $dG_l = dG_g$ . From that the **Clausius-Clapeyron equation** ((4.19), Vol. 5) is derived:

$$\frac{dp}{dT} = \frac{\Delta Q}{T(v_g - v_l)}. \quad (4.3)$$

$\Delta Q = T(s_g - s_l)$  is the *latent heat* per particle, which is needed for overcoming the cohesive forces.  $v_g$  ( $v_l$ ) and  $s_g$  ( $s_l$ ) are, respectively, the volume and the entropy per particle in the gas (liquid) phase. In both cases, these are the first partial derivatives of the free enthalpy. Obviously they must be different for the two phases, *gas* and *liquid*, because otherwise (4.3) would not make any sense. When traversing the coexistence line, the free enthalpy by itself behaves continuously, while its first derivatives exhibit discontinuities. These are the characteristics of a *first-order phase transition*.

### 4.1.2 First-Order Phase Transition

In the experiment one observes different types of phase transitions. Their oldest classification traces back to Ehrenfest (1933), which ascribes an *order* to the phase transition. An

#### ***n*-th order phase transition**

is thereby characterized by the observation that the  $(n - 1)$  first partial derivatives of the free enthalpy  $G$  with respect to its *natural* variables ( $T$  and  $p$  for the *fluid system*,  $T$  and  $B_0 = \mu_0 H$  for the *magnet*) are continuous at the *transition point*, while at least one of the  $n$ -th derivatives exhibit a discontinuity there. With increasing order of the phase transition, however, the physical differences between the phases, which

coexist at the transition point, will become more and more insignificant so that the question arises, up to which order it actually makes sense to speak of two *different* phases. Only the lowest orders can be of practical interest. The

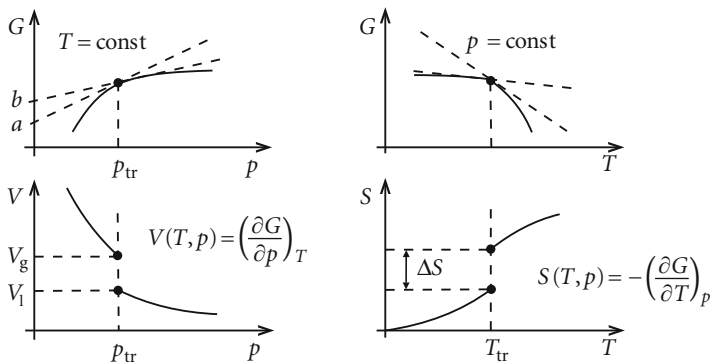
**first-order phase transition**

we have already briefly broached. For this transition the *Clausius-Clapeyron equation* (4.3) is valid. Let us recall at this stage for a moment the *geometrical interpretation* of the first-order transition from subsection 4.2.1 in Vol. 5, and that too at first for the fluid system. Starting point is the assertion (subsection 4.2.1, Vol. 5) that the free enthalpy  $G(T, p)$  in both the variables  $T$  and  $p$  is a **concave function**, which can be easily proved by means of the *stability conditions*  $c_p \geq 0$ ,  $\kappa_T \geq 0$  for the heat capacity and the compressibility. In this connection, one calls a function  $f(x)$  *concave at  $x$* , if it holds for all  $\lambda$  with  $0 \leq \lambda \leq 1$  and for arbitrary pairs of points  $x_1, x_2$  ( $x_1 > x_2$ ):

$$f(\lambda x_1 + (1 - \lambda)x_2) \geq \lambda f(x_1) + (1 - \lambda)f(x_2) .$$

On the other hand, one calls  $f(x)$  a *convex function*, if  $-f(x)$  is concave, i.e., when in the above relation the inequality-sign is reversed. For a concave (convex) function  $f(x)$ , the secant, which connects the points  $f(x_1)$  and  $f(x_2)$ , is always in the region  $x_1 \leq x \leq x_2$  above (below) the curve  $f(x)$ . If  $f(x)$  is even two times differentiable, then concavity (convexity) follows for all  $x$  from  $f''(x) \leq 0$  ( $\geq 0$ ).

The free enthalpy  $G(T, p)$ , at the transition point, is represented qualitatively by the picture, which is sketched in Fig. 4.2. The potential by itself is continuous, while the first derivatives exhibit continuity-jumps. The jump  $\Delta S$  of the entropy defines the *latent heat*  $\Delta Q = T_{tr}\Delta S$ . The *free energy*  $F(T, V)$  is as function of  $T$  **concave** and as function of  $V$  **convex**. As function of  $T$  at a fixed volume  $V$  the free energy behaves qualitatively very similar to the free enthalpy  $G$  at fixed  $p$ . At  $T = T_{tr}$  also  $S(T, V) = -(\partial F/\partial T)_V$  shows a discontinuity. The volume-dependence of the free energy allows to recognize, however, the first-order phase transition by a linear



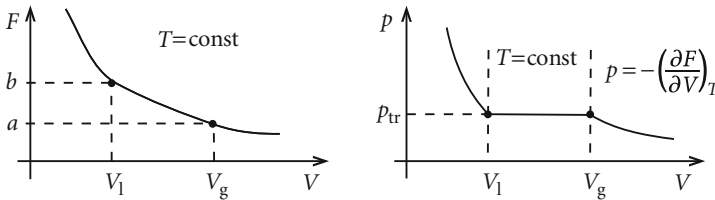
**Fig. 4.2** Qualitative behavior of the free enthalpy and its first derivatives with respect to the natural variables at the transition point of a phase transition of first order

segment in the region  $V_l \leq V \leq V_g$  (Fig. 4.3). There:

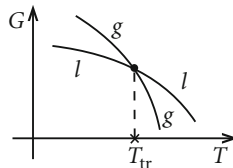
$$F(T, V) = -p_l V + G(T, p_l) .$$

In the  $pV$ -diagram this corresponds to a horizontal piece of the isotherm. A typical feature of first-order transitions is the experimentally proved existence of **metastable** phases, e.g., *overheated liquid, supersaturated vapor,...*). These suggest the idea that thermodynamic potentials such as  $G(T, p)$  are represented for each phase by a *stand-alone* analytic expression, which can be continued into the respective other phase (Fig. 4.4). At a given pressure  $p$  the two enthalpy-curves intersect at  $T = T_{tr}$  ( $g$ : gaseous,  $l$ : liquid). The phase with the smaller  $G$  is stable. The resulting *stable*  $G$ -curve then has a *kink* at  $T = T_{tr}$ , being thus still continuous there, but with a discontinuous first derivative.

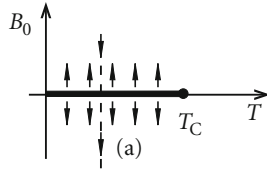
Fully analogous considerations can be applied for the magnetic system, if one takes the magnetic induction  $B_0 = \mu_0 H$  in analogy to the pressure  $p$  and the magnetic moment  $m$  in analogy to the volume  $V$ . In detail considerations, however, one has to take into account some minor differences (Fig. 4.5). The phase diagram already exhibits a peculiarity. A phase transition can take place in the magnetic system only in the zero-field and for temperatures  $T < T_C$  ( $T_C$ : *critical temperature*), which is then of first order. The magnetic moment changes its sign when one traverses the phase boundary, which is identical to the line segment  $0 \leq T \leq T_C$  of the  $T$ -axis (path (a) in Fig. 4.5). Because of the positive-definite heat capacities, the thermodynamic potentials  $G(T, B_0)$  and  $F(T, m)$  are both, as in the fluid system, concave as functions of  $T$ .



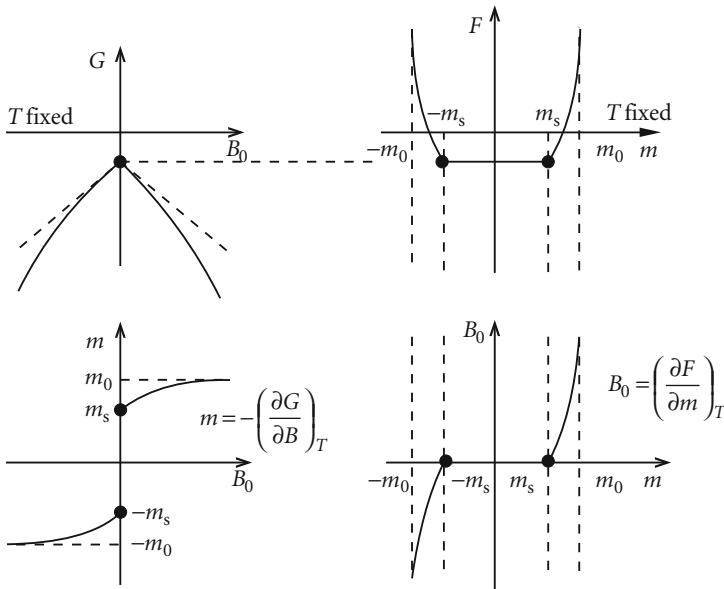
**Fig. 4.3** Qualitative behavior of the free energy and the pressure of a fluid system at the first-order phase transition.  $V_l$  ( $V_g$ ): volume of the liquid (gaseous) part in the two-phase regime



**Fig. 4.4** Schematic representation of the free enthalpy of a fluid system for the explanation of metastable phases at a first order transition ( $l$ : liquid;  $g$ : gaseous)



**Fig. 4.5** Phase diagram of the magnetic system



**Fig. 4.6** Qualitative behavior of the free enthalpy  $G$  and the free energy  $F$  as well as that of their first partial derivatives with respect to the field  $B_0$  and the magnetic moment  $m$ , respectively, at the first-order transition

However, since the susceptibility  $\chi_T$ , the *magnetic analog* to the compressibility  $\kappa_T$  of the fluid system, can also be negative (diamagnetism!), the statements about the  $B_0$ - and the  $m$ -dependencies are actually not unique. But if one excludes diamagnetism from the following consideration, then it can be stated that  $G(T, B_0)$  is concave as function of  $B_0$ , and  $F(T, m)$  convex as function of  $m$ . The first-order transition can therewith be qualitatively sketched easily also for the magnetic system (Fig. 4.6).

Because of  $B_0 = 0$  at the phase-transition point, the linear segment of the free energy in the *transition region* (Fig. 4.3) is now horizontal. The magnetic moment  $m$  is an odd function of the field. At the pole reversal of the field the magnetic moment flips into the opposite direction. That is possible, on the other hand, only if  $F$  as function of  $m$  is even. The first-order phase transition manifests itself by the discontinuous jump of the moment at  $B_0 = 0$ . With increasing field strength

the moment steadily increases and approaches asymptotically the *saturation value*  $\pm m_0$ . The free enthalpy  $G(T, B_0)$  thus becomes for large fields a linear function of  $B_0$ , while the free energy as function of  $m$  diverges at  $\pm m_0$ , and is of course not defined for  $|m| \geq m_0$ .

### 4.1.3 Second-Order Phase Transition

The phase transition of first order is correctly described by the Ehrenfest-scheme, while for the second- and higher-order transitions doubts and critics are indicated. In the *strict Ehrenfest sense* at a second-order phase transition the following conditions should be fulfilled:

1.  $G(T, p)$  continuous at the transition point;
2.  $S(T, p)$ ,  $V(T, p)$  continuous at the transition point;
3.  $C_p$ ,  $\kappa_T$  discontinuous at the transition point;
4. *phase-boundary curve* fixed by the

**Ehrenfest equations:**

$$\frac{dp}{dT} = \frac{1}{TV} \frac{C_p^{(1)} - C_p^{(2)}}{\beta^{(1)} - \beta^{(2)}} = \frac{\beta^{(1)} - \beta^{(2)}}{\kappa_T^{(1)} - \kappa_T^{(2)}}. \quad (4.4)$$

The indexes (1) and (2) refer to the two phases, which are at equilibrium at the *phase boundary*.  $\beta$  means here the isobaric expansion coefficient ( $\beta = (1/V)(\partial V/\partial T)_p$ ) and not the reciprocal temperature. The derivation of the Ehrenfest equations was performed in connection with equation (4.41) in Vol. 5. Thereby the above point 2. is exploited, i.e. more precisely, the fact that along the coexistence line it must be:  $dS^{(1)} = dS^{(2)}$  and  $dV^{(1)} = dV^{(2)}$ .

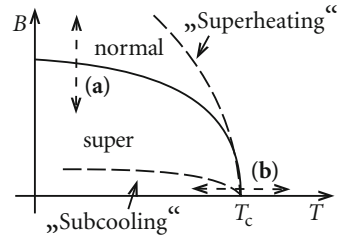
The Ehrenfest-definition of a second-order phase transition has been accepted for a long time, because at first any counter-example was not known, and because it was strictly confirmed by the *classical theories* (Sect. 4.3). A prominent experimental realization represents the superconductor. The *superconducting phase*, being present below the critical temperature  $T_C$  can be destroyed by a magnetic field. For  $B \geq B_C = \mu_0 H_C$  the respective metal becomes again normal-conducting (Fig. 4.7). When at a temperature  $T < T_C$  the coexistence line is passed (path (a) in Fig. 4.7), then it results evidently a first-order transition. Even the already mentioned metastable phases can be observed. For extremely pure aluminum one could restore the normal-conducting phase down to  $\approx 1/20 B_C$  (*subcooling*).

If, on the other hand, the transition takes place in the zero-field (path (b) in Fig. 4.7), then it is of second order in the *strict Ehrenfest sense*. The heat capacity  $C_{H=0}$  exhibits a finite jump at  $T_C$  (see Fig. 4.8).

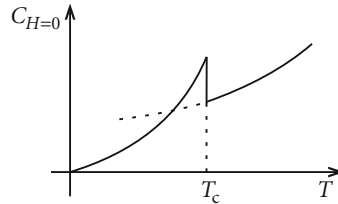
The present day criticism of the Ehrenfest classification is quite manifold. Phase transitions, which are not of first order, are characterized in the experiment, except

**Fig. 4.7**

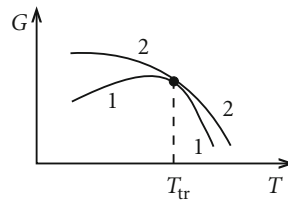
Temperature-behavior of the critical magnetic field of a superconductor



**Fig. 4.8** Temperature behavior of the zero-field heat capacity of a superconductor



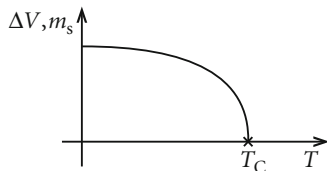
**Fig. 4.9** Hypothesis of two different enthalpy-curves at the second-order phase transition, one each for the two phases 1 and 2, which are at equilibrium at the transition point



for the superconductor, rather by singularities than by finite jumps of the heat capacities and compressibilities (susceptibilities). Strictly speaking, it is of course experimentally hardly possible to distinguish a singularity from a *very big jump*. The indications, however, very strongly point to real divergences. The exact *Onsager-solution* of the  $d = 2$ -Ising model (Sect. 4.4) leads to a *logarithmic*  $C_V$ -singularity, which does not fit the scheme, either. The criticism that the Ehrenfest classification is **too restrictive** is surely with a good basis.

Also the *metastable phases* can lead to a certain confusion, because they suggest the idea of **two** enthalpy-curves, a stand-alone one for each of the two participating phases. That seems to be indeed reasonable for first-order phase transitions. If, on the other hand, that applied also to second-order transitions, then there would arise serious contradictions. Concavity and continuous differentiability of the *stable* enthalpy-curve do namely prevent an intersection point of  $G_1$  and  $G_2$ . The two curves thus must '*huddle against each other*' at  $T_{tr}$  (Fig. 4.9). But then one may not be able to recognize a phase transition. The phase 1 would be stable everywhere. This contradiction can be resolved only such that in the above argumentation a wrong analogy of first-order and second-order phase transitions was taken. Indeed, *metastable phases*, which actually are the reason for the assumption of two independent enthalpy-curves, are realized only for first-order transitions. This is impressively to observe for the superconductor (see Fig. 4.7).





**Fig. 4.10** Temperature-dependence of the discontinuities in the first partial derivatives of thermodynamical potentials at the first-order phase transition: volume-jump  $\Delta V$  of the fluid system and spontaneous magnetic moment  $m_s$  of the magnetic system

Ultimately, from the above mentioned reasons, the *Ehrenfest scheme* could not assert itself. Today one distinguishes only two types of phase transitions, namely those of *first order*, which are also denoted as **discontinuous**, and those of *second order*, which are called **continuous transitions**. The first-order transitions remain so as defined in Sect. 4.1.2. They can be observed by certain discontinuities of the first partial derivatives of the thermodynamic potentials, as for instance by the ‘*volume jump*’  $\Delta V = V_g - V_l$  (see Fig. 4.2) or by the *spontaneous* total magnetic moment  $m_s$  (see Fig. 4.6). But the *magnitude* of these jumps turns out to be temperature-dependent. Normally it decreases with increasing temperature, in order to vanish at the *critical temperature*  $T_C$  (Fig. 4.10). The first derivatives thereafter are then again continuous. In the fluid system, e.g., there no longer appears a latent heat. However, if it turns out that at least one of the second partial derivatives is *non-analytical* at  $T_C$ , then this means that there is a *second-order phase transition*. This is experimentally observable via the so-called *response functions*:

*heat capacity*:

$$C_{V(m)} = T \left( \frac{\partial S}{\partial T} \right)_{V(m)} = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{V(m)},$$

$$C_{p(H)} = T \left( \frac{\partial S}{\partial T} \right)_{p(H)} = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{p(H)}.$$

*compressibility*:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial p^2} \right)_T.$$

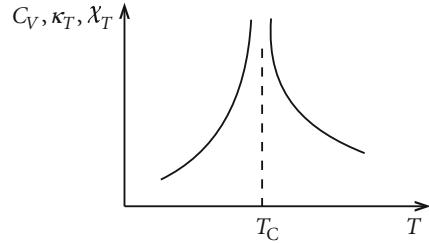
*susceptibility*:

$$\chi_T = \frac{1}{V} \left( \frac{\partial m}{\partial H} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial H^2} \right)_T$$

( $H$ : magnetic field) .

The *non-analyticities* can be finite discontinuities (see the superconductor) or real divergences (Fig. 4.11). That the second-order transitions are normally denoted as *continuous transitions* is due to the continuity of the first derivatives.

**Fig. 4.11** Schematic illustration of a second-order phase transition



#### 4.1.4 Order Parameter

Besides the mentioned *non-analyticities*, to indicate as further typical characteristics of the continuous phase transitions, there are the so-called **order parameters**. By these one understands the macroscopic variables, which can be reasonably defined exclusively only in one of the phases which participate in the transition. The nomenclature expresses that these variables have something to do with the change of the order in the state at the transition. In a thermodynamic many-particle system namely, two opposing tendencies are always competing, which can be easily understood with the *free energy*  $F = U - TS$ . This potential must come to a minimum at the equilibrium. An internal energy  $U$  as small as possible is thus *convenient*, which normally, as a consequence of the particle interactions, is achieved by a high order in the system. For the Ising model, described by the Hamilton function (4.1), for instance, a collective orientation of *all spins* parallel to an external magnetic field makes, for positive coupling constants  $J > 0$ , the internal energy  $U = \langle H \rangle$  minimal. On the other hand, a large entropy  $S$  would also be *convenient*. But this implies now a disorder as high as possible. These two obviously opposing tendencies require a compromise, which certainly will depend on the temperature  $T$ . At high temperature the disorder-tendency will dominate, and at low temperatures the order-tendency. If it comes therewith to a phase transition, then the low-temperature phase will be acclaimed, compared to the high-temperature phase, as a higher state of order. We list some examples of *order parameters*:

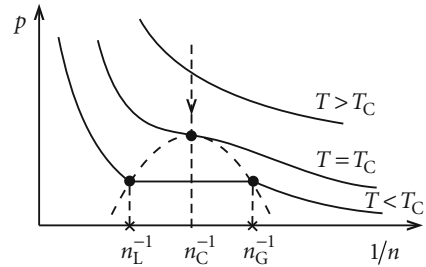
##### 1. Gas-liquid

If one cools along the path, indicated in Fig. 4.12, at the critical particle density  $n_C = N/V_C$ , then below  $T_C$ , the system, being before homogeneous, decays into two phases, liquid and gas, with different particle densities  $n_{L,G} = N_{L,G}/V_{L,G}$ . A new variable is therewith defined,

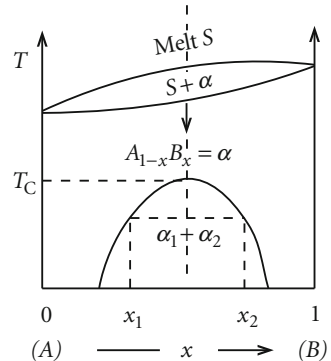
$$\Delta n = n_L - n_G, \quad (4.5)$$

which is meaningless in the high-temperature phase ( $T > T_C$ ).  $\Delta n$  is the *order parameter* of the gas-liquid system.

**Fig. 4.12** Isotherms of the fluid system (gas-liquid) for the definition of the order parameter



**Fig. 4.13** Phase diagram of a mixed crystal  $A_{1-x}B_x$  for fixing the order parameter



## 2. Ferromagnet

Below the Curie temperature ( $T < T_C$ ) the ferromagnet possesses a *spontaneous*, i.e. not enforced by an external field, magnetic moment  $m_S$ . Order parameter of the phase transition ferromagnet-paramagnet is therefore the *spontaneous magnetization*  $M_S = m_S/V$ , i.e. the *spontaneous* magnetic moment per volume.

## 3. Mixed Crystal

Below the critical temperature  $T_C$  the mixed crystal  $A_{1-x}B_x$ , which consists of the two components  $A$  and  $B$ , decays into two different mixed crystals  $\alpha_1$  and  $\alpha_2$  with different concentrations  $x_1$  and  $x_2$  of the component  $B$  (Fig. 4.13). The difference of the concentrations

$$\Delta x = x_2 - x_1 \quad (4.6)$$

is the *order parameter* of the mixed crystal.

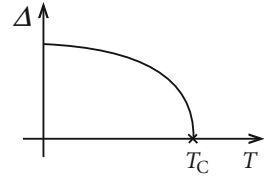
## 4. Superconductor

The *superconducting* state is characterized by an energy gap  $\Delta$  in the one-electron excitation spectrum (exercise 3.3.2, Vol. 9):

$$E(\mathbf{k}) = \sqrt{(\varepsilon(\mathbf{k}) - \mu)^2 + \Delta^2}. \quad (4.7)$$

$\varepsilon(\mathbf{k})$  are the one-particle energies of the *normal-conducting* state;  $\mu$  is the chemical potential. The *gap parameter*  $\Delta$  proves to be temperature-dependent

**Fig. 4.14**  
Temperature-dependence of the energy gap  $\Delta$  in the excitation spectrum of a superconductor



(Fig. 4.14). The microscopic *BCS theory* (**Bardeen, Cooper, Schrieffer**) yields the implicit condition equation

$$\Delta = \frac{1}{2} \Delta V \sum_{\mathbf{k}} \frac{\tanh\left((1/2)\beta \sqrt{(\varepsilon(\mathbf{k}) - \mu)^2 + \Delta^2}\right)}{\sqrt{(\varepsilon(\mathbf{k}) - \mu)^2 + \Delta^2}}. \quad (4.8)$$

Above a certain critical temperature  $T_C$  there does not exist a solution  $\Delta \neq 0$  (Fig. 4.14); the system behaves as a *normal conductor*. The gap parameter  $\Delta$  thus is different from zero only in the *superconducting* low-temperature phase ( $T < T_C$ ) being therewith a suitable *order parameter*.

### 4.1.5 Critical Fluctuations

A deep insight into the behavior of the thermodynamic systems in their *critical regions*, i.e. in those regions, where phase transitions take place, is provided by the so-called

**correlation function of the physical quantity X**

$$g(\mathbf{r}, \mathbf{r}') = \langle x(\mathbf{r})x(\mathbf{r}') \rangle - \langle x(\mathbf{r}) \rangle \langle x(\mathbf{r}') \rangle. \quad (4.9)$$

$x(\mathbf{r})$  is here the *density* of the quantity X:

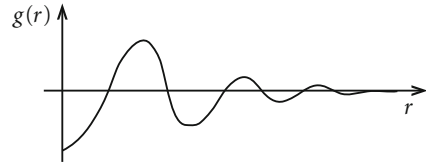
$$X = \int d^3r x(\mathbf{r}).$$

$g(\mathbf{r}, \mathbf{r}')$  represents a measure for the *correlation* between the positions  $\mathbf{r}$  and  $\mathbf{r}'$  with respect to the physical property X. In the case of *spatial homogeneity* it must hold

$$g(\mathbf{r}, \mathbf{r}') = g(|\mathbf{r} - \mathbf{r}'|).$$

If there are *no correlations* between the positions  $\mathbf{r}$  and  $\mathbf{r}'$ , then the first term in (4.9) will factorize,  $\langle x(\mathbf{r})x(\mathbf{r}') \rangle \rightarrow \langle x(\mathbf{r}) \rangle \langle x(\mathbf{r}') \rangle$ , and  $g(\mathbf{r}, \mathbf{r}')$  becomes zero. We look at two examples:

**Fig. 4.15** Typical distance-dependence of the pair-correlation function



### 1. density correlation, pair correlation

$$\begin{aligned}
 x(\mathbf{r}) &= n(\mathbf{r}) && (\text{particle density}) \\
 X &= N && (\text{particle number}) \\
 g(\mathbf{r}, \mathbf{r}') &= \langle n(\mathbf{r})n(\mathbf{r}') \rangle - \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle. && (4.10)
 \end{aligned}$$

In the case of spatial homogeneity  $g$  usually exhibits a damped oscillatory behavior (Fig. 4.15). With increasing distance  $|\mathbf{r} - \mathbf{r}'|$  the correlations become weaker and weaker:

$$\langle n(\mathbf{r})n(\mathbf{r}') \rangle \xrightarrow{|\mathbf{r}-\mathbf{r}'| \rightarrow \infty} \left( \frac{N}{V} \right)^2.$$

Particles, far away from each other, ‘do not know anything about each other’.

### 2. spin correlation

Let the Ising model (4.1) be the reference system:

$$\begin{aligned}
 X &= m = \mu \sum_i S_i : \text{total magnetic moment}, \\
 x(\mathbf{r}) &\longleftrightarrow S_i : \text{Ising spin}.
 \end{aligned}$$

In the definition (4.9)  $x(\mathbf{r})$  is now a discrete function of the position:

$$g_{ij} = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle. \quad (4.11)$$

We will later get to know that in the *critical regions* the correlation function  $g(\mathbf{r}, \mathbf{r}')$  takes approximately the form

$$g(\mathbf{r}, \mathbf{r}') = c_0 \frac{\exp(-|\mathbf{r} - \mathbf{r}'|/\xi(T))}{|\mathbf{r} - \mathbf{r}'|} \quad (4.12)$$

(Ornstein-Zernike behavior, see Sect. 4.3.9), by which a further important quantity is introduced, namely the

**correlation length**  $\xi(T)$

It represents a measure of the *range* of the correlation.

We will now derive, for the example of the Ising model (4.1), a connection between the correlation function (4.11) and the isothermal susceptibility:

$$\chi_T = \frac{1}{V} \left( \frac{\partial m}{\partial H} \right)_T = \frac{\mu_0}{V} \left( \frac{\partial m}{\partial B_0} \right)_T, \quad (4.13)$$

With the canonical partition function,

$$Z(T, B_0) = \sum_{\{S_i\}} \exp \left[ -\beta \left( -J \sum_{ij} S_i S_j - \mu B_0 \sum_i S_i \right) \right], \quad (4.14)$$

the average magnetic moment  $m$  of the Ising-spin system can be written as:

$$\begin{aligned} m &= \frac{1}{Z} \sum_{\{S_i\}} \left[ \left( \mu \sum_i S_i \right) \exp \left( \beta J \sum_{ij} S_i S_j + \beta \mu B_0 \sum_i S_i \right) \right] \\ &= \frac{1}{\beta} \left( \frac{\partial}{\partial B_0} \ln Z(T, B_0) \right)_T. \end{aligned} \quad (4.15)$$

In the expressions (4.14) and (4.15) it is summed over all possible spin configurations. By inserting (4.15) into (4.13) and executing the differentiations with respect to the field, one easily finds the mentioned connection between the susceptibility  $\chi_T$  and the spin correlation  $g_{ij}$  (4.11), which is known as **fluctuation-dissipation theorem**:

$$\chi_T = \beta \mu^2 \frac{\mu_0}{V} \sum_{ij} g_{ij}. \quad (4.16)$$

Because of

$$-1 \leq \langle S_i S_j \rangle \leq +1 \iff -2 \leq g_{ij} \leq +2$$

each summand in (4.16) is finite. On the other hand, it is observed in experiments on the magnetic systems that, in the case of second-order phase transitions, the susceptibility  $\chi_T$  diverges at the critical point:

$$\chi_T \xrightarrow{T \rightarrow T_c} \infty.$$

This behavior, however, can be understood with (4.16) only under two conditions:

1. *The number of summands in the double sum must be infinitely large!*

That is a further hint that Statistical Physics can be correct only for the *asymptotically large* system. We find therewith a further motive to deal in more detail with the *thermodynamic limit* ( $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = n$ ) in Sect. 4.5.

2. *The range of the correlation has to diverge in order that infinitely many terms in the sum are unequal zero.*

We have encountered therewith an important characteristic of the second-order phase transitions. The *correlation length*, introduced via (4.12), diverges in the critical region:

$$\xi(T) \xrightarrow{T \rightarrow T_C} \infty. \quad (4.17)$$

This leads to the concept of the

### **critical fluctuations,**

which are spoken of, when  $\xi(T)$  is of a macroscopic order of magnitude. In order to get a certain impression of it, the following typical numerical values may help:

$$\left| \frac{T - T_C}{T_C} \right| \approx 10^{-2} \quad (10^{-3}, 10^{-4}) \iff \xi \approx 100 \quad (500, 2000) \text{ \AA}.$$

In the region of *critical fluctuations* the *correlation length*  $\xi$  is essentially larger than the effective range of normal particle interactions, which in general amount to few atomic distances. This has the remarkable consequence that physical properties are not so much determined by the particular form of the particle interactions, but rather by the *extension*  $\xi$  of the coherent fluctuations of these properties around their average values. This leads to an astonishingly *universal* behavior of physical quantities near the critical point. Very different properties of very different systems obey near the critical temperature  $T_C$ , which by itself can still vary from system to system by orders of magnitude, completely analogous laws and rules. One speaks of **critical phenomena**. Their universality is the reason for the intense interest in these phenomena, although they appear only in the region of the *critical fluctuations*, i.e. in a very narrow temperature interval.

Since the correlation length  $\xi$  remains finite for first-order phase transitions, *critical phenomena* are observed only in connection with second-order phase transitions.

## 4.1.6 Exercises

### Exercise 4.1.1

Show that for the Ising model (4.1),

$$H = -J \sum_{i,j} S_i S_j - \mu B_0 \sum_i S_i, \quad S_i = \pm 1,$$

the free energy  $F(T, m)$  is an even function of the magnetic moment  $m = \mu \sum_i S_i$ .

**Exercise 4.1.2**

Let  $\hat{H}$  be the Hamilton operator of a magnetic system, which is in a homogeneous magnetic field  $B_0$ . The operator of the magnetic moment  $\hat{m}$  is defined by

$$\hat{m} = -\frac{d}{dB_0}\hat{H}$$

(equation (5.125) in Vol. 7). Let  $\hat{m}$  be a permanent magnetic moment, diamagnetic effects are excluded, i.e.

$$\frac{d}{dB_0}\hat{m} = 0$$

Magnetization  $M$  and susceptibility  $\chi_T$  are essentially determined by the statistical average of the magnetic moment:

$$M = \frac{1}{V}\langle\hat{m}\rangle; \chi_T = \mu_0 \left(\frac{\partial M}{\partial B_0}\right)_T$$

$\mu_0$  is the vacuum permeability. Verify the following connection between the susceptibility and the fluctuations of the magnetic moment (*fluctuation-dissipation theorem*):

$$\chi_T = \frac{1}{k_B T} \frac{\mu_0}{V} \langle(\hat{m} - \langle\hat{m}\rangle)^2\rangle$$

**Exercise 4.1.3**

For a first-order phase transition in a fluid system derive the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{S_2 - S_1}{V_2 - V_1}.$$

The indexes 1, 2 refer to the two phases which are at equilibrium on the phase boundary.  $S_i$  are the entropies and  $V_i$  the volumes of the two phases  $i = 1, 2$ .

**Exercise 4.1.4**

For a second-order phase transition in a fluid system prove the Ehrenfest equations:

$$\frac{dp}{dT} = \frac{1}{TV} \frac{C_p^{(1)} - C_p^{(2)}}{\beta^{(1)} - \beta^{(2)}} = \frac{\beta^{(1)} - \beta^{(2)}}{\kappa_T^{(1)} - \kappa_T^{(2)}}.$$

The indexes 1, 2 refer to the two phases which are at equilibrium on the phase boundary.  $\beta$  is the isobaric expansion coefficient,

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p,$$



and  $\kappa_T$  the isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

### Exercise 4.1.5

(Gorter model) A container of the volume  $V$  contains a small amount of liquid (volume  $V_L$ ). The rest of the volume ( $V_G = V - V_L$ ) is filled by the saturated vapor (pressure  $p_i$ ) of the liquid. Treat the vapor as an ideal gas. The walls of the container have a negligible heat capacity. They are, however, not fixed, but react elastically on the excess pressure,

$$\pi = p - p_i ,$$

where  $p$  means the external pressure, and the elasticity is given by

$$\frac{dV}{d\pi} = -a \quad a > 0 .$$

If the system is heated at  $p = \text{const}$ , then liquid vaporizes. Let  $T = T_C$  be the temperature at which the last drop is vaporized. Show that the system at  $T_C$  undergoes a second-order phase transition in the 'strict Ehrenfest sense'. For this purpose work out the following partial steps:

1. Calculate the slope  $dp/dT$  of the coexistence curve!
2. Show that the isobaric expansion coefficient,

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p ,$$

makes a finite jump at  $T_C$ !

3. How does the isothermal compressibility,

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T ,$$

behave at the transition point?

4. Demonstrate the validity of the Ehrenfest equation:

$$\frac{dp}{dT} = \frac{\Delta\beta}{\Delta\kappa_T} .$$

**Exercise 4.1.6**

Show that the Gorter model from Exercise 4.1.5 fulfills also the second Ehrenfest equation

$$\frac{dp}{dT} = \frac{1}{TV} \frac{C_p^{(1)} - C_p^{(2)}}{\beta^{(1)} - \beta^{(2)}} .$$

The indexes 1, 2 again refer to the two phases which are at equilibrium on the phase boundary.  $\beta^{(i)}$  is the isobaric expansion coefficient and  $C_p^{(i)}$  the heat capacity.

**Exercise 4.1.7**

By the use of the first law of Thermodynamics for a magnetic system,

$$dU = \delta Q + B_0 dm \quad (B_0 = \mu_0 H) ,$$

derive for the heat capacities,

$$C_m = \left( \frac{\delta Q}{\partial T} \right)_m \quad C_{H(B_0)} = \left( \frac{\delta Q}{\partial T} \right)_{H(B_0)}$$

the following equivalent connections:

$$C_H - C_m = \left( \left( \frac{\partial U}{\partial m} \right)_T - B_0 \right) \left( \frac{\partial m}{\partial T} \right)_H \quad (1)$$

$$C_H - C_m = -T \left( \frac{\partial B_0}{\partial T} \right)_m \left( \frac{\partial m}{\partial T} \right)_H \quad (2)$$

$$C_H - C_m = \frac{\mu_0}{V} T \chi_T^{-1} \left[ \left( \frac{\partial m}{\partial T} \right)_H \right]^2 \quad (3)$$

$$C_H - C_m = \frac{V}{\mu_0} T \chi_T \left[ \left( \frac{\partial B_0}{\partial T} \right)_m \right]^2 \quad (4)$$

$\chi_T$  is the isothermal susceptibility.

**Exercise 4.1.8**

When one brings a superconductor of the first kind into a magnetic field  $\mathbf{H}$ , it shows the so-called Meißner-Ochsenfeld effect, i.e., except for a thin negligible surface layer, in its inside

$$\mathbf{B}_0 = \mu_0(\mathbf{H} + \mathbf{M}) = 0 .$$

When  $\mathbf{H}$  exceeds a critical temperature-dependent field strength  $H_C$ , then a phase transition into the normal-conducting state takes place. To a good approximation

one finds:

$$H_C(T) = H_0 \left[ 1 - (1 - \alpha) \left( \frac{T}{T_C} \right)^2 - \alpha \left( \frac{T}{T_C} \right)^4 \right]$$

( $T_C$  = critical temperature,  $\alpha$ : material constant).

1. Calculate the latent heat at the phase transition by the use of the Clausius-Clapeyron equation. Thereby, the magnetization of the normal-conducting phase ( $M_n$ ) can be neglected compared to that of the superconducting phase ( $M_s$ ).
2. Calculate the *stabilization energy*  $\Delta G$  of the superconductor:

$$\Delta G = G_s(T, H = 0) - G_n(T, H = 0)$$

(n: normal-conducting, s: superconducting). Use once more  $M_n \ll M_s$ .

3. Calculate the entropy difference

$$\Delta S = S_s(T) - S_n(T)$$

using part 2. Compare the result with that from part 1.

4. What follows from the third law of Thermodynamics for

$$\left( \frac{dH_C}{dT} \right)_{T=0} ?$$

5. Calculate the difference  $\Delta C = C_s - C_n$  of the heat capacities!
6. Classify the phase transition!

## 4.2 Critical Phenomena

### 4.2.1 Critical Exponents

In the *critical regions* of the second-order phase transitions, the behavior of many physical quantities can each be characterized by a certain number, the *critical exponent*. One observes, for instance, very often that a physical property  $F$  depends on the *reduced* temperature,

$$\varepsilon = \frac{T - T_C}{T_C}, \quad (4.18)$$

in the following form:

$$F(\varepsilon) = a\varepsilon^\varphi (1 + b\varepsilon^x + \dots); \quad x > 0.$$

For  $\varepsilon \rightarrow 0$ , i.e.,  $T \rightarrow T_C$ , all terms in the bracket vanish except of the 1, so that  $F(\varepsilon)$  follows in the immediate neighborhood of  $T_C$  a **power law**. This is expressed by the shorthand notation

$$F(\varepsilon) \sim \varepsilon^\varphi, \tag{4.19}$$

which is to be read as: ‘ $F(\varepsilon)$  behaves in the critical region as  $\varepsilon^\varphi$ ’. The number  $\varphi$  therewith ultimately determines the temperature behavior in the critical region. The number is called the *critical exponent*.

The power-law behavior is typical, and, as mentioned, is rather often indeed observed. However, there are also deviations. We will see, for instance, that the heat capacity of the Ising model diverges logarithmically. The assumption of a power-law behavior thus is too restrictive. One therefore generalizes:

**critical exponent**

$$\varphi = \lim_{\varepsilon \xrightarrow{>} 0} \frac{\ln |F(\varepsilon)|}{\ln \varepsilon}, \tag{4.20}$$

$$\varphi' = \lim_{\varepsilon \xrightarrow{<} 0} \frac{\ln |F(\varepsilon)|}{\ln(-\varepsilon)}. \tag{4.21}$$

By  $\varphi$  and  $\varphi'$  it is at first distinguished, *from which side* the critical point is approached. It need not necessarily be  $\varphi = \varphi'$ . The power-law behavior is contained in the definitions (4.20) and (4.21). Though, other situations also are allowed. Corresponding examples we will get to know later. The symbolic shorthand notation (4.19), however, will be retained also for those cases, which do not really follow a power law.

There exists a finite set of critical exponents, a part of which we have already introduced in subsection 4.2.3 of Vol. 5. These we will gather briefly here once more and extend them by a few important other exponents, which were not yet accessible for us with the preconditions in Vol. 5.

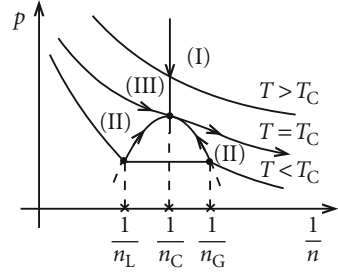
For the definition of a critical exponent the exact definition of the path is necessary, on which the state change takes place. For the gas-liquid system (*real gas*) the three paths I, II und III, sketched in Fig. 4.16 come into question. For the magnet the change of the state has in general to be performed in the zero field.

**1. heat capacities:  $\alpha, \alpha'$**

It holds for the real gas:

$$C_V \sim \begin{cases} (-\varepsilon)^{-\alpha'}: & \text{path II, } T \xrightarrow{<} T_C, \quad n = n_{G,L}, \\ \varepsilon^{-\alpha}: & \text{path I, } T \xrightarrow{>} T_C, \quad n = n_C. \end{cases} \tag{4.22}$$

**Fig. 4.16** Fixing the paths in the  $pV$ -diagram of the real gas ( $n = N/V$ ), on which the critical exponents are defined



$C_V$  has thus to be measured for  $T < T_C$  at a particle density, which steadily changes towards  $n_C$ . Because of  $n = n_{G,L}(T)$  this particle density is at equilibrium, on the path II, uniquely connected to the temperature.

For the magnet one schedules:

$$C_H \sim \begin{cases} (-\varepsilon)^{-\alpha'}: & T < T_C, \quad B_0 = \mu_0 H = 0, \\ \varepsilon^{-\alpha}: & T > T_C, \quad B_0 = \mu_0 H = 0. \end{cases} \quad (4.23)$$

**2. order parameter:  $\beta$**

Real gas:

$$\Delta n \sim (-\varepsilon)^\beta: \quad \text{path II} . \quad (4.24)$$

Magnet:

$$M_S \sim (-\varepsilon)^\beta: \quad B_0 = \mu_0 H = 0 . \quad (4.25)$$

The prime on the critical exponent  $\beta$  is here left out, although the change of the state takes place according to  $T \overset{\leftarrow}{\rightarrow} T_C$ . The distinction of  $\beta$  and  $\beta'$  is superfluous for the order parameter because the latter is defined only in the low-temperature phase.

**3. compressibilities, susceptibilities:  $\gamma, \gamma'$**

Real gas:

$$\kappa_T \sim \begin{cases} (-\varepsilon)^{-\gamma'}: & \text{path II} , \\ \varepsilon^{-\gamma}: & \text{path I} . \end{cases} \quad (4.26)$$

Magnet:

$$\chi_T \sim \begin{cases} (-\varepsilon)^{-\gamma'}: & T \overset{\leftarrow}{\rightarrow} T_C, \quad B_0 = \mu_0 H = 0, \\ \varepsilon^{-\gamma}: & T \overset{\rightarrow}{\leftarrow} T_C, \quad B_0 = \mu_0 H = 0. \end{cases} \quad (4.27)$$

#### 4. critical isotherm: $\delta$

Real gas:

$$p - p_C \sim (1/n - 1/n_C)^\delta: \quad \text{path III, } T = T_C . \quad (4.28)$$

Magnet:

$$B_0 \sim M^\delta: \quad T = T_C . \quad (4.29)$$

#### 5. correlation length: $\nu$ , $\nu'$ , $\eta$

The correlation length  $\xi(T)$  is introduced by (4.12). It diverges when the critical point is approached:

Real gas:

$$\xi \sim \begin{cases} (-\varepsilon)^{-\nu'}: & \text{path II ,} \\ \varepsilon^{-\nu}: & \text{path I .} \end{cases} \quad (4.30)$$

Magnet:

$$\xi \sim \begin{cases} (-\varepsilon)^{-\nu'}: & T \xrightarrow{<} T_C , \quad B_0 = \mu_0 H = 0 , \\ \varepsilon^{-\nu}: & T \xrightarrow{>} T_C , \quad B_0 = \mu_0 H = 0 . \end{cases} \quad (4.31)$$

Via the following ansatz for the correlation function  $g(\mathbf{r}, \mathbf{r}')$  at the critical temperature  $T_C$  one introduces a further *critical exponent*

$$g(\mathbf{r}, \mathbf{r}') \approx \frac{1}{|\mathbf{r} - \mathbf{r}'|^{d-2+\eta}} \begin{cases} T = T_C , p = p_C: & \text{real gas ,} \\ T = T_C , B_0 = 0: & \text{magnet .} \end{cases} \quad (4.32)$$

$d$  is the dimension of the system. Since according to (4.31)  $\xi = \infty$  for  $T = T_C$ , it should be, according to (4.12),  $\eta = 3 - d$ . The introduction of  $\eta$  would therewith be superfluous. The indeed a *bit unimaginative* exponent  $\eta$  expresses, how the correlation function of a real system deviates at  $T = T_C$  from the simple formula (4.12) (*Ornstein-Zernike behavior*, Sect. 4.3.9).

The Greek letters, chosen in the above relations for the critical exponents, are convention, and should not be replaced by others, in order to avoid misunderstandings. They are all non-negative numbers.

Why at all is one interested in *critical exponents*, although these are relevant only in a very narrow temperature region? Firstly, they are measurable. According to the definitions (4.20) and (4.21) the plot of  $\ln |F(\varepsilon)|$  versus  $\ln(\pm\varepsilon)$  should yield for sufficiently small  $\varepsilon$  a straight line with the slope  $\varphi$ .

From a fundamental point of view, however, above all the **universality** of physical properties at the phase transition is fascinating, which manifests itself in the *concept of the critical exponents*:

### Universality Hypothesis

(R. B. Griffiths: Phys. Rev. Lett. **24**, 1479 (1970)). The critical exponents are *almost universal*, i.e., practically for all thermodynamic systems the same. They only depend on:

1. the **dimension**  $d$  of the system,
2. the **range** of the particle interaction,
3. the **spin dimensionality**  $n$ .

The points 2 and 3 should be commented on. For the classification of the *range* of a particle interaction, we assume that the interaction decreases with the distance  $r$  of the interacting particles as

$$r^{-(d+2+x)} .$$

If  $x > 0$ , then one denotes the interaction as **short range**. Because of the diverging correlation length  $\xi$ , details of the particle interaction then do not play any role. Then really universal behavior appears. On the other hand, if one has to assume  $x < (d/2) - 2 < 0$ , then the interaction is considered as **long range**. In such a case the so-called *classical theories*, which will be discussed in Sect. 4.3, become valid, with a special set of critical exponents.—For **intermediate range** interactions ( $d/2 - 2 < x < 0$ ) one finds rather complicated behavior. The exponents can then depend also on  $x$ .

The *spin dimensionality*  $n$  becomes important for magnetic systems, which are often modeled as interacting spin systems:

$$H = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j , \quad (4.33)$$

By  $n$  one then understands the number of relevant components of the spin vectors  $\mathbf{S}_i$ :

- $n = 1$  : Ising model (4.1) ,
- $n = 2$  : XY model (two-dimensional spin vectors) ,
- $n = 3$  : Heisenberg model (three-dimensional spin vectors) .

We list some typical numerical values for the critical exponents  $\alpha$ ,  $\alpha'$ ,  $\beta$ ,  $\gamma$ ,  $\gamma'$ , and  $\delta$ :

	$\alpha$	$\alpha'$	$\beta$	$\gamma$	$\gamma'$	$\delta$
real gas, exp.	0	0	0.35	1.37	1.0	4.4
	(log)	(log)		$\pm 0.2$	$\pm 0.3$	$\pm 0.4$
magnet, exp.	0	0	0.34	1.33	1.33	$\geq 4.2$
	(log)	(log)		$\pm 0.03$	$\pm 0.03$	
class. theories	0	0	0.5	1	1	3
	(dis)	(dis)				
$d = 2$ -Ising, exact	0	0	0.125	1.75	1.75	15
	(log)	(log)				
$d = 3$ -Ising, approx.	0.11	0.11	0.325	1.24	1.24	$\approx 4.82$
$d = 3$ -Heisenberg, approx. ?	?	?	0.365	1.39	1.39	4.80

The critical exponent 0 is not unique. It can be a logarithmic singularity, but it can also characterize a finite discontinuity in the respective physical property. This is indicated accordingly in the above table.

We further add typical values for the exponents  $\nu$ ,  $\nu'$ , and  $\eta$ :

	$\nu$	$\nu'$	$\eta$
real gas, exp.	0.64	0.64	$\gtrsim 0$
magnet, exp.	0.65	0.65	$\gtrsim 0$
	$\pm 0.03$	$\pm 0.03$	
class. theories	0.25	0.25	0
$d = 2$ -Ising, exact	1	1	0.25
$d = 3$ -Ising, approx.	0.63	0.63	$\approx 0.03$
$d = 3$ -Heisenberg, approx.	0.705	0.705	0.034

It should be noted that the listed numerical values of the experimentally determined exponents are to be considered as *typical values*. Even today the published values still vary a little bit, depending on the method by which they have been measured. So one finds in the literature for the exponent  $\beta$  of the order parameter instead of 0.34 also 0.36 or 0.37. The values for  $\alpha$  and  $\eta$  are the most uncertain ones. The theoretical results for the  $d = 3$ -Ising model and the  $d = 3$ -Heisenberg model are based on unavoidable, but in the meantime extremely trustworthy approximations. The values for the *classical theories* are rigorously derivable (Sect. 4.3). This also holds for  $\alpha$ ,  $\alpha'$  and  $\beta$  of the  $d = 2$ -Ising model.



The calculated exponents of the  $d = 2$ - and  $d = 3$ -Ising model ( $n = 1$ ) as well as of the  $d = 3$ -Heisenberg model ( $n = 3$ ) clearly demonstrate the dependences on the lattice dimension  $d$  and the spin dimension  $n$ .

The universality hypothesis has shown its worth and is considered as practically proven after the development of the *Nobel-prize awarded* renormalization group theory by K. Wilson.

Interestingly, the different critical exponents are not completely independent of each other. There exist thermodynamically exact relations (*inequalities*) between them, the most important ones of which we have already derived in subsection 4.2.4 in Vol. 5:

$$\text{Rushbrooke inequality:} \quad \alpha' + 2\beta + \gamma' \geq 2, \quad (4.34)$$

$$\text{Griffiths inequality:} \quad \alpha' + \beta(1 + \delta) \geq 2, \quad (4.35)$$

$$\text{Widom inequality:} \quad \gamma' \geq \beta(\delta - 1). \quad (4.36)$$

There are strong hints that these exponent-inequalities are to be read even as equalities. The above table shows that this is true in any case for the *classical theories* and for the  $d = 2$ -Ising model. A further confirmation can be drawn from the scaling laws, which will be discussed in the next subsection.

## 4.2.2 Scaling Laws

With a consideration concerning the Ising model (4.1) we want to make plausible in this subsection, why the thermodynamically exact exponent-inequalities (4.34) to (4.36) are presumably to be read even as equalities. These relations are then called **scaling laws** for reasons which will become clear in the following. The mentioned consideration traces back to a heuristic argument of L.P. Kadanoff (*Kadanoff construction*), which will be illustrated here in connection with the Ising model, but which should have a substantially more general validity. The decisive aspect is namely the diverging of the correlation length  $\xi(T)$  at the critical point  $T_C$ . The spatial extension of the *fluctuations*, i.e., the coherent deviations of physical quantities from their mean values, will then become arbitrarily large, so that special details of the particle interactions do no longer play a role. That Kadanoff's idea indeed hits the point is quantitatively reasoned by the *renormalization group theory* of Wilson, into which, though, we cannot go in detail in this basic course of Theoretical Physics.

The result of the *Kadanoff construction* tells us that the *critical part* of the *free enthalpy*  $G(T, B_0)$  represents a *generalized homogeneous function*. This means that there exist two fixed numbers  $a_\varepsilon$  and  $a_B$ , with which it follows for all  $\lambda \in \mathbb{R}$ :

$$G(\lambda^{a_\varepsilon} \varepsilon, \lambda^{a_B} B_0) = \lambda G(\varepsilon, B_0). \quad (4.37)$$

Before we draw conclusions from this **scaling hypothesis**, also called **homogeneity postulate**, let us try to make it plausible in the framework of the Ising model. The numbers  $a_\varepsilon$  and  $a_B$  will not be further specified thereby, so that one cannot derive from (4.37) concrete numerical values for the critical exponents. It will, however, be possible to construct relationships between different exponents (*scaling laws*). The Hamilton function  $H$  appears, via the (grand-)canonical partition function, in the thermodynamic potentials exclusively in the form  $\beta H$ . We therefore investigate for the Ising-spin system instead of (4.1) directly the combination:

$$\beta H = -j \sum_{i,j} S_i S_j - b \sum_i S_i, \tag{4.38}$$

$$j = \frac{J}{k_B T}; \quad b = \frac{\mu B_0}{k_B T}. \tag{4.39}$$

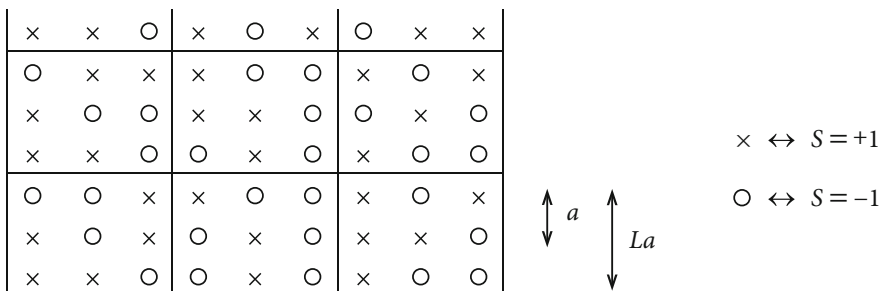
The first step consists in the decomposition of the spin lattice into elementary cells (*blocks*), in each of which there are  $L^d$  single spins (Fig. 4.17).  $d$  is again the lattice dimension. To the  $L^d$  spins of the elementary cell there can now be ascribed a common **block spin**. Since in the critical region the correlation length increases over all limits, the **scaling-transformation factor**  $L$  can always be chosen so that

$$a \ll La \ll \xi. \tag{4.40}$$

In a cluster of correlated, i.e., predominantly parallel spins there are then many *cells* (*blocks*) of the edge length  $La$ . We introduce the notation:

$$\text{block } \alpha \quad (\alpha = 1, 2, \dots, A) ; \quad \text{block spin } \widehat{S}_\alpha = \sum_{i \in \alpha} S_i. \tag{4.41}$$

For the ‘normal’ Ising-spins only  $S_i = \pm 1$  is possible. If the block lies entirely inside a cluster of correlated spins, then the block spin, too, has only two possibilities



**Fig. 4.17** Definition of the block (cell) spin in the Ising-spin lattice with the lattice constant  $a$

of orientation:

$$\widehat{S} \approx \pm L^d . \quad (4.42)$$

Slight deviations will appear for the blocks at the margin of the cluster. Furthermore, the correlated spins within the cluster of course are oriented in a preferred direction, single spins, however, can still 'break ranks'. For this reason we have put in (4.42) the 'approximation-sign'. For  $T \rightarrow T_C$  ( $\varepsilon \rightarrow 0$ ), because of  $\xi \rightarrow \infty$ , one can consider the Ising-system in the same manner as being composed of clusters of correlated single spins as well as of clusters of correlated block spins. In connection with (4.42) that must then mean that block spins interact with each other and with an external magnetic field in completely analogous manner as the single spins: **Block spins behave in the critical region like Ising spins!** We can therefore also expect that the non-analytical behavior of thermodynamic potentials at the critical point is described in both *pictures* likewise correctly. The respective partition functions should thermodynamically be completely equivalent. The expression corresponding to (4.38) will have in the *block-spin system* a very similar structure, though surely with modified coupling constants:

$$\widehat{\beta H} = -\widehat{j} \sum_{\alpha, \beta} \widehat{S}_\alpha \widehat{S}_\beta - \widehat{b} \sum_{\alpha} \widehat{S}_\alpha . \quad (4.43)$$

Just because of the modified coupling constant ( $j \rightarrow \widehat{j}$ ), the *critical region* in the *single-spin picture* will be different from that in the *block-spin picture*. That holds of course also for the *reduced temperature*:

$$\varepsilon \rightarrow \widehat{\varepsilon} .$$

The *thermodynamic equivalence* of the block-spin and the single-spin partition functions transfers to the thermodynamic potentials. In the critical region, the free enthalpy per single spin will exhibit as function of the variables  $\varepsilon$  and  $b$  the same *critical behavior* as the free enthalpy per block spin as function of the variables  $\widehat{\varepsilon}$  and  $\widehat{b}$ :

$$g_{\text{block spin}}(\widehat{\varepsilon}, \widehat{b}) \iff g_{\text{single spin}}(\varepsilon, b) .$$

Therefore we can omit already now the indexes *block spin* and *single spin* because both  $g$ 's have the same functional form. When we still recall the extensivity of the thermodynamic potentials, then we can represent the free enthalpy per block spin in two different ways what leads to the equation:

$$g(\widehat{\varepsilon}, \widehat{b}) = L^d g(\varepsilon, b) \quad (4.44)$$

This relation can of course be correct only for that part of the potential, which produces the *critical behavior*, but not necessarily also for the part which is regular at the critical point. The latter can be drastically different in the two pictures. It is, however, of no significance for the *critical phenomena*, which we are here interested in.

It now remains to establish the relationship between  $(\varepsilon, b)$  and  $(\hat{\varepsilon}, \hat{b})$ . The critical points must of course be identical:

$$(\varepsilon = 0, b = 0) \iff (\hat{\varepsilon} = 0, \hat{b} = 0) . \quad (4.45)$$

For the *field-term* it should hold in the *critical region*

$$-\hat{b} \sum_{\alpha} \hat{S}_{\alpha} \stackrel{!}{\sim} -b \sum_i S_i = -b \sum_{\alpha} \sum_{j \in \alpha} S_j$$

so that  $\hat{b} \sim b$ . Because the transformation is determined by  $L$ , we choose the following ansatz

$$\hat{b} = f(L)b \quad (4.46)$$

with an at first still unknown function  $f$ . Since in both systems the same *critical behavior* is to be expected, in particular with the same critical exponents, it must analogously be assumed

$$\hat{\varepsilon} = p(L)\varepsilon . \quad (4.47)$$

Equation (4.45) is therewith also fulfilled. The *equivalence relation* (4.44) now reads:

$$g(p(L)\varepsilon, f(L)b) = L^d g(\varepsilon, b) . \quad (4.48)$$

Although this is already completely sufficient for the confirmation of the homogeneity postulate (4.37), we will fix  $p$  and  $f$  still a bit more precisely. For this purpose we connect in series two scaling transformations:

$$\begin{aligned} (LM)^d g(\varepsilon, b) &= g(p(L)p(M)\varepsilon, f(L)f(M)b) \\ &\stackrel{!}{=} g(p(LM)\varepsilon, f(LM)b) . \end{aligned}$$

It follows from this relation:

$$p(LM) = p(L)p(M) ; \quad f(LM) = f(L)f(M) .$$

We presume  $f$  and  $p$  to be differentiable:

$$\frac{\partial}{\partial L} p(LM) = Mp'(LM) = \frac{\partial}{\partial L} (p(L)p(M)) = p(M)p'(L) .$$

With

$$p'(L = 1) = y$$

it then results:

$$p(M) = M^y .$$

The fully analogous consideration for  $f(L)$  yields:

$$f(L) = L^x .$$

Hence we can write instead of (4.48):

$$g(L^y \varepsilon, L^x b) = L^d g(\varepsilon, b) .$$

$x$  and  $y$  are thereby still undetermined numbers. It eventually follows with  $\lambda = L^d$ :

$$g(\lambda^{y/d} \varepsilon, \lambda^{x/d} b) = \lambda g(\varepsilon, b) . \quad (4.49)$$

Except for the restriction

$$1 \ll L \ll \frac{\xi}{a} \xrightarrow{T \rightarrow T_C} \infty ,$$

$L$  is arbitrarily selectable and therewith also  $\lambda$ . When one overlooks this restriction, then  $g(\varepsilon, b)$  indeed represents a *generalized homogeneous function* of the type (4.37):

$$a_\varepsilon = \frac{y}{d}; \quad a_B = \frac{x}{d} . \quad (4.50)$$

That we work here with  $b = \beta\mu B_0$  instead of  $B_0$ , does not falsify the statements concerning the critical exponents. These are explained for state changes, which are all performed in the zero field or, if not (exponent  $\delta!$ ), along the critical isotherm (see (4.22) to (4.32)).  $B_0 = 0$  entails  $b = 0$ , while on the critical isotherm the pre-factor  $\beta_c \mu = \mu/k_B T_C$  becomes trivial.

We will show in the next step how the numbers  $x$  and  $y$  in (4.49) can be expressed by critical exponents. For this purpose we differentiate (4.49) with respect to the

field  $b$ ,

$$\lambda^{x/d} \left[ \frac{\partial}{\partial (\lambda^{x/d} b)} g(\lambda^{y/d} \varepsilon, \lambda^{x/d} b) \right]_{\varepsilon} = \lambda \left[ \frac{\partial}{\partial b} (g(\varepsilon, b)) \right]_{\varepsilon},$$

and obtain then, using the thermodynamic relation,

$$\left( \frac{\partial G}{\partial B_0} \right)_T = -m(T, B_0) = -VM(T, B_0),$$

a useful relation for the magnetization  $M$  as function of the variables  $\varepsilon$  and  $b$ :

$$\lambda^{x/d} M(\lambda^{y/d} \varepsilon, \lambda^{x/d} b) = \lambda M(\varepsilon, b). \quad (4.51)$$

The changes of state, which are relevant for the critical exponents, take place in the zero-field ( $b = 0$ ), so that  $M$  becomes the *spontaneous* magnetization  $M_S$ ,

$$\lambda^{x/d} M_S(\lambda^{y/d} \varepsilon, 0) = \lambda M_S(\varepsilon, 0), \quad (4.52)$$

or they are performed on the critical isotherm ( $\varepsilon = 0$ ):

$$\lambda^{x/d} M(0, \lambda^{x/d} b) = \lambda M(0, b). \quad (4.53)$$

These relations are valid for arbitrary  $\lambda$ . If one chooses in (4.53)

$$\lambda = b^{-d/x},$$

it remains:

$$b^{-1} M(0, 1) = b^{-d/x} M(0, b).$$

$M(0, 1)$  is a constant number, so that one can also write:

$$b \sim [M(0, b)]^{x/(d-x)}. \quad (4.54)$$

The sign  $\sim$  is here, as explained in (4.19), to be understood as ‘*behaves in the critical region as ...*’. The comparison of (4.54) with (4.29) thus yields a connection between the critical exponent  $\delta$  and the number  $x$ :

$$\delta = \frac{x}{d-x}. \quad (4.55)$$

If one chooses in (4.52)

$$\lambda = (-\varepsilon)^{-d/y},$$

an analogous consideration leads to

$$M_S(\varepsilon, 0) \sim (-\varepsilon)^{(d-x)/y} . \quad (4.56)$$

The comparison with (4.25) then yields for the critical exponent of the order parameter:

$$\beta = \frac{d-x}{y} . \quad (4.57)$$

$x$  and  $y$  are now already determined by (4.55) and (4.57):

$$x = d \frac{\delta}{1+\delta} ; \quad y = \frac{d}{\beta} \frac{1}{1+\delta} . \quad (4.58)$$

If we are now able to express a further exponent by  $x$  and  $y$ , then this will lead eventually to relations between the exponents.

For the isothermal susceptibility

$$\chi_T = \mu_0 \left( \frac{\partial M}{\partial B_0} \right)_T$$

we have to differentiate (4.51) once more with respect to the field:

$$\lambda^{2x/d} \left[ \frac{\partial}{\partial (\lambda^{x/d} b)} M(\lambda^{y/d} \varepsilon, \lambda^{x/d} b) \right]_{\varepsilon} = \lambda \left( \frac{\partial}{\partial b} M(\varepsilon, b) \right)_{\varepsilon} .$$

From that we get for the susceptibility in the zero-field:

$$\lambda^{2x/d} \chi_T(\lambda^{y/d} \varepsilon, 0) = \lambda \chi_T(\varepsilon, 0) . \quad (4.59)$$

If we now insert here

$$\lambda = (\pm \varepsilon)^{-d/y} ,$$

we have:

$$\chi_T(\varepsilon, 0) \sim (\pm \varepsilon)^{-(2x-d)/y} . \quad (4.60)$$

This means according to (4.27) a connection of  $x$  and  $y$  with the critical exponents  $\gamma$  and  $\gamma'$ , respectively:

$$\gamma = \gamma' = \frac{2x-d}{y} . \quad (4.61)$$

In order to finally fix the critical exponents of the heat capacity,

$$C_H = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{B_0} ,$$

we have to differentiate the *homogeneity relation* (4.49) twice with respect to  $\varepsilon$ :

$$\lambda^{2y/d} \left[ \frac{\partial^2}{\partial (\lambda^{y/d} \varepsilon)^2} g(\lambda^{y/d} \varepsilon, \lambda^{x/d} b) \right]_b = \lambda \left( \frac{\partial^2}{\partial \varepsilon^2} g(\varepsilon, b) \right)_b .$$

The critical behavior of the zero-field heat capacity results therewith from the relation:

$$\lambda^{2y/d} C_H(\lambda^{y/d} \varepsilon, 0) = \lambda C_H(\varepsilon, 0) . \quad (4.62)$$

If we insert

$$\lambda = (\pm \varepsilon)^{-d/y} ,$$

it follows:

$$C_H(\varepsilon, 0) \sim (\pm \varepsilon)^{-(2-d/y)} . \quad (4.63)$$

The comparison with (4.23) leads to

$$\alpha = \alpha' = \frac{2y - d}{y} . \quad (4.64)$$

The critical exponents  $\alpha, \alpha', \beta, \gamma, \gamma', \delta$  are now all expressed by  $x$  and  $y$ . This means, on the other hand, that the measurement of two exponents uniquely fixes all the other exponents, provided that the *scaling hypothesis* (*homogeneity postulate* (4.49)), which could be made plausible by the *Kadanoff construction*, is indeed exact. One important consequence consists in the statement that the critical exponents are independent of whether the critical point is approached *from below* ( $T < T_C$ ) or *from above* ( $T > T_C$ ) ( $\alpha = \alpha', \gamma = \gamma'$ ). A further important consequence concerns the thermodynamically exact exponent-inequalities (4.34) to (4.36). One easily verifies with (4.55), (4.57), (4.61), and (4.64) that they are to be read as **equalities**:

$$\alpha + 2\beta + \gamma = 2 , \quad (4.65)$$

$$\alpha + \beta (1 + \delta) = 2 , \quad (4.66)$$

$$\gamma = \beta (\delta - 1) . \quad (4.67)$$



These equations, together with  $\alpha = \alpha'$  and  $\gamma = \gamma'$ , are denoted as **scaling laws**. Further scaling laws, which concern the critical exponents  $\nu$ ,  $\nu'$  and  $\eta$ , we will get to know in the next subsection.

### 4.2.3 Correlation Function

We will now show that the *correlation function* defined in (4.9) also represents a *generalized homogeneous function*. That will lead to statements about the critical exponents  $\nu$ ,  $\nu'$ , and  $\eta$ , where it will even be possible to connect these with the exponents  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , i.e. with quantities, which regulate the critical behavior of certain derivatives of the thermodynamic potentials. As in the last subsection, our plausibility-consideration concerns the Ising model:

$$g(r, \varepsilon) = \langle S_i S_j \rangle - \langle S \rangle^2. \quad (4.68)$$

We presume a spatially homogeneous system so that the correlation  $g$  (not to be confused with the free enthalpy!) will depend only on the distance

$$r = \frac{|\mathbf{R}_i - \mathbf{R}_j|}{a}.$$

We choose the distance as dimensionless, because the absolute distance of course does not matter, but only the number of interacting spins in between the two points under consideration. Furthermore, the spatial homogeneity manifests itself also in the fact that the average values,  $\langle S_i \rangle = \langle S \rangle \quad \forall i$ , do not depend on the special lattice site.

With the same justification as that before Eq. (4.44) we exploit here also the *plausible* assumption that the correlation function in the *block-spin picture*,

$$g(\hat{r}, \hat{\varepsilon}) = \langle \widehat{S}_\alpha \widehat{S}_\beta \rangle - \langle \widehat{S} \rangle^2, \quad (4.69)$$

should have as function of the *scaled* variables  $\hat{r}$  and  $\hat{\varepsilon}$  the same functional form as the correlation function in the *single-spin picture* (4.68) as function of the variables  $r$  and  $\varepsilon$ . The connection between the reduced temperatures  $\varepsilon$  and  $\hat{\varepsilon}$  we know already from the last subsection:

$$\hat{\varepsilon} = L^y \varepsilon; \quad y = \frac{d}{\beta} \frac{1}{1 + \delta}. \quad (4.70)$$

For  $\hat{r}$  we have simply:

$$\hat{r} = \frac{|\widehat{\mathbf{R}}_\alpha - \widehat{\mathbf{R}}_\beta|}{La} = \frac{r}{L}. \quad (4.71)$$

For the right-hand side of this equation it is thereby presumed that  $i$  and  $j$  denote equivalent positions in the blocks  $\alpha$  and  $\beta$ .

Somewhat differently from what we used in the preceding subsection, we normalize by

$$L^{-d} \sum_{i \in \alpha} S_i \equiv p \widehat{S}_\alpha \quad (\widehat{S}_\alpha = \pm 1) \tag{4.72}$$

the **block spin**  $\widehat{S}_\alpha$  exactly to 1, which is regulated by the factor  $p$ .  $p$  by itself should be of the order 1.

In the critical region ( $\xi \rightarrow \infty$ ) the average value  $\langle S_i S_j \rangle$  will be same, to a good approximation, for all  $i \in \alpha$  and all  $j \in \beta$ . This means:

$$\langle S_i S_j \rangle = L^{-2d} \sum_{i \in \alpha} \sum_{j \in \beta} \langle S_i S_j \rangle = p^2 \langle \widehat{S}_\alpha \widehat{S}_\beta \rangle .$$

For the same reason we have:

$$\langle S_i \rangle = L^{-d} \sum_{i \in \alpha} \langle S_i \rangle = p \langle \widehat{S}_\alpha \rangle .$$

This yields the following relation between the correlation functions in the two pictures:

$$g(r, \varepsilon) = p^2 g(\hat{r}, \hat{\varepsilon}) . \tag{4.73}$$

We can find out something about the number  $p$  with the aid of the field term in the Ising-Hamilton function: we can find out something with the aid of the field term in the Ising-Hamilton function:

$$\begin{aligned} \hat{b} \sum_\alpha \widehat{S}_\alpha &\stackrel{!}{=} b \sum_\alpha \sum_{i \in \alpha} S_i = b L^d \sum_\alpha (p \widehat{S}_\alpha) \\ \implies \hat{b} &= (p L^d) b . \end{aligned}$$

When we combine this with the previous result  $\hat{b} = L^x b$  (4.46), we get:

$$p = L^{x-d} . \tag{4.74}$$

Equation (4.73) therewith takes the form:

$$g(r, \varepsilon) = L^{2(x-d)} g\left(\frac{r}{L}, L^y \varepsilon\right) . \tag{4.75}$$

If we further use

$$L \rightarrow \lambda^{-1/(2(x-d))} ,$$

then we realize that the *critical part* of the correlation function indeed represents a *generalized homogeneous function*:

$$g(\lambda^{\alpha_r} r, \lambda^{\alpha_\varepsilon} \varepsilon) = \lambda g(r, \varepsilon) , \quad (4.76)$$

$$\alpha_r = \frac{1}{2(x-d)} \quad ; \quad \alpha_\varepsilon = -\frac{y}{2(x-d)} .$$

According to (4.12), (4.31) and (4.32) we have in the critical region:

$$g(r, \varepsilon) \sim \frac{\exp(-r/\xi(\varepsilon))}{r^{d-2+\eta}} ; \quad \xi(\varepsilon) \sim (\pm\varepsilon)^{-\nu'} . \quad (4.77)$$

This we will exploit, in order to search out, by means of (4.76), *scaling laws* for the critical exponents  $\nu$ ,  $\nu'$  and  $\eta$ .

At first we use in (4.76) for the case  $\varepsilon = 0$  ( $\Leftrightarrow T = T_C$ ):

$$\lambda = r^{-2(x-d)} .$$

This leads to:

$$g(r, 0) = r^{2(x-d)} g(1, 0) .$$

$g(1, 0)$  is here an unimportant number so that the comparison with (4.77) yields:

$$d - 2 + \eta = -2(x-d) \quad (4.78)$$

If we choose instead

$$\lambda = (\pm\varepsilon)^{2(x-d)/y} ,$$

it follows from (4.76):

$$g(r, \varepsilon) = (\pm\varepsilon)^{-2(x-d)/y} g(r(\pm\varepsilon)^{1/y}, \pm 1) .$$

This we insert into (4.77):

$$\frac{\exp\left(-\frac{r}{\xi(\varepsilon)}\right)}{r^{d-2+\eta}} \sim (\pm\varepsilon)^{-2(x-d)/y} \frac{\exp\left(-\frac{r(\pm\varepsilon)^{1/y}}{\xi(\pm 1)}\right)}{r^{d-2+\eta} (\pm\varepsilon)^{(d-2+\eta)/y}} .$$

From this we get with (4.78):

$$\xi(\varepsilon) \sim \xi(\pm 1)(\pm \varepsilon)^{-1/\nu}. \quad (4.79)$$

According to (4.31) this means:

$$\nu = \nu' = \frac{1}{\gamma}. \quad (4.80)$$

The results (4.78) and (4.80), derived from the property (4.76) of the correlation function, lead with our previous results (4.58) for  $x$  and  $y$  to a series of new **scaling laws**. One immediately obtains, for instance, with (4.80) in (4.64):

$$\alpha = \alpha' = 2 - d\nu = 2 - d\nu'. \quad (4.81)$$

If one combines (4.58), (4.66), (4.78), and (4.81), one easily finds:

$$d - 2 + \eta = \frac{2d\beta}{2 - \alpha} = \frac{2d}{1 + \delta} = \frac{2\beta}{\nu}. \quad (4.82)$$

It follows from (4.65) with (4.81) and (4.82):

$$\gamma = (2 - \eta)\nu, \quad (4.83)$$

$$d \frac{\delta - 1}{\delta + 1} = \frac{d\gamma}{2\beta + \gamma} = 2 - \eta. \quad (4.84)$$

To the last scaling law there exist the thermodynamically exact **Buckingham-Guntton inequalities**:

$$\frac{d\gamma'}{2\beta + \gamma'} \geq 2 - \eta; \quad d \frac{\delta - 1}{\delta + 1} \geq 2 - \eta. \quad (4.85)$$

The scaling laws, which contain the lattice dimension  $d$  (*hyperscaling*), are of special importance. It is a shortcoming of the *classical theories*, which we investigate in the next section, that their critical exponents are all independent of  $d$ . Only for  $d = 4$  the *classical theories* fulfill also the *hyperscaling*. The multitude of scaling laws offers a series of possibilities for testing the *scaling hypothesis*. So one finds, for instance, for the product  $d\nu$  several relations, which are checkable by model calculations or by the experiment:

$dv = 2 - \alpha$	2	2
$= 2 - \alpha'$	2	2
$= \gamma + 2\beta$	2	2
$= \gamma' + 2\beta$	2	2
$= \beta(\delta + 1)$	2	2
$= dv'$	2	1.5
$= \frac{d\gamma}{2-\eta}$	2	1.5
$= \frac{d\gamma'}{2-\eta}$	2	1.5
$= dv$	2	1.5
$\uparrow$	$\uparrow$	$\uparrow$
scaling laws	$d = 2$ -Ising model	$d = 3$ -classical theories

The scaling laws are fully confirmed by the exactly calculable  $d = 2$ -Ising model. They have been derived here on the basis of the *Kadanoff construction*, which, however, because of the various assumptions, can be considered as only *plausible* and not at all as exact. The scaling laws are actually confirmed only when the free enthalpy and the correlation function are indeed generalized homogeneous functions.

#### 4.2.4 Exercises

##### Exercise 4.2.1

A physical quantity  $f$  behaves in the critical region as

$$f(T) = aT \ln|T - T_c| + bT^2 .$$

What is the corresponding critical exponent?

##### Exercise 4.2.2

Show that for second-order phase transitions in the *Ehrenfest sense* only critical exponents  $\varphi = 0$  are possible.

**Exercise 4.2.3**

Determine the critical exponents of

1.  $f(T) = aT^{5/2} - b$ ,
2.  $f(T) = aT^2 + c(T - T_c)^{-1}$ ,
3.  $f(T) = a\sqrt{|T - T_c|} + d$ ,

$a, b, c, d$ : constants, unequal zero.

**Exercise 4.2.4**

Let the ratio of the heat capacities

$$R = \frac{C_m}{C_H}$$

be temperature-independent. Show that the equal-sign in the Rushbrooke relation

$$\alpha' + 2\beta + \gamma' \geq 2$$

holds only if  $R \neq 1$ .

**Exercise 4.2.5**

Derive for a magnetic system with the scaling hypothesis the following relation for the magnetization  $M$ :

$$\frac{M(\varepsilon, H)}{(\pm\varepsilon)^\beta} = M(\pm 1, (\pm\varepsilon)^{-\beta\delta} H).$$

Do you see a possibility to check by this equation experimentally the scaling hypothesis?

**Exercise 4.2.6**

Prove by the use of the scaling hypothesis the following exponent equations:

1.  $\gamma(\delta + 1) = (2 - \alpha)(\delta - 1)$ ,
2.  $\delta = \frac{2 - \alpha + \gamma}{2 - \alpha - \gamma}$ .

## 4.3 Classical Theories

### 4.3.1 Landau Theory

Problems of Statistical Physics can be considered as being *solved* as soon as a relevant thermodynamic potential, as for instance the free enthalpy  $G(T, p)$ , could be completely determined. Rigorously in a strict mathematical sense, that is rarely possible, though. The surprisingly universal behavior of physical quantities in the neighborhood of phase transition points, however, gives hope that possibly the *problem: phase transition*, at least in the *critical region*, is treatable in a very general way. The first attempt of such a general description stems from L. D. Landau (1937). The idea consists in a representation of the behavior of the free enthalpy  $G$  in the *critical region* as a functional of the order parameter  $\varphi$ , which we introduced in Sect. 4.1.4, or of its *density*  $\psi(\mathbf{r})$ :

$$\varphi = \int d^3r \psi(\mathbf{r}) \begin{cases} = 0 & \text{for } T > T_C, \\ \neq 0 & \text{for } T < T_C. \end{cases} \quad (4.86)$$

One may think for instance of the ferromagnet, for which  $\varphi$  means the magnetic moment  $\mathbf{m}$  and  $\psi(\mathbf{r})$  the local magnetization  $\mathbf{M}(\mathbf{r})$ . The observation that  $\psi$  tends continuously to zero for  $T \xrightarrow{\leftarrow} T_C$ , suggests for the *critical region* something like a power series expansion:

$$G(T; \varphi) = \int d^3r g(T; \psi(\mathbf{r})) = \int d^3r [g_0(\mathbf{r}) - \pi(\mathbf{r})\psi(\mathbf{r}) + a(T)\psi^2(\mathbf{r}) + b(T)\psi^4(\mathbf{r}) + c(T)(\nabla\psi(\mathbf{r}))^2]. \quad (4.87)$$

$\varphi$  (or  $\psi$ ) can of course not be considered as a thermodynamic variable like the temperature  $T$ , but must ultimately be fixed by thermal equilibrium conditions. At a given temperature, the equilibrium value of  $\varphi$  will be that for which  $G(T; \varphi)$  becomes minimal.—The second thermodynamic variable besides  $T$ , e.g. the pressure  $p$ , is not interesting for the following, and can therefore be suppressed in (4.87). The expansion (4.87) is of course not *a priori* clear, but represents at first a more or less arbitrary assumption of the theory. It appears indeed not unproblematic, since the phase transition provokes a singular point in the thermodynamic potential. That can transfer to the coefficients of the expansion. The magnitude of the individual terms in (4.87) must therefore not exclusively be determined by the power of  $\psi$ . When using (4.87) it is implicitly assumed that the coefficients  $a$ ,  $b$ ,  $c$  behave *smoothly*.

In (4.87)  $\pi(\mathbf{r})$  denotes the *conjugate force*, which belongs to the order-parameter density  $\psi(\mathbf{r})$ , as for instance the magnetic induction  $\mathbf{B}_0(\mathbf{r})$  to the magnetization  $\mathbf{M}(\mathbf{r})$  for the ferromagnet.  $g_0(\mathbf{r})$  is the enthalpy density at vanishing order parameter

( $T > T_C$ ). Due to symmetry reasons, the expansion (4.87) contains only even powers of  $\psi(\mathbf{r})$ , because  $G(T; \varphi)$  should not change with a simultaneous sign-change of  $\psi$  and  $\pi$  (see ferromagnet). For the same reason only rotation-invariant combinations of the gradient of  $\psi$  come into question.

All the statements of the *Landau theory* are consequences of the expansion (4.87), which is universal, i.e. independent of the material. We will at first begin with the important special case that the order-parameter density  $\psi$  and the conjugate force  $\pi$  are position-independent. Then (4.87) simplifies to:

$$G(T; \varphi) = G(T; \varphi = 0) - \pi\varphi + \frac{1}{V}a(T)\varphi^2 + \frac{1}{V^3}b(T)\varphi^4. \quad (4.88)$$

At vanishing force ( $\pi = 0$ ) the equilibrium value of  $\varphi$  must be zero for  $T > T_C$  and for  $T < T_C$  unequal zero (Fig. 4.18). For  $T > T_C$  the extreme-value condition of the free enthalpy,

$$\left(\frac{\partial G}{\partial \varphi}\right)_T \stackrel{!}{=} 0 = \frac{2}{V}a(T)\varphi + \frac{4}{V^3}b(T)\varphi^3,$$

is indeed fulfilled by  $\varphi = 0$ , while the minimum-requirement,

$$\left(\frac{\partial^2 G}{\partial \varphi^2}\right)_T (\varphi = 0) = \frac{2}{V}a(T) \stackrel{!}{>} 0,$$

can be realized only with

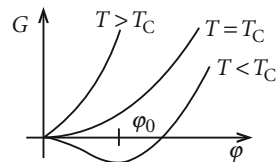
$$a(T) > 0 \quad \text{for } T > T_C.$$

No statement about  $b(T)$  is at first possible for  $T > T_C$ .

In the low-temperature phase ( $T < T_C$ ) the extreme-value condition reads, because of  $\varphi_0 \neq 0$  (Fig. 4.18),

$$a(T) + \frac{2}{V^2}b(T)\varphi_0^2 = 0, \quad (4.89)$$

**Fig. 4.18** Schematic behavior of the free enthalpy as function of the order parameter  $\varphi$  at constant temperature





which is fulfilled by

$$\varphi_0 = \pm \sqrt{-V^2 \frac{a(T)}{2b(T)}} . \quad (4.90)$$

The extremum is a minimum if it holds additionally

$$a(T) + \frac{6}{V^2} b(T) \varphi_0^2 > 0 . \quad (4.91)$$

When one subtracts (4.89) from (4.91), it remains to require:

$$b(T) > 0 \quad \text{for } T < T_C . \quad (4.92)$$

But because of (4.89) that has also the consequence

$$a(T) < 0 \quad \text{for } T < T_C .$$

The coefficient  $a(T)$  thus changes its sign at  $T = T_C$  what suggests the ansatz

$$a(T) = a_0 (T - T_C) , \quad a_0 > 0 . \quad (4.93)$$

This step of course involves once more a certain arbitrariness, because each other odd power of  $(T - T_C)$  would also guarantee the sign-change. However, later we will be able to demonstrate that higher powers of  $(T - T_C)$  lead to contradictions in other respects.

At the critical temperature  $T_C$  it holds for the order parameter  $\varphi_0 = 0$ , so that for  $T = T_C$  the first three derivatives of  $G$  with respect to  $\varphi$  vanish. The minimum-condition must therefore refer to the fourth derivative:

$$\left( \frac{\partial^4 G}{\partial \varphi^4} \right)_{T=T_C} (\varphi = \varphi_0 = 0) \stackrel{!}{>} 0 .$$

From that we read off

$$b(T_C) > 0 . \quad (4.94)$$

Because of (4.92) and for reasons of continuity one can thus assume for the entire, very small *critical region*

$$b(T) \approx b(T_C) \equiv b > 0 . \quad (4.95)$$

We have motivated (4.93) and (4.95) for a system with position-independent  $\psi$  and  $\pi$ . Because of the universality of the *Landau ansatz* (4.87), however, the structures

of the two equations should be generally valid. Only the concrete numerical values for the constants  $a_0$ ,  $b$  and  $T_C$  will be material-specific.

### 4.3.2 Spatial Fluctuations

Before we explicitly calculate the critical exponents of the Landau theory, we will have to still look at the important **correlation function** of the order parameter, for which it must hold according to (4.9):

$$\begin{aligned} g(\mathbf{r}, \mathbf{r}') &= \langle \psi(\mathbf{r})\psi(\mathbf{r}') \rangle - \langle \psi(\mathbf{r}) \rangle \langle \psi(\mathbf{r}') \rangle \\ &= \left\langle (\psi(\mathbf{r}) - \langle \psi(\mathbf{r}) \rangle)(\psi(\mathbf{r}') - \langle \psi(\mathbf{r}') \rangle) \right\rangle. \end{aligned} \quad (4.96)$$

It describes the connection between the deviations of the order-parameter density from its average values at the positions  $\mathbf{r}$  and  $\mathbf{r}'$ . We apply the Hamilton operator in the following form,

$$H = H_0 - \int d^3 r' \pi(\mathbf{r}') \psi(\mathbf{r}'), \quad (4.97)$$

where  $H_0$  means the *force-free* operator. We are at first interested in the *response*  $\delta\langle\psi(\mathbf{r})\rangle$  of the order-parameter density to a variation  $\delta\pi(\mathbf{r}')$  of the *conjugate force*. We calculate the average value  $\langle\psi(\mathbf{r})\rangle$  in the canonical ensemble:

$$\begin{aligned} \langle\psi(\mathbf{r})\rangle &= \frac{1}{Z} \text{Tr} [\psi(\mathbf{r}) e^{-\beta H}] , \\ Z &= \text{Tr}(e^{-\beta H}) . \end{aligned} \quad (4.98)$$

The variation

$$\begin{aligned} \delta\langle\psi(\mathbf{r})\rangle &= \frac{1}{Z} \text{Tr} [\psi(\mathbf{r})(-\beta\delta H)e^{-\beta H}] \\ &\quad - \frac{1}{Z^2} \text{Tr} [(-\beta\delta H)e^{-\beta H}] \text{Tr} [\psi(\mathbf{r})e^{-\beta H}] \\ &= -\beta \{ \langle\psi(\mathbf{r})\delta H\rangle - \langle\delta H\rangle\langle\psi(\mathbf{r})\rangle \} \end{aligned}$$

yields with

$$\delta H = - \int d^3 r' \psi(\mathbf{r}') \delta\pi(\mathbf{r}')$$

a connection between the *response* of the order parameter to the *external perturbations* and the internal fluctuations of the system:

$$\delta\langle\psi(\mathbf{r})\rangle = \beta \int d^3r' g(\mathbf{r}, \mathbf{r}') \delta\pi(\mathbf{r}') . \quad (4.99)$$

This is nothing else but the, compared to (4.16), generalized

**fluctuation-dissipation theorem**

In the homogeneous case ( $\delta\langle\psi\rangle$  and  $\delta\pi$  are position-independent!) it follows from (4.99) the to (4.16) corresponding connection between susceptibility ( $k$ : constant),

$$\chi_T = \frac{k}{V} \left( \frac{\partial\varphi_0}{\partial\pi} \right)_T = k \left( \frac{\partial\psi_0}{\partial\pi} \right)_T ,$$

and correlation function:

$$\chi_T = k\beta \int d^3r' g(\mathbf{r}, \mathbf{r}') . \quad (4.100)$$

Here we have presumed that the *most probable* and the *average* order-parameter density are same:

$$\bar{\psi}_0 \stackrel{!}{=} \langle\psi\rangle . \quad (4.101)$$

Equation (4.101) is in general surely correct, but becomes questionable just in the region of strong fluctuations and has therefore later still to be commented on.

The further discussion will be performed again for the compared to (4.100) more general expression (4.99) of the fluctuation-dissipation theorem. The most probable value (equilibrium value) of the order parameter is that which minimizes  $G(T; \varphi)$ . The first variation of the free enthalpy with respect to  $\psi$  must therefore vanish at  $\psi_0$ :

$$0 \stackrel{!}{=} \int d^3r [-\pi(\mathbf{r}) + 2a(T)\psi_0(\mathbf{r}) + 4b(T)\psi_0^3(\mathbf{r}) - 2c(T)\Delta\psi_0(\mathbf{r})] \delta\psi(\mathbf{r}) . \quad (4.102)$$

Maybe the origin of the last term in the bracket should be commented on a bit. We made ourselves somewhat familiar with the *calculus of variation* in subsection 1.3.2 of Vol. 2. It is common for all functions  $\psi(\mathbf{r})$ , which are admitted to the so-called *competing ensemble*, that they coincide on the surface of the integration volume, so that their variation there vanishes. According to (4.87) we need then for  $\delta G$ , among

other things, the following contribution:

$$\begin{aligned} \delta \int_V d^3r (\nabla \psi(\mathbf{r}))^2 &= 2 \int_V d^3r \nabla \psi(\mathbf{r}) \delta \nabla \psi(\mathbf{r}) \\ &= 2 \int_V d^3r [\operatorname{div}(\nabla \psi \delta \psi) - \delta \psi \Delta \psi] . \end{aligned}$$

We have here exploited:  $\delta(\nabla \psi) = \nabla(\delta \psi)$ . The first term in the bracket vanishes,

$$\int_V d^3r \operatorname{div}(\nabla \psi \delta \psi) = \int_{\partial V} d\mathbf{f} \cdot \nabla \psi \delta \psi = 0 ,$$

because  $\delta \psi$  is zero on the surface  $\partial V$  of  $V$ . The variation of the last term in (4.87) yields

$$\delta \int_V d^3r c(T) (\nabla \psi(\mathbf{r}))^2 = \int_V d^3r (-2c(T) \Delta \psi) \delta \psi(\mathbf{r}) ,$$

which explains (4.102).—Since  $\delta \psi$  can be arbitrarily chosen, except for the already used boundary condition, it must even hold, beyond (4.102),

$$\pi(\mathbf{r}) = 2a(T)\psi_0(\mathbf{r}) + 4b(T)\psi_0^3(\mathbf{r}) - 2c(T)\Delta\psi_0(\mathbf{r}) . \quad (4.103)$$

When we now still accept (4.101) in (4.103), i.e. identifying the most probable order-parameter density with the average one, and vary (4.103) with respect to the force  $\pi$ , then it remains after exploiting the fluctuation-dissipation theorem:

$$\begin{aligned} \delta\pi(\mathbf{r}) &= \int d^3r' \delta(\mathbf{r} - \mathbf{r}') \delta\pi(\mathbf{r}') \\ &= \beta \left( 2a(T) + 12b(T)\langle\psi(\mathbf{r})\rangle^2 - 2c(T)\Delta_r \right) \int d^3r' g(\mathbf{r}, \mathbf{r}') \delta\pi(\mathbf{r}') . \end{aligned}$$

Since  $\delta\pi$ , too, can be arbitrarily chosen, it finally results the following conditional equation for the correlation function  $g(\mathbf{r}, \mathbf{r}')$ :

$$\left( 2a(T) + 12b(T)\langle\psi(\mathbf{r})\rangle^2 - 2c(T)\Delta_r \right) g(\mathbf{r}, \mathbf{r}') = k_B T \delta(\mathbf{r} - \mathbf{r}') . \quad (4.104)$$

This equation will be integrable only with simplifying assumptions concerning  $\langle\psi(\mathbf{r})\rangle$ . Let  $\psi(\mathbf{r})$  be almost homogeneous, i.e. only weakly position-dependent. Furthermore,  $g(\mathbf{r}, \mathbf{r}')$  interests us only with respect to its critical behavior, i.e.

according to (4.31) for the case  $\pi \rightarrow 0$ . But then we can use approximately (4.90):

$$T > T_C: \langle \psi(\mathbf{r}) \rangle^2 \rightarrow 0, \quad T < T_C: \langle \psi(\mathbf{r}) \rangle^2 \rightarrow -\frac{a(T)}{2b(T)}, \quad (4.105)$$

and (4.104) simplifies to

$$(\alpha_1 - \alpha_2 \Delta_r)g(\mathbf{r}, \mathbf{r}') = k_B T \delta(\mathbf{r} - \mathbf{r}'), \quad (4.106)$$

where it must be taken  $(\alpha_1, \alpha_2) = (2a, 2c)$  for  $T > T_C$  and  $(\alpha_1, \alpha_2) = (-4a, 2c)$  for  $T < T_C$ . After Fourier transformation,

$$g(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int d^3k g(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')},$$

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int d^3k e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')},$$

(4.106) goes over into the algebraic equation :

$$g(\mathbf{k}) = \frac{k_B T}{(\alpha_1 + \alpha_2 k^2)} = g(k).$$

Inverse transformation with trivial angle integration leads to:

$$g(\mathbf{r}, \mathbf{r}') = g(\mathbf{r} - \mathbf{r}')$$

$$= \frac{k_B T}{8\pi^2 \alpha_2 i |\mathbf{r} - \mathbf{r}'|} \int_{\mathcal{C}} dk \left( \frac{1}{k + i\sqrt{\frac{\alpha_1}{\alpha_2}}} + \frac{1}{k - i\sqrt{\frac{\alpha_1}{\alpha_2}}} \right) e^{ik|\mathbf{r} - \mathbf{r}'|}.$$

Only the second term possesses a pole in the upper half-plane. According to the *residue theorem* ((4.425), Vol. 3) it thus follows

$$g(\mathbf{r}, \mathbf{r}') = \frac{k_B T}{8\pi c(T)} \frac{\exp\left(-\frac{|\mathbf{r} - \mathbf{r}'|}{\xi(T)}\right)}{|\mathbf{r} - \mathbf{r}'|} \quad (4.107)$$

as solution for the correlation function of the order parameter in a **three**-dimensional system. Thereby it holds for the **correlation length**  $\xi$ :

$$T > T_C: \xi(T) = \sqrt{\frac{c(T)}{a(T)}}, \quad T < T_C: \xi(T) = \sqrt{\frac{-c(T)}{2a(T)}}. \quad (4.108)$$

### 4.3.3 Critical Exponents

The *Landau ansatz* (4.87) is much more detailed than the *scaling hypothesis* (4.37). In contrast to the latter, the *Landau theory* is therefore able to deliver concrete numerical values for the critical exponents.

The temperature-dependence of the order parameter in the critical region can be read off from (4.90), when one inserts (4.93) into (4.95):

$$\varphi_0 = \pm V \sqrt{\frac{a_0}{2b}} |T - T_C|^{1/2} \quad (T < T_C) .$$

The critical exponent of the order parameter is therewith directly available:

$$\beta = \frac{1}{2} . \quad (4.109)$$

For the heat capacity,

$$C_{\pi=0} = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_{\pi=0} ,$$

the temperature-dependence of the free enthalpy is decisive, which we find for the homogeneous system ( $\psi(\mathbf{r}) \equiv \psi$ ,  $\varphi = V\psi$ ) by insertion of (4.90) into (4.88):

$$\begin{aligned} T > T_C: G(T) &= G(T, \varphi = 0) , \\ T < T_C: G(T) &\stackrel{(\pi=0)}{=} G(T; \varphi = 0) + \frac{1}{V} a(T) \varphi_0^2 + \frac{1}{V^3} b \varphi_0^4 \\ &\stackrel{(4.90)}{=} G(T; \varphi = 0) - V \frac{a^2(T)}{4b} . \end{aligned}$$

From that it follows with (4.93):

$$C_{\pi=0}(T = T_C^{(-)}) = C_{\pi=0}(T = T_C^{(+)}) + T_C V \frac{a_0^2}{2b} . \quad (4.110)$$

The heat capacity thus exhibits a finite jump at  $T_C$ . According to (4.20) and (4.21) this corresponds to a critical exponent:

$$\alpha = \alpha' = 0 . \quad (4.111)$$

Note that the choice of a higher odd power of  $T - T_C$  in (4.93) would guarantee the sign-change of  $a(T)$  at  $T_C$ , but, on the other hand, it would cause  $C_{\pi=0}(T_C^{(-)}) = C_{\pi=0}(T_C^{(+)})$ . The heat capacity would then not show at  $T_C$  any peculiarity. That excludes  $a(T) \sim (T - T_C)^{2n+1}$  with  $n \geq 1$ .

For the derivation of the exponent  $\delta$  we exploit the extremal condition

$$\left(\frac{\partial G}{\partial \varphi}\right)_T = 0 = -\pi + \frac{2}{V}a(T)\varphi + \frac{4}{V^3}b(T)\varphi^3 \quad (4.112)$$

for the case of a non-vanishing *conjugate* force  $\pi$ . Since the coefficients  $a(T)$ ,  $b(T)$  in (4.88) should be independent of  $\pi$ , it can be assumed, according to (4.93),  $a(T_C) = 0$  and, according to (4.95),  $b(T) = b(T_C) \equiv b$ . It holds therewith on the critical isotherm  $T = T_C$ :

$$\pi = \frac{4}{V^3}b\varphi^3 \quad (T = T_C) .$$

We read off

$$\delta = 3 \quad (4.113)$$

(see (4.28) and (4.29), respectively).

For the (generalized) isothermal susceptibility, defined before Eq. (4.100), one differentiates the extremum condition (4.112) with respect to  $\pi$ :

$$1 = \frac{2a}{k}\chi_T + \frac{12b}{kV^2}\varphi_0^2\chi_T .$$

If one approaches the critical temperature  $T_C$  in the low-temperature phase ( $T \rightarrow T_C^{(-)}$ ), then one has to insert (4.90) for  $\varphi_0$ :

$$1 = -\frac{4a(T)}{k}\chi_T .$$

This means because of (4.93):

$$\chi_T = \frac{k}{4a_0} |T - T_C|^{-1} \quad (T \xrightarrow{<} T_C) . \quad (4.114)$$

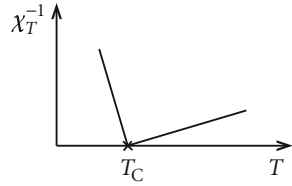
If one approaches the critical point in the high-temperature phase, then one has to take  $\varphi_0 = 0$ :

$$\chi_T = \frac{k}{2a_0} |T - T_C|^{-1} \quad (T \xrightarrow{>} T_C) . \quad (4.115)$$

The critical exponents  $\gamma$ ,  $\gamma'$  are therefore determined in the framework of the *Landau theory*:

$$\gamma = \gamma' = 1 . \quad (4.116)$$

**Fig. 4.19** Temperature profile of the inverse isothermal susceptibility close to a second-order phase transition



The ratio of the so-called *critical amplitudes* in (4.114) and (4.115) yields the value  $C'/C = 1/2$  typical for all *classical theories* (Fig. 4.19).

The *remaining* critical exponents  $\nu$ ,  $\nu'$  and  $\eta$  are to be derived via the correlation function (4.107). When one assumes, without being able, though, to precisely justify it, that the coefficient  $c(T)$  in the *Landau expansion* (4.87) does not, or *only uncritically*, depend on the temperature in the critical region ( $c(T) \approx c(T_C)$ ), then it holds for the **correlation length**  $\xi(T)$ , when one inserts (4.93) into (4.108):

$$\begin{aligned}\xi(T) &\approx \sqrt{\frac{c(T_C)}{a_0}} |T - T_C|^{-1/2} \text{ for } T > T_C, \\ \xi(T) &\approx \sqrt{\frac{c(T_C)}{2a_0}} |T - T_C|^{-1/2} \text{ for } T < T_C.\end{aligned}\quad (4.117)$$

The Landau theory therewith confirms the diverging of the correlation length when one approaches the critical point. The comparison with (4.31) yields the critical exponent:

$$\nu = \nu' = \frac{1}{2}.\quad (4.118)$$

Because of the diverging correlation length, Eq. (4.107) simplifies for  $T = T_C$  to:

$$g(\mathbf{r}, \mathbf{r}') = \frac{k_B T_C}{8\pi c(T_C)} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \quad (T = T_C).$$

The relation (4.107) has been calculated for a three-dimensional system ( $d = 3$ ). The definition (4.32) of the exponent  $\eta$  then fixes for the Landau theory

$$\eta = 0.\quad (4.119)$$

The critical exponents, which we derived in this subsection, have already been listed in Sect. 4.2.1.



### 4.3.4 Region of Validity of the Landau Theory

After the considerations of the last three subsections it remains to be stated that the Landau theory is based, in a not insignificant manner, on unproven assumptions. The concrete conclusions are accordingly uncertain. We should therefore give some thought to the region of validity of the theory. Let us at first consider once more the *fluctuation-dissipation theorem* (4.99), into which we insert for the correlation function  $g(\mathbf{r}, \mathbf{r}')$  the expression (4.107):

$$\int d^3 r' g(\mathbf{r}, \mathbf{r}') = \frac{k_B T}{2c} \int_0^\infty x x e^{-x/\xi} = \frac{k_B T}{2c} \xi^2 .$$

Hence, there exists for the infinitely large system ( $V \rightarrow \infty$ ) a simple connection between the susceptibility  $\chi_T$  and the correlation length  $\xi(T)$ :

$$\chi_T = \frac{k}{2c} \xi^2(T) \sim |T - T_C|^{-1} . \quad (4.120)$$

The results (4.116) for  $\gamma$ ,  $\gamma'$  and (4.118) for  $\nu$ ,  $\nu'$  are obviously consistent. As already discussed in Sect. 4.1.5, the diverging of the susceptibility at  $T = T_C$  is directly tied in with the existence of *critical fluctuations*, which manifest themselves in the long range of  $g(\mathbf{r}, \mathbf{r}')$ . But here the Landau theory seems to contradict itself, because large fluctuations of the order parameter in the critical region put into question the basic ansatz (4.87). Note that the fluctuations found their way into the Landau theory only by the *fluctuation-dissipation theorem* (4.99) (see the derivation of (4.104)). In the ansatz (4.87) they do not appear, because then this ansatz would have to incorporate besides the terms of the form  $\psi^2(\mathbf{r})$  also such of the type  $\psi(\mathbf{r})\psi(\mathbf{r}')$ . Furthermore, in the case of strong fluctuations, the validity of (4.101) is no longer guaranteed. The most probable order-parameter density, which realizes  $\delta G = 0$ , must not necessarily be identical to the average value  $\langle \psi \rangle$ . The Landau theory can therefore be valid only as long as the fluctuations are small compared to the thermal average of the order parameter:

$$\langle (\psi - \langle \psi \rangle)^2 \rangle \ll \langle \psi \rangle^2 . \quad (4.121)$$

This should be fulfilled particularly for all distances  $|\mathbf{r} - \mathbf{r}'|$  within the correlation length  $\xi$ . Now one can estimate for a  $d$ -dimensional system,

$$\chi_T = k\beta \int d^d r g(\mathbf{r}) \approx k\beta \xi^d g(\mathbf{r}_0) \approx k\beta \xi^d \langle (\psi - \langle \psi \rangle)^2 \rangle$$

with  $0 < r_0 < \xi$ . We assume that it is even in the general  $d$ -dimensional system possible to associate the correlation length  $\xi$  by (4.120) with the susceptibility  $\chi_T$ .

Then it results with (4.114) for  $T \rightarrow T_C^{(-)}$ :

$$\begin{aligned} \langle (\psi - \langle \psi \rangle)^2 \rangle &\approx \frac{k^{d/2-1}}{\beta_C (2c(T_C))^{d/2}} \chi_T^{-d/2} \chi_T \\ &= \frac{k^{d/2-1}}{\beta_C (2c(T_C))^{d/2}} \frac{k^{1-d/2}}{(4a_0)^{1-d/2}} |T - T_C|^{d/2-1} . \end{aligned}$$

Thus it remains to be required, if the validity of (4.93) and (4.95) can be assumed:

$$\frac{k_B T_C}{(2c(T_C))^{d/2}} \left( 4a_0 |T - T_C| \right)^{d/2-1} \ll \frac{a_0}{2b} |T - T_C| .$$

This leads for the critical region ( $T \rightarrow T_C^{(-)}$ ) to the so-called **Ginzburg criterion** for the region of validity of the Landau theory:

$$\frac{2b}{(c(T_C))^{d/2}} k_B T_C \left( 2a_0 |T - T_C| \right)^{d/2-2} \ll 1 \quad (4.122)$$

For  $d > 4$  the criterion is satisfiable, for  $d < 4$  it is always violated. It is therefore not astonishing that the critical exponents of the Landau theory deviate rather substantially from the experimentally found values for one-, two-, and three-dimensional systems. The superconductor represents an exception, for which the pre-factor in (4.122) is very small, so that the criterion can be fulfilled even for  $d = 3$  very close to  $T_C$ .—We had already pointed out in connection with the table at the end of Sect. 4.2.3 that for  $d = 4$  the classical Landau theory even fulfills the scaling laws, which contain the dimension  $d$  ('*hyperscaling*').

In the next subsections we want to present some simple model systems, which are to be considered as concrete microscopic realizations of the Landau theory.

### 4.3.5 Model of a Paramagnet

By *paramagnetism* one understands the reaction of a system of permanent magnetic moments to an external magnetic field  $\mathbf{B}_0 = \mu_0 \mathbf{H}$ . These permanent moments may be, e.g., those of the itinerant conduction electrons in a metallic solid. The corresponding *Pauli spin-paramagnetism* we have extensively discussed in Sect. 3.2.6. The topic of this subsection shall therefore be the paramagnetism of insulators (*Langevin paramagnetism*). This phenomenon underlies the perception that permanent magnetic moments are fixedly localized at certain lattice sites of a solid. They stem from incompletely filled atomic electron shells, e.g., from the 3*d*-shell of the *transition metals*, from the 4*f*-shell of the *rare earths* or the 5*f*-shell of the *actinides*. At first we assume that there are no *appreciable* interactions

between these moments. In an external magnetic field  $\mathbf{B}_0$  the moments (vectors!) try to orient themselves parallel to the field, because then the internal energy  $U$  of the system decreases. This tendency is counteracted by the temperature  $T$ , which tries to maximize the entropy  $S$  by an as large as possible *disorder*. The total magnetization at a finite temperature is then fixed by the requirement that the free energy  $F = U - TS$  has to become minimal. The magnetization will therefore be a function of the temperature  $T$  and the field  $B_0$ .

The just described paramagnet is characterized by the following Hamilton operator:

$$H_0 = - \sum_{i=1}^N \boldsymbol{\mu}_i \cdot \mathbf{B}_0 . \quad (4.123)$$

$\boldsymbol{\mu}_i$  is the operator of the magnetic moment at the  $i$ -th lattice site:

$$\boldsymbol{\mu}_i = -\frac{1}{\hbar} g_J \mu_B \mathbf{J}_i . \quad (4.124)$$

$\mathbf{J}_i$  is the operator of the total angular momentum of the  $i$ -th particle,  $g_J$  is the Landé-factor, and  $\mu_B$  the Bohr magneton. Let  $\mathbf{B}_0$  be a homogeneous magnetic field:

$$H_0 = \frac{1}{\hbar} g_J \mu_B \sum_{i=1}^N \mathbf{J}_i \cdot \mathbf{B}_0 . \quad (4.125)$$

The quantum-mechanical directional quantization permits for the vector  $\mathbf{J}_i$  only  $(2J + 1)$  different directions relative to the field:

$$\begin{aligned} \mathbf{J}_i \cdot \mathbf{B}_0 &= \hbar m_i B_0 , \\ m_i &= -J, -J + 1, \dots, +J . \end{aligned}$$

Hence,  $H_0$  possesses  $(2J + 1)^N$  eigen-states. The canonical partition function can then be formulated as follows:

$$\begin{aligned} Z_N(T, B_0) &= \text{Tr} e^{-\beta H_0} \\ &= \sum_{m_1=-J}^{+J} \cdots \sum_{m_N=-J}^{+J} \exp \left( -\beta b \sum_{i=1}^N m_i \right) , \\ b &\equiv g_J \mu_B B_0 . \end{aligned}$$

Because of missing interactions, these are  $N$  independent summations, which can be easily performed:

$$\begin{aligned} Z_N(T, B_0) &= \prod_{i=1}^N \left( \sum_{m_i=-J}^{+J} e^{(-\beta b m_i)} \right) \\ &= [e^{\beta b J} (1 + e^{-\beta b} + e^{-2\beta b} + \dots + e^{-2\beta b J})]^N \\ &= \left[ e^{\beta b J} \frac{1 - e^{-\beta b (2J+1)}}{1 - e^{-\beta b}} \right]^N = \left[ \frac{e^{\beta b (J+1/2)} - e^{-\beta b (J+1/2)}}{e^{(1/2)\beta b} - e^{-(1/2)\beta b}} \right]^N . \end{aligned}$$

The partition function is therewith already completely determined:

$$Z_N(T, B_0) = \left\{ \frac{\sinh[\beta b (J + 1/2)]}{\sinh((1/2)\beta b)} \right\}^N \quad (4.126)$$

The magnetization has a component unequal to zero only in field direction:

$$\begin{aligned} M(T, B_0) &= -g_J \mu_B \frac{1}{V} \sum_{i=1}^N \langle m_i \rangle = \frac{g_J \mu_B}{V \beta Z_N} \frac{d}{db} Z_N \\ &= \frac{1}{V \beta} g_J \mu_B \frac{d}{db} \ln Z_N . \end{aligned}$$

It follows after simple rearrangements:

$$M(T, B_0) = M_0 B_J (\beta g_J \mu_B J B_0) . \quad (4.127)$$

Here we have used

$$M_0 = \frac{N}{V} g_J \mu_B J \quad (4.128)$$

as the *saturation magnetization*, while

$$B_J(x) = \frac{2J+1}{2J} \coth \left( \frac{2J+1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right) \quad (4.129)$$

is the so-called *Brillouin function*. Let us list some of the most important properties of this function, which is so essential for the *theory of magnetism*:

1.  $J = 1/2$  .

For this special case ( $L = 0, J = S = 1/2$ ) the Brillouin function simplifies to:

$$B_{1/2}(x) = \tanh x . \quad (4.130)$$

2.  $J \rightarrow \infty$ .

In this so-called *classical limiting case*  $B_J(x)$  is identical to the *Langevin function*  $L(x)$ , which appears in a classical treatment of the paramagnet ((1.23), Vol. 5), which, in particular, disregards the *directional quantization* of the angular momentum:

$$B_\infty(x) = \coth x - \frac{1}{x} \equiv L(x) . \quad (4.131)$$

3. *Small argument.*

When one uses the series expansion of the hyperbolic cotangent,

$$\coth x = \frac{1}{x} + \frac{1}{3}x - \frac{1}{45}x^3 + O(x^5) ,$$

in the definition Eq. (4.129), then one finds:

$$B_J(x) = \frac{J+1}{3J}x - \frac{J+1}{3J} \frac{2J^2+2J+1}{30J^2}x^3 + \dots \quad (4.132)$$

This has especially the consequence (Fig. 4.20)

$$B_J(0) = 0 . \quad (4.133)$$

According to (4.127) the magnetization will thus vanish for  $B_0 = 0$  or  $T \rightarrow \infty$ . Therefore there does not exist a *spontaneous* magnetization, which is characteristic for the *ferromagnet* at temperatures below the *Curie temperature*  $T_C$ .

4. *Symmetry.*

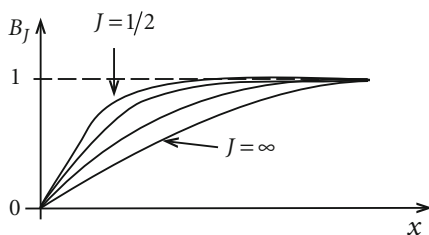
Because of  $\coth(-x) = -\coth x$  it is also:

$$B_J(-x) = -B_J(x) . \quad (4.134)$$

Referred to (4.127) this means that with a *pole reversal* of the external field ( $B_0 \rightarrow -B_0$ ) the magnetization, too, turns over.

5. *Saturation.*

**Fig. 4.20** Qualitative behavior of the Brillouin function for different quantum numbers  $J$  of the angular momentum



Because of  $\coth x \rightarrow 1$  for  $x \rightarrow \infty$  the Brillouin function runs asymptotically towards a finite limiting value (Fig. 4.20):

$$B_J(x) \xrightarrow{x \rightarrow \infty} 1. \quad (4.135)$$

That means physically that the magnetization (4.127) is driven by a strong field ( $B_0 \rightarrow \infty$ ) into *saturation*. When all magnetic moments are oriented parallel,  $M$  has reached its maximum value  $M_0$ , and can no longer increase even with a further enhancement of the field strength.

Eventually the **high-temperature behavior** ( $\beta\mu_B B_0 \ll 1$ ) of the magnetization is still interesting, for which it approximately holds with (4.132):

$$M(T, B_0) \approx \frac{C}{\mu_0 T} B_0, \quad (4.136)$$

$$C = \frac{N}{V} (g_J \mu_B)^2 \mu_0 \frac{J(J+1)}{3k_B} \quad (\text{Curie constant}).$$

The susceptibility of the paramagnet,

$$\chi = \mu_0 \left( \frac{\partial M}{\partial B_0} \right)_T = \frac{C}{T}, \quad (4.137)$$

shows for high temperatures a characteristic  $(1/T)$ -dependence, which is known as **Curie law**.

### 4.3.6 Mean-Field Approximation of the Heisenberg Model

Equation (4.133) points out that without particle interactions no *spontaneous* magnetization can appear. The paramagnet therefore does not exhibit any phase transition. For the description of the phenomenon *ferromagnetism* the model (4.125) has to be accordingly extended. In simplest form, the interaction between the localized moments can be written as scalar product between the participating operators of angular momentum. This corresponds to the extensively discussed **Heisenberg model**

$$H = - \sum_{ij} \hat{J}_{ij} \mathbf{J}_i \cdot \mathbf{J}_j + \frac{1}{\hbar} g_J \mu_B \sum_i \mathbf{J}_i \cdot \mathbf{B}_0, \quad (4.138)$$

from which one knows in the meantime that, in many cases, it comes to very realistic statements about magnetic properties of insulators. One can find microscopic reasons for the operator (4.138) and, in particular, for the so-called **exchange**

**integrals**  $\widehat{J}_{ij}$ , which, however, we will not present here in detail. We restrict ourselves only to the remark that the coupling constants  $\widehat{J}_{ij}$ ,

$$\widehat{J}_{ij} = \widehat{J}_{ji} ; \quad \widehat{J}_{ii} = 0 , \quad (4.139)$$

are due to an only quantum-mechanically justifiable *exchange interaction*. The Heisenberg model finds its best realizations among *magnetic insulators* such as

$$\begin{aligned} \text{EuO, EuS, CdCr}_2\text{Se}_4, \text{ HgCr}_2\text{Se}_4, \dots & \quad (d = 3) \\ \text{K}_2\text{CuF}_4, \text{ CrBr}_3, \dots & \quad (d = 2) , \\ \text{CsCuCl}_3, \dots & \quad (d = 1) . \end{aligned}$$

But also in magnetic metals like Gadolinium, the magnetism is due to localized moments. These materials are successfully described by this model, as long as only their purely magnetic properties are concerned. In spite of its rather simple structure, the Heisenberg model could exactly be solved up to now only for a few special cases. In general, approximations cannot be avoided. We will here perform the really simplest approximation, the so-called *mean-field approximation*, because this proves to be equivalent to the *Landau theory*.

At first we bring the model-Hamilton operator (4.138) by the use of (4.139) into a somewhat different form:

$$\widehat{H} = - \sum_{ij} \widehat{J}_{ij} (J_i^+ J_j^- + J_i^z J_j^z) + \frac{1}{\hbar} g_J \mu_B B_0 \sum_i J_i^z . \quad (4.140)$$

The homogeneous field  $\mathbf{B}_0$  defines the  $z$ -direction ( $\mathbf{B}_0 = B_0 \mathbf{e}_z$ ). The *mean-field approximation* now consists in a linearization of the operator products. In the following still exact expression for the product of two operators  $\widehat{A}$  and  $\widehat{B}$ ,

$$\widehat{A} \cdot \widehat{B} = (\widehat{A} - \langle \widehat{A} \rangle)(\widehat{B} - \langle \widehat{B} \rangle) + \widehat{A} \langle \widehat{B} \rangle + \langle \widehat{A} \rangle \widehat{B} - \langle \widehat{A} \rangle \langle \widehat{B} \rangle ,$$

one neglects the first summand which represents the *fluctuations* of the operators  $\widehat{A}$ ,  $\widehat{B}$  around their mean values:

$$\widehat{A} \widehat{B} \xrightarrow{\text{MFA}} \widehat{A} \langle \widehat{B} \rangle + \langle \widehat{A} \rangle \widehat{B} - \langle \widehat{A} \rangle \langle \widehat{B} \rangle . \quad (4.141)$$

If one applies this approximation to the operator products in (4.140), then just the ‘*exchange terms of the angular momentum*’ are suppressed,

$$J_i^+ J_j^- \xrightarrow{\text{MFA}} 0 , \quad (4.142)$$

since for reasons of the angular-momentum conservation it must be

$$\langle J_i^+ \rangle = \langle J_i^- \rangle = 0 \quad \forall i .$$

It thus remains:

$$\widehat{H} \rightarrow - \sum_{ij} \widehat{J}_{ij} (J_i^z \langle J_j^z \rangle + \langle J_i^z \rangle J_j^z) + \frac{1}{\hbar} g_J \mu_B B_0 \sum_i J_i^z + D(T, B_0) .$$

$D(T, B_0)$  is a temperature-dependent and a field-dependent number, i.e. not an operator,

$$D(T, B_0) = \sum_{ij} \widehat{J}_{ij} \langle J_i^z \rangle \langle J_j^z \rangle ,$$

which for our purposes can be neglected here. In any case, it would later drop out during the calculation of the magnetization.—We concentrate ourselves in the following on the **homogeneous ferromagnet**, for which translational symmetry can be assumed in the form

$$\langle J_i^z \rangle \equiv \langle J^z \rangle \quad \forall i .$$

If one further defines

$$\widehat{J}_0 = \sum_i \widehat{J}_{ij} = \sum_j \widehat{J}_{ij} , \quad (4.143)$$

the Heisenberg-Hamilton operator (4.138, 4.140) in the *mean-field approximation* reads:

$$H_{\text{MFA}} = \frac{1}{\hbar} g_J \mu_B (B_0 + B_{\text{ex}}) \sum_{i=1}^N J_i^z . \quad (4.144)$$

$B_{\text{ex}}$  is an *effective field*, which is called the ‘*exchange field*’:

$$B_{\text{ex}} = -2 \langle J^z \rangle \widehat{J}_0 \frac{\hbar}{g_J \mu_B} .$$

It turns out to be proportional to the magnetization,

$$M = - \frac{N}{V} g_J \mu_B \frac{1}{\hbar} \langle J^z \rangle ,$$



so that we can write:

$$B_{ex} = \mu_0 \lambda M, \quad (4.145)$$

$$\lambda = \frac{V}{N} \frac{2\widehat{J}_0 \hbar^2}{\mu_0 (g_J \mu_B)^2}.$$

The mean-field version (4.144) of the Heisenberg-Hamilton operator (4.138) obviously has the same structure as the Hamilton operator (4.125) of a paramagnet. The many-particle problem has reduced into a one-particle one. The influence of the particle interactions is simulated, to a first approximation, by an *effective* magnetic field, which must be determined *self-consistently*, since it depends by itself on the magnetization of the system. We can accordingly adopt all the results of the last subsection. For the magnetization we get an expression of the form (4.127):

$$M(T, B_0) = M_0 B_J (\beta g_J \mu_B J (B_0 + B_{ex})). \quad (4.146)$$

We are only interested in the *spontaneous* magnetization, since a phase transition is to be expected exclusively in the zero-field:

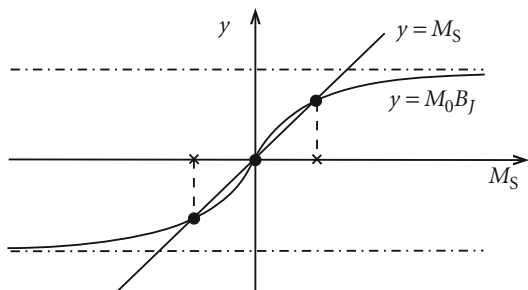
$$M_S(T) \equiv M(T, 0) = M_0 B_J (\beta g_J \mu_0 \mu_B J \lambda M_S). \quad (4.147)$$

This is an implicit conditional equation for  $M_S$ . Because of (4.133),  $M_S = 0$  (paramagnetism!) is always a solution. The question is, whether and under which conditions there exists an additional solution  $M_S \neq 0$ . In an illustrative manner, this can *graphically be discussed* (see *Weiss ferromagnet*, subsection 1.4.4 in Vol. 5), when one plots the left-hand side and the right-hand side of (4.147) both as functions of  $M_S$  searching for intersection points (Fig. 4.21). There obviously exists such an  $M_S \neq 0$ -solution, when the initial slope of the right-hand side of Eq. (4.147) is greater than 1:

$$\left. \frac{d}{dM_S} M_0 B_J (\beta g_J \mu_0 \mu_B J \lambda M_S) \right|_{M_S=0} \stackrel{(4.132)}{=} \frac{J+1}{3J} M_0 (\beta g_J \mu_0 \mu_B J \lambda)$$

$$\stackrel{(4.128)}{=} \frac{N J + 1}{V} \frac{1}{3} \beta (g_J \mu_B)^2 \mu_0 J \lambda = C \frac{\lambda}{T}.$$

**Fig. 4.21** Graphic solution for the spontaneous magnetization of a Heisenberg ferromagnet in the mean-field approximation



$C$  is the Curie constant defined in (4.136). The slope of  $M_0 B_J$  increases with decreasing temperature. For all  $T < T_C$  there exists a non-trivial solution for the *spontaneous* magnetization, where the **Curie temperature**  $T_C$  results from the requirement

$$C \frac{\lambda}{T_C} \stackrel{!}{=} 1 \iff T_C = \lambda C . \quad (4.148)$$

One easily realizes that, as soon as a solution  $M_S \neq 0$  exists, this will be more stable compared to the always present  $M_S = 0$ -solution. Accordingly, at the temperature  $T = T_C$  a phase transition indeed takes place:

$$\begin{aligned} T < T_C: & \text{ ferromagnetism } (M_S \neq 0) , \\ T > T_C: & \text{ paramagnetism } (M_S = 0) . \end{aligned}$$

However, it must be considered as a serious shortcoming of the mean-field approximation that it indicates this phase transition **independently** of the lattice dimension  $d$ , already as soon as  $\widehat{J}_0$ , and therewith  $\lambda$  are unequal zero. This result strongly conflicts with the experiment as well as with a few **exact** model calculations, but is typical for all the *classical theories*, in particular also for the Landau theory.

Finally we will derive a characteristic result of the mean-field approximation, which concerns the susceptibility  $\chi_T$  in the paramagnetic phase ( $T > T_C$ ) for  $B_0 \xrightarrow{>} 0$ . It then holds in any case

$$\beta g_J \mu_B J (B_0 + B_{\text{ex}}) \ll 1 , \quad (4.149)$$

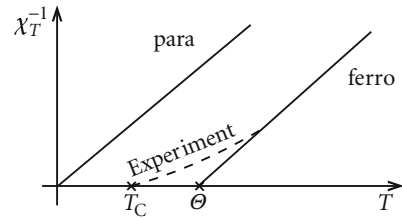
so that the magnetization (4.146) can be simplified when one uses the expansion (4.132) for the Brillouin function:

$$\begin{aligned} M(T, B_0) & \approx \left( \frac{N}{V} g_J \mu_B J \right) \frac{J+1}{3J} \beta g_J \mu_B J (B_0 + B_{\text{ex}}) \\ & \stackrel{(4.136)}{=} \stackrel{(4.148)}{=} \frac{C}{\mu_0 T} B_0 + \frac{T_C}{T} M(T, B_0) , \\ M(T, B_0) & = \frac{C}{T - T_C} \frac{1}{\mu_0} B_0 . \end{aligned} \quad (4.150)$$

The expression for the susceptibility, which results from that,

$$\chi_T = \mu_0 \left( \frac{\partial M}{\partial B_0} \right)_{T, B_0 \xrightarrow{>}} = \frac{C}{T - T_C} , \quad (4.151)$$

**Fig. 4.22** High-temperature behavior of the inverse isothermal susceptibility of, respectively, a paramagnet and a ferromagnet in its paramagnetic phase. The broken line shows a typical experimental course



is called **Curie-Weiss law**. This is, at least for high temperatures, experimentally excellently confirmed. The inverse susceptibility shows in every case a linear high-temperature behavior (Fig. 4.22). The extrapolation of this linear behavior onto the  $T$ -axis defines the

### paramagnetic Curie temperature $\Theta$

In the mean-field approximation  $\Theta$  is identical to  $T_C$ . In the experiment,  $\Theta$  is always a bit higher than  $T_C$ . According to (4.137) one can consider the paramagnet as a limiting case of the ferromagnet with  $T_C = 0$  (Fig. 4.22).

We will extend the expansion (4.150) by a further step, but we will thereby now presume that the magnetic system is in its *critical region* ( $T \xrightarrow{\leftarrow} T_C$ ,  $B_0 \xrightarrow{\sim} 0$ ,  $M \approx M_S$ ):

$$M_S \approx M_0 \left[ \frac{J+1}{3J} \beta g_J \mu_B J (B_0 + B_{\text{ex}}) - \frac{J+1}{3J} \frac{2J^2 + 2J + 1}{30J^2} (\beta g_J \mu_B J (B_0 + B_{\text{ex}}))^3 \right].$$

$B_0$  can always be chosen so that

$$B_0 \ll B_{\text{ex}} = \lambda \mu_0 M_S$$

can be assumed. Therefore, we can neglect, in the last term of the bracket,  $B_0$  in relation to  $B_{\text{ex}}$ :

$$M_S \stackrel{(4.136)}{\approx} \frac{C}{\mu_0 T} B_0 + \frac{T_C}{T} M_S - \frac{2J^2 + 2J + 1}{30J^2} \frac{C}{\mu_0 T} (\beta g_J \mu_B J)^2 (\mu_0 \lambda M_S)^3.$$

This can also be written as follows:

$$B_0 \approx m_S \left( \frac{2}{V} a(T) + \frac{4b(T)}{V^3} m_S^2 \right). \quad (4.152)$$

$m_S = VM_S$  is thereby the *spontaneous* magnetic moment. Furthermore, the following abbreviations were used:

$$a(T) = a_0 (T - T_C); \quad a_0 = \frac{\mu_0}{2C}, \quad (4.153)$$

$$b(T) = \frac{2J^2 + 2J + 1}{120J^2} \left( \frac{g_J \mu_B J}{k_B T} \right)^2 \left( \frac{\mu_0 T_C}{C} \right)^3. \quad (4.154)$$

In the *critical region* it can be taken  $b(T) \approx b(T_C) = b > 0$ .

$m_S = VM_S$  corresponds to the *order parameter*  $\varphi$  of the Landau theory.  $B_0$  is the force  $\pi$  which is conjugate to  $m_S$ .

Equation (4.152) is therewith the exact counterpart to the conditional equation (4.112) for the order parameter in the Landau theory. The equivalence of the mean-field approximation of the Heisenberg model (4.144) with the Landau theory is thus shown. By the example of the ferromagnet we have been able to demonstrate a microscopic realization of the more general Landau theory. Above all, the characteristics of the approximation thereby became clear, which consists in the neglect of fluctuations (4.141).

Because of the equivalence of (4.112) and (4.152), we can identify, without further calculation, the **critical exponents** of the ferromagnet in the mean-field approximation with those of the Landau theory:

$$\beta = \frac{1}{2}, \quad \delta = 3, \quad \gamma = \gamma' = 1, \quad \alpha = \alpha' = 0. \quad (4.155)$$

$\gamma = 1$  was explicitly shown with (4.151). The Landau theory yields for the susceptibility in the paramagnetic phase the expression (4.115), where the constant is to be chosen as  $k = \mu_0$  (cf. the  $\chi_T$ -definitions (4.100) and (4.151)). This means:

$$\chi_T = \frac{\mu_0}{2a_0} \frac{1}{T - T_C}.$$

If one inserts into this Eq. (4.153) for  $a_0$ , then it results exactly the *Curie-Weiss law* (4.151). That confirms once more the equivalence of the two theories.

It is recommended to the reader, as an exercise, to explicitly re-calculate the other exponents of the ferromagnet in (4.155).

### 4.3.7 Van der Waals Gas

In the introduction of this chapter we have marked the dissertation thesis of van der Waals on the real gas (gas-liquid) as the hour of birth of the *new-age* theory of phase transition. Because of this, we should still give some thought to the fitting of this theory into the context of the considerations of this chapter. The van der Waals model was already the topic of extensive considerations in Vol. 5 of this

basic course in Theoretical Physics, which we will not repeat here. Instead, we are now mainly focussed on the thermodynamic equivalence of the model with the just discussed mean-field approximation of the Heisenberg ferromagnet and therewith also with the more general Landau theory. The typical of the mean-field approximation consists in replacing the microscopic particle interactions by an effective, infinitely long-range magnetic field, along which the localized moments then have to orient themselves independently of each other. By this, the actual many-particle problem becomes a one-particle problem, being therewith solvable. We will now show that also the *van der Waals equation of state* ((1.14), Vol. 5) can be derived by the introduction of a *mean field*.

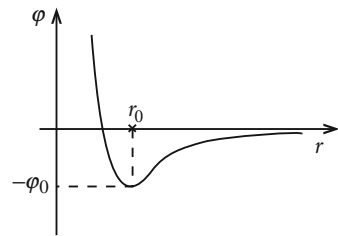
We think of a **real gas**, whose properties are affected by two-particle interactions. A typical interaction potential, as for instance that by Lennard-Jones,

$$\varphi(r) = \varphi_0 \left\{ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right\} ,$$

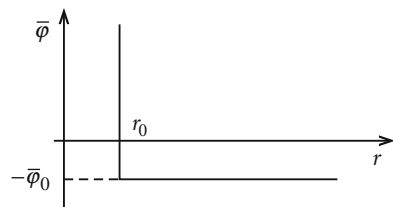
possesses a repulsive '*hard core*'-region, a minimum in the attractive part, after which very rapidly drops down to zero with increasing distance  $r$  of the interaction partners (Fig. 4.23). In a rough approximation the entirety of **all** particle interactions will now be replaced by an average infinitely long-range potential field  $\bar{\varphi}$  (Fig. 4.24). The single particle thus moves in a homogeneous mean field built by all the other particles,

$$\bar{\varphi}(r) = \begin{cases} \infty & \text{if } r < r_0 , \\ -\bar{\varphi}_0 & \text{if } r > r_0 , \end{cases} \quad (4.156)$$

**Fig. 4.23** Pair-interaction potential as function of the particle distance



**Fig. 4.24** Strongly simplified pair-interaction potential as a function of the particle distance



where of course a ‘hard core’ remains to be taken into consideration, because the *classical* particles can not approach each other arbitrarily closely, because of their finite volumes. In a magnetic system, the rigid arrangement of the spins on the lattice correspond to the ‘hard core’.

But if the effective field is built up by all the other particles, then the constant  $\bar{\varphi}_0$  should be proportional also to the particle density  $N/V$ :

$$\bar{\varphi}_0 = \frac{a}{N_A} \frac{N}{V} = \frac{an^2}{NV}. \quad (4.157)$$

$a$  is an unknown coefficient,  $N_A$  is the *Avogadro number* ((1.8), Vol. 5), and  $n = N/N_A$  is the number of moles in the considered gas. The classical partition function  $Z_N$  will factorize because of the missing particle interactions,

$$Z_N \sim \left\{ \int d^3p \int d^3r \exp \left[ -\beta \left( \frac{\mathbf{p}^2}{2m} + \bar{\varphi}(r) \right) \right] \right\}^N,$$

where we are interested only in the spatial part, which can easily be calculated with (4.156):

$$Z_N \sim [(V - nb)e^{\beta\bar{\varphi}_0}]^N.$$

Here

$$V_{\min} = nb$$

means the entirety of all the ‘hard core’-volumes.  $b$  is thus the ‘**proper volume**’ of all particles of a mole. We now can formulate the pressure of the gas:

$$\begin{aligned} p &= - \left( \frac{\partial F}{\partial V} \right)_T = k_B T \left( \frac{\partial}{\partial V} \ln Z_N \right)_T \\ &= Nk_B T \frac{1 + (V - nb)\beta \partial\bar{\varphi}_0/\partial V}{V - nb} = Nk_B T \left( \frac{1}{V - nb} - \beta \frac{an^2}{NV^2} \right). \end{aligned}$$

But that is just the **van der Waals equation of state** ((1.14), Vol. 5):

$$\left( p + \frac{an^2}{V^2} \right) (V - nb) = Nk_B T = nRT. \quad (4.158)$$

It is shown therewith that the van der Waals model indeed corresponds to a mean-field approximation and must therefore be ascribed to the *classical theories*. We have calculated the critical exponents of the van der Waals gas as exercise 4.3.8 in Vol. 5. They are identical to those of the *Landau theory* (Sect. 4.3.3).

### 4.3.8 Pair Correlation and Structure Factor

In this subsection we will consider a further example of a *classical theory*, namely the *Ornstein-Zernike theory*. It refers to the gas-liquid system, and thereby especially to the *density-correlation function*  $g(\mathbf{r}, \mathbf{r}')$ , which is also called *pair correlation*, which we got to know already with (4.10) and (4.96). We therefore know already that it plays a decisive role in connection with critical phenomena:

$$\begin{aligned} g(\mathbf{r}, \mathbf{r}') &= \left\langle (n(\mathbf{r}) - \langle n(\mathbf{r}) \rangle)(n(\mathbf{r}') - \langle n(\mathbf{r}') \rangle) \right\rangle \\ &= \langle n(\mathbf{r}) \cdot n(\mathbf{r}') \rangle - n^2 . \end{aligned} \quad (4.159)$$

$n(\mathbf{r})$  is the microscopic *particle density*:

$$n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{R}_i) . \quad (4.160)$$

$\langle n(\mathbf{r})n(\mathbf{r}') \rangle$  can be understood as the *conditional probability* to find a particle at the position  $\mathbf{r}$ , if there is definitely another particle at the position  $\mathbf{r}'$ . The pair correlation by itself represents a measure for the correlation between the deviations of the particle density  $n(\mathbf{r})$  from its average value  $\langle n(\mathbf{r}) \rangle$  at the positions  $\mathbf{r}$  and  $\mathbf{r}'$ .—We will presume a homogeneous system:

$$\langle n(\mathbf{r}) \rangle = n = \frac{\langle N \rangle}{V}; \quad g(\mathbf{r}, \mathbf{r}') = g(|\mathbf{r} - \mathbf{r}'|) . \quad (4.161)$$

The exact form of  $g(\mathbf{r}, \mathbf{r}')$  of course depends on the type of the particle interaction. However, it holds always:

$$\begin{aligned} \langle n(\mathbf{r})n(\mathbf{r}') \rangle &\xrightarrow{|\mathbf{r}-\mathbf{r}'| \rightarrow \infty} n^2 , \\ g(\mathbf{r}, \mathbf{r}') &\xrightarrow{|\mathbf{r}-\mathbf{r}'| \rightarrow \infty} 0 . \end{aligned}$$

For infinitely large distances  $|\mathbf{r} - \mathbf{r}'|$ , the events at  $\mathbf{r}$  and  $\mathbf{r}'$  are no longer correlated, i.e., they are independent of each other.

The *pair correlation* can be associated with the compressibility  $\kappa_T$  of the *fluid system*. The latter could be connected in Eq. (1.200) with the particle fluctuations:

$$\frac{\kappa_T}{\kappa_T^{(0)}} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} .$$

$\kappa_T^{(0)} = \beta V / \langle N \rangle = 1/p$  is thereby the compressibility of the ideal gas. We have previously used this formula, in order to prove the equivalence of the statistical

descriptions (canonical and grand-canonical ensembles). Here we are interested in another connection:

$$\begin{aligned} \langle (N - \langle N \rangle)^2 \rangle &= \int d^3r \int d^3r' \langle (n(\mathbf{r}) - \langle n(\mathbf{r}) \rangle)(n(\mathbf{r}') - \langle n(\mathbf{r}') \rangle) \rangle \\ &= \int d^3r \int d^3r' g(|\mathbf{r} - \mathbf{r}'|) = V \int d^3r g(r) . \end{aligned}$$

This leads to the analog of the *fluctuation-dissipation theorem* (4.16) for the fluid system:

$$\frac{\kappa_T}{\kappa_T^{(0)}} = \frac{1}{n} \int_V d^3r g(r) . \tag{4.162}$$

A diverging  $\kappa_T$  for  $T \rightarrow T_C$  is conceivable only with a diverging range of the correlation, as we have already realized in connection with (4.16) for the special example of the Ising-spin system.

The spatial Fourier transform of the pair correlation is the **static structure factor**:

$$S(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} g(r) . \tag{4.163}$$

This quantity is directly accessible in the experiment, e.g. via the scattering of radiation (X-rays, neutrons, light) on the liquid or on the gas. If we denote with  $\mathbf{k}_0$  ( $\mathbf{k}_s$ ) the wave vector of the incident (scattered) radiation, and with  $\hbar\mathbf{q}$  the momentum transfer in the case of **quasi-elastic scattering** (Fig. 4.25),

$$|\mathbf{k}_0| \approx |\mathbf{k}_s| = k ,$$

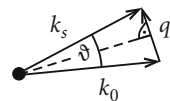
then we have at a *scattering angle*  $\vartheta$ :

$$|\mathbf{q}| = 2k \sin \frac{\vartheta}{2} . \tag{4.164}$$

Let  $I(\mathbf{q})$  be the intensity of the radiation scattered by  $\mathbf{q}$ , and  $f_i(\mathbf{q})$  be the *scattering amplitude* for the corresponding scattering at the  $i$ -th particle. The ‘*scattering ability*’ for each of the  $N$  identical particles each is the same. The scattering amplitudes can therefore differ at most by a phase factor:

$$f_i(\mathbf{q}) = f_j(\mathbf{q}) e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} .$$

**Fig. 4.25** Definition of the scattering angle for quasi-elastic scattering





For the *scattered intensity* it then holds ((9.14), Vol. 7):

$$\begin{aligned} I(\mathbf{q}) &\sim \left\langle \left| \sum_i f_i(\mathbf{q}) \right|^2 \right\rangle = \left\langle \sum_{ij} f_i(\mathbf{q}) f_j^*(\mathbf{q}) \right\rangle \\ &= |f_0(\mathbf{q})|^2 \left\langle \sum_{ij} e^{-i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \right\rangle. \end{aligned}$$

In the case of missing particle correlations we would have:

$$I_0(\mathbf{q}) \sim \langle N \rangle |f_0(\mathbf{q})|^2.$$

The intermediate result

$$\frac{I(\mathbf{q})}{I_0(\mathbf{q})} = \frac{1}{\langle N \rangle} \left\langle \sum_{ij} e^{-i\mathbf{q}(\mathbf{R}_i - \mathbf{R}_j)} \right\rangle$$

can be further reformulated:

$$\begin{aligned} \frac{I(\mathbf{q})}{I_0(\mathbf{q})} &= \frac{1}{\langle N \rangle} \int d^3 r \int d^3 r' e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \\ &\quad \cdot \left\langle \left( \sum_i \delta(\mathbf{r} - \mathbf{R}_i) \right) \left( \sum_j \delta(\mathbf{r}' - \mathbf{R}_j) \right) \right\rangle \\ &= \frac{1}{\langle N \rangle} \int d^3 r \int d^3 r' e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \langle n(\mathbf{r}) n(\mathbf{r}') \rangle \\ &\stackrel{(4.159)}{=} \frac{1}{n} \int d^3 r e^{-i\mathbf{q} \cdot \mathbf{r}} g(r) + n \int d^3 r e^{-i\mathbf{q} \cdot \mathbf{r}}. \end{aligned}$$

The second summand only concerns the non-deflected radiation,

$$n \int d^3 r e^{-i\mathbf{q} \cdot \mathbf{r}} = \langle N \rangle \delta(\mathbf{q}),$$

and is therefore normally left out. We now recognize with (4.163) the connection between the scattered intensity and the static structure factor:

$$\frac{I(\mathbf{q})}{I_0(\mathbf{q})} = \frac{1}{n} S(\mathbf{q}). \quad (4.165)$$

$S(\mathbf{q})$  thus describes how the intensity  $I(\mathbf{q})$  of the radiation, which is scattered by  $\mathbf{q}$ , deviates from the intensity, which would come out in the absence of particle correlations. The structure factor represents therewith a measure of the influence of the particle correlations.

If one combines (4.165) and (4.162),

$$\lim_{\mathbf{q} \rightarrow 0} \frac{I(\mathbf{q})}{I_0(\mathbf{q})} = \frac{\kappa_T}{\kappa_T^{(0)}} , \quad (4.166)$$

then one sees that the *criticality* of the compressibility leads to an enormous increase of the scattered intensity for small deflections. This phenomenon is experimentally observable as the so-called *critical opalescence*.

### 4.3.9 Ornstein-Zernike Theory

The critical behavior of the correlation function  $g(\mathbf{r})$  will now be investigated. According to (4.12) and (4.32) it is to be expected:

$$g(\mathbf{r}) \sim \frac{\exp\left(-\frac{r}{\xi(T)}\right)}{r^{d-2+\eta}} .$$

The temperature-dependence of the *correlation length*,

$$\xi(T) \sim \begin{cases} (-\varepsilon)^{-\nu'} , & \text{if } T \xrightarrow{<} T_C , \\ \varepsilon^{-\nu} , & \text{if } T \xrightarrow{>} T_C , \end{cases}$$

defines the critical exponents  $\nu$  and  $\nu'$ . In the following, we are interested in a determination of the exponents  $\nu$ ,  $\nu'$ , and  $\eta$  for the fluid system, which are accessible only with some difficulty. For this purpose we reformulate the pair correlation a bit:

$$\begin{aligned} g(\mathbf{r}-\mathbf{r}') &= \langle n(\mathbf{r})n(\mathbf{r}') \rangle - n^2 = \left\langle \sum_{ij} \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j) \right\rangle - n^2 \\ &= \delta(\mathbf{r}-\mathbf{r}') \left\langle \sum_i \delta(\mathbf{r}-\mathbf{R}_i) \right\rangle + \left\langle \sum_{\substack{ij \\ i \neq j}} \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j) \right\rangle - n^2 . \end{aligned}$$

In the last step we have extracted the *self-correlation function* ( $i = j$ ). We define,

$$\Gamma(\mathbf{r}-\mathbf{r}') = \frac{1}{n^2} \left\langle \sum_{\substack{ij \\ i \neq j}} \delta(\mathbf{r}-\mathbf{R}_i)\delta(\mathbf{r}'-\mathbf{R}_j) \right\rangle - 1 , \quad (4.167)$$

and obtain:

$$g(\mathbf{r}-\mathbf{r}') = n\delta(\mathbf{r}-\mathbf{r}') + n^2\Gamma(\mathbf{r}-\mathbf{r}') . \quad (4.168)$$

The criticality of  $g$  transfers to  $\Gamma$ . For the following series expansions it is therefore recommendable to introduce the **direct correlation function**  $D(\mathbf{r} - \mathbf{r}')$ :

$$\Gamma(\mathbf{r} - \mathbf{r}') = D(\mathbf{r} - \mathbf{r}') + n \int d^3 r'' D(\mathbf{r} - \mathbf{r}'') \Gamma(\mathbf{r}'' - \mathbf{r}'). \quad (4.169)$$

The reason for the introduction of  $D$  becomes evident when one Fourier-transforms the so-called **Ornstein-Zernike integral equation** (4.169) by the use of the convolution theorem ((4.188), Vol. 3):

$$\Gamma(\mathbf{q}) = \int d^3 r \Gamma(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} = D(\mathbf{q}) + nD(\mathbf{q})\Gamma(\mathbf{q}).$$

This means:

$$D(\mathbf{q}) = \frac{\Gamma(\mathbf{q})}{1 + n\Gamma(\mathbf{q})}. \quad (4.170)$$

For  $T \rightarrow \infty$  the correlation  $\Gamma$  vanishes ( $\Gamma(\mathbf{q}) \rightarrow 0$ ), so that  $D(\mathbf{q}) \approx \Gamma(\mathbf{q})$ . For  $T \rightarrow T_C$   $\Gamma$  diverges ( $\Gamma(\mathbf{q} = 0) \rightarrow \infty$ ), but  $D$  remains finite ( $D(\mathbf{q} = 0) \approx 1/n$ ). Contrary to the other correlations  $D$  thus does not become critical, so that one can assume that this function can be expanded at each temperature, i.e. also at  $T = T_C$ , as a Taylor series around  $q = 0$ :

$$D(\mathbf{q}) = D(0) + \sum_{\alpha=1}^{\infty} c_{\alpha} q^{\alpha}. \quad (4.171)$$

This formulation presumes, in addition, an *isotropic system*, so that angle-dependences are not to be taken into account. Because of  $D(\mathbf{r}) = D(r)$  and therewith

$$\begin{aligned} c_{\alpha} &= \frac{1}{\alpha!} \left\{ \frac{\partial^{\alpha}}{\partial q^{\alpha}} D(\mathbf{q}) \right\}_{\mathbf{q}=0} = \frac{1}{\alpha!} \left\{ \frac{\partial^{\alpha}}{\partial q^{\alpha}} 2\pi \int_{-1}^{+1} dx \int_0^{\infty} dr e^{-iqr x} r^2 D(r) \right\}_{\mathbf{q}=0} \\ &= 2\pi \frac{(-i)^{\alpha}}{\alpha!} \int_{-1}^{+1} dx x^{\alpha} \int_0^{\infty} dr r^{\alpha+2} D(r) \end{aligned}$$

all the coefficients  $c_{\alpha}$  with odd  $\alpha$  are zero:

$$D(\mathbf{q}) = D(q) = D(0) + \sum_{\alpha=1}^{\infty} c_{2\alpha} q^{2\alpha}.$$

The region of small wave-number transfers is of special interest. The **Ornstein-Zernike approximation** therefore consists in terminating the expansion of  $D(\mathbf{q})$  after the first non-vanishing term:

$$D(\mathbf{q}) \approx D(0) + c_2 q^2 . \quad (4.172)$$

We use it to calculate the *static structure factor*, for which we get with (4.163), (4.168), and (4.170):

$$S(\mathbf{q}) = n + n^2 \Gamma(\mathbf{q}) = \frac{n}{1 - nD(\mathbf{q})} .$$

With the abbreviation

$$\xi^2 = \frac{-nc_2}{1 - nD(0)} \quad (4.173)$$

and the Ornstein-Zernike approximation (4.172) one finds:

$$S(\mathbf{q}) \approx -\frac{1}{c_2} \frac{1}{\xi^{-2} + q^2} \stackrel{(4.165)}{=} n \frac{I(\mathbf{q})}{I_0(\mathbf{q})} . \quad (4.174)$$

The scattered intensity thus exhibits at  $q = 0$  a *Lorentz peak*, whose half width is obviously given by  $\xi^{-1}$ . That the quantity  $\xi$  defined in (4.173) is indeed related to the *correlation length* one recognizes after inverse transformation into the three-dimensional ( $d = 3$ ) position space (Exercise 4.3.9):

$$g(r) = -\frac{2\pi^2}{c_2 V} \frac{\exp\left(-\frac{r}{\xi}\right)}{r} . \quad (4.175)$$

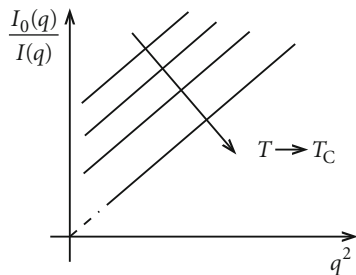
In the Ornstein-Zernike approximation the pair correlation has therewith exactly the form (4.12). The other way round, one ascribes to every system, whose correlation function has the structure (4.175), an **Ornstein-Zernike behavior**. Note that with the transformation from (4.174) to (4.175) it is integrated over **all** wave vectors  $\mathbf{q}$ , which makes the *Ornstein-Zernike approximation* (4.172) somewhat questionable. The comparison of (4.175) with (4.32) fixes the critical exponent  $\eta$  ( $d = 3$ ):

$$\eta = 0 . \quad (4.176)$$

Strictly speaking, this result was of course to be expected, since the exponent  $\eta$  actually characterizes just the *deviation* from the *Ornstein-Zernike behavior*. For fixing the exponents  $\nu$  and  $\nu'$  we use (4.174) and (4.166):

$$\xi^2 = -c_2 S(0) = -nc_2 \frac{\kappa_T}{\kappa_T^{(0)}} .$$

**Fig. 4.26** Prediction of the Ornstein-Zernike theory with respect to the inverse scattered intensity when one approaches the critical point



$\xi^2$  therefore becomes critical in the same manner as the compressibility so that, consequently, it must be

$$\nu^{(l)} = \frac{1}{2} \gamma^{(l)}. \quad (4.177)$$

Equations (4.176) and (4.177) correspond to the statements (4.116), (4.118), and (4.119) of the *superordinate* Landau theory.

The correlation length  $\xi$  is experimentally observable by the scattered light intensity  $I(q)$ . Because of (4.174) the plot of  $I_0(q)/I(q)$  as function of  $q^2$  (Fig. 4.26) should yield a straight line with the slope  $-nc_2(T)$  and an axis intercept  $-nc_2/\xi^2$ . The latter approaches zero for  $T \rightarrow T_C$ .—These predictions of the Ornstein-Zernike theory are qualitatively very well confirmed by the experiment.

### 4.3.10 Exercises

#### Exercise 4.3.1

Show that the internal energy of the van der Waals gas is of the form

$$U(T, V) = f(T) - a \frac{n^2}{V},$$

where  $f(T)$  is a not in detail determined function of the temperature. Let the mole number  $n$ , and therewith also the particle number  $N$  be constant. Calculate the entropy  $S(T, V)$  and therewith the latent heat  $\Delta Q = T_0(S_G - S_L)$  at the phase transition!

#### Exercise 4.3.2

A ferromagnetic solid is described by the Heisenberg model of interacting localized spins  $\mathbf{S}_i$  in the homogeneous magnetic field  $\mathbf{B} = B\mathbf{e}_z$ :

$$H = - \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - 2\mu_B B \sum_i S_i^z.$$

These are thought to be  $S = \frac{1}{2}$ -spins, whose exchange interactions are restricted to next neighbors:

$$J_{ij} = \begin{cases} J & \text{if } i \text{ and } j \text{ next neighbors} \\ 0 & \text{otherwise} \end{cases}$$

1. Introduce as 'test system' the paramagnet  $H^*$  from Exercise 2.3.9:

$$H^* = -2\mu_B B^* \sum_i S_i^z$$

$B^*$ : 'mean field' (variational parameter!)

Calculate therewith by using (2.139)

$$F \leq F^* + \langle H - H^* \rangle^* = \widehat{F}^*$$

an upper boundary  $\widehat{F}^*$  for the free energy  $F$  of the spin system.

2. Calculate the *optimal mean field*  $B_0^*$  as that field  $B^*$ , which makes  $\widehat{F}^*$  to the best possible approximation for  $F$ .  
3. Define with

$$k_B T_C = \frac{1}{2} z J$$

( $z$ : number of next neighbors of a given lattice point) the Curie temperature  $T_C$ . Show that there is a phase transition at  $T_C$ :

$T < T_C$  : ferromagnetism

$T > T_C$  : paramagnetism

4. Show that for  $T > T_C$ ,  $B \rightarrow 0^+$  the susceptibility

$$\begin{aligned} \chi(T) &= \left. \frac{\partial}{\partial B} M(T, B) \right|_{B=0} \\ &= 2\mu_B \left. \frac{\partial}{\partial B} \langle S^z \rangle^* \right|_{B=0} \end{aligned}$$

( $M(T, B)$ : magnetization) fulfills the Curie-Weiss law

$$\chi(T) \sim \frac{1}{T - T_C} .$$

**Exercise 4.3.3**

Calculate the critical exponents  $\beta$ ,  $\gamma$ ,  $\gamma'$ , and  $\delta$  of the van der Waals gas:

1. Show at first that the van der Waals-equation of state, by the use of the reduced quantities

$$p_r = \frac{p}{p_c} - 1; \quad V_r = \frac{V}{V_c} - 1; \quad \varepsilon = \frac{T}{T_c} - 1,$$

can be written as follows:

$$p_r (2 + 7V_r + 8V_r^2 + 3V_r^3) = -3V_r^3 + 8\varepsilon (1 + 2V_r + V_r^2).$$

2. How does the reduced volume  $V_r$  behave for  $T \xrightarrow{<} T_c$  and  $T \xrightarrow{>} T_c$ ?
3. Determine the critical exponent  $\beta$ .
4. Show that it holds on the critical isotherm

$$p_r = -\frac{3}{2} V_r^3 \left( 1 - \frac{7}{2} V_r + \dots \right)$$

5. Determine the critical exponent  $\delta$ .
6. Derive with the compressibility  $\kappa_T$  the values for the critical exponents  $\gamma$  and  $\gamma'$ .  
What can be said about the critical amplitudes  $C$  and  $C'$ ?

**Exercise 4.3.4**

Investigate the *critical behavior* of the isobaric thermal expansion coefficient

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

for the van der Waals gas.

**Exercise 4.3.5**

Discuss the critical behavior of the Weiss ferromagnet. This obeys the equation of state ((1.4.4), Vol. 5):

$$M = M_0 L \left( m \frac{B_0 + \lambda \mu_0 M}{k_B T} \right)$$

1. Show that, with the reduced quantities

$$\widehat{M} = \frac{M}{M_0}; \quad b = \frac{m B_0}{k_B T}; \quad \varepsilon = \frac{T - T_c}{T_c}$$

( $m$ : magnetic moment;  $M_0 = \frac{N}{V} m$ : saturation magnetization), the equation of state can be written as follows:

$$\widehat{M} = L \left( b + \frac{3\widehat{M}}{\varepsilon + 1} \right)$$

( $L(x) = \coth x - \frac{1}{x}$ : Langevin function). It further holds  $T_c = \lambda C$  with

$$C = \mu_0 \frac{N m^2}{V 3k_B}$$

2. Calculate the critical exponent  $\beta$ .
3. What is the value of the critical exponent  $\delta$ ?
4. Derive the critical exponents  $\gamma, \gamma'$  and determine the ratio  $C/C'$  of the critical amplitudes.

**Exercise 4.3.6**

The Landau theory for the homogeneous ferromagnet leads, in the critical region, to the following ansatz of the free energy:

$$F(T, m) = \sum_{n=0}^{\infty} L_{2n}(T) m^{2n}$$

$$L_n(T) = \sum_{j=0}^{\infty} l_{nj} (T - T_C)^j .$$

$l_{nj}$ : constants;  $T_C$ : Curie temperature

1. Determine the equation of state

$$B_0 = B_0(T, m) \quad (B_0 = \mu_0 H) . \quad (1)$$

2. Calculate the susceptibility

$$\chi_T = \frac{\mu_0}{V} \left( \frac{\partial m}{\partial B_0} \right)_T = \chi_T(T, m) \quad (2)$$

and show that from the experimentally observed divergence of  $\chi_T$  for  $T \rightarrow T_C$  it must necessarily follow

$$l_{20} = 0 . \quad (3)$$

3. Calculate the critical exponents

$$\beta, \gamma, \gamma' \quad \text{and} \quad \delta \quad (4)$$



under the presumption:

$$l_{40} > 0 ; l_{21} \neq 0 ; l_{02} \neq 0 \quad (5)$$

Can  $l_{40} > 0$  be justified?

### Exercise 4.3.7

The Landau theory of the homogeneous ferromagnet leads to the following ansatz for the free energy in the critical region (see Exercise 4.3.6):

$$F(T, m) = \sum_{n=0}^{\infty} L_{2n}(T) m^{2n}$$

$$L_n(T) = \sum_{j=0}^{\infty} l_{nj} (T - T_C)^j$$

$l_{nj}$ : constants;  $T_C$ : Curie temperature  
Calculate the heat capacity

$$C_H = T \left( \frac{\partial S}{\partial T} \right)_{H(B_0)}$$

Show that it performs at the Curie point  $T_C$  a finite jump  $\Delta C_H \neq 0$ ! Is this also true for  $C_m$ ? What follows for the critical exponents  $\alpha$  and  $\alpha'$ ?

### Exercise 4.3.8

Consider as in Exercise 4.3.6 the homogeneous ferromagnet in the Landau formulation. A certain arbitrariness seems to be due to the choice of the expansion coefficients  $l_{nm}$ .  $l_{20} = 0$  is necessary according to Exercise 4.3.6. Which values result for the critical exponents  $\beta$ ,  $\gamma$ ,  $\gamma'$ ,  $\delta$ ,  $\alpha$ ,  $\alpha'$ , if it is additionally assumed

$$l_{40} = 0, l_{60} > 0 ?$$

Discuss in particular the thermodynamically **exact** inequality:  $\gamma(\delta + 1) \geq (2 - \alpha)(\delta - 1)$ .

### Exercise 4.3.9

Show that the expression (4.175) follows by Fourier transformation from Eq. (4.174)!

## 4.4 Ising Model

With the Hamilton operator (4.138) we have got to know the **Heisenberg model**, which is known today to be able to provide a rather realistic description of ferromagnets and antiferromagnets, whose *spontaneous* magnetization results from strictly **localized** magnetic moments (EuO, EuS, EuTe, Gd,...). The Heisenberg model allows for further specializations, if one decomposes the product of the angular-momentum operators  $\mathbf{J}_i \cdot \mathbf{J}_j$  into weighted components:

$$\mathbf{J}_i \cdot \mathbf{J}_j \rightarrow \alpha J_i^x J_j^x + \beta J_i^y J_j^y + \gamma J_i^z J_j^z ,$$

$$\alpha = \beta = \gamma = 1: \quad \text{Heisenberg model,}$$

$$\alpha = \beta = 1; \quad \gamma = 0: \text{XY-model,}$$

$$\alpha = \beta = 0; \quad \gamma = 1: \text{Ising model.}$$

In this subsection we will concentrate ourselves on the *Ising model*, which was already mentioned several times in the preceding subsections. Its importance lies even today in the fact that it represents so far the only quasi-realistic model of an interacting many-particle system, which shows a phase transition and can be treated, within certain limits, in a rigorous mathematical manner.

The idea of the model has already been briefly interpreted in connection with Eq. (4.1). At each of  $N$  lattice points, which build a  $d$ -dimensional periodic lattice ( $d = 1, 2, 3$ ), there is a permanent magnetic moment,

$$\mu_i = \mu S_i, \quad S_i = \pm 1 \quad i = 1, 2, \dots, N, \quad (4.178)$$

which can adopt only two possibilities of orientation relative to an somewhat given direction. That is regulated by the *classical* spin variable  $S_i = \pm 1$ . The localized moments interact with each other; otherwise there of course could not be expected a phase transition. Let us denote the *coupling constants*, a bit more generally as in (4.1), by  $J_{ij}/\mu^2$ . The Hamilton function then reads:

$$H = - \sum_{i,j} J_{ij} S_i S_j - \mu B_0 \sum_i S_i . \quad (4.179)$$

The magnetic induction  $\mathbf{B}_0 = (0, 0, B_0)$  defines the  $z$ -direction, relative to which the moments will align themselves parallel or antiparallel.

The significance of the Ising model is, not the least, due to the multitude of exact results, atypical for many-particle models. The one-dimensional ( $d = 1$ ) model with and without field  $B_0$  can rigorously be treated (Sects. 4.4.1, 4.4.2), if the interactions  $J_{ij}$  are restricted to next neighbors, only. The  $d = 2$ -model is also mathematically strictly tractable (Sect. 4.4.4), though only for  $B_0 = 0$ . The exact solution for the

three-dimensional ( $d = 3$ )-Ising system is so far not available. There exist, however, so-called *extrapolation methods*, the results of which are judged as quasi-exact. The application spectrum of the Ising model is of rather multifaceted nature. In the first place, it is, according to the original objective, a simple **model for magnetic insulators**. The restriction to the  $z$ -component of the spin vectors, though, is reasonable only for systems with strongly uniaxial symmetry, for which the permanent moments are fixed to a special direction in space ( $\text{DyPO}_4$ ,  $\text{CoCs}_3\text{Cl}$ , ...). In the region of magnetism, the Ising model is therefore today rather seldom applied. In fact, it has developed into a general **demonstration model of Statistical Physics**. As certainly the simplest microscopic model, which exhibits a second-order phase transition for  $d \geq 2$ , it is in the center of many considerations and investigations concerning the general theory of *phase transitions and critical phenomena*.

#### 4.4.1 The One-Dimensional Ising Model ( $B_0 = 0$ )

We are interested in finding out whether or not the  $d = 1$ -Ising spin system (Fig. 4.27) exhibits a phase transition, i.e., whether a critical temperature  $T_C$  exists, below which the spins order themselves *spontaneously*. Therefore, at first, no magnetic field is switched on. The interaction may be restricted to directly neighboring spins:  $J_{i+1} \rightarrow J_i$ .

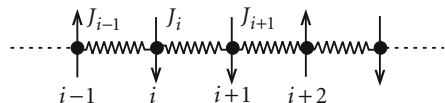
$$H = - \sum_{i=1}^{N-1} J_i S_i S_{i+1} . \quad (4.180)$$

We calculate with the Hamilton function the classical canonical partition function. Because in the latter  $H$  appears only in the form of  $\exp(-\beta H)$  the following abbreviation

$$j_i = \frac{J_i}{k_B T} = \beta J_i \quad (4.181)$$

turns out to be reasonable. Each *Ising spin*  $S_i$  has two possibilities for its orientation. There are therefore altogether  $2^N$  different spin arrangements and accordingly  $2^N$  different states of the system, over which it must be summed in the partition

**Fig. 4.27** Symbolic representation of the Ising-spin chain



function:

$$Z_N = Z_N(j_1, j_2, \dots, j_{N-1}) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} \exp \left( \sum_{i=1}^{N-1} j_i S_i S_{i+1} \right).$$

We determine  $Z_N$  by a *recursion formula*, for the derivation of which we extend the chain by one Ising spin:

$$Z_{N+1} = \sum_{S_1} \cdots \sum_{S_N} \exp \left( \sum_{i=1}^{N-1} j_i S_i S_{i+1} \right) \sum_{S_{N+1}} \exp(j_N S_N S_{N+1}).$$

The factor to the right can easily be calculated:

$$\sum_{S_{N+1}}^{\pm 1} \exp(j_N S_N S_{N+1}) = 2 \cosh(j_N S_N) = 2 \cosh(j_N).$$

We have therewith already found the mentioned recursion formula,

$$Z_{N+1} = 2Z_N \cosh(j_N),$$

which leads to

$$Z_{N+1} = Z_1 2^N \prod_{i=1}^N \cosh(j_i)$$

where  $Z_1$  means the partition function of the single spin. The latter has two eigenstates ( $|\uparrow\rangle, |\downarrow\rangle$ ), both with zero energy, because the single spin has no possibility of interaction:

$$Z_1 = \sum_{S_1} e^0 = 2. \quad (4.182)$$

The partition function of the  $N$ -spin Ising system on the one-dimensional lattice is therewith determined:

$$Z_N(T) = 2^N \prod_{i=1}^{N-1} \cosh(\beta J_i). \quad (4.183)$$

This function further simplifies for the usual special case  $J_i \equiv J \forall i$  to:

$$Z_N(T) = 2^N \cosh^{N-1}(\beta J). \quad (4.184)$$

Using the partition function we calculate in the next step the *spin correlation function* (4.11) ( $J > 0$ ):

$$\begin{aligned}
 \langle S_i S_{i+j} \rangle &= \frac{1}{Z_N} \sum_{\{S_i\}} (S_i S_{i+j}) \exp \left[ \sum_{m=1}^{N-1} J_m S_m S_{m+1} \right] \\
 &= \frac{1}{Z_N} \sum_{\{S_i\}} (S_i \underbrace{S_{i+1}}_{+1}) (\underbrace{S_{i+1}}_{+1} \underbrace{S_{i+2}}_{+1}) \cdots (\underbrace{S_{i+j-1}}_{+1} S_{i+j}) \exp[\dots] \\
 &= \frac{1}{Z_N} \left( \frac{\partial}{\partial j_i} \frac{\partial}{\partial j_{i+1}} \cdots \frac{\partial}{\partial j_{i+j-1}} \right) Z_N \\
 &= \frac{\cosh j_1 \cdots \sinh j_i \cdots \sinh j_{i+j-1} \cdots \cosh j_{N-1}}{\cosh j_1 \cdots \cosh j_i \cdots \cosh j_{i+j-1} \cdots \cosh j_{N-1}} .
 \end{aligned}$$

For  $\langle S_i S_{i+j} \rangle$  we have therewith found:

$$\langle S_i S_{i+j} \rangle = \prod_{k=1}^j \tanh(\beta J_{i+k-1}) . \quad (4.185)$$

In spite of the extremely short-range interaction (next neighbors!) there result nevertheless long-range correlations between the Ising spins. For the usual special case  $J_i \equiv J \forall i$  the spin correlation becomes independent of  $i$ , and depends only on the *distance*  $j$  between the two spins:

$$\langle S_i S_{i+j} \rangle \equiv \tanh^j(\beta J) . \quad (4.186)$$

We are now in a position to calculate the **spontaneous magnetization** of the Ising chain, being therewith able to investigate the possibility of a phase transition (Fig. 4.28). In the case of *homogeneous interactions*  $J_i = J \forall i$  the average value  $\langle S_i \rangle \equiv \langle S \rangle$  is same for all  $i$ , possibly except for the edge points of the chain. We get the spontaneous magnetization,

$$M_S(T) = \mu \langle S \rangle ,$$

**Fig. 4.28** Spontaneous magnetization of the linear Ising chain



by the fact that it must hold in the infinitely large system

$$\langle S_i S_{i+j} \rangle \xrightarrow{j \rightarrow \infty} \langle S_i \rangle \langle S_{i+j} \rangle = \langle S \rangle^2 .$$

That means

$$M_S^2(T) = \mu^2 \lim_{j \rightarrow \infty} \langle S_i S_{i+j} \rangle . \quad (4.187)$$

Because it is always  $|\tanh x| < 1$  for  $x \neq \pm\infty$ , it follows after insertion of (4.186) into (4.187):

$$M_S(T) = \begin{cases} 0 & \text{for } T > 0 , \\ \mu & \text{for } T = 0 . \end{cases} \quad (4.188)$$

At finite temperatures a spontaneous magnetization is impossible in the one-dimensional Ising model (Fig. 4.28)! Consequently, **there does not exist a phase transition!**

#### 4.4.2 Transfer-Matrix Method

The one-dimensional Ising model, in the presence of an external magnetic field ( $B_0 \neq 0$ ), shall now be investigated. For the calculation of the partition function we use the *transfer-matrix method*, which was introduced in 1944 by Onsager for the solution of the two-dimensional Ising model. Because we will investigate the two-dimensional model in Sect. 4.4.4 applying a graphical method, we will demonstrate here the transfer-matrix method on the one-dimensional model. We restrict ourselves again to next-neighbor interactions, which from the beginning shall be same for all pairs of spins:

$$\beta H = -j \sum_{i=1}^N S_i S_{i+1} - b \sum_{i=1}^N S_i \quad j = \beta J ; \quad b = \beta \mu B_0 . \quad (4.189)$$

We now use *periodic boundary conditions* by closing the linear spin chain to a ring:

$$S_{N+1} = S_1 .$$

We have already previously worked out that such special boundary conditions do not mean any restriction in the *thermodynamic limit*  $N \rightarrow \infty$  (see Sect. 4.5), but of course can have certain effects for the finite system.

For the calculation of the canonical partition function we now introduce the **transfer function**:

$$T_{i,i+1} = \exp \left[ jS_i S_{i+1} + \frac{1}{2}b (S_i + S_{i+1}) \right] . \quad (4.190)$$

Because of the agreed periodic boundary conditions it can be written:

$$e^{-\beta H} = T_{1,2} T_{2,3} \cdots T_{N,1} .$$

Obviously there are for  $T_{i,i+1}$  four different spin combinations ( $S_i = \pm 1, S_{i+1} = \pm 1$ ), by which the elements of the **transfer matrix** are calculated:

$$\widehat{T} \equiv \begin{pmatrix} e^{j+b} & e^{-j} \\ e^{-j} & e^{j-b} \end{pmatrix} . \quad (4.191)$$

With the spin states,

$$|S_i = +1\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} ; \quad |S_i = -1\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix} ,$$

one gets the relation,

$$\langle S_i | \widehat{T} | S_{i+1} \rangle = T_{i,i+1} , \quad (4.192)$$

which helps to formulate the partition function:

$$\begin{aligned} Z_N(T, B_0) &= \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} T_{1,2} T_{2,3} \cdots T_{N,1} \\ &= \sum_{S_1} \cdots \sum_{S_N} \langle S_1 | \widehat{T} | S_2 \rangle \langle S_2 | \widehat{T} | S_3 \rangle \cdots \langle S_N | \widehat{T} | S_1 \rangle \\ &= \sum_{S_1} \langle S_1 | \widehat{T}^N | S_1 \rangle = \text{Tr} \widehat{T}^N . \end{aligned}$$

Here the completeness of the spin states was exploited. The *trace* is independent of the basis which is used for the representation of the matrix. In its *eigen-basis*,  $\widehat{T}$  is diagonal:

$$Z_N(T, B_0) = \text{Tr} \widehat{T}^N = E_+^N + E_-^N . \quad (4.193)$$

$E_+$  and  $E_-$  are the two eigen-values of the  $2 \times 2$ -matrix (4.191)

$$\det |\widehat{T} - E\mathbf{1}| \stackrel{!}{=} 0 .$$

One easily finds:

$$E_{\pm} = e^j \left[ \cosh b \pm \sqrt{\cosh^2 b - 2e^{-2j} \sinh(2j)} \right]. \quad (4.194)$$

Because of  $E_+ > E_-$  only  $E_+$  plays a role for the asymptotically large system (thermodynamic limit):

$$Z_N(T, B_0) = E_+^N \left[ 1 + \left( \frac{E_-}{E_+} \right)^N \right] \xrightarrow{N \gg 1} E_+^N. \quad (4.195)$$

When the field is switched off ( $B_0 = 0$ ) the eigen-values  $E_{\pm}$  simplify to

$$E_{\pm} \xrightarrow{B_0=0} e^j \left[ 1 \pm \sqrt{1 - e^{-2j}(e^{2j} - e^{-2j})} \right] = e^j \pm e^{-j}.$$

This means for the partition function:

$$\begin{aligned} Z_N(T, 0) &= 2^N \cosh^N(\beta J) [1 + \tanh^N(\beta J)] \\ &\xrightarrow{N \gg 1} 2^N \cosh^N(\beta J) \quad (T \neq 0). \end{aligned} \quad (4.196)$$

The comparison with (4.184) confirms the equivalence of the results for the ring and for the open chain in the case of the asymptotically large system. For a finite number of spins, though, the special boundary conditions actually become noticeable.

### 4.4.3 Thermodynamics of the $d = 1$ -Ising Model

At first, we will derive the **thermal equation of state** of the one-dimensional *Ising magnet*. That can be done via the magnetic moment and the magnetization, respectively:

$$M(T, B_0) = \frac{1}{Z_N} \sum_{\{S\}} \left( \mu \sum_i S_i \right) e^{-\beta H} = \frac{1}{\beta} \left( \frac{\partial}{\partial B_0} \ln Z_N(T, B_0) \right)_T.$$

It follows with (4.195):

$$M(T, B_0) = \frac{N}{\beta} \frac{1}{E_+} \frac{\partial E_+}{\partial B_0}.$$



That is easily evaluated:

$$M(T, B_0) = N\mu \frac{\sinh(\beta\mu B_0)}{\sqrt{\cosh^2(\beta\mu B_0) - 2e^{-2\beta J} \sinh(2\beta J)}} . \quad (4.197)$$

For all finite temperatures the magnetic moment (the magnetization) vanishes when the field is *switched off* ( $B_0 = 0$ ) (Fig. 4.29). As already stated in (4.188) there is no *spontaneous* magnetization. The  $d = 1$ -Ising model is for all temperatures  $T \neq 0$  paramagnetic.—For very strong fields  $B_0$  the magnetization runs into *saturation* (Fig. 4.29):

$$M(T, B_0) \approx N\mu \tanh(\beta\mu B_0) \rightarrow N\mu .$$

The  $M$ - $B_0$ -isotherms look very much like those of the ideal  $S = 1/2$ -paramagnet in Sect. 4.3.5.

The **free energy**  $F$  of the field-free ( $B_0 = 0$ ) one-dimensional Ising model can directly be read off from (4.196):

$$F(T) = -k_B T \ln Z_N(T, 0) = -Nk_B T \ln [2 \cosh(\beta J)] . \quad (4.198)$$

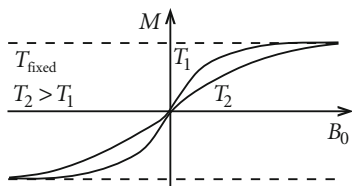
With this function we calculate the **entropy**  $S$ :

$$S = -\frac{\partial F}{\partial T} = Nk_B \{ \ln [2 \cosh(\beta J)] - \beta J \tanh(\beta J) \} . \quad (4.199)$$

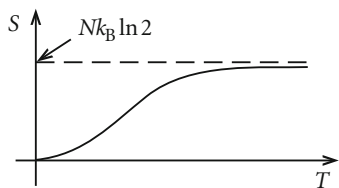
It fulfills the third law of Thermodynamics (Fig. 4.30)

$$S \xrightarrow{T \rightarrow 0} Nk_B \{ \beta J - \beta J \} = 0 .$$

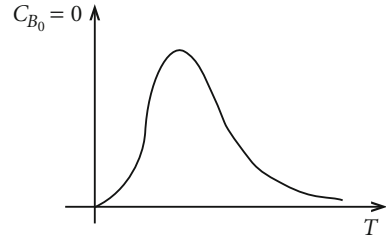
**Fig. 4.29** Isotherms of the paramagnetic  $d = 1$ -Ising model



**Fig. 4.30** Temperature behavior of the entropy of the  $d = 1$ -Ising model



**Fig. 4.31** Temperature behavior of the zero-field heat capacity of the  $d = 1$ -Ising model



For very high temperatures it results a thermal equivalence of all the  $2^N$  spin states. That means (Fig. 4.30):

$$S \xrightarrow{T \rightarrow \infty} k_B \ln 2^N = Nk_B \ln 2 .$$

By the entropy we get the **heat capacity**:

$$C_{B_0=0} = T \left( \frac{\partial S}{\partial T} \right)_{B_0=0} = Nk_B \frac{\beta^2 J^2}{\cosh^2(\beta J)} . \quad (4.200)$$

$C_{B_0=0} \rightarrow 0$  for  $T \rightarrow 0$  (Fig. 4.31) is a further hint that the third law of Thermodynamics is fulfilled.

For the calculation of the isothermal susceptibility  $\chi_T$  we conveniently start at the *fluctuation-dissipation theorem* (4.16), which we have actually derived there for the Ising-spin system:

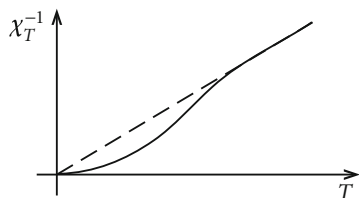
$$\begin{aligned} \chi_T(B_0 = 0) &= \beta \mu^2 \frac{\mu_0}{V} \sum_{ij} (\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle) \\ &\stackrel{(4.186)}{=} \beta \mu^2 \mu_0 \frac{N}{V} \sum_j \tanh^j(\beta J) . \end{aligned}$$

Because of  $B_0 = 0$ , the expectation values  $\langle S_i \rangle$  and  $\langle S_j \rangle$  vanish. The remaining sum is just twice the *geometric series* except for the  $j = 0$ -term :

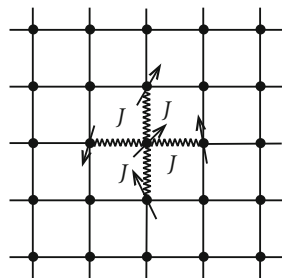
$$\chi_T(B_0 = 0) = \frac{N}{V} \beta \mu^2 \mu_0 \frac{1 + \tanh(\beta J)}{1 - \tanh(\beta J)} = \frac{N}{V} \beta \mu^2 \mu_0 e^{2\beta J} . \quad (4.201)$$

This expression agrees with the susceptibility in (4.13), which one finds with (4.197) for  $B_0 \rightarrow 0$ . The susceptibility fulfills for high temperatures the *Curie law* (4.137) of the paramagnet and diverges for  $T \rightarrow 0$  (Fig. 4.32).

**Fig. 4.32** Temperature behavior of the inverse isothermal susceptibility of the  $d = 1$ -Ising model



**Fig. 4.33** Two-dimensional Ising-spin lattice with isotropic spin coupling



#### 4.4.4 Partition Function of the Two-Dimensional Ising Model

The evaluation of the  $d = 2$ -model turns out to be very much more complicated than that of the one-dimensional system. However, since it is a problem statement typical for the theory of phase transitions, we will perform the due derivations in a very detailed manner. Thereby we will follow a method, which was proposed by M. L. Glasser (Am. J. Phys. **38**, 1033 (1970)).

Starting point is again the Hamilton function (4.179), where, however, only isotropic *next-neighbor interactions* shall be taken into consideration (Fig. 4.33). An external field is **not** switched on ( $B_0 = 0$ ):

$$H = -J \sum_{(i,j)} S_i S_j . \quad (4.202)$$

The calculation will at first be performed for a **finite** system of  $N$  Ising-spins on a quadratic lattice. The transition into the *thermodynamic limit* will be done only at the end of the calculation. The summation in (4.202) runs over all pairs  $(i, j)$  of next neighbors on the lattice. The objective is the calculation of the **canonical partition function**:

$$Z_N(T) = \sum_{\{S_i\}} \exp(-\beta H) . \quad (4.203)$$

The summation comprises all the  $2^N$  spin configurations.

We begin with a suitable **high-temperature expansion** of the partition function. The spin variable can only take the values +1 or -1. It therefore holds for arbitrary  $n \in \mathbf{Z}$ :

$$(S_i S_j)^{2n} = 1 ; \quad (S_i S_j)^{2n+1} = S_i S_j .$$

When one uses this in the series expansion of the exponential function, it follows immediately:

$$e^{\beta J S_i S_j} = \cosh(\beta J) + (S_i S_j) \sinh(\beta J) = \cosh(\beta J) [1 + v (S_i S_j)] .$$

By  $v$  we have introduced a variable convenient for high-temperature expansions:

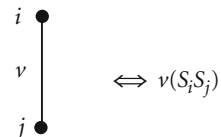
$$v = \tanh(\beta J) . \tag{4.204}$$

On the quadratic lattice, each Ising-spin has four next neighbors. If one neglects boundary effects, because later the transition to the infinitely large system is performed anyway, then one counts  $2N$  different pairs of next neighbors. One finds therewith, rather directly, the following first intermediate result for the canonical partition function:

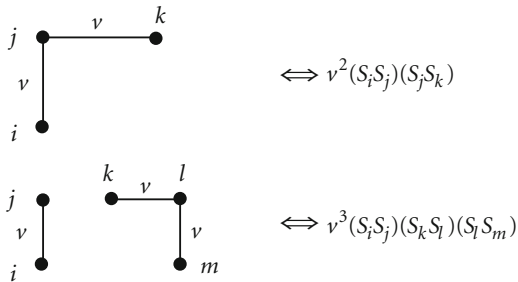
$$\begin{aligned} Z_N(T) &= \sum_{\{S_i\}} \prod_{(i,j)} e^{\beta J S_i S_j} \\ &= \cosh^{2N}(\beta J) \sum_{\{S_i\}} \left[ 1 + v \sum_{\nu=1}^{2N} S_{i_\nu} S_{j_\nu} \right. \\ &\quad \left. + v^2 \sum_{\substack{\nu, \mu=1 \\ \nu \neq \mu}}^{2N} (S_{i_\nu} S_{j_\nu})(S_{i_\mu} S_{j_\mu}) + \dots \right] . \end{aligned} \tag{4.205}$$

In the next step the spin products are graphically represented by **diagrams**. The *interaction*  $v$  corresponds to a solid line between respective lattice points (Fig. 4.34). Each line carries the factor  $v$  and links two next neighbors. The points are called **vertexes**. To each vertex an **order** can be ascribed, defined by the number of interaction lines which are coupled to this point (Fig. 4.35). Thus there are the orders 1 to 4.

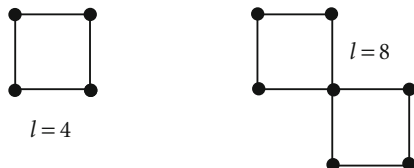
**Fig. 4.34** Elementary module of the diagram expansion for the canonical partition function of the  $d = 2$ -Ising model



**Fig. 4.35** Typical spin products in the diagram expansion for the canonical partition function of the  $d = 2$ -Ising model



**Fig. 4.36** Examples of diagrams, which give a finite contribution to the canonical partition function of the  $d = 2$ -Ising model



In a typical spin product of (4.205),

$$\sum_{\{S_i\}} (S_{i_1} S_{j_1}) \cdots (S_{i_l} S_{j_l}) ,$$

it is summed over all  $2^N$  spin configurations. If there appear in the product one or more spins  $S_i^*$  with odd powers (1 or 3), the total expression vanishes, because then there exists to each summand in  $\{S_i\}$  a counterpart, which differs from it only by the fact that  $S_i^* = \pm 1$  is replaced by  $-S_i^*$ . These terms compensate each other. When, however, all spins appear in the above product even-numbered (two times or four times), then the total product yields the value  $+1$ , and, after summation over all spin configurations, the contribution  $2^N$ . Therefore one can obviously write instead of (4.205):

$$Z_N(T) = 2^N \cosh^{2N}(\beta J) \sum_{l=0}^{\infty} g_l v^l . \tag{4.206}$$

$g_l$  is thereby the number of diagrams, which are built by  $l$  lines with exclusively even vertexes ( $g_0 \equiv 1$ ). Only closed polylines possess nothing but even vertexes (Fig. 4.36).  $l = 4$  is thus the lowest finite power of  $v$  in (4.206).

The remaining task consists in fixing  $g_l$ . For this purpose, we introduce at first two new terms:

**Node:** vertex of the fourth order (Fig. 4.37).

**Loop:** closed polyline **without** nodes.

In order to avoid later ambiguities, we agree upon a prescription how to unlock nodes. That is sketched in Fig. 4.38. As shown, each node can be *unlocked* in three different ways. The third variant we will call **self-intersection** (SIS). Each diagram

Fig. 4.37 Node of a diagram

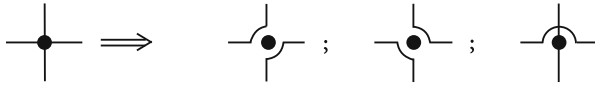


Fig. 4.38 Prescription for the unlocking of nodes

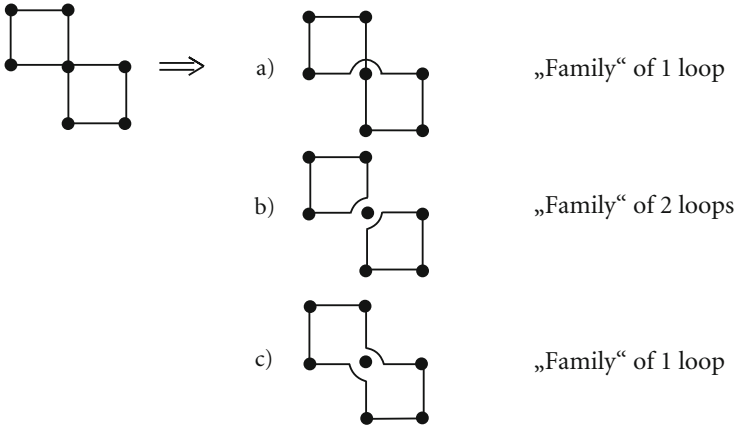


Fig. 4.39 Definition of a ‘family of loops’

with  $k$  nodes decays, according to this prescription, into  $3^k$  **families of loops**. We present an example for  $k = 1$  in Fig. 4.39.

The unlocking of the nodes leads of course to a substantial multiplication of the number of diagrams, which can again be outweighed by the introduction of weight factors  $\eta$  for *loops* and *families*, respectively:

$$\eta(\text{loop}) = (-1)^{\text{number of SIS}},$$

$$\eta(\text{family}) = (-1)^{\text{number of SIS in the family}}.$$

In the sketched example in Fig. 4.39 it is  $\eta(a) = -1$ ,  $\eta(b) = +1$ ,  $\eta(c) = +1$ . The sum of the  $\eta$ 's is thus equal to 1! That can be generalized:

$$g_l = \text{sum of the weights of all families of loops of altogether } l \text{ lines.}$$

This one understands as follows:

1. A diagram **without** nodes consists of one single loop or of a family of loops without SIS, and is therefore counted with the weight  $\eta = (-1)^0 = +1$ .
2. For a diagram with  $k$  nodes we have  $\binom{k}{j}$  possibilities to choose  $j$  nodes, which an SIS should have after the unlocking. For each of the  $(k-j)$  nodes, which after the unlocking are without SIS, there are two possibilities. Thus there are altogether  $2^{k-j}\binom{k}{j}$  possibilities to build from a diagram with  $k$  nodes a family of loops with  $j$  self-intersections. Each of these families carries the weight  $(-1)^j$ .—The total weight of all families of loops, which can be built from a diagram with  $k$  nodes, amounts to:

$$\sum_{j=0}^k \binom{k}{j} 2^{k-j} (-1)^j = (2-1)^k = 1.$$

After unlocking the nodes, according to the above prescription, the number of diagrams has multiplied. The weight factors, however, take care for the fact that all families of loops, which arise from a given diagram, yield the total weight  $+1$ . The quantity  $g_l$ , which was introduced for (4.206) as the number of diagrams built up by  $l$  lines with exclusively even vertexes, can now also be seen as sum of the weights of all families of loops with altogether  $l$  lines.

We define in the next step:

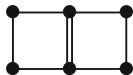
$D_l =$  sum of the weights of all loops of  $l$  lines.

Since each family is composed by one or more loops,  $g_l$  can be expressed by  $D_l$ :

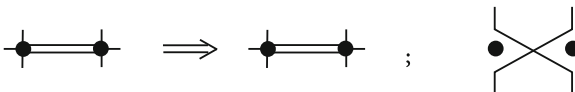
$$g_l = \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{\substack{l_1, \dots, l_n \\ \sum l_i = l}} D_{l_1} D_{l_2} \cdots D_{l_n}; \quad l \neq 0 \quad (4.207)$$

( $g_0 = 1$ ). The product  $D_{l_1} D_{l_2} \cdots D_{l_n}$  comprises all possible decompositions of a family of  $l$  lines into loops, where of course the constraint  $\sum l_i = l$  must be fulfilled. Summands in (4.207), which differ only by the sequence of the factors ( $D_{l_i}$ ), describe the same family, therefore must be counted actually only once. This is regulated by the factor  $(1/n!)$ . The summation over  $n$  in (4.207) can formally run up to infinity, since for  $l_i < 4$   $D_{l_i} = 0$ , because loops with less than four lines do not exist.

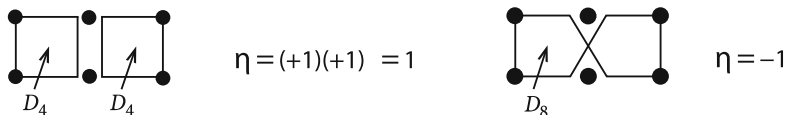
It still remains, however, to clarify a problem in connection with the representation (4.207). Since the  $l_i$  summations are to be performed completely independently of each other, at least except for the constraint  $\sum l_i = l$ , there will appear also *double occupancies* of single lines (Fig. 4.40). These belong to non-existing loops on the quadratic lattice, therefore do not appear in the initial equation (4.205). We thus have to weight them in such a way that they do not yield any contribution. Simply to extract them out from (4.207) would be too complicated. We agree to treat a *double occupancy* as sketched in Fig. 4.41, i.e., to count them twice. In the



**Fig. 4.40** Double occupancy of lines in the diagram expansion for the canonical partition function of the  $d = 2$ -Ising model



**Fig. 4.41** Resolving a double occupancy of lines in the diagram expansion for the canonical partition function of the  $d = 2$ -Ising model



**Fig. 4.42** Example for the resolving of a double occupancy of lines in the diagram expansion for the canonical partition function of the  $d = 2$ -Ising model

second version a *self-intersection* is produced, while in the first no self-interaction is produced. The weights of the two types of diagrams thus compensate each other. We can therefore formally take into consideration even the in principle forbidden *double occupancies* in (4.207). An example is given in Fig. 4.42.

With this description, (4.207) can now be used, in order to get a further intermediate result for the canonical partition function. We need in (4.206):

$$g_l v^l \stackrel{(4.207)}{=} \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{\substack{l_1, \dots, l_n \\ \sum l_i = l}} (D_{l_1} v^{l_1}) \cdots (D_{l_n} v^{l_n}) \quad (l \neq 0).$$

When we sum this expression over all  $l$  from 1 to  $\infty$ , then all the  $l_i$ -summations become independent of each other. The constraint  $\sum l_i = l$  is then meaningless:

$$\sum_{l=0}^{\infty} g_l v^l = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left[ \sum_{l^*=1}^{\infty} D_{l^*} v^{l^*} \right]^n = \exp \left[ \sum_{l=1}^{\infty} D_l v^l \right].$$

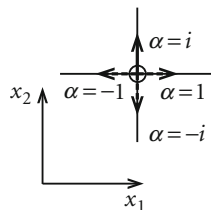
We can now replace (4.206) by the new intermediate result:

$$Z_N(T) = 2^N \cosh^{2N}(\beta J) \exp \left[ \sum_{l=1}^{\infty} D_l v^l \right]. \tag{4.208}$$

It thus remains, because of  $D_l$ , to add together the weights of all the loops, which can be built by  $l$  lines.



**Fig. 4.43** Introduction of 'directed paths' in the diagram expansion for the canonical partition function of the  $d = 2$ -Ising model



The remaining task consists in counting the self-intersections within a loop. This can be done in an elegant manner by the introduction of **directed paths** (Fig. 4.43). For this purpose we represent the two-dimensional Ising-lattice in the complex plane,

$$z = x_1 + ix_2 ,$$

with integral real and imaginary parts for the individual lattice points.

A **single step**  $p = (z, \alpha)$  is defined by its starting point  $z$  and its

$$\text{direction} \quad \alpha = 1, i, -1, -i ,$$

so that  $z + \alpha$  represents the endpoint of the step. A *path from  $z$  to  $z'$  in  $m$  steps* is a sequence of  $m$  single steps,

$$p_0 = (z_0, \alpha_0), p_1, p_2, \dots, p_{m-1} = (z_{m-1}, \alpha_{m-1}) ,$$

with

$$z_0 = z ; \quad z_{i+1} = z_i + \alpha_i ; \quad z_m = z' .$$

In order to avoid turning points, we still require:

$$\alpha_{i+1} \neq -\alpha_i .$$

For fixing  $D_l$  we need the *weight* of a loop. This we will relate to the following **weight of the path**:

$$\eta(\text{path}) = \exp \left[ \frac{i}{2} \left( \arg \frac{\alpha_1}{\alpha_0} + \dots + \arg \frac{\alpha_m}{\alpha_{m-1}} \right) \right] . \tag{4.209}$$

Because of  $\alpha_{i+1}/\alpha_i = 1, \pm i$  it can be

$$\arg \frac{\alpha_{i+1}}{\alpha_i} = 0, \pm \frac{\pi}{2} .$$

It represents the change of direction between the  $i$ -th and the  $(i + 1)$ -st *single step*.  $\arg(\alpha_{i+1}/\alpha_i) = \pm\pi$  does not appear, because direct reversal steps shall be excluded.

We now introduce the matrix  $M_m$ , whose elements are defined as follows:

$$\langle p | M_m | p' \rangle = \text{sum of the weights of all paths from } p \text{ to } p' \text{ in } m \text{ single steps.}$$

The matrix element shall be zero, if  $p'$  cannot be reached from  $p$  by  $m$  steps. Of course, for  $m = m_1 + m_2$  it also holds:

$$\begin{aligned} \langle p | M_m | p' \rangle &= \sum_{p''} \langle p | M_{m_1} | p'' \rangle \langle p'' | M_{m_2} | p' \rangle \\ &\iff M_m = M_{m_1} M_{m_2} . \end{aligned}$$

The decomposition can be continued:

$$M_m = M_1^m .$$

Since there are for  $N$  lattice sites and four possibilities for  $\alpha$  (boundary effects neglected)  $4N$  different single steps  $p$ ,  $M_1$  must be a  $4N \times 4N$ -matrix. However, the matrix contains a lot of zeros, namely for all the  $p, p'$ , which are not bridgeable by a single step.

The matrix  $M_l$  has a direct relationship to the quantity  $D_l$  we are actually interested in:

$$D_l = -\frac{1}{2l} \sum_p \langle p | M_l | p \rangle = -\frac{1}{2l} \text{Tr} M_l^l . \tag{4.210}$$

One recognizes the validity of this relation as follows: At first,  $D_l$  refers to *loops*, i.e., to closed paths, so that only the diagonal elements  $p = p'$  will play a role. In the sum over  $p$  each of the  $l$  points of the loop can be the starting point. Furthermore, the loop can be run through in two different directions. This ambiguity is accounted for by the factor  $1/2l$ . In addition, for a closed path, the total angle of rotation is always an integral multiple of  $2\pi$ . This means in every case

$$\eta(\text{path}) = \pm 1 .$$

This statement can still be formulated a bit more precisely. If there is *no self-intersection* or *an even number of self-intersections*, then the angle of rotation is  $\pm 2\pi$ . In the case of an odd number of SIS the angle is zero. The examples plotted in Fig. 4.44 may help to clarify this point ( $\varphi$ : total angle of rotation).

According to (4.209) we thus have

$$\eta(\text{path}) = -\eta(\text{loop}) ,$$

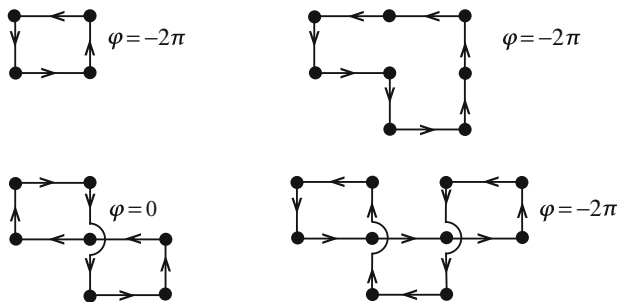


Fig. 4.44 Examples for the evaluation of directed paths

which explains the minus sign in (4.210). When the eigen-values  $m_1, m_2, \dots, m_{4N}$  of the matrix  $M_1$  are known, then we can write:

$$\text{Tr}M_1^l = \sum_{j=1}^{4N} (m_j)^l .$$

For (4.208) we need:

$$\begin{aligned} \sum_{l=1}^{\infty} D_l v^l &= -\frac{1}{2} \sum_{j=1}^{4N} \sum_{l=1}^{\infty} \frac{(m_j v)^l}{l} = \frac{1}{2} \sum_{j=1}^{4N} \ln(1 - v m_j) \\ &= \ln \left[ \prod_{j=1}^{4N} (1 - v m_j)^{1/2} \right] = \ln [ \det(\mathbb{1} - v M_1) ]^{1/2} . \end{aligned}$$

We have therewith found a further intermediate result for the partition function:

$$Z_N(T) = 2^N \cosh^{2N}(\beta J) [ \det(\mathbb{1} - v M_1) ]^{1/2} . \tag{4.211}$$

To avoid edge points we now introduce *periodic boundary conditions*, which is allowed only now, because otherwise the counting would have been erroneous. A path, which takes course from the left edge to the right edge of the plane lattice, would be on the torus, which originates by periodic boundary conditions, also a loop.

The elements of the matrix  $M_1$  read:

$$\langle p | M_1 | p' \rangle = \exp \left[ \frac{i}{2} \arg \frac{\alpha'}{\alpha} \right] (1 - \delta_{\alpha, -\alpha'}) \delta_{z+\alpha, z'} . \tag{4.212}$$

The first term explains itself by (4.209) as the weight of the single step, the second prevents turning points, and the third takes care that the step from  $z$  to  $z'$  takes place

in direction  $\alpha$ . By the boundary conditions translational symmetry is guaranteed. The matrix element (4.212) will depend, for given  $\alpha$ ,  $\alpha'$ , only on the distance  $z - z'$ . Therefore a Fourier transformation recommends itself, because the transformed matrix  $\widehat{M}_1$  will then be diagonal as function of the variable  $q$ , which is conjugate to  $z$ :

$$N = N_1 N_2; \quad z = x_1 + ix_2, \quad x_i = 1, \dots, N_i \quad (i = 1, 2),$$

$$q = q_1 + iq_2; \quad q_i = \frac{2\pi}{N_i}(1, 2, \dots, N_i),$$

$$\begin{aligned} \langle q\alpha | \widehat{M}_1 | q'\alpha' \rangle &= \frac{1}{N^2} \sum_{\substack{x_1 x_2 \\ \bar{x}_1 \bar{x}_2}} e^{-i(q_1 x_1 + q_2 x_2)} \langle z\alpha | M_1 | z'\alpha' \rangle e^{i(q'_1 x'_1 + q'_2 x'_2)} \\ &= e^{\frac{i}{2} \arg \frac{\alpha'}{\alpha}} (1 - \delta_{\alpha, -\alpha'}) \frac{1}{N^2} \sum_{\substack{x_1 x_2 \\ \bar{x}_1 \bar{x}_2}} \delta_{x_1 + \text{Re}\alpha x'_1} \\ &\quad \cdot \delta_{x_2 + \text{Im}\alpha x'_2} e^{i(q'_1 x'_1 + q'_2 x'_2 - q_1 x_1 - q_2 x_2)} \\ &= e^{\frac{i}{2} \arg \frac{\alpha'}{\alpha}} (1 - \delta_{\alpha, -\alpha'}) \frac{1}{N^2} \sum_{x_1 x_2} e^{i(q'_1 - q_1)x_1} \\ &\quad \cdot e^{i(q'_2 - q_2)x_2} e^{i(q'_1 \text{Re}\alpha + q'_2 \text{Im}\alpha)} \\ &= e^{i(q_1 \text{Re}\alpha + q_2 \text{Im}\alpha)} e^{\frac{i}{2} \arg \frac{\alpha'}{\alpha}} (1 - \delta_{\alpha, -\alpha'}) \delta_{q_1 q'_1} \delta_{q_2 q'_2}. \end{aligned}$$

The matrix  $\widehat{M}_1$  consists of  $4 \times 4$ -blocks along the diagonal, and otherwise of only zeros:

$$\langle q\alpha | \widehat{M}_1 | q'\alpha' \rangle = \delta_{qq'} \langle \alpha | m(q) | \alpha' \rangle, \quad (4.213)$$

$$\langle \alpha | m(q) | \alpha' \rangle = e^{i(q_1 \text{Re}\alpha + q_2 \text{Im}\alpha)} e^{\frac{i}{2} \arg \frac{\alpha'}{\alpha}} (1 - \delta_{\alpha, -\alpha'}) .$$

With  $\alpha$  in the order  $+1, +i, -1, -i$  as row index, and  $\alpha'$  accordingly as column index, as well as with the abbreviations,

$$\lambda = e^{i\pi/4}, \quad Q_1 = e^{iq_1}, \quad Q_2 = e^{iq_2},$$

the matrix  $m(q)$  reads:

$$m(q) \equiv \begin{pmatrix} Q_1 & \lambda Q_1 & 0 & \lambda^* Q_1 \\ \lambda^* Q_2 & Q_2 & \lambda Q_2 & 0 \\ 0 & \lambda^* Q_1^* & Q_1^* & \lambda Q_1^* \\ \lambda Q_2^* & 0 & \lambda^* Q_2^* & Q_2^* \end{pmatrix}. \quad (4.214)$$

For the partition function (4.211) the determinant

$$\det(\mathbb{1} - vM_1) = \det(\mathbb{1} - v\widehat{M}_1) = \prod_q \det(\mathbb{1} - vm(q))$$

is needed:

$$Z_N(T) = 2^N \cosh^{2N}(\beta J) \left[ \prod_q \det(\mathbb{1} - vm(q)) \right]^{1/2}. \quad (4.215)$$

Therewith we have reached our goal, because the determinant of the  $4 \times 4$ -matrix is rather easily determined:

$$Z_N(T) = 2^N \cosh^{2N}(\beta J) \left[ \prod_{q_1, q_2} \{(1 + v^2)^2 - 2v(1 - v^2)(\cos q_1 + \cos q_2)\} \right]^{1/2}. \quad (4.216)$$

#### 4.4.5 The Phase Transition

A possible phase transition becomes noticeable as some *anomaly* of a suitable thermodynamic potential. We therefore calculate now by the canonical partition function (4.216) the free energy. Because of the mandatory transition into the thermodynamic limit, of course only the free energy per spin is interesting:

$$f(T) = \lim_{N \rightarrow \infty} \frac{1}{N} (-k_B T \ln Z_N(T)) = -k_B T \left\{ \ln 2 + 2 \ln \cosh(\beta J) \right. \quad (4.217) \\ \left. + \lim_{N \rightarrow \infty} \frac{1}{2N} \sum_{q_1, q_2} \ln [(1 + v^2)^2 - 2v(1 - v^2)(\cos q_1 + \cos q_2)] \right\}.$$

The double sum can be turned into a double integral. Since in the  $q$ -space per raster volume  $2\pi/N_i$  there is just one  $q_i$ -value ( $i = 1, 2$ ;  $N_1 N_2 = N$ ), the transition-prescription reads:

$$\sum_{q_1, q_2} \dots \rightarrow \frac{N}{4\pi^2} \iint_0^{2\pi} dq_1 dq_2 \dots$$

If one still uses

$$\begin{aligned} \ln \cosh(\beta J) &= \ln \frac{1}{\sqrt{1-v^2}} = \frac{1}{4} \ln(1-v^2)^{-2} \\ &= \frac{1}{16\pi^2} \iint_0^{2\pi} dq_1 dq_2 \ln(1-v^2)^{-2}, \\ \left( \frac{1+v^2}{1-v^2} \right)^2 &= \cosh^2(2\beta J) = (1 - \sinh(2\beta J))^2 + 2 \sinh(2\beta J), \\ \frac{2v}{1-v^2} &= 2 \sinh(\beta J) \cosh(\beta J) = \sinh(2\beta J), \end{aligned}$$

then one gets the following expression for the free energy:

$$\begin{aligned} f(T) &= -k_B T \left\{ \ln 2 + \frac{1}{8\pi^2} \iint_0^{2\pi} dq_1 dq_2 \right. \\ &\quad \left. \cdot \ln \left[ (1 - \sinh(2\beta J))^2 + \sinh(2\beta J)(2 - \cos q_1 - \cos q_2) \right] \right\}. \end{aligned} \quad (4.218)$$

Even at a possible phase transition, the free energy remains continuous, but not the derivatives. Unfortunately, the double integral can not further be treated analytically. Something *anomalous* is actually to be expected only for the case that the argument of the logarithm vanishes. But then both summands must be zero, in particular it must be fulfilled

$$1 \stackrel{!}{=} \sinh \frac{2J}{k_B T_C}, \quad (4.219)$$

whereby the critical temperature would be fixed:

$$\frac{J}{k_B T_C} = \frac{1}{2} \ln(1 + \sqrt{2}) = 0.4407. \quad (4.220)$$

That indeed at  $T_C$  it is a **second-order phase transition** we will analyze by an estimation of the integral in (4.218). For this purpose we use the following Taylor expansion around  $T = T_C$ :

$$\begin{aligned} \sinh(2\beta J) &= \sinh(2\beta_C J) + (T - T_C) \cosh(2\beta_C J) \left( -\frac{2J}{k_B T_C^2} \right) + \dots \\ &= 1 - \frac{T - T_C}{T_C} (2\beta_C J \cosh(2\beta_C J)) + \dots \\ &= 1 - a\varepsilon + \dots \end{aligned}$$

The constant  $a$  is of the order of magnitude 1:

$$a \equiv 2\beta_C J \cosh(2\beta_C J) = 0.8814 \frac{2 + \sqrt{2}}{1 + \sqrt{2}} = 1.2465 .$$

According to (4.218) near  $T_C$ , the free energy should thus be of the form

$$f(T) \approx -k_B T \left\{ \ln 2 + \frac{1}{8\pi^2} \iint_0^{2\pi} dq_1 dq_2 \cdot \ln [a^2 \varepsilon^2 + (1 - a\varepsilon)(2 - \cos q_1 - \cos q_2)] \right\} .$$

Only the double integral can become critical:

$$I(\varepsilon) \equiv \iint_0^{2\pi} dq_1 dq_2 \ln [a^2 \varepsilon^2 + (1 - a\varepsilon)(2 - \cos q_1 - \cos q_2)] .$$

The first derivative

$$\frac{dI}{d\varepsilon} = \iint_0^{2\pi} dq_1 dq_2 \frac{2a^2 \varepsilon - a(2 - \cos q_1 - \cos q_2)}{a^2 \varepsilon^2 + (1 - a\varepsilon)(2 - \cos q_1 - \cos q_2)} \xrightarrow{\varepsilon \rightarrow 0} -4\pi^2$$

does not show for  $T \rightarrow T_C$  ( $\varepsilon \rightarrow 0$ ) any anomaly. The phase transition, if there is any, is certainly not of first order.

However, the second derivative

$$\begin{aligned} \left. \frac{d^2 I}{d\varepsilon^2} \right|_{\varepsilon \rightarrow 0} &= \iint_0^{2\pi} dq_1 dq_2 \frac{a^2 (\cos q_1 + \cos q_2)}{2 - \cos q_1 - \cos q_2} \\ &= -a^2 4\pi^2 + 2a^2 \iint_0^{2\pi} \frac{dq_1 dq_2}{2 - \cos q_1 - \cos q_2} \end{aligned}$$

exhibits a **logarithmic divergence**. That one sees most clearly, when one investigates the integral close to the lower integration limit,

$$2 - \cos q_1 - \cos q_2 \approx -\frac{1}{2}(q_1^2 + q_2^2) ,$$

and introduces plane polar coordinates:

$$q_1 = q \cos \varphi, \quad q_2 = q \sin \varphi: \quad dq_1 dq_2 = q dq d\varphi.$$

Then one can estimate:

$$\iint_0^{2\pi} \frac{dq_1 dq_2}{2 - \cos q_1 - \cos q_2} \longrightarrow \int_0^{\infty} q dq \frac{1}{q^2} = \ln q \Big|_0^{\infty}.$$

The second derivative of  $I$  with respect to  $\varepsilon$  thus indeed diverges logarithmically for  $\varepsilon \rightarrow 0$  ( $T \rightarrow T_C$ ). That transfers to the second derivative of the free energy with respect to the temperature, and therewith to the heat capacity:

$$C_{B_0=0} = -T \frac{d^2 f}{dT^2}.$$

The two-dimensional Ising model undergoes a **second-order phase transition** at a critical temperature  $T_C$ , which is defined by (4.220). The logarithmic divergence of the heat capacity corresponds to a *critical exponent*:

$$\alpha = 0. \quad (4.221)$$

The temperature behavior of the spontaneous magnetization  $M_S(T)$  ultimately justifies the assumption of a phase transition at  $T = T_C$ :

$$M_S(T) = \begin{cases} (1 - \sinh^{-4}(2\beta J))^{1/8}: & T < T_C, \\ 0: & T > T_C. \end{cases} \quad (4.222)$$

Normally one would find the *spontaneous* magnetization by differentiating the free energy with respect to the field with a subsequent limiting process  $B_0 \rightarrow 0$ . However, since for the  $d = 2$ -model the free energy in a finite field ( $B_0 \neq 0$ ) could not be calculated so far, one has to determine  $M_S(T)$  by the relation (4.187). Such a calculation was first performed by C. N. Yang (1952), after in 1944 L. Onsager had already made known the result (4.222) as a contribution to a seminar discussion, without publishing, though, its derivation. One reads off from (4.222) the **critical exponent of the order parameter of the two-dimensional Ising model**:

$$\beta = \frac{1}{8} \quad (4.223)$$



### 4.4.6 The Lattice-Gas Model

The lattice-gas model represents, according to its original intention, a simple modeling of the fluid system (gas-liquid), where, however, interestingly enough, a close correspondence to the Ising model is recognizable. That is the reason why we will briefly discuss it at this stage.

Assume that the system possesses the constant volume  $V$  and the constant particle number  $N$ . One now decomposes  $V$  into small parcels of the volume  $\tilde{v}$ , which corresponds approximately to the (classical) particle volume. That means that each parcel can be occupied by at most one (classical) particle. The particles are thereby, in fact, not arranged on a rigid lattice, but are freely mobile. At the moment, when the center of the particle (molecule) is in a certain cell, this cell is considered as 'occupied'. For the fractional amount of the **occupied** cells in the entire  $V$  it then holds:

$$x(V) = \frac{N}{\frac{V}{\tilde{v}}} . \quad (4.224)$$

$\frac{V}{\tilde{v}}$  is the total number of the cells in  $V$ , and thus corresponds to the highest possible particle number. The particle number in  $V$  is constant. But that does not hold, because of the particle movements, for any macroscopic partial volume  $\Delta V$  of  $V$ . The partial system in  $\Delta V$  is thus statistically to be described in the framework of the grand-canonical ensemble.

How can one recognize a phase transition in such a lattice gas?

- $T > T_C$

The free motion of the particles takes care for strong fluctuations of the particle number  $N(\Delta V)$  in  $\Delta V$ . For the individual parcels there is a rapid change between 'occupied' and 'unoccupied'. On an average, however, the fractional amount of the occupied cells in  $\Delta V$  will agree with that in the entire  $V$  (4.224):

$$x(\Delta V) = x(V) . \quad (4.225)$$

The system is in its *gas phase*!

- $T \approx T_C$

Because of the strongly increasing correlation length there will appear larger regions being occupied or unoccupied, respectively. The fractional amount of occupied cells in  $\Delta V$  will thus distinctly deviate from its average value (4.224). A *formation of droplets (clusters)* sets in:

$$x(\Delta V) < x(V) \quad \text{or} \quad x(\Delta V) > x(V) . \quad (4.226)$$

- $T \ll T_C$

Now there will be macroscopic, occupied and unoccupied regions. Except for certain edge effects,  $\Delta V$  will be completely occupied or completely unoccupied,

where hardly any fluctuations of the particle number will be observed. The system is in its *liquid phase*. Thereby it is to be taken into consideration that the model disregards the gravitational force. Therefore there can not exist a horizontal interface between gas and liquid.

If one ascribes to the parcels a *cell variable*

$$n_i = \begin{cases} 1, & \text{if cell } i \text{ occupied} \\ 0, & \text{if cell } i \text{ unoccupied} \end{cases} \quad (4.227)$$

and compares that with the Ising model

$$S_i = \begin{cases} +1, & \text{if spin } i \text{ equals } \uparrow \\ -1, & \text{if spin } i \text{ equals } \downarrow \end{cases},$$

then one finds already here indications of a close correspondence between lattice-gas model and Ising model:

$$S_i \Leftrightarrow 2n_i - 1. \quad (4.228)$$

That shall in detail be investigated in the following.

It proves to be convenient to distinguish two types of lattice gases, which turn out, though, to be thermodynamically equivalent, as we will see later.

### Lattice gas I:

We fix

$K$  : set of *all* parcels of the partial volume  $\Delta V$

$X$  : set of the *occupied* parcels of the partial volume  $\Delta V$ .

We choose here, differently from the above considerations, a somewhat more abstract formulation, in order to distinguish, which properties are due to the (compact) region  $K$  (or  $X$ ), and which are determined by the corresponding volume  $\Delta V$ . There might be properties, which do not depend only on  $\Delta V$  but also on the special shape of the volume. In fact, however, this will not play a major role in what follows.

The interaction energy reads in its *natural* version:

$$U_I(X) = \frac{1}{2} \sum_{\substack{i \in X \\ j \in X}} \varphi_I(i, j). \quad (4.229)$$

$\varphi_I(i, j)$  is a translational-invariant pair potential of finite range. There is no need, however, to further specify it. Because each cell can only be occupied by at most one particle, it is automatically a *hard-core*-potential, and represents therewith, according to the considerations in the later following Sect. 4.5.3, a *stable* potential,

for which a physically reasonable grand-canonical partition function can be defined (see (4.263)):

$$\Xi_{\mu}^{(l)}(T, K) = \sum_{X \subset K} \exp(\beta(\mu N(X) - U_I(X))) \quad (4.230)$$

It is summed over all conceivable subsets  $X$  of  $K$ .  $N(X)$  is the number of elements of  $X$ , i.e. the number of the occupied parcels ( $\cong$  number of the lattice-gas particles in  $\Delta V$ ).  $\mu$  is as usual the chemical potential.  $\Xi_{\mu}^{(l)}(T, K)$  is obviously a polynomial of the fugacity

$$z = \exp(\beta\mu)$$

of the degree  $N(K)$ :

$$\Xi_z^{(l)}(T, K) = \sum_{X \subset K} z^{N(X)} \prod_{\substack{i \in X \\ j \in X}} \exp\left(-\frac{1}{2}\beta\varphi_I(i, j)\right) \quad (4.231)$$

When we formulate the volume  $\Delta V = N(K) \tilde{v}$  in units of  $\tilde{v}$ , we can also interpret  $N(K)$  already as the *volume* of the partial lattice  $K$ . According to Eq. (2.86) it then follows for the *pressure of the lattice gas*:

$$p_I(T, \mu, K) = \frac{1}{\beta N(K)} \ln \Xi_{\mu}^{(l)}(T, K) . \quad (4.232)$$

With (2.79) one finds the *specific volume*  $v = N(K)/N(X)$  and the *particle density*  $n = v^{-1}$ , respectively:

$$n = \frac{1}{v} = \frac{1}{\beta N(K)} \frac{\partial}{\partial \mu} \ln \Xi_{\mu}^{(l)}(T, K) = \frac{\partial}{\partial \mu} p_I(T, \mu, K) . \quad (4.233)$$

With the Eqs. (4.232) and (4.233) the chemical potential  $\mu$  can be eliminated, at least in principle, and one then gets the *pv*-isotherms of the lattice gas.

An alternative to the lattice gas I represents the

### Lattice gas II:

One can normalize the interaction energy also such that it is composed by (*particle-hole*)-pair potentials between occupied and unoccupied parcels:

$$U_{II}(X) = \sum_{\substack{i \in X \\ j \notin X}} \varphi_{II}(i, j) . \quad (4.234)$$

In the case of symmetric pair interaction it must hold:

$$U_{II}(X) = U_{II}(K - X) .$$

By this one finds some symmetry relations for the grand-canonical partition function of the lattice gas II:

$$\begin{aligned}
 \Xi_{\mu}^{(II)}(T, K) &= \sum_{X \subset K} \exp(\beta(\mu N(X) - U_{\text{II}}(X))) \\
 &= \sum_{X \subset K} \exp(\beta\mu N(K) + \beta(-\mu)(N(K) - N(X)) \\
 &\quad \times \exp(-\beta U_{\text{II}}(K - X))) \\
 &= \exp(\beta\mu N(K)) \sum_{Y \subset K} \exp(\beta(-\mu N(Y) - U_{\text{II}}(Y))) .
 \end{aligned}$$

It thus holds:

$$\Xi_{\mu}^{(II)}(T, K) = \exp(\beta\mu N(K)) \Xi_{-\mu}^{(II)}(T, K) . \quad (4.235)$$

As an immediate consequence of this symmetry it follows for the *pressure of the lattice gas*:

$$p_{\text{II}}(T, \mu, K) \stackrel{(2.84)}{=} \frac{\ln \Xi_{\mu}^{(II)}(T, K)}{\beta N(K)} = \mu + p_{\text{II}}(T, -\mu, K) \quad (4.236)$$

and for the *particle density* ( $n = (\partial p / \partial \mu)_{T, N(K)}$ ):

$$n_{\text{II}}(T, \mu, K) = 1 - n_{\text{II}}(T, -\mu, K) . \quad (4.237)$$

Let us now check the

### **Equivalence of the two lattice gases:**

For this purpose we reformulate a bit the interaction energy of the lattice gas II (4.234):

$$U_{\text{II}}(X) = \sum_{\substack{i \in X \\ j \in K}} \varphi_{\text{II}}(i, j) - \sum_{\substack{i \in X \\ j \in X}} \varphi_{\text{II}}(i, j) .$$

Because of the assumed translational symmetry, the first term can be simplified:

$$\sum_{\substack{i \in X \\ j \in K}} \varphi_{\text{II}}(i, j) = N(X) \sum_{j \in K} \varphi_{\text{II}}(0, j) \equiv N(X) \varphi_{\text{II}}^{(0)}(K) .$$

For given  $K$   $\varphi_{\text{II}}^{(0)}(K)$  is only an unimportant constant. It thus holds:

$$U_{\text{II}}(X) = N(X) \varphi_{\text{II}}^{(0)}(K) - \sum_{\substack{i \in X \\ j \in X}} \varphi_{\text{II}}(i, j) . \quad (4.238)$$

We now choose a lattice gas I such that

$$\varphi_I(i, j) = -2\varphi_{II}(i, j) . \quad (4.239)$$

Then we can write:

$$\begin{aligned} \mu N(X) - U_{II}(X) &= \left( \mu - \varphi_{II}^{(0)}(K) \right) N(X) - \frac{1}{2} \sum_{\substack{i \in X \\ j \in X}} \varphi_I(i, j) \\ &= \left( \mu - \varphi_{II}^{(0)}(K) \right) N(X) - U_I(X) . \end{aligned}$$

It follows eventually for the partition function and the lattice-gas pressure:

$$\Xi_{\mu}^{(II)}(T, K) = \Xi_{\mu - \varphi_{II}^{(0)}}^{(I)}(T, K) \quad (4.240)$$

$$p_{II}(T, \mu, K) = p_I(T, \mu - \varphi_{II}^{(0)}, K) \quad (4.241)$$

Under the presumption (4.239), the two lattice gases are thus thermodynamically equivalent. They both have, for instance, the same  $p$ - $v$ -diagram. Only the chemical potential is shifted due to the different energy normalizations.

#### 4.4.7 *Thermodynamic Equivalence of Lattice-Gas Model and Ising Model*

We now will show that the lattice gases of the preceding subsection are thermodynamically equivalent to the Ising model with external magnetic field  $B_0$  (!). The energy of a certain configuration  $S$  of Ising-spins on the lattice  $K$  in the presence of a magnetic field reads:

$$U(S) = - \sum_{\substack{i \in K \\ j \in K}} J_{ij} S_i S_j - b \sum_{i \in K} S_i \quad (b = g\mu_B B_0) . \quad (4.242)$$

We assume thereby, somewhat more general as usual, that the coupling constants can actually still depend on the lattice site:

$$J_{ii} = 0 ; \quad J_{ij} = J_{ji} ; \quad J_0 = \sum_{i \in K} J_{ij} = \sum_{j \in K} J_{ij} . \quad (4.243)$$

Let

$X$  be the set of the lattice points with  $S_i = +1$

and

$$n_i = \begin{cases} 1, & \text{if } i \in X \\ 0, & \text{if } i \notin X. \end{cases} \quad (4.244)$$

This means:

$$S_i = 2n_i - 1. \quad (4.245)$$

Therewith the interaction energy  $U(S(X))$  reads:

$$\begin{aligned} U(S(X)) &= - \sum_{\substack{i \in K \\ j \in K}} J_{ij} (2n_i - 1)(2n_j - 1) - b \sum_{i \in K} (2n_i - 1) \\ &= -4 \sum_{\substack{i \in X \\ j \in X}} J_{ij} + 2 \sum_{\substack{i \in X \\ j \in K}} J_{ij} + 2 \sum_{\substack{i \in K \\ j \in X}} J_{ij} - \sum_{\substack{i \in K \\ j \in K}} J_{ij} \\ &\quad - 2b \sum_{i \in X} 1 + b \sum_{i \in K} 1 \\ &= 2 \sum_{\substack{i \in X \\ j \notin X}} J_{ij} + 2 \sum_{\substack{i \notin X \\ j \in X}} J_{ij} - N(K)J_0 - 2bN(X) + bN(K). \end{aligned}$$

It thus remains:

$$U(S(X)) = 4 \sum_{\substack{i \in X \\ j \notin X}} J_{ij} + N(K)(b - J_0) - 2bN(X). \quad (4.246)$$

We now search for the equivalence to the lattice gas II. That succeeds with the choice

$$\varphi_{\text{II}}(i, j) \equiv 4J_{ij}, \quad (4.247)$$

because then it remains:

$$U(S(X)) = U_{\text{II}}(X) + (b - J_0)N(K) - 2bN(X). \quad (4.248)$$

Because of the constant number of spin-lattice sites the ‘*natural*’ framework for the Ising model should be the canonical ensemble. With respect to the lattice-gas model, only the  $\uparrow$ -sites are considered as ‘*particles*’. Their number, however, is not constant. The goal must therefore be to find a connection between the canonical

partition function of the Ising model and the grand-canonical partition function of the lattice gas.

$$\begin{aligned}
 Z_K(T, B_0) &= \sum_{\{S\}} \exp(-\beta U(S)) = \sum_{X \subset K} \exp(-\beta U(S(X))) \\
 &= \sum_{X \subset K} \exp(-\beta(U_{\text{II}}(X) - 2bN(X))) \exp(-\beta(b - J_0)N(K)) \\
 &= \Xi_{\mu=2b}^{(\text{II})}(T, K) \exp(-\beta(b - J_0)N(K)) . \tag{4.249}
 \end{aligned}$$

One recognizes a close relationship between the two partition functions, if one identifies the chemical potential  $\mu$  of the lattice gas with the field term  $2b = 2g\mu_B B_0$  of the Ising system.

The free energy per spin of the Ising model corresponds to the pressure of the lattice gas:

$$f(T, B_0, M) = -\frac{1}{\beta N(K)} \ln Z_K(T, B_0) = -p_{\text{II}}(T, \mu = 2b, K) + (b - J_0) . \tag{4.250}$$

With the symmetry relation (4.236), we control:

$$\begin{aligned}
 f(T, -B_0, K) &= -p_{\text{II}}(T, -2b, K) + (-b - J_0) = -p_{\text{II}}(T, 2b, K) + (b - J_0) \\
 &= f(T, B_0, K) . \tag{4.251}
 \end{aligned}$$

The free energy per spin is thus an even function of the field, as it must be, in order to make the magnetization, as the first derivative with respect to  $B_0$ , an odd function of the magnetic field.

We have finally still to think about what in the Ising model corresponds to the specific volume  $v$  of the lattice gas.  $v$  is the volume, which, on an average, is available for every 'particle'. We had identified  $N(K)$  in suitable units as the total volume. Therefore it can be taken (see (4.233))  $v = N(K)/N(X)$ . For comparison we consider the (dimensionless) magnetization of the Ising model:

$$M = \frac{N_{\uparrow} - N_{\downarrow}}{N} = \frac{2N(X) - N(K)}{N(K)} = \frac{2}{v} - 1 .$$

It thus holds:

$$v = \frac{2}{M + 1} . \tag{4.252}$$

The correspondence is thus complete. The lattice-gas problem, having regard to (4.247), is identical to that of an Ising-spin system in the magnetic field. Because of this fact, the results found for the Ising model can rather directly be transferred to the lattice-gas model.

We compile once more the most important assignments:

- The volume  $\Delta V$  of the lattice gas  $\Pi$  corresponds to the number of spins in the Ising lattice.
- The number of gas atoms (occupied cells) correlates with the number of  $\uparrow$ -Ising spins.
- The average particle volume  $v$  in the lattice gas is related via Eq. (4.252) to the magnetization  $M$  of the Ising spins.
- The role of the chemical potential  $\mu$  of the lattice gas undertakes, according to (4.249), in the Ising model the magnetic field  $B_0$  ( $\mu \leftrightarrow 2b = 2g\mu_B B_0$ ).
- The grand-canonical partition function  $\Xi_\mu^{(II)}(T, K)$  of the lattice gas corresponds, according to equation (4.249), to the canonical partition function of the Ising model.
- The pressure  $p_{II}(T, \mu, K)$  of the lattice gas is, according to equation (4.250), equivalent to the free energy per spin  $f(T, B_0, K)$  of the Ising model.

### 4.4.8 Exercises

#### Exercise 4.4.1

A magnetic system is described by the Ising model ( $N$  localized spins).

1. Express the canonical partition function  $Z_N(T, B_0)$  by the moments  $m_l$  of the Hamilton function  $H$ :

$$m_l = \frac{\text{Tr}(H^l)}{\text{Tr}(\mathbb{I})} ; \quad l = 1, 2, 3, \dots$$

What is the meaning of  $\text{Tr}(\mathbb{I})$  for the Ising system?

2. Verify for the heat capacity  $C_{B_0}$  the high-temperature expansion

$$C_{B_0} = \frac{1}{k_B T^2} (m_2 - m_1^2) + \mathcal{O}(1/T^3) .$$

#### Exercise 4.4.2

Consider a spin system with the total magnetic moment

$$\hat{m} = \mu \sum_i S_i ,$$

described by the Ising model. By the use of the *fluctuation-dissipation theorem* (4.16) express the isothermal susceptibility  $\chi_T$  by the spin correlation  $\langle S_i S_j \rangle$ .

1. Calculate therewith the 'field-free' ( $B_0 = 0$ )-susceptibility of an 'open' chain of  $N$  Ising spins. Find  $\chi_T$  as a function of  $v = \tanh \beta J$ .



2. Discuss the result for the thermodynamic limit  $N \rightarrow \infty$ , and compare it with the results from Sect. 4.4.3.

### Exercise 4.4.3

1. Calculate for the one-dimensional Ising model (linear open chain), without external magnetic field, the four-spin-correlation function

$$\langle S_i S_{i+1} S_j S_{j+1} \rangle .$$

2. Calculate with the result in 1. the heat capacity  $C_{B_0=0}$ .

### Exercise 4.4.4

According to (4.206), the partition function of the Ising model ( $N$  spins, only isotropic next-neighbor interactions) can be formulated as follows:

$$Z_N(T) = 2^N \cosh^p(\beta J) \sum_{l=0}^{\infty} g_l v^l$$

$g_l$  is thereby the number of diagrams of  $l$  lines with exclusively even vertexes. A line corresponds to an *interaction*

$$v = \tanh(\beta J)$$

between Ising spins at respective lattice sites. Only closed paths of lines possess exclusively even vertexes. Details can be found in Sect. 4.4.4.  $p$  is the number of the pairwise different interactions between next-neighbor spins. For the two-dimensional quadratic lattice, e.g., it holds  $p = 2N$  if edge effects are neglected (see (4.206)).

The above expression for the partition function is valid independently of the dimension of the lattice. Evaluate  $Z_N(T)$

1. for the linear open spin chain,
2. for the closed ring of Ising spins!

### Exercise 4.4.5

Consider an Ising model of  $N$  spins with an isotropic interaction restricted to next neighbors  $J$ .

1. Use the diagram technique of Sect. 4.4.4, which has led to the expression (4.206) for the partition function  $Z_N(T)$ , in order to expand also the spin correlation  $\langle S_m S_n \rangle$  in powers of the high-temperature variable  $v = \tanh(\beta J)$ :

$$\langle S_m S_n \rangle = A(\beta J) \sum_{l=?}^{\infty} \rho_{mn}(l) v^l$$

Find  $A(\beta J)$  and interpret  $\rho_{mn}(l)$ !

2. Evaluate the so obtained expression of the spin correlation for the linear open spin chain!
3. What is the result for the closed ring?

#### Exercise 4.4.6

The fluctuation-dissipation theorem (4.16) and the results from Exercise 4.4.5 for the spin correlation  $\langle S_i S_j \rangle$  show that the isothermal susceptibility  $\chi_T$  can be expanded as series in powers of  $\beta J$ :

$$\chi_T = \sum_l \alpha_l (\beta J)^l .$$

In the case of a phase transition at  $T = T_C$ ,  $\chi_T$  becomes singular. The series can thus have only a finite radius of convergence  $R$ . There can exist of course further singularities in the complex plane. We will, however, assume that the *physical singularity*  $j_c = \beta_c J$  is the nearest one, and determines therewith the radius of convergence,

$$R = j_c = \beta_c J = \left( \lim_{l \rightarrow \infty} \frac{\alpha_l}{\alpha_{l-1}} \right)^{-1} .$$

Since  $\chi_T$  becomes critical at  $T_C$ , the following representation is also valid:

$$\chi_T = c \left( \frac{T - T_C}{T_C} \right)^{-\gamma} \left( 1 + a \left( \frac{T - T_C}{T_C} \right)^x + \dots \right) .$$

The second term on the right-hand side can explicitly have, as *correction term* ( $x > 0$ ), a completely different form. It is only important here that it becomes negligible for  $T \rightarrow T_C$ .

1. For a real system it is normally impossible to determine all coefficients  $\alpha_l$  in the above expansion of  $\chi_T$ . Show how one can, nevertheless, infer the critical temperature  $T_C$  and the critical exponent  $\gamma$  from the calculation of only a finite number of  $\alpha_l$  with a suitable *extrapolation*.
2. Show that the procedure from 1. yields for the mean-field approximation (Curie-Weiss law)

$$\chi_T = \frac{C}{T - T_C} \quad (C : \text{Curie constant})$$

the correct  $T_C$  and the correct exponent  $\gamma$ .

3. Investigate the one-dimensional Ising model (linear open chain in the thermodynamic limit  $N \rightarrow \infty$ ). Show that  $\chi_T$  can be brought into the above form, and determine via the ratio of subsequent coefficients  $\alpha_l$  the radius of convergence  $R$ !

**Exercise 4.4.7**

A powerful method for the determination of critical quantities at the second-order phase transition is delivered by the renormalization-group theory. The basic idea will be worked out in this exercise on the exactly calculable one-dimensional Ising model, although it actually represents an unrealistic example because it does not exhibit a phase transition. Its partition function as well as its free energy can be determined also with such a renormalization procedure.

1. Discuss the canonical partition function  $Z_N(j)$  ( $j = \beta J$ ) of a ring of interacting Ising spins without external field (4.189):

$$H = -J \sum_{i=1}^N S_i S_{i+1} \quad (S_{N+1} = S_1) .$$

Show by the use of suitable spin summations that  $Z_N(j)$  can be expressed by the partition function  $Z_{N/2}(j')$  for half the original particle number and for a weaker effective coupling  $j'$ :

$$Z_N(j) = 2^{N/2} \cosh^{N/4}(2j) Z_{N/2}(j') \\ j' = \frac{1}{2} \ln (\cosh(2j)) .$$

Show that indeed  $j' < j$ , where weaker effective coupling at fixed  $J$  means higher temperature.

2. Because the free energy as thermodynamic potential is an extensive quantity, it must hold:

$$\ln Z_N(j) = N P(j) .$$

Express  $P(j)$  by  $j'$  and  $P(j')$ . Consider how one can get from that, iteratively ('by renormalization'), the free energy for any arbitrary temperature.

3. Show that the renormalization formula from 2. reproduces the known exact result (4.198) for the free energy of the Ising ring.

**Exercise 4.4.8**

Verify, starting at equation (4.215), the expression (4.216) for the partition function  $Z_N(T)$  of the two-dimensional Ising model!

## 4.5 Thermodynamic Limit

### 4.5.1 Set of Problems

At several stages of the theories developed so far, we already met the necessity to extrapolate the respective considerations on the *infinitely large system*. This has to be done for an  $N$ -particle system in the volume  $V$  according to the following prescription:

$$\left. \begin{array}{l} N \rightarrow \infty \\ V \rightarrow \infty \end{array} \right\} n = \frac{N}{V} \rightarrow \text{const} \quad (4.253)$$

The particle density  $n$  remains finite during the process. One calls this limiting process *thermodynamic limit*. It is necessary, among others, for

1. the validity of the usual thermodynamic relations (equations of state, intensive/extensive quantities),
2. the equivalence of the various statistical descriptions,
3. the appearance of phase transitions.

Thermodynamic potentials of a macroscopic system are considered as *extensive* quantities ( $\sim V$ ,  $\sim N$ ). When one now decomposes the system at constant temperature  $T$  and at constant particle density  $n$  into macroscopic partial systems, then the *extensivity* means that the total energy is equal to the sum of the energies of the partial systems. Strictly speaking, that can of course be correct only if the interactions between particles of different partial systems can be neglected, and that is the case only in the *thermodynamic limit*, in principle, we have already used this limit very often without explicitly mentioning it. When discussing the equations of state of real gases we have, for instance, presumed, more or less unconsciously, that the pressure of the gas does not depend on the concrete form of the container, but only on the temperature and on the density of the gas. Also this can surely be correct only in the *thermodynamic limit*, when surface effects do not play any role (counterexample:  $\text{H}_2\text{O}$ -droplet).

We know from the preceding sections that only in the *thermodynamic limit* micro-canonical, canonical, and grand-canonical ensembles lead to strictly the same results.

If one wants to recognize a *phase transition* by the means of *Statistical Physics*, the partition function must exhibit certain *non-analyticities*. We will realize in the next subsections that partition functions of **finite** systems are analytical in the entire physical region. In this connection, also the *fluctuation-dissipation theorem* (4.16) may be recalled, which permits only in the *thermodynamic limit* a diverging of the susceptibility  $\chi_T$  for  $T \rightarrow T_C$ .

With the *thermodynamic limit*, however, there are also connected some non-trivial questions and problems, which shall be outlined by the example of a *classical continuous system*

We let  $N$  particles be in the volume  $V$  with the particle-coordinates,

$$\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}; \quad \mathbf{p} = \{\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N\},$$

and the Hamilton function:

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \varphi(\mathbf{r}_i - \mathbf{r}_j) = T(\mathbf{p}) + U(\mathbf{r}). \quad (4.254)$$

For the *canonical partition function* it holds according to (1.138):

$$\begin{aligned} Z_N(T, V) &= \frac{1}{h^{3N} N!} \int d^{3N} p \int d^{3N} r e^{-\beta H(\mathbf{p}, \mathbf{r})} \\ &= \frac{1}{\lambda^{3N} N!} \int_V d^{3N} r e^{-\beta U(\mathbf{r})}. \end{aligned} \quad (4.255)$$

$\lambda(T)$  is thereby the thermal de Broglie wave length (1.137). In the **finite** system the *free energy per particle*  $f_N$ ,

$$f_N(T, V) = -k_B T \frac{1}{N} \ln Z_N(T, V),$$

can definitely still depend on the particle number  $N$ . The reversal reads:

$$Z_N(T, V) = \exp(-N\beta f_N(T, V)).$$

In the expression (1.159) for the grand-canonical partition function,

$$\Xi_z(T, V) = \sum_{N=0}^{\infty} z^N Z_N(T, V) = \exp(\beta V p_V(T, z)), \quad (4.256)$$

the pressure  $p_V(T, z)$  is also that of a finite system.

In the *thermodynamic limit* one has the *limiting functions*:

$$f(T, v) = \lim_{\substack{N \rightarrow \infty \\ V \rightarrow \infty \\ V/N \rightarrow v}} f_N(T, V), \quad (4.257)$$

$$p(T, z) = \lim_{V \rightarrow \infty} p_V(T, z). \quad (4.258)$$

At first we have to know whether these functions really exist. This is actually not a matter of course, as we will get to know in the next subsection. In the second step we have to fulfill the *stability criteria* ( $C_V \geq 0$ ,  $\kappa_T \geq 0$ ), and to guarantee the equivalence of canonical and grand-canonical statistics. That means, for instance, that the *canonically* determined free energy  $f$  and the *grand-canonically* derived pressure must be connected with each other by the thermodynamic relation

$$\left(\frac{\partial f}{\partial v}\right)_T = -p. \quad (4.259)$$

We will work out in the next subsection at first the conditions for the existence of the limiting functions (4.257), (4.258).

### 4.5.2 ‘Catastrophic’ Potentials

Interaction potentials are called *catastrophic* if one cannot define with them, even for a finite volume  $V$ , a grand-canonical partition function  $\Xi$  so that from the very beginning the requirements on the thermodynamic limit, which we formulated after (4.258), are not satisfiable.

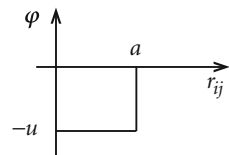
We start with an example: Let the interaction potential  $\varphi$  in the Hamilton function (4.254) be constant, equal to  $-u$  for particle distances  $r_{ij} \leq a$  and otherwise zero (Fig. 4.45). It is then easy to write down the partition function for a volume  $V_0$  of a sphere of the radius  $r_0 \leq a$

$$Z_N(T, V_0) = \frac{1}{N!} \left(\frac{V_0}{\lambda^3}\right)^N \exp\left(\frac{1}{2}\beta u N(N-1)\right).$$

$(1/2)N(N-1)$  is the number of pair interactions for  $N$  particles. The integrand in the definition (4.255) of  $Z_N$  is positive definite. It follows therefore with  $V > V_0$

$$Z_N(T, V) \geq Z_N(T, V_0),$$

**Fig. 4.45** Simple example for a ‘catastrophic potential’



and for the grand-canonical partition function it even holds:

$$\Xi_z(T, V) \geq \sum_{N=0}^{\infty} \frac{z^N}{N!} \left( \frac{V_0}{\lambda^3} \right)^N \exp \left( \frac{1}{2} \beta u N (N-1) \right) = \infty .$$

The divergence results from the  $N^2$ -term in the argument of the exponential function.  $\Xi_z$  diverges for all  $V \geq V_0$  and  $z \neq 0$ .  $\varphi(\mathbf{r})$  is therewith a **catastrophic potential!** This statement can be generalized:

#### Assertion 4.5.1

Let  $\varphi(\mathbf{r})$  be an interaction potential with the following properties:

1.  $\varphi(\mathbf{r})$  is continuous, i.e. in particular that  $\varphi(0)$  is finite!
2. There exists at least one configuration

$$\mathbf{r}_1, \dots, \mathbf{r}_n \quad (n \text{ arbitrary}),$$

for which

$$\sum_{i,j}^{1,\dots,n} \varphi(\mathbf{r}_i - \mathbf{r}_j) < 0 . \quad (4.260)$$

Note that the sum contains also the diagonal terms  $\varphi(0)$ !

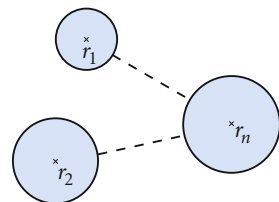
Then the grand-canonical partition function  $\Xi_z(T, V)$  diverges for sufficiently large  $V$  and for all  $z \neq 0$ .  $\varphi(\mathbf{r})$  is therefore ‘catastrophic’.

*Proof* We assume that there exists such a configuration  $\mathbf{r}_1, \dots, \mathbf{r}_n$ . Let us then consider a *special situation*, for which there are each  $k$  particles located in certain neighborhoods of the  $\mathbf{r}_1, \dots, \mathbf{r}_n$  (Fig. 4.46):

$$N = kn .$$

In the *general* definition of the partition function  $Z_N$  it is to integrate over **all** conceivable arrangements, which all lead to positive contributions. The special case, sketched in Fig. 4.46, thus represents only a lower bound for  $Z_N$ . The potential

**Fig. 4.46** Special particle configuration for the investigation whether or not a pair potential is ‘catastrophic’



energy  $U(\mathbf{r})$  can be estimated for this special case as follows:

$$\frac{1}{2}k(k-1)n\varphi(0) + \frac{1}{2}k^2 \sum_{i \neq j} \varphi(\mathbf{r}_i - \mathbf{r}_j) \approx \frac{k^2}{2} \sum_{i,j}^{1,\dots,n} \varphi(\mathbf{r}_i - \mathbf{r}_j) < 0 .$$

The first summand represents the interactions within the clusters and exploits the continuity of  $\varphi$ . The second summand embraces the interactions between particles from different clusters. The right-hand side is negative because of the assumption 2., and finite because of the assumption 1.. In every case it holds:

$$U(\mathbf{r}) \approx -k^2b = -N^2 \frac{b}{n^2}; \quad b > 0 .$$

For the partial volume  $V_0$ , consisting of the  $n$  clusters, we thus have:

$$Z_N(T, V_0) \approx \frac{1}{N!} \left( \frac{V_0}{\lambda^3} \right)^N \exp \left( \beta b \frac{N^2}{n^2} \right) ,$$

$$Z_N(T, V) \geq Z_N(T, V_0) , \quad \text{if } V \geq V_0 .$$

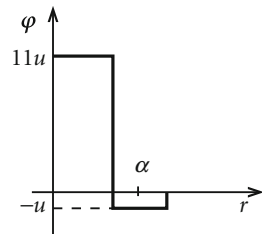
Because of the square of the particle number in the exponential function, the grand-canonical partition function  $\Xi_z$  diverges in the above example for each  $z \neq 0!$  That proves the assertion.

*Catastrophic* behavior obviously seems to arise always when arbitrarily many particles can be pulled together in a confined region. *Physical* potentials should have something like a repulsive ‘hard core’.

*Example* As to the potential course, plotted in Fig. 4.47, one can imagine that the edges are a bit *rounded off* to make  $\varphi$  continuous. Then  $\varphi$  might simulate the potential of a solid with interactions only between nearest neighbors. Let the configuration  $\mathbf{r}_1, \dots, \mathbf{r}_n$  correspond to a segment of a face-centered cubic lattice. Each lattice atom has then 12 nearest neighbors with the distance  $a$ :

$$\sum_{i,j}^{1,\dots,n} \varphi(\mathbf{r}_i - \mathbf{r}_j) = n\varphi(0) + 12n\varphi(a) = 11nu - 12nu < 0 .$$

**Fig. 4.47** Example of a pair potential with ‘hard core’, which nevertheless is ‘catastrophic’





According to the just proven assertion this  $\varphi(r)$  is thus also *catastrophic*. The repulsion at the zero-point is still too weak.

### 4.5.3 ‘Stable’ Potentials

For a **continuous**  $\varphi(r)$ , which in particular gives rise to a finite  $\varphi(0)$ , it must hold, in accordance with the assertion proven in the last subsection, in order to guarantee the convergence of the grand-canonical partition function:

$$\frac{1}{2} \sum_{i,j}^{1,\dots,n} \varphi(\mathbf{r}_i - \mathbf{r}_j) \geq 0 \quad \forall n \quad \text{and} \quad \forall \mathbf{r}_1, \dots, \mathbf{r}_n. \quad (4.261)$$

This requirement turns out to be a sufficient condition for a ‘*physically acceptable*’ potential. One namely realizes, when one brings the diagonal terms to the right-hand side of the inequality,

$$U(\mathbf{r}) = \frac{1}{2} \sum_{i,j}^{i \neq j} \varphi(\mathbf{r}_i - \mathbf{r}_j) \geq -\frac{1}{2} N \varphi(0),$$

that there exists a finite constant  $B$ , by which the potential energy can be estimated as follows:

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) \geq -NB \quad \forall N, \quad \forall \mathbf{r}_1, \dots, \mathbf{r}_N. \quad (4.262)$$

That is the **basic condition for stable potentials**. In this case the canonical partition function possesses an upper bound,

$$Z_N(T, V) \leq \frac{1}{N!} \left( \frac{V}{\lambda^3} e^{\beta B} \right)^N,$$

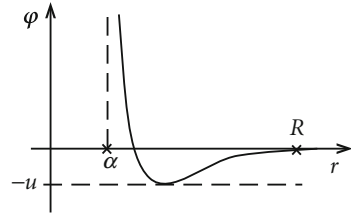
so that the grand-canonical partition function definitely converges:

$$\Xi_z(T, V) \leq \sum_{N=0}^{\infty} \frac{1}{N!} \left( z \frac{V}{\lambda^3} e^{\beta B} \right)^N = \exp \left( z \frac{V}{\lambda^3} e^{\beta B} \right) < \infty.$$

For the finite system,  $\Xi_z(T, V)$  is then well-defined for all values of the fugacity  $z$  and all temperatures  $T$ .

For continuous potentials  $\varphi$  the condition (4.261) is not only sufficient, but also necessary, in order to be *stable*. There are, however, also discontinuous stable potentials, for instance those with a ‘*hard core*’ and an effective finite range  $R$  (Fig. 4.48). Each (classical) particle can then interact only with a maximal number

**Fig. 4.48** Typical curve of a particle-pair potential



$n$  of other particles. This corresponds to the number of particles (*spheres of radii  $a$* ), which will go in the volume  $(4\pi/3)R^3$ . For all  $\mathbf{r}_1, \dots, \mathbf{r}_N$  we have therewith:

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) \geq -Nnu . \tag{4.263}$$

The ‘*hard core*’-potential is therefore stable!

### 4.5.4 Canonical Ensemble

From now on we restrict our considerations to interacting particle systems, which fulfill the following conditions:

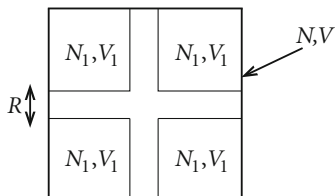
1.  $\varphi(\mathbf{r})$  is stable,
2.  $\varphi(\mathbf{r}) \leq 0$  for  $r \geq R$ .

We let  $R$  thereby be any typical microscopic length. For non-stable potentials Statistical Physics is absolutely impossible. But even for stable  $\varphi(\mathbf{r})$  we have to ask ourselves whether in every case the *thermodynamic limit* exists. This question will be investigated at first for the canonical ensemble. Above all, we are thereby interested in the free energy per particle. Does the limiting function (4.257) really exist?

$$f(T, v) = \lim_{\substack{V \rightarrow \infty \\ N \rightarrow \infty \\ V/N \rightarrow v}} f_N(T, V) .$$

In order to investigate this, we construct at first a *suitable* sequence  $V \rightarrow \infty$ . The starting volume  $V$  may be a cube, which contains  $N$  particles. The partition function is then of the form (4.255). In the next step we distribute the  $N$  particles into equal portions  $N_1$  over eight smaller cubes  $V_1$  ( $N = 8N_1$ ), which are located in the corners of the initial cube (Fig. 4.49). Between the ‘*sub-cubes*’ there are *corridors* of the width  $R$ , which do not contain particles. When we integrate in (4.255) exclusively over the sub-cubes, we get a lower bound for  $Z_N$ , since, because of  $8V_1 < V$ , the positive integrand is integrated over a smaller volume. Furthermore, the configuration space is additionally restricted by the requirement  $N_1 = \text{const}$  in each cube  $V_1$ . Eventually, we still suppress the interactions between particles

**Fig. 4.49** Nesting of cubes for the demonstration of the limiting function of the free energy in the canonical ensemble



from different cubes. Because of the condition 2., it holds for these interactions  $\varphi(\mathbf{r}) \leq 0$ , since  $r \geq R$ . The exponential function  $\exp(-\beta\varphi(\mathbf{r}))$  is thus greater than 1. The neglect of these interactions makes the estimation, as a lower bound of the partition function, even safer. When, however, no interactions exist between the *sub-cubes*, then the partition function will factorize. One should notice that the *correct Boltzmann counting* (1.129) requires, because of the absence of contacts between the sub-cubes, as factor in front of the partition-function integral in (4.255),  $(N_1!)^{-8}$  instead of  $(N!)^{-1}$ . (Only the interchange of two particles from the same sub-cube does not lead to a new state; see the explanatory statement after (1.129)). Hence we obtain the estimation:

$$Z_{N=8N_1}(T, V) > (Z_{N_1}(T, V_1))^8 .$$

This also means

$$\exp(-\beta N f_N(T, V)) > \exp(-8\beta N_1 f_{N_1}(T, V_1)) ,$$

so that the free energy per particle increases with the subdivision:

$$f_N(T, V) < f_{N_1}(T, V_1) .$$

The *stability* of the interaction potential  $\varphi(\mathbf{r})$  has, according to (4.262), the consequence

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) \geq -NB \quad (B \text{ finite})$$

and therewith

$$Z_N(T, V) \leq \frac{1}{N!} \left( \frac{V}{\lambda^3} e^{\beta B} \right)^N .$$

Let  $N$  be so large that the *Stirling formula* ( $\ln N! \approx N(\ln N - 1)$ ) is applicable:

$$-\beta N f_N(T, V) = \ln Z_N(T, V) \leq N(\beta B + 1) + N \ln \left( \frac{V}{\lambda^3 N} \right) .$$

All in all we have found therewith the following estimation for the free energy:

$$-B - k_B T \left[ 1 + \ln \left( \frac{V}{\lambda^3 N} \right) \right] \leq f_N(T, V) < f_{N_1}(T, V_1) .$$

When we now understand the **thermodynamic limit** as a sequence of cubes in the above described *nesting*,

$$N \rightarrow \infty, \quad V \rightarrow \infty, \quad V/N \rightarrow v \quad (\text{finite}),$$

then the free energy  $f_N(T, V)$  turns out to be a bounded below, monotonically decreasing function. It is shown therewith that the **limiting function**  $f(T, v)$  (4.257) **does exist** for all potentials, which fulfill the two conditions formulated at the beginning of this subsection!

It is recommended to the reader, to show as an exercise, that the considered *cube-sequence* let the ratio  $V/N$  indeed approach asymptotically a finite particle volume  $v$ .—The proof of existence for  $f(T, v)$  was performed here only by the special cube-nesting. It contains, however, already all the essentials. We therefore retain from the generalization to arbitrary volumes at the limiting process  $V \rightarrow \infty$ .

But we still have to concern ourselves with the **stability conditions of the canonical ensemble**:

$$C_V \geq 0; \quad \kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T \geq 0 . \quad (4.264)$$

The criterion, which refers to the heat capacity, has already been proven with (1.148) for every finite system. The second condition is identical to

$$\left( \frac{\partial p}{\partial v} \right)_T = - \left( \frac{\partial^2 f}{\partial v^2} \right)_T \leq 0 \quad (4.265)$$

and states that  $f$  as a function of  $v$  must be **convex**. This in turn means that it should hold for all  $0 \leq \lambda \leq 1$ :

$$f(\lambda v_1 + (1 - \lambda)v_2) \leq \lambda f(v_1) + (1 - \lambda)f(v_2) . \quad (4.266)$$

For the proof we modify the above line of thought in such a way that we take the same cube-nesting, but we fill four of the cubes each with  $\widehat{N}_1$  particles and the other four each with  $\widehat{N}_2$  particles:

$$N = 4\widehat{N}_1 + 4\widehat{N}_2 .$$

The same considerations as those above, then lead to the estimation

$$Z_N(T, V) \geq (Z_{\widehat{N}_1}(T, V_1))^4 (Z_{\widehat{N}_2}(T, V_1))^4 ,$$

and equivalently therewith to:

$$f_N(T, V) \leq \frac{4\widehat{N}_1}{N} f_{\widehat{N}_1}(T, V_1) + \frac{4\widehat{N}_2}{N} f_{\widehat{N}_2}(T, V_1) .$$

In the *thermodynamic limit*,

$$\begin{aligned} \frac{V_1}{\widehat{N}_1} &\longrightarrow v_1 ; & \frac{V_1}{\widehat{N}_2} &\longrightarrow v_2 , \\ \frac{4\widehat{N}_1}{N} &= \frac{\frac{\widehat{N}_1}{V_1}}{\frac{\widehat{N}_1}{V_1} + \frac{\widehat{N}_2}{V_1}} \longrightarrow \frac{\frac{1}{v_1}}{\frac{1}{v_1} + \frac{1}{v_2}} = \frac{v_2}{v_1 + v_2} , \\ \frac{4\widehat{N}_2}{N} &\longrightarrow \frac{v_1}{v_1 + v_2} , \end{aligned}$$

one thus finds for the free energy per particle:

$$\lim_{\substack{V \rightarrow \infty \\ N \rightarrow \infty \\ V/N \rightarrow v}} f_N(T, V) \equiv f(T, v) \leq \frac{v_2}{v_1 + v_2} f(T, v_1) + \frac{v_1}{v_1 + v_2} f(T, v_2) .$$

As consecutive members of the cube-nesting,  $V/N$  and  $V_1/\frac{1}{2}(\widehat{N}_1 + \widehat{N}_2)$  have of course the same limiting value  $v$ . But otherwise it also holds:

$$\frac{V_1}{\frac{1}{2}(\widehat{N}_1 + \widehat{N}_2)} \longrightarrow \frac{2}{\frac{1}{v_1} + \frac{1}{v_2}} = \frac{2v_1v_2}{v_1 + v_2} .$$

The above inequality therewith reads:

$$f\left(T, \frac{2v_1v_2}{v_1 + v_2}\right) \leq \frac{v_2}{v_1 + v_2} f(T, v_1) + \frac{v_1}{v_1 + v_2} f(T, v_2) .$$

If one takes

$$\lambda = \frac{v_2}{v_1 + v_2} ,$$

then one finds exactly (4.266). The *limiting function*  $f(T, v)$  is therefore indeed as a function of  $v$  convex. The stability conditions (4.264) are therewith fulfilled.

### 4.5.5 Grand-Canonical Ensemble

As to the interaction potential we agree upon the same preconditions as those at the beginning of Sect. 4.5.4. Furthermore, we use for the transition into the *thermodynamic limit* the same volume-nesting, now, however, with **variable** particle numbers in the cubes. Since, as before, *corridors* of the width  $R$  are left open, and interactions between particles of different cubes are again neglected, one gets the following inequality:

$$Z_N(T, V) > \sum_{\substack{\sum_i N_i = N \\ N_1, \dots, N_8}} Z_{N_1}(T, V_1) \cdots Z_{N_8}(T, V_1) .$$

We multiply this expression by  $z^N$  and sum over all particle numbers from 0 to  $\infty$ . By this summation the constraint  $\sum_i N_i = N$  becomes redundant:

$$\begin{aligned} \sum_{N=0}^{\infty} z^N Z_N(T, V) &> \sum_{N_1, \dots, N_8=0}^{\infty} z^{N_1+N_2+\dots+N_8} Z_{N_1}(T, V_1) \cdots Z_{N_8}(T, V_1) \\ &= \left[ \sum_{N_1=0}^{\infty} z^{N_1} Z_{N_1}(T, V_1) \right]^8 . \end{aligned}$$

For this we can also write:

$$\Xi_z(T, V) = \exp(\beta V p_V(T, z)) > (\Xi_z(T, V_1))^8 = \exp(8\beta V_1 p_{V_1}(T, z)) . \tag{4.267}$$

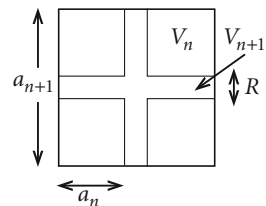
In the sense of the cube-nesting one can read off from this result the following inequality for the pressure

$$p_{V_{n+1}}(T, z) > \frac{8V_n}{V_{n+1}} p_{V_n}(T, z) . \tag{4.268}$$

$V_n$  is the volume of the cube in the  $n$ -th step of the nesting. One takes from Fig. 4.50:

$$a_{n+1} = 2a_n + R .$$

**Fig. 4.50** Volume-nesting for the investigation of the thermodynamic limit in the grand-canonical ensemble



This means:

$$\frac{8V_n}{V_{n+1}} = \frac{1}{\left(1 + \frac{R}{2a_n}\right)^3} \xrightarrow{n \rightarrow \infty} 1. \quad (4.269)$$

The inequality sign in (4.267) results to a great extent from the neglected interactions between particles of different cubes. Their percentage of the total number of the interactions is, however, in each step practically the same, so that, because of (4.269), for sufficiently large  $n$ , it must even hold instead of (4.268)

$$p_{V_{N+1}}(T, z) > p_{V_n}(T, z).$$

On the other hand, we had found, very generally, for stable potentials

$$\Xi_z(T, V) \leq \exp\left(z \frac{V}{\lambda^3} e^{\beta B}\right),$$

where  $B$  is any finite constant. For the pressure this has the consequence

$$p_V(T, z) = \frac{1}{V\beta} \ln \Xi_z(T, V) \leq \frac{1}{\beta} \frac{z}{\lambda^3} e^{\beta B}.$$

The right-hand side of this inequality remains unaffected by the limiting process  $V \rightarrow \infty$ , so that  $p_V(T, z)$  turns out to be an upper-bounded monotonously increasing function. The *limiting function*

$$p(T, z) = \lim_{V \rightarrow \infty} p_V(T, z) \quad (4.270)$$

therefore does exist.

The stability conditions of the grand-canonical ensemble are fulfilled, on the basis of fluctuation formulas, already for finite systems. So we have for instance proven with (1.199) that  $\kappa_T \geq 0$ .

## 4.6 Microscopic Theory of the Phase Transition

When we now want to summarize at the end of this section, what really characterizes and defines a phase transition, then we could come to the following qualitative statement:

**phase transition**  $\iff$

*singularity, non-analyticity or discontinuity of a **relevant** thermodynamic function, which otherwise is everywhere analytical.*

A *theory of phase transitions* therefore consists in an investigation, whether thermodynamic functions are piecewise analytical, and in a discussion of the

nature of possibly existing singularities. The *complete* theory must be able to interpret macroscopic phenomena as condensation, spontaneous magnetization, . . . as consequences of microscopic (atomic) interactions. In this section we will discuss a proposal by C. N. Yang and T. D. Lee (Phys. Rev. **87**, 404 (1952)), which seems to be acceptable, although one does not know whether it represents the only access to the phenomenon *phase transition*, and whether it really covers the full, very complex problem.

### 4.6.1 Finite Systems

We concentrate our considerations on a **classical system of  $N$  particles in the volume  $V$**  with the Hamilton function:

$$H = T(\mathbf{p}) + U(\mathbf{r}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \varphi(\mathbf{r}_i - \mathbf{r}_j) .$$

Let  $\varphi(r)$  be a pair interaction with ‘hard core’ (Fig. 4.51). Hence, it is definitely a *stable* potential. The grand-canonical partition function exists and converges for all values of the fugacity  $z = \exp(\beta\mu)$ :

$$\Xi_z(T, V) = 1 + \sum_{n=1}^{\infty} z^n Z_n(T, V) . \tag{4.271}$$

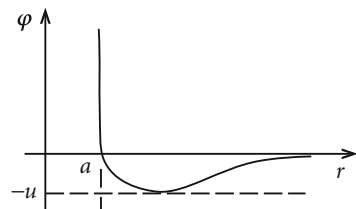
For the pressure we had found in (1.180)

$$p = \frac{1}{V\beta} \ln \Xi_z(T, V) , \tag{4.272}$$

while the *specific volume*  $v = V/\langle N \rangle$  was calculated in (1.168):

$$\frac{1}{v} = \frac{1}{V} z \frac{\partial}{\partial z} \ln \Xi_z(T, V) = \beta z \frac{\partial}{\partial z} p . \tag{4.273}$$

**Fig. 4.51** Pair-interaction potential with ‘hard core’





From the two last equations  $z$  must be eliminated in order to get the **equation of state**

$$p = p(T, v) .$$

When will this equation of state show an anomalous behavior, which might indicate a *phase transition*? The partition function by itself converges for all  $z$ , and therefore is in particular finite. Consequently, something can happen only at the zeros of  $\Xi_z$ , for which the logarithm diverges ( $\ln \Xi_z \rightarrow -\infty$ ). Thus we state:

**zeros of  $\Xi_z(T, V) \iff$  phase transitions.**

Where are these zeros and how can we find them? Because  $\varphi(r)$  is a ‘hard core’-potential, we can imagine the (classical) particles as *hard spheres*. That, however, means that there is a maximal number of particles  $N^*(V)$  which will fit into the (finite) volume  $V$ . For  $N > N^*$  we have  $U(r) = \infty$  and therewith

$$Z_N(T, V) \equiv 0 , \quad \text{if } N > N^*(V) .$$

The grand-canonical partition function therewith is a polynomial in  $z$  of the degree  $N^*$ :

$$\Xi_z(T, V) = 1 + zZ_1(T, V) + z^2Z_2(T, V) + \dots + z^{N^*}Z_{N^*}(T, V) . \quad (4.274)$$

The canonical partition function  $Z_N$  is positive definite, i.e., all coefficients of the polynomial are positive. We therefore state:

**$\Xi_z(T, V)$  has no real positive zero as long as  $V$  is finite.**

The  $N^*$  zeros of the polynomial are either *negative real* or are *pairwise conjugate complex* (Fig. 4.52). In the *physical region*

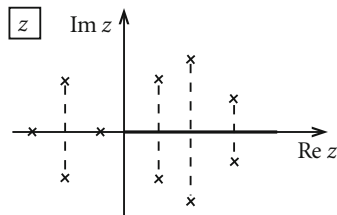
$$0 \leq z = e^{\beta\mu} < \infty$$

there is no zero. This forces us to state:

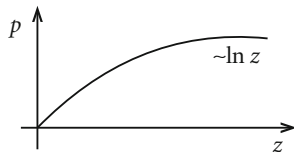
**in a finite system a phase transition does not appear.**

In order to substantiate this, we build the *equation of state of a finite system*. According to (4.272) the pressure  $p$  is positive in the *physical region*  $0 \leq z < \infty$  and is a monotonically increasing function of  $z$ , because  $\Xi_z$  represents a polynomial in  $z$  with only positive coefficients. Because of  $\Xi_{z=0} \equiv 1$  one finds  $p(z = 0) = 0$

**Fig. 4.52** Distribution of the zeros of the grand-canonical partition function of a finite system as function of the fugacity  $z$



**Fig. 4.53** Pressure as a function of the fugacity for a finite system



(Fig. 4.53). For large  $z$  the highest power of the polynomial dominates,

$$\Xi_z(T, V) \xrightarrow{z \rightarrow \infty} z^{N^*} Z_{N^*}(T, V),$$

so that, according to (4.272), the pressure  $p$  can be estimated to (Fig. 4.53)

$$p \rightarrow \frac{1}{V\beta} [N^* \ln z + \ln Z_{N^*}] \xrightarrow{z \rightarrow \infty} \frac{N^*}{V\beta} \ln z.$$

For the *specific volume*  $v$  it remains to be evaluated, according to (4.273),

$$\frac{1}{v} = \frac{1}{V} z \frac{1}{\Xi_z} \frac{\partial}{\partial z} \Xi_z.$$

The denominator does not possess any zero in the *physical region*.  $1/v$  therewith is analytical in a region, which contains the real positive axis. We eventually investigate the derivative of  $1/v$  with respect to  $z$ :

$$\begin{aligned} \frac{\partial}{\partial z} \frac{1}{v} &= \frac{1}{V} \left[ \frac{1}{\Xi_z} \sum_N N z^{N-1} Z_N - z \frac{1}{\Xi_z^2} \left( \frac{\partial}{\partial z} \Xi_z \right)^2 + \frac{z}{\Xi_z} \frac{\partial^2}{\partial z^2} \Xi_z \right] \\ &= \frac{1}{V} \left[ \frac{\langle N \rangle}{z} - z \frac{1}{z^2} \langle N \rangle^2 + \frac{1}{z} \langle N(N-1) \rangle \right] \\ &= \frac{1}{Vz} [\langle N^2 \rangle - \langle N \rangle^2]. \end{aligned}$$

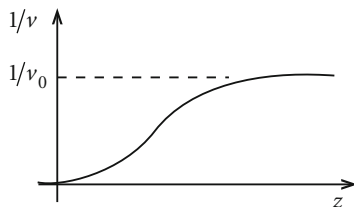
$1/v$  obviously is also a monotonically increasing function of  $z$  (Fig. 4.54):

$$z \frac{\partial}{\partial z} \frac{1}{v} = \frac{1}{V} \langle (N - \langle N \rangle)^2 \rangle \geq 0. \tag{4.275}$$

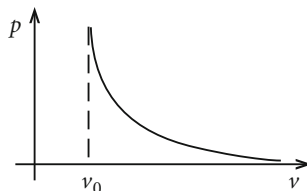
Because of  $\Xi_{z=0} \equiv 1$  it holds, as for the pressure  $p$ :

$$\frac{1}{v}(z=0) = 0.$$

**Fig. 4.54** Inverse specific volume as a function of the fugacity for a finite system



**Fig. 4.55** Pressure-volume isotherm of a finite system



It follows asymptotically:

$$\frac{1}{v} = \beta z \frac{\partial}{\partial z} p \xrightarrow{z \rightarrow \infty} \beta z \frac{\partial}{\partial z} \left( \frac{N^*}{V\beta} \ln z \right) = \frac{N^*}{V} = \frac{1}{v_0} .$$

$v_0$  is the minimal specific volume, the smallest possible volume per particle.

We have seen that both  $p(z)$  and  $v^{-1}(z)$  are analytical and monotonically increasing in a neighborhood of the positive real axis. Hence, there exist also the respective inverse functions, for instance  $z = z(v^{-1})$ . Without explicitly determining it we know that  $z(v^{-1})$  is a monotonically increasing function of  $v^{-1}$  in the interval  $0 \leq v^{-1} \leq v_0^{-1}$ . Consequently,  $z$  is monotonically decreasing as a function of  $v$  in the region  $v_0 \leq v < \infty$ . This transfers to the pressure and to the equation of state of the system:  $p(v)$  is continuous and monotonically decreasing for  $v_0 \leq v < \infty$  (Fig. 4.55). The equation of state does not exhibit any peculiarities. Indications of a phase transition are not recognizable.

We formulate a **first conclusion**:

1. It is not easy to recognize a phase transition for a finite  $V$ , as large as it may be, if the equation of state is not explicitly available:

**phase transition  $\iff$  limiting property.**

This already came up in the discussion of the *fluctuation-dissipation theorem* (4.16), but there only in connection with second-order phase transitions.

2. To recognize a phase transition, one has to investigate the respective system in the **thermodynamic limit**,

what leads to the non-trivial question whether this limit actually exists for  $p$  and  $v$ :

$$p(T, z) = \lim_{V \rightarrow \infty} p_V(T, z) , \tag{4.276}$$

$$\frac{1}{v}(T, z) = \beta \lim_{V \rightarrow \infty} z \frac{\partial}{\partial z} p_V(T, z) . \tag{4.277}$$

According to Sect. 4.5 the answer depends on the type of the interaction potential. No problems arise for classical systems with ‘hard core’-potentials.

3. If in the experiment, for instance by an horizontal segment of the  $p$ - $v$ -isotherms, a first-order phase transition is *recognized* (Fig. 4.56), so, nevertheless,  $p$  can not be strictly constant in the transition region for a finite  $V$ , because  $p$  is an analytic function of  $v$ . It could, however, be that the derivative  $\partial p/\partial v$  is so extremely small that macroscopically the difference to  $p = \text{const}$  is not detectable. The experiment would then decide that there is a *phase transition*, while for the theory there does not exist a simple possibility to recognize that, by inspecting the partition function. For this purpose an explicit determination of  $p = p(v)$  would be necessary!

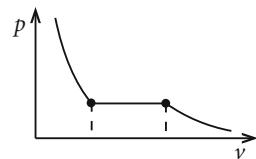
### 4.6.2 The Theorems of Yang and Lee

What can change in the *thermodynamic limit* compared to the finite system (Fig. 4.57)?

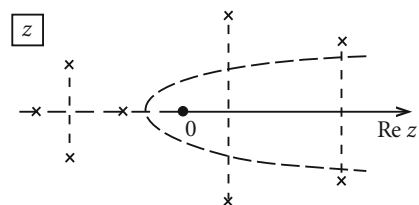
1. The number of zeros increases, since the degree  $N^*(V)$  of the polynomial  $\Xi_z$  tends to infinity.
2. The positions of the zeros in the complex  $z$ -plane will change.
3. Zeros, which are at first isolated, can be shifted to build continuous distributions (Fig. 4.58).
4. **Single points of the real  $z$ -axis can become accumulation points of the zero set of  $\Xi_z$ .**

The *theorems of Yang and Lee* are of decisive importance in this connection. We present them here without proof (Fig. 4.58).

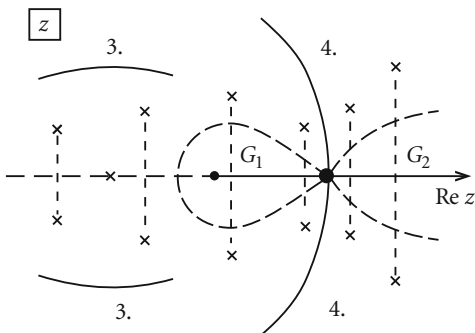
**Fig. 4.56**  $p$ - $V$ -isotherm of a real gas with a first-order phase transition



**Fig. 4.57** Distribution of the  $z$ -zero set of the grand-canonical partition function of a finite system



**Fig. 4.58** Conceivable  $z$ -zero distribution of the grand-canonical partition function of a thermodynamic system in the thermodynamic limit



**Theorem 4.6.1** For a stable interaction potential  $\varphi(r)$ , the limiting function

$$F_\infty(z, T) = \lim_{V \rightarrow \infty} \frac{1}{V} \ln \Xi_z(T, V) = \beta p(z, T) \tag{4.278}$$

exists for all  $z > 0$ , i.e., in the entire physical region. It is independent of the form of the volumes during the limiting process, and it represents a **continuous non-decreasing** function of  $z$ .

**Theorem 4.6.2**

Let  $G_1$  be a simply connected region of the complex  $z$ -plane, which contains a part of the positive-real  $z$ -axis, but **no** zero of  $\Xi_z(T, V)$  (Fig. 4.58). Then it holds:

1.  $(1/V) \ln \Xi_z(T, V) \xrightarrow{V \rightarrow \infty} F_\infty(z, T)$  converges **uniformly** for all  $z$  in the inside of  $G_1$ !
2.  $F_\infty(z, T)$  is **analytical** in  $G_1$ !

The proof of Theorem 4.6.1 was essentially performed in Sect. 4.5.5. We discuss here the **consequences** of these two theorems:

1. Because of the uniform convergence, the limiting process  $\lim_{V \rightarrow \infty}$  and the differentiation  $\partial/\partial z$  can be interchanged. Therewith also  $1/v$  is analytical in  $G_1$ , i.e., arbitrarily often differentiable:

$$\beta p(z, T) = F_\infty(z, T) , \tag{4.279}$$

$$v^{-1}(z, T) = z \frac{\partial}{\partial z} F_\infty(z, T) . \tag{4.280}$$

With the statement of Theorem 4.6.1 and the same considerations as in the last subsection for the finite system, one realizes that the equation of state does not exhibit any peculiarity in the region  $G_1$ . There is **no** phase transition in  $G_1$ !

2. As **phase** of the system one can interpret the set of all the thermodynamic states, which correspond to a  $z > 0$  from the inside of  $G_1$ .

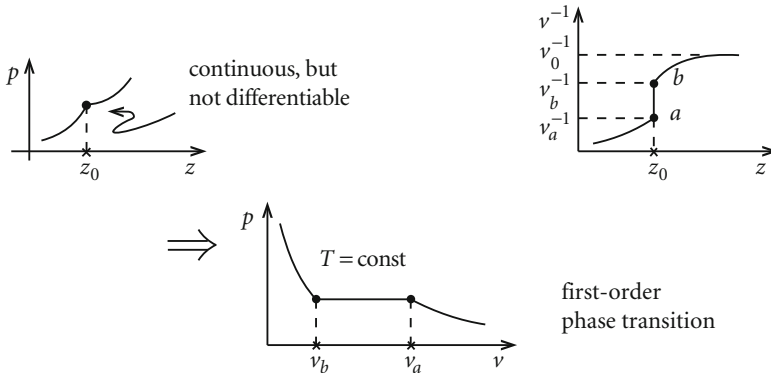


Fig. 4.59 Illustration of a phase transition of first order

3. Under which conditions is actually a **phase transition** possible? In the thermodynamic limit the  $\Xi_z$ -zeros can shift in such a way that a certain  $z_0$  ( $0 \leq z_0 < \infty$ ) becomes an accumulation point of these zeros (Fig. 4.58). The point  $z_0$  separates two regions  $G_1$  and  $G_2$  of the kind as meant in the Theorem 4.6.2. As edge point,  $z_0$  is neither in the inside of  $G_1$  nor in the inside of  $G_2$ , so that Theorem 4.6.1 is still valid for  $z_0$ , but not the Theorem 4.6.2. This means that  $p(z, T)$  is still continuous in  $z_0$ , but possibly no longer analytical, i.e., not arbitrarily often differentiable (see Fig. 4.59).

4. Illustration (Fig. 4.59):

$v^{-1}(z, T)$  must indeed take **all** values between the points  $a$  and  $b$ , because  $v^{-1}(z, T)$  represents a limiting function for  $V \rightarrow \infty$ , and because  $v^{-1}$  is for every value of  $V$  a continuous, non-decreasing function of  $z$ .

5. It would also be thinkable:

$$\frac{\partial^v p(z, T)}{\partial z^v} \text{ continuous at } z_0 \text{ for } v = 0, 1, \dots, n - 1,$$

$$\frac{\partial^n p(z, T)}{\partial z^n} \text{ discontinuous at } z_0.$$

The result would be a phase transition of higher order. Also singularities in any derivative can appear. The type of the phase transition is thus determined by the analytical behavior of  $p(z)$  at  $z_0$ .

In order to prove or disprove the correctness of the Yang-Lee theory of the phase transition, the grand-canonical partition function  $\Xi_z$  would have to be explicitly calculated for real systems. That, however, almost always exceeds our mathematical capabilities. For this reason, simple models are of interest.

### 4.6.3 Mathematical Model of a Phase Transition

For an illustration of the *Yang-Lee theory* we consider a completely abstract model, at first without any claim of a relationship to a real system. This fictitious system shall possess the grand-canonical partition function:

$$\Xi_z(V) = (1+z)^V \frac{1-z^{V+1}}{1-z}. \quad (4.281)$$

At the transition into the *thermodynamic limit* the volume  $V$  shall be measured in suitable units, so that we can assume it to be an integer:

$$V = 1, 2, 3, \dots \rightarrow \infty.$$

When we insert the known series expansions

$$\frac{1-z^{V+1}}{1-z} = \sum_{k=0}^V z^k; \quad (1+z)^V = \sum_{q=0}^V \binom{V}{q} z^q$$

into (4.281) and arrange according to powers of  $z$ , then  $\Xi_z$  takes an *almost familiar* form:

$$\Xi_z(V) = \sum_{N=0}^{2V} z^N Z_N(V) \quad (4.282)$$

$$Z_N(V) = \begin{cases} \sum_{k=0}^N \binom{V}{k} & \text{if } 0 \leq N \leq V \\ \sum_{k=N-V}^V \binom{V}{k} & \text{if } V \leq N \leq 2V. \end{cases} \quad (4.283)$$

The temperature-dependence of the *canonical partition function*  $Z_N$  shall not play a decisive role during the limiting process  $V \rightarrow \infty$  and is therefore not explicitly covered by the model.

#### Where are the $\Xi_z$ -zeros?

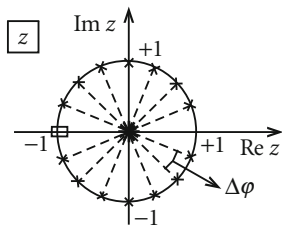
One reads off from (4.281):

1.  $z = -1$ :  $V$ -fold zero,
2.  $z = \sqrt[V+1]{1} \implies z_n = e^{i\varphi_n}$  with  $\varphi_n = \frac{2\pi}{V+1}n$ ,  $n = 1, 2, \dots, V$ ;  $V$  simple zeros.

$\Xi_z$  is a polynomial of the degree  $2V$ , and possesses therefore  $2V$  zeros, which are all located on the unit circle in the complex  $z$ -plane with angular distances (Fig. 4.60)

$$\Delta\varphi = \frac{2\pi}{V+1}. \quad (4.284)$$

**Fig. 4.60** Distribution of the zeros of the grand-canonical partition function in the mathematical model



$z = +1$  is **not** a zero, because according to l'Hospital's rule:

$$\lim_{z \rightarrow +1} \frac{1 - z^{V+1}}{1 - z} = \lim_{z \rightarrow +1} \frac{-(V + 1)z^V}{-1} = V + 1 \neq 0$$

We see that there is **no** zero on the positive-real axis (*physical region*), as long as a *finite* system is considered ( $V < \infty$ ). **There is no phase transition in the finite system!**

We now investigate the **thermodynamic limit**. The two zeros  $z_1$  and  $z_V$ , which are next to the real  $z$ -axis, have an angular distance from the axis of

$$\Delta\varphi = \frac{2\pi}{V + 1} \xrightarrow{V \rightarrow \infty} 0,$$

which becomes zero in the infinitely large system. That holds also for all the other angular distances between neighboring zeros. In the thermodynamic limit the zeros thus build a **continuous covering of the unit circle**, which even comes up to the positive-real axis. According to the general theory,

**a phase transition at  $z = +1$**

is therefore possible! We have to investigate in the following whether this is indeed the case, and if yes, of which kind the phase transition will be.

At first we calculate the **pressure  $p$**  of the system in the **thermodynamic limit** using (4.279):

$|z| < 1$ :

$$\begin{aligned} \lim_{V \rightarrow \infty} \frac{1}{V} \ln \Xi_z(V) &= \lim_{V \rightarrow \infty} \left[ \ln(1 + z) + \frac{1}{V} \ln(1 - z^{V+1}) - \frac{1}{V} \ln(1 - z) \right] \\ &= \ln(1 + z). \end{aligned}$$

$|z| > 1$ :

$$\begin{aligned} \lim_{V \rightarrow \infty} \frac{1}{V} \ln \Xi_z(V) &= \ln(1 + z) + \lim_{V \rightarrow \infty} \frac{1}{V} \left( \ln z^V + \ln \frac{1 - \frac{1}{z^{V+1}}}{1 - \frac{1}{z}} \right) \\ &= \ln(1 + z) + \ln z. \end{aligned}$$



The pressure  $p(z)$  is obviously represented by two analytic functions, neither of which exhibits something special at  $z = +1$ :

$$\beta p(z) = \begin{cases} \ln(1+z) & \text{for } |z| < 1, \\ \ln z(1+z) & \text{for } |z| > 1. \end{cases} \quad (4.285)$$

As required by the first theorem of the Yang-Lee theory,  $p(z)$  is continuous and non-decreasing for all  $0 \leq z < \infty$ , also for  $z = +1$ .

For the calculation of the **specific volume** we take the formula (4.280):

$$v(z) = \left( \beta z \frac{\partial}{\partial z} p(z) \right)^{-1}.$$

One easily finds with (4.285):

$$v(z) = \begin{cases} \frac{1+z}{z} & \text{for } |z| < 1, \\ \frac{1+z}{1+2z} & \text{for } |z| > 1. \end{cases} \quad (4.286)$$

With this in mind we realize already that at  $z = +1$  a **phase transition** indeed takes place:

$$\lim_{|z| \rightarrow 1^+} v(z) = \frac{2}{3} \neq \lim_{|z| \rightarrow 1^-} v(z) = 2.$$

Furthermore, one easily verifies that, for all positive-real  $z$ ,  $v(z)$  is a monotonically decreasing function of  $z$ :

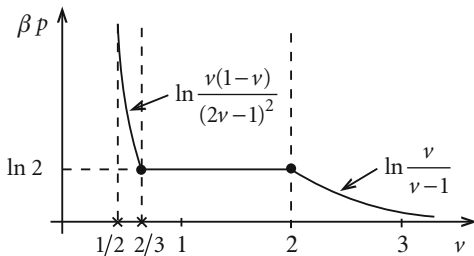
$$\frac{d}{dz} v(z) < 0$$

Because of  $v(z) \rightarrow \frac{1}{2}$  for  $|z| \rightarrow \infty$  there is a **minimal specific volume**:  $v_0 = 1/2$ .

This means:

$$\begin{aligned} |z| < 1 &\iff v \geq 2: && \text{'gas'}, \\ |z| > 1 &\iff v_0 \leq v \leq \frac{2}{3}: && \text{'liquid'}. \end{aligned} \quad (4.287)$$

**Fig. 4.61** Phase transition of first order in the mathematical model



It eventually remains to evaluate the **equation of state**:

**gaseous phase** ( $|z| < 1$ ):

$$v = \frac{1+z}{z} \implies 1+z = \frac{v}{v-1} .$$

This is inserted into (4.285):

$$p = \frac{1}{\beta} \ln \frac{v}{v-1} . \tag{4.288}$$

For  $v \rightarrow \infty$  the pressure vanishes.

**liquid phase** ( $|z| > 1$ ):

$$v = \frac{1+z}{1+2z} \implies z = \frac{1-v}{2v-1} , \quad 1+z = \frac{v}{2v-1} .$$

This yields the pressure:

$$p = \frac{1}{\beta} \ln \frac{v(1-v)}{(2v-1)^2} . \tag{4.289}$$

The pressure becomes infinitely large when  $v$  approaches the minimal volume  $v_0 = 1/2$ .  $p$  is in both phases monotonically decreasing as a function of  $v$ . The saturation pressure at the phase transition ( $z = +1$ ) amounts to

$$\beta p(1) = \ln 2 ,$$

according to (4.285). Our model fulfills therefore all the details of the general theory with a phase transition of first order, which exhibits an astonishing similarity to the real gas-liquid system (Fig. 4.61)!

### 4.6.4 Exercises

#### Exercise 4.6.1

Consider the possibility of a phase transition in the one-dimensional Ising model with ferromagnetic coupling ( $J > 0$ ) in the framework of the Yang-Lee theory.

1. Represent the canonical partition function  $Z_N(T, B_0)$  as a function of the *fugacity*  $z = \exp(2\beta b)$  with  $b = g\mu_B B_0$ . The here actually unimportant factor  $g\mu_B$  is the magnetic moment connected with the Ising-spin. Why is here the variable  $z$  reasonable?
2. Determine the distribution of the zeros  $\{z_n\}$  of the partition function of the finite system.
3. What happens to the distribution of the zeros in the thermodynamic limit ( $N \rightarrow \infty$ )? How does one recognize that in the one-dimensional Ising system no phase transition can appear?

#### Exercise 4.6.2

Let  $\{z_n\}$  be the (complex) zeros of the grand-canonical partition function  $\Xi_z^{(II)}(T, K)$  of the lattice gas II. The pair potential shall be of the form  $\varphi_{II}(i, j) \geq 0$  for all parcels  $i, j$ . (Notations as in Sect. 4.4.6).

1. Why should each of the two (non-real) zeros be conjugate complex?
2. Show that with  $z_n$  also  $z_n^{-1}$  is a zero of the grand-canonical partition function.
3. Since both the  $\{z_n\}$  and the  $\{z_n^{-1}\}$  build a complete set of zeros, there must be a connection between these two sets. The most obvious assumption would be to identify each  $z_n$  with  $1/z_n$  or with  $1/z_n^*$  (see Exercise 4.6.1). Which of the two assumptions were conceivable, and what would follow from that for the distribution of the zeros in the complex  $z$ -plane?
4. Start from the validity of the assumption in part 3., in order to show that the lattice gas, independent of the range of the interaction and also independent of the dimension of the system, can **not** perform a phase transition for  $\mu \neq 0$ !
5. Can there exist a phase transition in the Ising model of arbitrary lattice dimension if a field is switched on ( $B_0 \neq 0$ )?

## 4.7 Self-Examination Questions

### To Section 4.1

1. What does one understand by the term *phase*?
2. What is stated by the Gibbs phase rule?
3. State the Clausius-Clapeyron equation? To which type of phase transition is the equation applicable?

4. What does one understand, *according to Ehrenfest*, by the *order* of a phase transition?
5. When is a function  $f(x)$  *concave*, and when it is *convex*? What can be said in this respect about  $G(T, p)$ ?
6. How does a first-order phase transition manifests itself in the volume-dependence of the free energy  $F$ ?
7. Sketch the phase diagram of the magnet in the  $B_0$ - $T$ -plane?
8. How does a first-order phase transition of a magnetic system presents itself in the  $m$ -dependence of the free energy?
9. How does the heat capacity  $C_{H=0}$  of the superconductor behave at the critical temperature?
10. What does one understand by *continuous* and *discontinuous* phase transitions?
11. By which measured quantities can the continuous phase transition be experimentally observed?
12. Which meaning does the *order parameter* have?
13. Which order parameter determines the gas-liquid transition?
14. What does one understand by the correlation function of a physical quantity  $x$ ?
15. What does the *correlation length*  $\xi(T)$  represent?
16. Which connection can be built up, in the framework of the Ising model, between isothermal susceptibility  $\chi_T$  and spin correlation  $g_{ij}$ ?
17. What follows from the divergence of  $\chi_T$  at the second-order phase transition for the correlation function  $g_{ij}$ ?
18. How does  $\xi(T)$  behave for  $T \rightarrow T_C$ ?
19. In which temperature region do the principles (laws) come into effect, which are called *critical phenomena*?

## To Section 4.2

1. How are critical exponents defined? For which type of phase transition are they introduced?
2. To which physical quantity are the critical exponents  $\nu$  and  $\nu'$  ascribed?
3. What does the universality hypothesis tell us?
4. Which situations can be described by the critical exponent zero?
5. Which parameters restrict the universality of the critical exponents?
6. Which thermodynamically exact exponent-inequalities do you know?
7. What does one understand by the *homogeneity postulate* and the *scaling hypothesis*, respectively?
8. What is the basic idea of the Kadanoff construction?
9. Which consequence does the thermodynamic equivalence of *single-spin picture* and *Block-spin picture* with respect to the free enthalpy have?
10. How does the lattice dimension  $d$  enter the homogeneity postulate?
11. What does one understand by scaling laws?

12. Which are the most important consequences of the scaling hypothesis?
13. Via which property of which function can the scaling laws for the critical exponents  $\nu$ ,  $\nu'$  and  $\eta$  be derived?

### To Section 4.3

1. How does the *Landau ansatz* for the free enthalpy in the critical region of a second-order phase transition read?
2. Could you list some points of criticism with respect of the *Landau ansatz*?
3. Which relation exists between the *response* of the order parameter to *external perturbations* and the internal fluctuations of the system, expressed by the correlation function of the order parameter?
4. Which structure does the correlation function  $g(\mathbf{r}, \mathbf{r}')$  of the order parameter in the Landau theory have?
5. Which are the numerical values of the critical exponents in the Landau theory?
6. Which connection exists in the critical region between the susceptibility  $\chi_T$  and the correlation length  $\xi$ ?
7. Which general precondition must be fulfilled for the applicability of the Landau theory?
8. What is the basic statement of the Ginzburg criterion?
9. What is a Langevin paramagnet? By which Hamilton operator is it described?
10. Of which structure is the canonical partition function of the paramagnet?
11. Which structure does the Brillouin function have? Which relation does it have to the magnetization?
12. Which characteristic properties of the Brillouin function do you know?
13. For which limiting case is the Brillouin function identical to the classical Langevin function?
14. Which characteristic high-temperature behavior does the susceptibility of the paramagnet show?
15. In which form is the particle interaction taken into consideration in the Hamilton operator of the Heisenberg model?
16. What is a *mean-field approximation*?
17. How does the Heisenberg-Hamilton operator look like in the mean-field approximation? How does it differ from the Hamilton operator of a paramagnet?
18. Does the lattice dimension  $d$  play a role for the phase transition *ferro- ↔ paramagnetism* in the mean-field approximation of the Heisenberg model?
19. What does the Curie-Weiss law tell us? How is the *paramagnetic Curie temperature* defined?
20. Which relationship exists between the mean-field approximation of the Heisenberg model and the general Landau theory?
21. Do the critical exponents of the mean-field approximation differ from those of the Landau theory?

22. In what way can the van der Waals model of a real gas be understood as mean-field approximation?
23. Which physical meaning does the *pair correlation*  $g(\mathbf{r}, \mathbf{r}')$  have?
24. Which connection exists between the compressibility  $\kappa_T$  and the pair correlation  $g(\mathbf{r}, \mathbf{r}')$ ?
25. How is the *static structure factor*  $S(\mathbf{q})$  defined?
26. What does one understand by *critical opalescence* and how can it be explained?
27. Which form does the structure factor  $S(\mathbf{q})$  take in the *Ornstein-Zernike approximation*?
28. Can the Ornstein-Zernike theory provide explicit numerical values for the critical exponents  $\nu$  and  $\nu'$ ?
29. How can the correlation length  $\xi$  be experimentally determined?

### To Section 4.4

1. By what do the Hamilton operators of the Heisenberg, the *XY*, and the Ising model differ?
2. What is the model conception of the Ising model?
3. How many eigen-states does a one-dimensional chain of  $N$  Ising spins have?
4. How can one calculate by means of the spin correlation  $\langle S_i S_j \rangle$  the magnetization of the Ising system?
5. Is there a phase transition in the one-dimensional Ising model?
6. Which connection exists between *transfer matrix* and *transfer function*?
7. How can the partition function of the  $d = 1$ -Ising model be expressed by the transfer matrix?
8. Which qualitative course do the  $M$ - $B_0$ -isotherms of the one-dimensional Ising model exhibit?
9. Which reasons are in favor, and which facts do not support the interpretation of the one-dimensional Ising model as a ferromagnet with  $T_C = 0^+$ ?
10. By which simple equation is the critical temperature of the  $d = 2$ -Ising model determined?
11. Which numerical values do the critical exponents  $\alpha$  and  $\beta$  of the  $d = 2$ -Ising model have?

### To Section 4.5

1. How is the *thermodynamic limit* performed for an  $N$ -particle system in the volume  $V$ ?
2. When is the thermodynamic limit indispensable?
3. When does one call an interaction potential *catastrophic*? What does that mean?
4. Under which conditions is a continuous potential  $\varphi(\mathbf{r}_i - \mathbf{r}_j)$  *catastrophic*?

5. What does one understand by a *stable* potential?
6. What is the basic condition for a *stable* potential?
7. Are classical '*hard core*'-potentials *stable*?
8. How do the *stability conditions* of the canonical ensemble read?
9. In the thermodynamic limit, why should the free energy per particle represent a *convex* function of the particle volume  $v$ ?

## To Section 4.6

1. How does a phase transition manifest itself in the grand-canonical partition function?
2. Which functional form does  $\Xi_z(T, V)$  take for a particle system with a '*hard core*'-interaction potential in the finite volume  $V$ ?
3. Why can no phase transition appear in a finite system?
4. Which course does the  $p$ - $v$ -isotherm of a particle system with '*hard core*'-interaction in the finite volume  $V$  show?
5. How can one explain the *discrepancy* that in the experiment phase transitions are observed always in finite systems, while the theory excludes such a transition?
6. Which are the essential changes, with respect to the *phase transition*, when one goes from the *finite* system to the *thermodynamic limit*?
7. Which are the statements of the *theorems of Yang and Lee*?
8. What does one understand in the *Yang-Lee theory* by the term *phase*?
9. Under which condition is a *phase transition* possible?
10. What determines the type of the phase transition?

# Appendix A

## Solutions of the Exercises

### Section 1.1.3

#### Solution 1.1.1

1. Trick: At first we consider  $p_1$  and  $p_2$  as independent variables, and set at the end of the calculation  $p_1 + p_2 = 1$ !

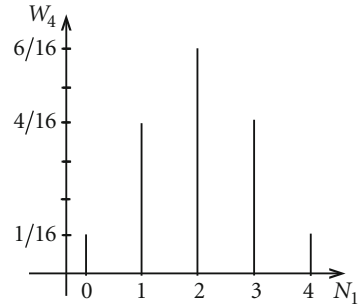
$$\begin{aligned}
 \langle N_1 \rangle &= p_1 \frac{\partial}{\partial p_1} \sum_{N_1=0}^N \frac{N!}{N_1! (N - N_1)!} p_1^{N_1} p_2^{N - N_1} \Big|_{p_1 + p_2 = 1} \\
 &= p_1 \frac{\partial}{\partial p_1} (p_1 + p_2)^N \Big|_{p_1 + p_2 = 1} = N p_1 (p_1 + p_2)^{N-1} \Big|_{p_1 + p_2 = 1} = N p_1, \\
 \langle N_1^2 \rangle &= p_1 \frac{\partial}{\partial p_1} \left[ p_1 \frac{\partial}{\partial p_1} (p_1 + p_2)^N \right] \Big|_{p_1 + p_2 = 1} = \left[ p_1 \frac{\partial}{\partial p_1} N p_1 (p_1 + p_2)^{N-1} \right] \Big|_{p_1 + p_2 = 1} \\
 &= \left[ N p_1 (p_1 + p_2)^{N-1} + N (N - 1) p_1^2 (p_1 + p_2)^{N-2} \right] \Big|_{p_1 + p_2 = 1} \\
 &= N p_1 + N (N - 1) p_1^2.
 \end{aligned}$$

Mean square deviation:

$$\overline{\Delta N_1} = \sqrt{\langle N_1^2 \rangle - \langle N_1 \rangle^2} = \sqrt{N p_1 (1 - p_1)}.$$



Fig. A.1



For  $p_1 = 0$  and  $p_1 = 1$  the deviation is of course equal to zero. Apart from that it increases with  $N$  over all limits.

Relative mean square deviation (Fig. A.1):

$$\frac{\overline{\Delta N_1}}{\langle N_1 \rangle} = \sqrt{\frac{1-p_1}{N p_1}} \xrightarrow{N \rightarrow \infty} 0.$$

2.

$$p_1 = p_2 = \frac{1}{2},$$

$$w_4(0) = w_4(4) = \frac{1}{16},$$

$$w_4(1) = w_4(3) = \frac{4}{16},$$

$$w_4(2) = \frac{6}{16}.$$

3.

$$\langle N_1 \rangle = \frac{1}{2} 10^{23}; \quad \overline{\Delta N_1} = \frac{1}{2} 10^{11.5},$$

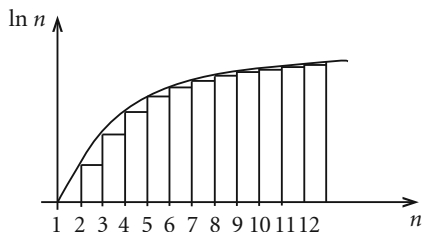
$$\frac{\overline{\Delta N_1}}{\langle N_1 \rangle} = 10^{-11.5},$$

$$w_N(10^{23}) = \left(\frac{1}{2}\right)^{10^{23}} = 2^{-10^{23}} \approx 0.$$

### Solution 1.1.2

$$S = \ln m! = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln m = \sum_{n=1}^m \ln n.$$

Fig. A.2



S: Area under the step curve in Fig. A.2. Obviously the estimate holds:

$$\int_2^m dx \ln(x-1) \leq S \leq \int_1^m dx \ln x .$$

The integrals can be easily evaluated:

$$\begin{aligned} \int_2^m dx \ln(x-1) &= \int_1^{m-1} dy \ln y = [y \ln y - y]_1^{m-1} \\ &= (m-1) \ln(m-1) - (m-1) + 1 \\ &= (m-1)(\ln(m-1) - 1) + 1 , \end{aligned}$$

$$\int_1^m dx \ln x = [x \ln x - x]_1^m = m(\ln m - 1) + 1$$

$$\implies (m-1)(\ln(m-1) - 1) \leq S - 1 \leq m(\ln m - 1) ;$$

$$m \rightarrow \infty: \quad S \rightarrow m(\ln m - 1) .$$

### Solution 1.1.3

$$N_1 \ll N, \quad p_1 \ll 1 .$$

Estimation:

$$\frac{N!}{(N - N_1)!} = N(N - 1)(N - 2) \cdots (N - N_1 + 1) \approx N^{N_1},$$

$$\ln p_2^{N - N_1} = (N - N_1) \ln(1 - p_1) \approx N \ln(1 - p_1) \approx -Np_1 = -\langle N_1 \rangle$$

$$\implies p_2^{N - N_1} \approx \exp(-\langle N_1 \rangle),$$

$$p_1^{N_1} = \left( \frac{\langle N_1 \rangle}{N} \right)^{N_1}$$

$$\implies w_N(N_1) = \frac{N!}{N_1! (N - N_1)!} p_1^{N_1} p_2^{N - N_1} \approx \frac{\langle N_1 \rangle^{N_1}}{N_1!} e^{-\langle N_1 \rangle}.$$

### Solution 1.1.4

$p$  = probability that a **particular** mistake appears on a **particular** page

$$= \frac{1}{500} \quad (\text{equal } a \text{ priori-probability}),$$

$N$  = total number of mistakes = 500

$\implies$  mean value per page:

$$\langle N_1 \rangle = Np = 1.$$

Poisson distribution:

$$w_N(N_1) \approx \frac{1}{N_1!} e^{-1}.$$

- $w_N(0) = e^{-1} = 0.368$ .
- $w_N(N_1 \geq 3) = 1 - w_N(0) - w_N(1) - w_N(2) = 1 - 0.368 - 0.368 - 0.184 = 0.080$   
(actually astonishingly small!).

### Solution 1.1.5

- There are  $N!$  possibilities to distribute  $N$  bullets over the  $N$  boxes. The first bullet has  $N$  possibilities, the second then  $N - 1$  possibilities, the third  $N - 2$ , and so on. We ask ourselves how many *pairwise different* occupancies of the  $k$  red boxes

exist. Among the  $N!$  possibilities of distribution there are of course also those, which differ from each other only by an interchange of bullets between the  $k$  red boxes and between the  $N - k$  blue boxes, respectively. Such distributions should be counted only once. The number of the pairwise different occupancies of the red boxes is therefore:

$$\alpha_N(k) = \frac{N!}{k!(N - k)!} .$$

All these occupancies are of the same probability. The probability to find a special set of  $k$  bullets just in the  $k$  red boxes is therewith:

$$w_k^N = \frac{1}{\alpha_N(k)} = \frac{k!(N - k)!}{N!} .$$

2. We consider again a particular set of  $k$  bullets. As just calculated, the probability that all are in red boxes is equal to  $w_k^N$ . Each other occupancy of the red boxes appears with the same probability. In the next step, out of the particular set of  $k$  bullets  $k' < k$  bullets shall be in the red boxes, the other  $k - k'$ , however, in the blue boxes. There are  $\alpha_k(k')$  possibilities to distribute  $k'$  objects over  $k$  sites, and  $\alpha_{N-k}(k - k')$  possibilities for the other  $k - k'$  objects to be distributed over the remaining  $N - k$  sites. There are thus

$$\alpha_k(k') \cdot \alpha_{N-k}(k - k')$$

realizations, for which from the  $k$  given bullets  $k'$  are put into red boxes and  $k - k'$  into blue boxes. Each of these realizations appears, according to 1., with the probability  $w_k^N$ . The probability to find from a chosen group of  $k$  bullets a special set of  $k'$  bullets in the red boxes and the other  $k - k'$  in the blue boxes is thus:

$$\begin{aligned} w_{k'}^N(k) &= w_k^N \alpha_k(k') \cdot \alpha_{N-k}(k - k') \\ &= \frac{k!(N - k)!}{N!} \frac{k!}{k'!(k - k')!} \frac{(N - k)!}{(k - k')!(N - 2k + k')!} \end{aligned}$$

3. The numbers, drawn by the lottery company, correspond to the  $k = 6$  ‘red boxes’. From the  $k = 6$  numbers I have tipped,  $k' < 6$  go into the ‘red boxes’, being therefore ‘hits’,  $k - k' = 6 - k'$  go into the ‘blue boxes’, belonging therefore to the  $N - k = 49 - 6 = 43$  not drawn numbers (‘blanks’).

(a) Six hits:

$$k' = k : w_6^{49}(6) = w_6^{49} = \frac{6!43!}{49!} \approx 7.15 \cdot 10^{-8}$$

(b) Five hits:

$$k' = k - 1 : w_5^{49}(6) = w_6^{49} \cdot \frac{6!}{5!1!} \frac{43!}{1!42!} = w_6^{49} \cdot 258 \approx 0.185 \cdot 10^{-4}$$

(c) Four hits:

$$k' = k - 2 : w_4^{49}(6) = w_6^{49} \cdot \frac{6!}{4!2!} \frac{43!}{2!41!} = w_6^{49} \cdot 13545 \approx 0.968 \cdot 10^{-3}$$

(d) Three hits:

$$k' = k - 3 : w_3^{49}(6) = w_6^{49} \cdot \frac{6!}{3!3!} \frac{43!}{3!40!} = w_6^{49} \cdot 246820 \approx 0.0176$$

### Solution 1.1.6

- (4, 0), (3, 1), (2, 2), (1, 3), (0, 4).
- Possibilities of realization (1.1):

$$\Gamma_4(n_a, n_b) = \frac{4!}{n_a! n_b!} .$$

$$\Gamma_4(4, 0) = 1: \quad |aaaa\rangle$$

$$\quad \quad \quad \uparrow\uparrow\uparrow\uparrow$$

$$\quad \quad \quad \text{particles} \quad 1234$$

$$\Gamma_4(3, 1) = 4: \quad |aaab\rangle$$

$$\quad \quad \quad |aaba\rangle$$

$$\quad \quad \quad |abaa\rangle$$

$$\quad \quad \quad |baaa\rangle$$

$$\Gamma_4(2, 2) = 6: \quad |aabb\rangle$$

$$\quad \quad \quad |bbaa\rangle$$

$$\quad \quad \quad |abab\rangle$$

$$\quad \quad \quad |baba\rangle$$

$$\quad \quad \quad |abba\rangle$$

$$\quad \quad \quad |baab\rangle$$

$$\Gamma_4(1, 3) = 4: \quad \begin{array}{l} |abbb\rangle \\ |babb\rangle \\ |bbab\rangle \\ |bbba\rangle \end{array}$$

$$\Gamma_4(0, 4) = 1: \quad |bbbb\rangle .$$

3. Equal *a priori*-probability for all the 16 *thinkable* states:

$$w(4, 0) = w(0, 4) = \frac{1}{16} ; \quad w(3, 1) = w(1, 3) = \frac{4}{16} ; \quad w(2, 2) = \frac{6}{16} .$$

## Section 1.2.5

### Solution 1.2.1

$$H(q, p) = E = \text{const} \implies \frac{p^2}{2mE} + \frac{q^2}{\frac{2E}{m\omega^2}} \stackrel{!}{=} 1 .$$

Areas of constant energy in the phase space are similar ellipses with the semi-axes:

$$p_0(E) = \sqrt{2mE}; \quad q_0(E) = \sqrt{\frac{2E}{m\omega^2}} .$$

Phase trajectory:

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{m} ; & \dot{p} &= -\frac{\partial H}{\partial q} = -m\omega^2 q \\ \implies dq &= \frac{p}{m} dt . \end{aligned}$$

$p$  from the equation of the ellipse:

$$\begin{aligned} p^2 &= p_0^2 \left( 1 - \frac{q^2}{q_0^2} \right) \\ \implies dq &= \frac{p_0}{m} \sqrt{1 - \frac{q^2}{q_0^2}} dt . \end{aligned}$$

Separation of variables:

$$\int_{q_1}^q \frac{dq'}{\sqrt{(1 - q'^2/q_0^2)}} = \frac{p_0}{m} \int_0^t dt' = \frac{p_0}{m} t, \quad \int \frac{dx}{\sqrt{a^2 - x^2}} = \arcsin \frac{x}{|a|} + c$$

$$\implies \frac{p_0}{m} t = q_0 \left[ \arcsin \frac{q}{q_0} - \arcsin \frac{q_1}{q_0} \right]$$

$$\implies q(t) = q_0 \sin(\omega t + \varepsilon(q_1, E)),$$

$$\varepsilon(q_1, E) = \arcsin \frac{q_1}{q_0}: \text{ fixed by initial conditions at } t = 0,$$

$$p^2 = \frac{p_0^2}{q_0^2} (q_0^2 - q^2) = m^2 \omega^2 q_0^2 \cos^2(\omega t + \varepsilon(q_1, E))$$

$$\implies p(t) = p_0 \cos(\omega t + \varepsilon(q_1, E)).$$

The phase trajectory is therewith determined:

$$\boldsymbol{\pi}(t | q_1, E) = \left( \sqrt{\frac{2E}{m\omega^2}} \sin(\omega t + \varepsilon), \sqrt{2mE} \cos(\omega t + \varepsilon) \right).$$

$q_1 = q(t = 0)$  as initial condition and  $E$  determine also the initial momentum  $p_1$ :

$$\boldsymbol{\pi}(t | q_1, E) \longrightarrow \boldsymbol{\pi}(t | q_1, p_1) = \boldsymbol{\pi}(t | \boldsymbol{\pi}(0)).$$

$\boldsymbol{\pi}(t)$  describes the motion of an oscillator, which is at the time  $t = 0$  at  $\boldsymbol{\pi}(0) = (q_1, p_1)$ , as a function of time. After the period  $\tau = 2\pi/\omega$  **each** point of the  $H(q, p) = E$ -hyper surface was run through. The quasi-ergodic hypothesis is therefore exact for the one-dimensional harmonic oscillator!

### Solution 1.2.2

$$H = H(\mathbf{q}, \mathbf{p}); \quad \rho = \rho(H, t)$$

$$\implies \nabla \rho = \frac{\partial \rho}{\partial H} \nabla H.$$

Because of

$$\begin{aligned}\nabla H &= \left( \frac{\partial H}{\partial q_1}, \dots, \frac{\partial H}{\partial q_s}, \frac{\partial H}{\partial p_1}, \dots, \frac{\partial H}{\partial p_s} \right) \\ &= \left( -\dot{p}_1, \dots, -\dot{p}_s, \dot{q}_1, \dots, \dot{q}_s \right), \\ \mathbf{v} &= \left( \dot{q}_1, \dots, \dot{q}_s, \dot{p}_1, \dots, \dot{p}_s \right)\end{aligned}$$

we have

$$\mathbf{v} \cdot \nabla H = 0$$

and therewith also:

$$\mathbf{v} \cdot \nabla \rho = 0 .$$

This means according to the Liouville equation:

$$\frac{\partial \rho}{\partial t} = 0 .$$

### **Solution 1.2.3**

It holds for  $\det F_t$  as for **every** determinant ((1.332), (1.336), Vol. 1):

$$\sum_{k=1}^{2s} a_{ik} U_{jk} = \delta_{ij} \det F^{(t,0)} .$$

Thereby

$$a_{ik} = \frac{\partial \pi_i(t)}{\partial \pi_k(0)} ; \quad U_{ik} = \frac{\partial(\det F^{(t,0)})}{\partial a_{ik}}$$

are the elements of the determinant and their algebraic complements ((1.327), Vol. 1), respectively. We build therewith:

$$\frac{d}{dt} \det F^{(t,0)} = \sum_{i,k} \frac{\partial(\det F^{(t,0)})}{\partial a_{ik}} \frac{da_{ik}}{dt} = \sum_{i,k} U_{ik} \frac{da_{ik}}{dt} .$$



For this expression we use:

$$\begin{aligned} \frac{da_{ik}}{dt} &= \frac{d}{dt} \left( \frac{\partial \pi_i(t)}{\partial \pi_k(0)} \right) = \frac{\partial}{\partial \pi_k(0)} (\dot{\pi}_i(t)) \\ &= \sum_j \frac{\partial \dot{\pi}_i(t)}{\partial \pi_j(t)} \frac{\partial \pi_j(t)}{\partial \pi_k(0)} = \sum_j a_{jk} \frac{\partial \dot{\pi}_i(t)}{\partial \pi_j(t)}. \end{aligned}$$

This is inserted into the above equation:

$$\begin{aligned} \frac{d}{dt} \det F^{(t,0)} &= \sum_{ijk} U_{ik} a_{jk} \frac{\partial \dot{\pi}_i(t)}{\partial \pi_j(t)} = \sum_{ij} \delta_{ij} \det F^{(t,0)} \frac{\partial \dot{\pi}_i(t)}{\partial \pi_j(t)} \\ &= \det F^{(t,0)} \sum_i \frac{\partial \dot{\pi}_i(t)}{\partial \pi_i(t)}, \\ \sum_i \frac{\partial \dot{\pi}_i(t)}{\partial \pi_i(t)} &= \sum_{j=1}^s \left( \frac{\partial^2 H}{\partial q_j(t) \partial p_j(t)} - \frac{\partial^2 H}{\partial p_j(t) \partial q_j(t)} \right) = 0. \end{aligned}$$

It follows:

$$\frac{d}{dt} \det F^{(t,0)} = 0 \implies \det F^{(t,0)} = \det F^{(0,0)} = 1.$$

This proves the assertion:  $\Gamma_t = \Gamma_0 = 1$ .

### **Solution 1.2.4**

1. Phase volume:

$$\begin{aligned} \varphi(E) &= \alpha \iint_{H < E} dq dp \\ &= \alpha \cdot \text{surface area of the phas-space ellipse (see Exercise 1.2.1)} \\ &= \alpha \cdot \pi p_0 q_0 \\ &= \alpha \cdot \pi \sqrt{2mE} \sqrt{\frac{2E}{m\omega^2}} \\ \implies \varphi(E) &= \alpha \cdot \frac{2\pi}{\omega} E. \end{aligned}$$

It follows therewith:

$$\Gamma(E) = \varphi(E + \Delta) - \varphi(E) = \alpha \cdot \frac{2\pi}{\omega} \Delta .$$

It holds:

$$\rho_0 = \frac{\alpha}{\Gamma(E)} = \frac{\omega}{2\pi\Delta} .$$

Normalized density-distribution function:

$$\rho(q, p, t) \equiv \rho(q, p) = \begin{cases} \omega/2\pi\Delta & \text{if } E < H(q, p) < E + \Delta , \\ 0 & \text{otherwise .} \end{cases}$$

2. Kinetic energy:

$$\begin{aligned} \langle T \rangle &= \frac{\rho_0}{2m} \iint_{E < H < E + \Delta} dq dp p^2 , \\ \iint_{H < E} dq dp p^2 &= \int_{p^2 < 2mE} dp p^2 \int_{q^2 < \frac{2E}{m\omega^2} - \frac{p^2}{m^2\omega^2}} dq = \int_{-\sqrt{2mE}}^{+\sqrt{2mE}} dp p^2 2\sqrt{\frac{2E}{m\omega^2} - \frac{p^2}{m^2\omega^2}} \\ &= \frac{2}{m\omega} \int_{-\sqrt{2mE}}^{+\sqrt{2mE}} dp p^2 \sqrt{2mE - p^2} . \end{aligned}$$

Formulary:

$$\int dx x^2 \sqrt{a^2 - x^2} = \frac{x}{8}(2x^2 - a^2)\sqrt{a^2 - x^2} + \frac{a^4}{8} \arcsin \frac{x}{|a|} + c .$$

Therewith:

$$\iint_{H < E} dq dp p^2 = \frac{2}{m\omega} \frac{4m^2 E^2}{8} (\arcsin 1 - \arcsin(-1)) = \frac{m\pi}{\omega} E^2 .$$

It follows:

$$\langle T \rangle = \frac{\omega}{4\pi\Delta m} \frac{m\pi}{\omega} \{(E + \Delta)^2 - E^2\} = \frac{1}{4\Delta} \{2E\Delta + \Delta^2\} ,$$

$$\langle T \rangle = \frac{1}{2}E + \frac{1}{4}\Delta .$$

Potential energy:

$$\begin{aligned} \langle V \rangle &= \frac{1}{2}m\omega^2\rho_0 \iint_{E < H < E + \Delta} dq dp q^2 , \\ \iint_{H < E} dq dp q^2 &= \int_{-\sqrt{\frac{2E}{m\omega^2}}}^{+\sqrt{\frac{2E}{m\omega^2}}} dq q^2 \int_{-\sqrt{2mE - m^2\omega^2 q^2}}^{+\sqrt{2mE - m^2\omega^2 q^2}} dp \\ &= 2 \int_{-\sqrt{\frac{2E}{m\omega^2}}}^{+\sqrt{\frac{2E}{m\omega^2}}} dq q^2 \sqrt{2mE - m^2\omega^2 q^2} \\ &= 2m\omega \int_{-\sqrt{\frac{2E}{m\omega^2}}}^{+\sqrt{\frac{2E}{m\omega^2}}} dq q^2 \sqrt{\frac{2E}{m\omega^2} - q^2} . \end{aligned}$$

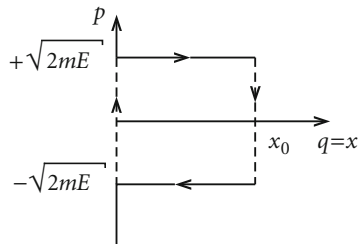
That is the same type of integral as that for the calculation of the average kinetic energy:

$$\iint_{H < E} dq dp q^2 = 2m\omega \frac{1}{8} \frac{4E^2}{m^2\omega^4} (\arcsin 1 - \arcsin(-1)) = \frac{\pi E^2}{m\omega^3} .$$

We calculate therewith:

$$\langle V \rangle = \frac{1}{2}m\omega^2 \frac{\omega}{2\pi\Delta} \frac{\pi}{m\omega^3} \{(E + \Delta)^2 - E^2\} = \frac{1}{4\Delta} (2E\Delta + \Delta^2) = \frac{1}{2}E + \frac{1}{4}\Delta = \langle T \rangle .$$

Fig. A.3



**Solution 1.2.5**

(Fig. A.3)

1.

$$V(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq x_0, \\ \infty & \text{otherwise} \end{cases}$$

$$\implies H = \frac{p^2}{2m} = E \iff p = \pm\sqrt{2mE} \quad \text{for } 0 \leq x \leq x_0.$$

2.

$$\varphi(E) = \alpha \int_0^{x_0} dq \int_{-\sqrt{2mE}}^{+\sqrt{2mE}} dp = \alpha 2x_0\sqrt{2mE}.$$

**Solution 1.2.6**

$$\rho(\mathbf{q}, \mathbf{p}) = \begin{cases} \rho_0, & \text{if } E < H(\mathbf{q}, \mathbf{p}) < E + \Delta, \\ 0 & \text{otherwise,} \end{cases}$$

$$\rho_0 = \frac{\alpha}{\Gamma(E)}; \quad \Gamma(E) = \alpha \iint_{E < H(\mathbf{q}, \mathbf{p}) < E + \Delta} d^s q d^s p \quad (s = 2N),$$

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^N H_i(\mathbf{q}_i, \mathbf{p}_i), \quad \text{where}$$

$$H_i(\mathbf{q}_i, \mathbf{p}_i) = \frac{1}{2m} (p_{ix}^2 + p_{iy}^2), \quad \text{if } 0 \leq q_{ix} \leq x_0 \quad \text{and} \quad 0 \leq q_{iy} \leq y_0.$$

When dealing with the phase volume

$$\varphi(E) = \alpha \iint_{H(\mathbf{q}, \mathbf{p}) \leq E} d^{2N} q d^{2N} p$$

the position-integrals are directly calculable:

$$\varphi(E) = \alpha (x_0 y_0)^N \cdot V_{2N}; \quad V_{2N} \equiv \int \dots \int_{\sum_{i=1}^{2N} p_i^2 \leq 2mE} dp_1 dp_2 \dots dp_{2N}.$$

$V_{2N}$  is the volume of the  $2N$ -dimensional sphere of the radius  $\sqrt{2mE}$ . Using spherical coordinates one finds:

$$V_{2N} = \Omega_{2N} \int_0^{\sqrt{2mE}} dp p^{2N-1} = \frac{\Omega_{2N}}{2N} (\sqrt{2mE})^{2N}.$$

$\Omega_{2N}$ : surface of the  $2N$ -dimensional unit sphere. This can be determined by the Gaussian integral in the  $2N$ -dimensional space:

$$G_{2N} = \int d^{2N} x e^{-(x_1^2 + \dots + x_{2N}^2)} = \prod_{i=1}^{2N} \int_{-\infty}^{+\infty} x_i e^{-x_i^2} = (\sqrt{\pi})^{2N} = \pi^N.$$

Alternately by the use of spherical coordinates:

$$G_{2N} = \int d^{2N} x e^{-x^2} = \Omega_{2N} \int_0^{\infty} dx x^{2N-1} e^{-x^2}.$$

With the substitution  $y = x^2 \curvearrowright dx = \frac{dy}{2\sqrt{y}}$  and the definition of the Gamma-function:

$$G_{2N} = \frac{1}{2} \Omega_{2N} \int_0^{\infty} y y^{N-1} e^{-y} = \frac{1}{2} \Omega_{2N} \Gamma(N) = \frac{1}{2} \Omega_{2N} (N-1)!$$

Comparison of the two results for  $G_{2N}$ :

$$\Omega_{2N} = \frac{2\pi^N}{\Gamma(N)} = \frac{2\pi^N}{(N-1)!}.$$

The volume of the  $2N$ -dimensional sphere of the radius  $\sqrt{2mE}$  is therewith determined:

$$V_{2N} = \frac{\pi^N}{N\Gamma(N)} (2mE)^N = \frac{\pi^N}{N!} (2mE)^N.$$

Insertion yields the phase volume and the required normalization constant of the micro-canonical ensemble:

$$\begin{aligned}\varphi(E) &= \frac{\alpha}{N!} (2\pi m x_0 y_0)^N \cdot E^N \\ \Gamma(E) &= \varphi(E + \Delta) - \varphi(E) = \frac{\alpha}{N!} (2\pi m x_0 y_0 E)^N \left[ \left(1 + \frac{\Delta}{E}\right)^N - 1 \right] \\ \rho_0 &= \frac{N!}{(2\pi m x_0 y_0 E)^N \left[ \left(1 + \frac{\Delta}{E}\right)^N - 1 \right]}.\end{aligned}$$

### Solution 1.2.7

1. Equation of motion ((2.109), Vol. 1):

$$m\ddot{q} + \bar{\alpha}\dot{q} = 0.$$

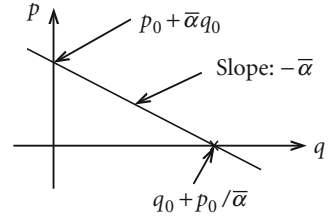
Solution ((2.111), Vol. 1):

$$\begin{aligned}q(t) &= a_1 + a_2 \exp\left(-\frac{\bar{\alpha}}{m}t\right), \\ p(t) &= m\dot{q}(t) = -\bar{\alpha}a_2 \exp\left(-\frac{\bar{\alpha}}{m}t\right).\end{aligned}$$

Initial conditions:

$$\begin{aligned}q(t=0) &= q_0; & p(t=0) &= p_0 \\ \implies p_0 &= -\bar{\alpha}a_2; & q_0 &= a_1 + a_2, \\ a_2 &= -\frac{p_0}{\bar{\alpha}}; & a_1 &= q_0 + \frac{p_0}{\bar{\alpha}}\end{aligned}$$

Fig. A.4



$$\Rightarrow q(t) = q_0 + \frac{p_0}{\bar{\alpha}} \left[ 1 - \exp\left(-\frac{\bar{\alpha}}{m}t\right) \right],$$

$$p(t) = p_0 \exp\left(-\frac{\bar{\alpha}}{m}t\right).$$

Phase trajectory (Fig. A.4):

$$p(t) + \bar{\alpha}q(t) = p_0 + \bar{\alpha}q_0 = \text{const}.$$

$$\begin{aligned} dq(t)dp(t) &= \frac{\partial(q(t), p(t))}{\partial(q(0), p(0))} dq(0)dp(0) = \begin{vmatrix} 1 & \frac{1}{\bar{\alpha}} [1 - \exp(-\frac{\bar{\alpha}}{m}t)] \\ 0 & \exp(-\frac{\bar{\alpha}}{m}t) \end{vmatrix} dq_0 dp_0 \\ &= \exp\left(-\frac{\bar{\alpha}}{m}t\right) dq_0 dp_0 \\ &\Rightarrow \text{temporally variable phase volume!} \end{aligned}$$

2. Equation of motion ((2.169), Vol. 1):

$$\ddot{q} + \frac{\bar{\alpha}}{m}\dot{q} + \omega^2 q = 0.$$

Solution for weak friction ((2.174), Vol. 1):

$$\begin{aligned} q(t) &= \exp\left(-\frac{\bar{\alpha}}{2m}t\right) \left( q_0 \cos \omega t + \frac{2p_0 + \bar{\alpha}q_0}{2m\omega} \sin \omega t \right) \\ \Rightarrow \dot{q}(t) &= \exp\left(-\frac{\bar{\alpha}}{2m}t\right) \left[ \left( \frac{2p_0 + \bar{\alpha}q_0}{2m} - \frac{\bar{\alpha}q_0}{2m} \right) \cos \omega t - \left( \frac{\bar{\alpha}}{2m} \frac{2p_0 + \bar{\alpha}q_0}{2m\omega} + q_0\omega \right) \sin \omega t \right], \\ p(t) &= \exp\left(-\frac{\bar{\alpha}}{2m}t\right) \left[ p_0 \cos \omega t - \left( \bar{\alpha} \frac{2p_0 + \bar{\alpha}q_0}{4m\omega} + m q_0\omega \right) \sin \omega t \right]. \end{aligned}$$

Weak friction:

$$\frac{\bar{\alpha}}{m\omega} \ll 1$$

$$\implies q(t) \approx \exp\left(-\frac{\bar{\alpha}}{2m}t\right) \left(q_0 \cos \omega t + \frac{p_0}{m\omega} \sin \omega t\right),$$

$$p(t) \approx \exp\left(-\frac{\bar{\alpha}}{2m}t\right) (p_0 \cos \omega t - mq_0\omega \sin \omega t).$$

It follows with  $\sin^2 x + \cos^2 x = 1$ :

$$\frac{1}{2m}p^2(t) + \frac{1}{2}m\omega^2 q^2(t) = \exp\left(-\frac{\bar{\alpha}}{m}t\right) \left[\frac{1}{2m}p_0^2 + \frac{1}{2}m\omega^2 q_0^2\right] = E_0 \exp\left(-\frac{\bar{\alpha}}{m}t\right).$$

This is an *equation of an ellipse* with time-dependent semi-axes:

$$a = \sqrt{2mE_0} \exp\left(-\frac{\bar{\alpha}}{2m}t\right),$$

$$b = \sqrt{\frac{2E_0}{m\omega^2}} \exp\left(-\frac{\bar{\alpha}}{2m}t\right)$$

$\implies$  phase trajectory: elliptical spiral,

$$\begin{aligned} dq(t)dp(t) &= \frac{\partial(q(t), p(t))}{\partial(q_0, p_0)} dq_0 dp_0 \\ &= \begin{vmatrix} \exp(-\frac{\bar{\alpha}}{2m}t) \cos \omega t & \exp(-\frac{\bar{\alpha}}{2m}t) \frac{1}{m\omega} \sin \omega t \\ -\exp(-\frac{\bar{\alpha}}{2m}t) m\omega \sin \omega t & \exp(-\frac{\bar{\alpha}}{2m}t) \cos \omega t \end{vmatrix} dq_0 dp_0 \\ &= \exp(-\frac{\bar{\alpha}}{m}t) dq_0 dp_0 \end{aligned}$$

$\implies$  temporally variable phase volume!

### **Solution 1.2.8**

Energy-volume relationship of a relativistic particle ((2.63), Vol. 4):

$$cp = \sqrt{E^2 - m^2 c^4}.$$



Phase volume:

$$\varphi(E) = \alpha \iint_{H \leq E} dqdp = \alpha V \frac{4\pi}{3} p^3(E) = \alpha V \frac{4\pi}{3} \left( \frac{E^2}{c^2} - m^2 c^2 \right)^{3/2}.$$

### Solution 1.2.9

Number of different possibilities to distribute  $N$  particles over the two levels and thereby to realize the energy  $E = E(N_1, N_2)$ :

$$\Gamma_N(E) = \frac{N!}{N_1! N_2!}.$$

Stirling formula:

$$\ln N! \approx N(\ln N - 1) = N \ln \frac{N}{e} = \ln \left( \frac{N}{e} \right)^N \rightsquigarrow N! \approx \left( \frac{N}{e} \right)^N$$

Therewith the phase volume  $\Gamma_N(E)$  can be estimated:

$$\Gamma_N(E) \approx \frac{N^N}{N_1^{N_1} N_2^{N_2}} = \left( \frac{N}{N_1} \right)^{N_1} \left( \frac{N}{N_2} \right)^{N_2} = \left[ \left( \frac{N}{N_1} \right)^{\frac{N_1}{N}} \left( \frac{N}{N_2} \right)^{\frac{N_2}{N}} \right]^N.$$

It holds:

$$\begin{aligned} E &= (2N_1 - N) \varepsilon = (N - 2N_2) \varepsilon \\ \rightsquigarrow \frac{N_1}{N} &= \frac{1}{2} \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right); \quad \frac{N_2}{N} = \frac{1}{2} \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right) \rightsquigarrow \frac{N_i}{N} = f_i \left( \frac{E}{N} \right) \\ \rightsquigarrow \Gamma_N(E) &= \left[ \mathcal{F} \left( \frac{E}{N} \right) \right]^N \quad \text{with} \quad \mathcal{F} \left( \frac{E}{N} \right) = \left( \frac{1}{f_1} \right)^{f_1} \left( \frac{1}{f_2} \right)^{f_2}. \end{aligned}$$

$\frac{E}{N}$  is an intensive variable. It thus follows:

$$\ln \Gamma_N(E) \propto N.$$

### Section 1.3.8

#### Solution 1.3.1

1. We calculate

$$I = \int_{-\infty}^{+\infty} dy_1 \cdots \int_{-\infty}^{+\infty} dy_N \exp(- (y_1^2 + \cdots + y_N^2))$$

in two different ways, on the one hand by factorization of the exponential-function,

$$I = \left( \int_{-\infty}^{+\infty} dy e^{-y^2} \right)^N = \pi^{N/2} ,$$

on the other hand by introducing spherical coordinates:

$$\begin{aligned} I &= \int_0^\infty dR S_N(R) e^{-R^2} = \quad (\text{isotropic problem}) \\ &= NC_N \int_0^\infty dR R^{N-1} e^{-R^2} \stackrel{(x=R^2)}{=} \frac{1}{2} NC_N \int_0^\infty dx x^{(N/2)-1} e^{-x} \\ &\implies I = \frac{1}{2} NC_N \Gamma\left(\frac{N}{2}\right) \\ &\implies C_N = \frac{2\pi^{N/2}}{N\Gamma\left(\frac{N}{2}\right)} . \end{aligned}$$

Gamma function:

$$\Gamma(x + 1) = x\Gamma(x) , \quad \Gamma(1) = 1 ; \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} .$$

N even  $N = 2n ; \quad n \in \mathbb{N}$ :

$$\begin{aligned} \Gamma\left(\frac{N}{2}\right) &= \Gamma(n) = (n - 1)! = \left(\frac{N}{2} - 1\right)! = \frac{2}{N} \left(\frac{N}{2}\right)! \\ &\implies C_N = \frac{\pi^{N/2}}{\left(\frac{N}{2}\right)!} . \end{aligned}$$

$N$  odd  $N = 2n + 1$ ;  $n \in \mathbb{N}$ :

$$\begin{aligned} \Gamma\left(\frac{N}{2}\right) &= \Gamma\left(n + \frac{1}{2}\right) = \left(n - \frac{1}{2}\right) \Gamma\left(n - \frac{1}{2}\right) \\ &= \left(n - \frac{1}{2}\right) \left(n - \frac{3}{2}\right) \Gamma\left(n - \frac{3}{2}\right) = \left(n - \frac{1}{2}\right) \left(n - \frac{3}{2}\right) \cdots \frac{1}{2} \Gamma\left(\frac{1}{2}\right) \\ &= \frac{1}{2^n} (2n-1)(2n-3) \cdots 1 \sqrt{\pi} = \frac{\sqrt{\pi}}{2^{(N-1)/2}} (N-2)(N-4) \cdots 1 \end{aligned}$$

$$\implies N \Gamma\left(\frac{N}{2}\right) = \frac{\sqrt{\pi}}{2^{(N-1)/2}} N!!$$

$$\implies C_N = \frac{2 (2\pi)^{(N-1)/2}}{N!!} .$$

2. Volume of the sphere:

$$V_N(R) = C_N R^N .$$

Volume of a surface layer of the thickness  $\Delta \ll R$ :

$$\begin{aligned} \Delta V_N(\Delta) &= V_N(R) - V_N(R - \Delta) = C_N [R^N - (R - \Delta)^N] \\ \implies \Delta V_N(\Delta) &= V_N(R) \left[ 1 - \left(1 - \frac{\Delta}{R}\right)^N \right] . \end{aligned}$$

$\Delta, R$  fixed:

$$\lim_{N \rightarrow \infty} \frac{\Delta V_N(\Delta)}{V_N(R)} = \lim_{N \rightarrow \infty} \left[ 1 - \underbrace{\left(1 - \frac{\Delta}{R}\right)^N}_{<1} \right] = 1, \quad \text{if } \Delta > 0 .$$

### **Solution 1.3.2**

Phase volume according to Exercise 1.2.9:

$$\Gamma_N(E) = \left(\frac{N}{N_1}\right)^{N_1} \left(\frac{N}{N_2}\right)^{N_2} .$$

Thereby it holds:

$$N_1 = \frac{N}{2} \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right) \quad N_2 = \frac{N}{2} \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right) .$$

Hence it follows for the entropy:

$$\begin{aligned} S(E, N) &= k_B \ln \Gamma_N(E) = k_B \left( N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2} \right) \\ &= -k_B \frac{N}{2} \left[ \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right) \ln \left( \frac{1}{2} \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right) \right) \right. \\ &\quad \left. + \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right) \ln \left( \frac{1}{2} \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right) \right) \right] . \end{aligned}$$

With (1.89) we then get for the temperature:

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial S(E, N)}{\partial E} \right)_N = -k_B \frac{N}{2} \left[ \frac{1}{\varepsilon N} \ln \left( \frac{1}{2} \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right) \right) \right. \\ &\quad \left. + \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right) \frac{1}{\frac{1}{2} \left( \frac{1}{\varepsilon} \frac{E}{N} + 1 \right)} \frac{1}{2\varepsilon N} \right. \\ &\quad \left. - \frac{1}{\varepsilon N} \ln \left( \frac{1}{2} \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right) \right) \right. \\ &\quad \left. + \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right) \frac{1}{\frac{1}{2} \left( 1 - \frac{1}{\varepsilon} \frac{E}{N} \right)} \left( -\frac{1}{2\varepsilon N} \right) \right] \\ &= \frac{k_B}{2\varepsilon} \ln \frac{1 - \frac{1}{\varepsilon} \frac{E}{N}}{1 + \frac{1}{\varepsilon} \frac{E}{N}} \\ \curvearrowright \exp(2\varepsilon\beta) &= \frac{1 - \frac{1}{\varepsilon} \frac{E}{N}}{1 + \frac{1}{\varepsilon} \frac{E}{N}} \quad \left( \beta = \frac{1}{k_B T} \right) . \end{aligned}$$

That can be resolved for the energy:

$$E = N\varepsilon \frac{1 - \exp(2\beta\varepsilon)}{1 + \exp(2\beta\varepsilon)} = -N\varepsilon \tanh(\beta\varepsilon) .$$

$N_1$  ( $N_2$ ) is the number of particles in the upper (lower) level  $+\varepsilon$  ( $-\varepsilon$ ). So  $N_1/N$  can be considered as *occupation probability* for the upper level and  $N_2/N$  for the lower

level!

$$\frac{N_1}{N} = \frac{1}{2} \left( 1 + \frac{1}{\varepsilon} \frac{E}{N} \right) = \frac{1}{2} \left( \frac{1 - \exp(2\beta\varepsilon)}{1 + \exp(2\beta\varepsilon)} + 1 \right) = \frac{1}{\exp(2\beta\varepsilon) + 1} \equiv n(T)$$

$$\frac{N_2}{N} = 1 - \frac{N_1}{N} = 1 - n(T).$$

It follows for the entropy:

$$S(T, N) = -k_B N \left( n(T) \ln n(T) + (1 - n(T)) \ln(1 - n(T)) \right).$$

Because of  $n(T) \rightarrow 0$  for  $T \rightarrow 0$ , one recognizes:

$$\lim_{T \rightarrow 0} S(T, N) = 0.$$

This corresponds to the *third law of Thermodynamics* (see subsection 2.2.2 and section 3.8 Vol. 5).

We started for the solution of this exercise with a classical particle system. The considerations, however, remain word-for-word the same for a quantum-mechanical system of distinguishable particles. That will be demonstrated in Exercise 2.2.2.

### Solution 1.3.3

1.

$$T^{-1} = \left( \frac{\partial S}{\partial E} \right)_{V, N} = k_B \frac{1}{\Gamma_N} \left( \frac{\partial \Gamma_N}{\partial E} \right)_{V, N} = k_B \frac{3}{2} N \frac{1}{E}$$

$$\implies U = E = \frac{3}{2} N k_B T.$$

2.

$$p = T \left( \frac{\partial S}{\partial V} \right)_{E, N} = T \frac{k_B}{\Gamma_N} \left( \frac{\partial \Gamma_N}{\partial V} \right)_{E, N} = k_B T \frac{N}{V} \implies pV = N k_B T.$$

3. *Adiabatic*:  $S = \text{const} \iff \Gamma_N = \text{const}$

$$0 = dE + pdV - \mu dN$$

$$\implies p = - \left( \frac{\partial E}{\partial V} \right)_{S, N},$$

$$E = \left( \frac{\Gamma_N}{f(N)V^N} \right)^{2/3N} = \left( \frac{\Gamma_N}{f(N)} \right)^{2/3N} V^{-2/3}$$

$$\begin{aligned} \Rightarrow \left( \frac{\partial E}{\partial V} \right)_{\Gamma, N} &= -\frac{2}{3} V^{-5/3} \left( \frac{\Gamma_N}{f(N)} \right)^{2/3N} \\ \Rightarrow p V^{5/3} &= \frac{2}{3} \left( \frac{\Gamma_N}{f(N)} \right)^{2/3N} = \text{const.} \end{aligned}$$

### Solution 1.3.4

#### 1. Equilibrium:

Ideal gases do not possess any interactions. Each state of gas 1 can thus be combined with each state of gas 2  $\Rightarrow$

$$\begin{aligned} \varphi_N(E, V) &= \sum_{E_1} \varphi_{N_1}(E_1, V) \varphi_{N_2}(E - E_1, V) \\ N_1 + N_2 &= N \quad E_1 + E_2 = E \end{aligned}$$

For the phase volume of the ideal gas we have Eq. (1.118) ( $i = 1, 2$ ):

$$\varphi_{N_i}(E_i, V) = \frac{1}{N_i!} \left( \frac{V}{h^3} \right)^{N_i} \frac{\pi^{\frac{3N_i}{2}}}{\left( \frac{3N_i}{2} \right)!} (2m_i E_i)^{\frac{3N_i}{2}}$$

'Equilibrium' ( $E_1 \Rightarrow \widehat{E}_1$ )  $\Leftrightarrow$  maximal summand of the phase volume! As usual it is convenient to investigate the logarithm:

$$\ln(\varphi_{N_1}(E_1, V) \varphi_{N_2}(E - E_1, V)) = \sum_{i=1}^2 \ln \varphi_{N_i}(E_i, V)$$

Stirling formula:

$$\ln \left( \frac{3N_i}{2} \right)! = \frac{3N_i}{2} \left( \ln \frac{3N_i}{2} - 1 \right) \quad \ln N_i! = N_i (\ln N_i - 1)$$

It follows therewith:

$$\begin{aligned} \ln \varphi_{N_i}(E_i, V) &= N_i \left( \ln \left[ \frac{V}{N_i} \left( \frac{4\pi m_i E_i}{3h^2 N_i} \right)^{3/2} \right] + \frac{5}{2} \right) \\ &= N_i \ln \frac{V}{N_i} + \frac{3}{2} N_i \ln \frac{E_i}{N_i} + N_i \ln c_i \end{aligned}$$

For the summand in the total phase volume it can then be written:

$$\begin{aligned} \ln(\varphi_{N_1}(E_1, V)\varphi_{N_2}(E_2, V)) &= N_1 \ln \frac{V}{N_1} + N_2 \ln \frac{V}{N_2} \\ &\quad + \frac{3}{2}N_1 \ln \frac{E_1}{N_1} + \frac{3}{2}N_2 \ln \frac{E - E_1}{N_2} \\ &\quad + N_1 \ln c_1 + N_2 \ln c_2 \end{aligned}$$

'Equilibrium' ( $E_1 \Rightarrow \widehat{E}_1$ )

$$\begin{aligned} 0 &= \frac{\partial}{\partial E_1} \ln(\varphi_{N_1} \cdot \varphi_{N_2}) \\ &= \frac{3}{2}N_1 \frac{1}{\widehat{E}_1} + \frac{3}{2}N_2 \frac{-1}{E - \widehat{E}_1} \\ &= \frac{3}{2} \left( \frac{N_1}{\widehat{E}_1} - \frac{N_2}{\widehat{E}_2} \right) \end{aligned}$$

Equilibrium is thus existent when the energy per particle is same for both gases!

$$\frac{\widehat{E}_1}{N_1} = \frac{\widehat{E}_2}{N_2} \quad \text{with} \quad \widehat{E}_1 + \widehat{E}_2 = E$$

2. Temperatures:

$$\frac{1}{T_i} = \frac{\partial}{\partial E_i} k_B \ln \varphi_{N_i}(E_i, V) \Big|_{E_i=\widehat{E}_i} = \frac{3}{2}N_i k_B \frac{1}{\widehat{E}_i}$$

'Partial gases' at equilibrium (see 1.):

$$T_1 = T_2 \quad \text{with} \quad \widehat{E}_{1,2} = \frac{3}{2}N_{1,2}k_B T_{1,2}$$

Temperature of the 'total gas':

$$\begin{aligned} \frac{1}{T} &= \frac{\partial}{\partial E} k_B \ln(\varphi_{N_1}(E_1, V)\varphi_{N_2}(E - E_1, V)) \Big|_{E_i=\widehat{E}_i} \\ &= \frac{3}{2}N_2 \frac{1}{E - \widehat{E}_1} = \frac{3}{2}N_2 \frac{1}{\widehat{E}_2} \\ &= \frac{1}{T_2} \end{aligned}$$

The temperatures of the 'partial gases' and of the 'total gas' are thus same!

$$T_1 = T_2 = T$$

## 3. Pressures:

It follows with

$$\frac{\widehat{E}_i}{N_i} = \frac{3}{2}k_B T \quad i = 1, 2$$

for the **entropy** of the ‘total system’ at equilibrium:

$$\begin{aligned} S &= k_B \ln(\varphi_{N_1} \cdot \varphi_{N_2}) \\ &= k_B \sum_{i=1}^2 \left( \frac{3N_i}{2} \ln \left( \frac{3}{2}k_B T \right) + N_i \ln \frac{V}{N_i} + N_i \ln c_i \right) \\ &= S_1 + S_2 \end{aligned}$$

**Partial pressures** of the ‘partial gases’:

$$p_i = T \left( \frac{\partial S_i}{\partial V} \right)_{N_i} = k_B T \frac{N_i}{V}$$

The result is the **total pressure** as sum of the partial pressures:

$$p = T \left( \frac{\partial S}{\partial V} \right)_N = k_B T \sum_{i=1}^2 \frac{N_i}{V} = \sum_{i=1}^2 p_i$$

**Solution 1.3.5**

1. We take from Exercise 1.2.6:

$$V = x_0 y_0 ; \quad \alpha = \frac{\alpha^*}{h^{2N}} \quad (1.45)$$

$$\varphi_N(E, V) = \frac{\alpha^*}{N!} \left( \frac{2\pi}{h^2} mV \right)^N E^N$$

$$\begin{aligned} \Gamma_N(E, V) &= \frac{\alpha^*}{N!} \left( \frac{2\pi}{h^2} mV \right)^N [(E + \Delta)^N - E^N] \\ &= \varphi_N(E, V) \left[ \left( 1 + \frac{\Delta}{E} \right)^N - 1 \right]. \end{aligned}$$

With

$$\ln N! \approx N(\ln N - 1)$$



it follows:

$$\begin{aligned}\ln \varphi_N(E, V) &= N \left[ \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} E \right) + 1 \right] + \ln \alpha^* \\ \ln \Gamma_N(E, V) &= \ln \varphi_N(E, V) + \ln \left[ \left( 1 + \frac{\Delta}{E} \right)^N - 1 \right].\end{aligned}$$

Because of  $\Delta \ll E$  it can further be approximated:

$$\ln \left[ \left( 1 + \frac{\Delta}{E} \right)^N - 1 \right] \approx \ln \left( N \frac{\Delta}{E} \right).$$

That means:

$$\ln \Gamma_N(E, V) = \ln \varphi_N(E, V) + \mathcal{O}(\ln N).$$

The equivalence is therewith shown, because  $\ln \varphi_N = \mathcal{O}(N)$  (see above) so that the second summand is negligible for large  $N$  in comparison to the first summand.

2. Temperature:

$$\begin{aligned}T^{-1} &= \left( \frac{\partial S}{\partial E} \right)_{V, N} = k_B N \frac{\partial}{\partial E} \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} E \right) = k_B N \frac{1}{E} \\ \curvearrowright k_B T &= \frac{E}{N}.\end{aligned}$$

Entropy:

$$\begin{aligned}S(E, V, N) &= k_B \ln \varphi_N(E, V) = N k_B \left[ \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} E \right) + 1 \right] + k_B \ln \alpha^* \\ \alpha^* &= \frac{1}{N!}; \quad \ln \alpha^* = -\ln N! \approx -N(\ln N - 1) \\ \curvearrowright S(E, V, N) &= N k_B \left[ \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} \frac{E}{N} \right) + 2 \right] \\ &= N k_B \left[ \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} k_B T \right) + 2 \right] = S(T, V, N).\end{aligned}$$

Free energy:

$$\begin{aligned}F &= U - TS; \quad U = E = N k_B T \\ \curvearrowright F(T, V, N) &= -N k_B T \left[ \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} k_B T \right) + 1 \right].\end{aligned}$$

## 3. Chemical potential:

$$\begin{aligned}\mu &= -T \left( \frac{\partial S}{\partial N} \right)_{E,V} \\ \left( \frac{\partial S}{\partial N} \right)_{E,V} &= k_B \left[ \ln \left( \frac{2\pi}{h^2} m \frac{V E}{N N} \right) + 2 \right] + N k_B N^2 \left( -\frac{2}{N^3} \right) \\ &= k_B \ln \left( \frac{2\pi}{h^2} m \frac{V E}{N N} \right) .\end{aligned}$$

It follows eventually with  $k_B T = E/N$ :

$$\mu(T, V, N) = -k_B T \ln \left( \frac{2\pi}{h^2} m \frac{V}{N} k_B T \right) .$$

This is obviously identical with

$$\mu(T, V, N) = \left( \frac{\partial F}{\partial N} \right)_{T,V} .$$

**Solution 1.3.6**

## 1. Hamilton function:

$$H(\mathbf{q}, \mathbf{p}) = \frac{1}{2m} \sum_{i=1}^N (p_i^2 + m^2 \omega^2 q_i^2) .$$

Phase volume:

$$\varphi_N(E) = \alpha \iint_{H(\mathbf{q}, \mathbf{p}) \leq E} d^N q d^N p; \quad \alpha = \frac{\alpha^*}{h^N} .$$

Transformation of variables:

$$\begin{aligned}x_i &= m\omega q_i \\ \implies H(\mathbf{x}, \mathbf{p}) &= \frac{1}{2m} \sum_{i=1}^N (p_i^2 + x_i^2) , \\ \varphi_N(E) &= \frac{\alpha^*}{(m\omega h)^N} \iint_{H(\mathbf{x}, \mathbf{p}) \leq E} d^N x d^N p .\end{aligned}$$

The multiple integral represents a  $2N$ -dimensional sphere of the radius  $\sqrt{2mE}$ :

$$\varphi_N(E) = \frac{\alpha^*}{(m\omega h)^N} C_{2N} (2mE)^N .$$

It holds thereby according to Exercise 1.3.1:

$$\begin{aligned} C_{2N} &= \frac{\pi^N}{N!} \\ \implies \varphi_N(E) &= \frac{\alpha^*}{N!} \left( \frac{2\pi}{\omega h} \right)^N E^N . \end{aligned}$$

2. Entropy:

$$S = k_B \left\{ \ln \left[ \frac{\alpha^*}{N!} \left( \frac{2\pi}{\omega h} \right)^N \right] + N \ln E \right\} .$$

Temperature:

$$T^{-1} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{Nk_B}{E} \iff E = Nk_B T .$$

### Solution 1.3.7

An *adiabatic* change of state results from an interaction of the system with exclusively *external* parameters. We formally consider them as time-dependent and calculate:

$$\frac{d}{dt} \langle H(\mathbf{q}, \mathbf{p}; \mathbf{z}(t)) \rangle = \frac{d}{dt} \iint d^s q d^s p H(\mathbf{q}, \mathbf{p}; \mathbf{z}(t)) \rho_{mce}(\mathbf{q}, \mathbf{p}; \mathbf{z}(t)) .$$

Exploitation of the Liouville equation (1.34),

$$\frac{d}{dt} \rho_{mce}(\mathbf{q}, \mathbf{p}, t) = 0 ,$$

leads to:

$$\begin{aligned} \frac{d}{dt} \langle H(\mathbf{q}, \mathbf{p}; \mathbf{z}(t)) \rangle &= \iint d^s q d^s p \sum_{i=1}^n \frac{\partial H}{\partial z_i} \dot{z}_i \rho_{mce}(\mathbf{q}, \mathbf{p}, t) \\ &= \sum_{i=1}^n \dot{z}_i \iint d^s q d^s p \frac{\partial H}{\partial z_i} \rho_{mce}(\mathbf{q}, \mathbf{p}, t) = \sum_{i=1}^n \frac{dz_i}{dt} \left\langle \frac{\partial H}{\partial z_i} \right\rangle \\ \implies \langle \dot{U} \rangle_{ad} &= (d\langle H \rangle)_{ad} = \sum_{i=1}^n \left\langle \frac{\partial H}{\partial z_i} \right\rangle dz_i . \end{aligned}$$

### Solution 1.3.8

1. In general it holds:

$$\begin{aligned} d\varphi(E; \mathbf{z}) &= \left( \frac{\partial \varphi}{\partial E} \right)_{\mathbf{z}} dE + \sum_{i=1}^n \left( \frac{\partial \varphi}{\partial z_i} \right)_{E, z_j (j \neq i)} dz_i \\ &= D(E, \mathbf{z}) dE + \sum_{i=1}^n \left( \frac{\partial \varphi}{\partial z_i} \right)_{E, z_j (j \neq i)} dz_i \end{aligned}$$

$D(E, \mathbf{z})$ : density of states (1.50).

We look at the second summand separately:

$$\left( \frac{\partial \varphi}{\partial z_i} \right)_{E, z_j (j \neq i)} = \lim_{\Delta z_i \rightarrow 0} \frac{\alpha}{\Delta z_i} \left[ \iint_{H(z_i + \Delta z_i) \leq E} d^s q d^s p - \iint_{H(z_i) \leq E} d^s q d^s p \right] .$$

Because of

$$H(z_i + \Delta z_i) = H(z_i) + \Delta z_i \frac{\partial H}{\partial z_i} + \dots$$

it further follows:

$$\begin{aligned}
 \left(\frac{\partial\varphi}{\partial z_i}\right)_{E, \mathbf{z}_j (j \neq i)} &= \lim_{\Delta z_i \rightarrow 0} \frac{\alpha}{\Delta z_i} \iint_{E \leq H(\mathbf{z}_i) \leq E - \Delta z_i \frac{\partial H}{\partial z_i}} d^s q d^s p \\
 &\stackrel{(1.54)}{=} \lim_{\Delta z_i \rightarrow 0} \frac{\alpha}{\Delta z_i} \int_{H(\mathbf{z}_i) = E} \frac{df_E}{|\nabla H|} \left(-\Delta z_i \frac{\partial H}{\partial z_i}\right) \\
 &= \alpha \int_{H(\mathbf{z}_i) = E} \frac{df_E}{|\nabla H|} \left(-\frac{\partial H}{\partial z_i}\right) \stackrel{(1.56)}{=} D(E, \mathbf{z}) \left\langle -\frac{\partial H}{\partial z_i} \right\rangle.
 \end{aligned}$$

This means altogether:

$$d\varphi(E; \mathbf{z}) = D(E, \mathbf{z}) \left( dE - \sum_{i=1}^n \left\langle \frac{\partial H}{\partial z_i} \right\rangle dz_i \right).$$

2. *Adiabatic* change of state (see Exercise 1.3.7):

$$dE = (dU)_{ad} = \sum_{i=1}^n \left\langle \frac{\partial H}{\partial z_i} \right\rangle dz_i \implies (d\varphi(E; \mathbf{z}))_{ad} = 0.$$

### Solution 1.3.9

1. Probability to find the momentum component of a particle in the interval  $(p_1; p_1 + dp_1)$ :

$$\begin{aligned}
 w(p_1) dp_1 &= dp_1 \frac{\int d\mathbf{q} \int \cdots \int dp_2 \cdots dp_{3N} \rho(\mathbf{q}, \mathbf{p})}{\iint d\mathbf{q} d\mathbf{p} \rho(\mathbf{q}, \mathbf{p})} \\
 &= dp_1 \frac{V^N \int \cdots \int dp_2 \cdots dp_{3N} \rho(\mathbf{q}, \mathbf{p})}{V^N \int d\mathbf{p} \rho(\mathbf{q}, \mathbf{p})} \\
 &\sim dp_1 \int \cdots \int dp_2 \cdots dp_{3N} \delta \left[ (p_2^2 + \cdots + p_{3N}^2) - (2mE - p_1^2) \right].
 \end{aligned}$$

On the right-hand side we have a volume-integral over the  $(3N - 1)$ -dimensional space with an isotropic integrand. After angle-integration over the  $(3N - 1)$ -dimensional unit sphere we find a contribution  $\sim p^{3N-2}$ , where  $p$  is the absolute value of the vector

$$\mathbf{p} = (p_2, p_3, \dots, p_{3N}).$$

It thus remains to be calculated:

$$w(p_1)dp_1 \sim \Theta(2mE - p_1^2)dp_1 \int_0^\infty dp p^{3N-2} \delta[p^2 - (2mE - p_1^2)].$$

Substitution:

$$y = p^2 - (2mE - p_1^2) \iff p = \sqrt{y + (2mE - p_1^2)},$$

$$dp = \frac{1}{2p} dy,$$

$$\begin{aligned} w(p_1)dp_1 &\sim \Theta(2mE - p_1^2)dp_1 \int_{-(2mE-p_1^2)}^\infty dy [y + (2mE - p_1^2)]^{(3N-3)/2} \delta(y) \\ &= \Theta(2mE - p_1^2)dp_1 (2mE - p_1^2)^{(3N-3)/2}. \end{aligned}$$

$m$  and  $E$  are constant:

$$w(p_1)dp_1 \sim \Theta(2mE - p_1^2)dp_1 \left(1 - \frac{p_1^2}{2mE}\right)^{(3N-3)/2}.$$

$N$  is of the order of magnitude  $10^{22}$ . We can thus confidently neglect in the numerator of the exponent the 3 compared to  $3N$ . The expression in the second bracket is smaller than 1. In order that the right-hand side actually is essentially different from zero in spite of the very large exponent, the value of the bracket by itself must be very close to 1. This means:

$$\frac{p_1^2}{2mE} \ll 1.$$

That permits the estimation:

$$\begin{aligned} 1 - \frac{p_1^2}{2mE} &\approx \exp\left(-\frac{p_1^2}{2mE}\right), \\ \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3N-3}{2}} &\approx \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3N}{2}} \approx \exp\left(-\frac{3N}{2} \frac{p_1^2}{2mE}\right). \end{aligned}$$

We further insert, according to (1.121),  $E = (3/2)Nk_B T$  and then have:

$$w(p_1)dp_1 \sim \Theta(2mE - p_1^2) \exp\left(-\frac{p_1^2}{2mk_B T}\right) dp_1.$$

It follows from that with  $p_1 = mv_1$  'almost' the Maxwell's velocity distribution:

$$w(v_1)dv_1 \sim \Theta\left(\frac{2E}{m} - v_1^2\right) \exp\left(-\frac{mv_1^2}{2k_B T}\right) dv_1 .$$

The 'almost' refers to the step function. The micro-canonical ensemble gives an upper limit for the velocity!—We will, however, disregard this restriction for the next partial solutions.

2. With 1. it also holds:

$$w(\mathbf{v})d^3v = c \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) d^3v .$$

The constant  $c$  follows from the normalization condition:

$$\begin{aligned} 1 &\stackrel{!}{=} \int w(\mathbf{v})d^3v = 4\pi c \int_0^\infty \exp(-\alpha v^2)v^2 dv = 4\pi c \left(-\frac{d}{d\alpha} \int_0^\infty \exp(-\alpha v^2)dv\right) \\ &= -2\pi c \frac{d}{d\alpha} \sqrt{\frac{\pi}{\alpha}} = \pi c \sqrt{\pi} \alpha^{-3/2} \\ &\implies c = \left(\frac{m}{2\pi k_B T}\right)^{3/2} . \end{aligned}$$

The probability distribution of the absolute value of the velocity follows by integration over the angles:

$$w(v)dv = \int_0^{2\pi} d\varphi \int_{-1}^{+1} d \cos \vartheta w(\mathbf{v})v^2 dv = 4\pi c \exp\left(-\frac{mv^2}{2k_B T}\right) v^2 dv .$$

3. Most probable absolute value of the velocity:

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{d}{dv} w(v) = 4\pi c \exp\left(-\frac{mv^2}{2k_B T}\right) \left(2v - 2v^3 \frac{m}{2k_B T}\right) \\ &\implies v_{\max} = \sqrt{\frac{2k_B T}{m}} . \end{aligned}$$

4. Mean values:

$$\langle v_x \rangle = \int v_x w(\mathbf{v})d^3v$$

$$v_x = v \sin \vartheta \cos \varphi ,$$

$$\langle v_x \rangle = c \int_0^\infty \exp\left(-\frac{mv^2}{2k_B T}\right) v^3 dv \int_0^{2\pi} d\varphi \cos \varphi \int_0^\pi d\vartheta \sin^2 \vartheta = 0$$

$$\text{because of } \int_0^{2\pi} d\varphi \cos \varphi = 0.$$

Analogously the other components:

$$\langle v_y \rangle = \langle v_z \rangle = 0$$

$\implies \langle \mathbf{v} \rangle = 0$ : isotropic velocity distribution.

Average absolute value of the velocity:

$$\begin{aligned} \langle v \rangle &= \int_0^\infty w(v) v dv = 4\pi c \int_0^\infty v^3 \exp(-\alpha v^2) dv \\ &= 4\pi c \left[ -\frac{d}{d\alpha} \int_0^\infty v \exp(-\alpha v^2) dv \right] \\ &= 4\pi c \left\{ -\frac{d}{d\alpha} \left[ -\frac{1}{2\alpha} \int_0^\infty \frac{d}{dv} \exp(-\alpha v^2) dv \right] \right\} \\ &= -4\pi c \frac{d}{d\alpha} \frac{1}{2\alpha} = 2\pi c \frac{1}{\alpha^2} = 2\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \left( \frac{2k_B T}{m} \right)^2 \\ &\implies \langle v \rangle = 2\sqrt{\frac{2k_B T}{\pi m}} = \frac{2}{\sqrt{\pi}} v_{\max}. \end{aligned}$$

Average square of velocity:

$$\begin{aligned} \langle v^2 \rangle &= \int_0^\infty w(v) v^4 dv = 4\pi c \int_0^\infty v^4 \exp(-\alpha v^2) dv \\ &= 4\pi c \frac{d^2}{d\alpha^2} \int_0^\infty \exp(-\alpha v^2) dv \\ &= 4\pi c \frac{d^2}{d\alpha^2} \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} = 2\pi^{3/2} c \frac{3}{4} \alpha^{-5/2} \end{aligned}$$



$$= \frac{3}{2}\pi^{3/2} \left( \frac{m}{2\pi k_B T} \right)^{3/2} \left( \frac{2k_B T}{m} \right)^{5/2} = 3 \frac{k_B T}{m}$$

$$\implies \sqrt{\langle \mathbf{v}^2 \rangle} = \sqrt{3 \frac{k_B T}{m}} = \sqrt{\frac{3}{2}} v_{\max}.$$

Comparison:

$$v_{\max} : \langle v \rangle : \sqrt{\langle \mathbf{v}^2 \rangle} = 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}} \approx 1 : 1.13 : 1.22.$$

### Solution 1.3.10

Taylor expansion for  $f(E)$ :

$$\begin{aligned} f(E) &= f(E_0) + f'(E_0)(E - E_0) + \dots \\ &= E_0^N + N E_0^{N-1}(E - E_0) + \dots \end{aligned}$$

Ratio of the first two terms:

$$\Delta = \frac{N E_0^{N-1}(E - E_0)}{E_0^N} = N \frac{E - E_0}{E_0}$$

Requirement:

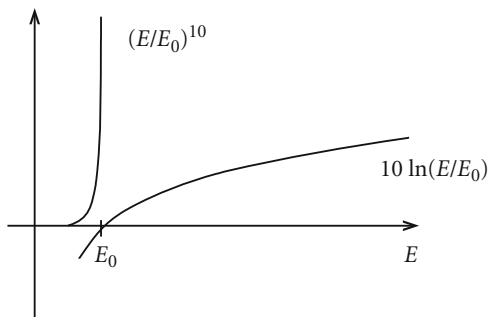
$$\Delta \ll 1 \iff \frac{\Delta E}{E_0} \ll \frac{1}{N}$$

i.e. for  $N = \mathcal{O}(10^{23})$ : extremely small region of convergence, Taylor expansion presumably unusable!

On the other hand, Taylor expansion for  $\ln f(E)$ :

$$\begin{aligned} \ln f(E) &= \ln f(E_0) + (E - E_0) \frac{f'(E_0)}{f(E_0)} + \dots \\ &= N \ln E_0 + (E - E_0) \frac{N E_0^{N-1}}{E_0^N} + \dots \\ &= N \ln E_0 + (E - E_0) \frac{N}{E_0} + \dots \\ \implies \Delta &= \frac{E - E_0}{E_0 \ln E_0} \end{aligned}$$

Fig. A.5



Requirement:

$$\Delta \ll 1 \iff \frac{\Delta E}{E_0} \ll \ln E_0 \sim \ln N ,$$

i.e., the Taylor expansion is now possibly useful. The behavior of the logarithm remains even for  $10^{23}$  'moderate' (Fig. A.5).

Discussion: In Statistical Physics one has to often deal with functions of the type  $E^N$  with  $N = \mathcal{O}(10^{23})$ , as for instance the phase volume of the micro-canonical ensemble  $\Gamma_N(E, V)$ . Necessary discussions of curves are therefore in general performed with the 'better-behaved' function  $\ln f(E)$ .

### Solution 1.3.11

The density of states was defined in (1.50):

$$D_N(E, V) = \frac{d}{dE} \varphi_N(E, V) .$$

The phase volume  $\varphi_N(E, V)$  of the ideal gas was calculated in (1.118):

$$D_N(E, V) = \frac{1}{N!} \left( \frac{V}{h^3} \right)^N \frac{\pi^{3N/2}}{\left( \frac{3N}{2} \right)!} \frac{3N}{2} (2m)^{3N/2} E^{(3N/2)-1} .$$

It holds for the temperature:

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial S}{\partial E} \right)_{N,V} = \frac{k_B}{D_N(E, V)} \left( \frac{\partial}{\partial E} D_N(E, V) \right)_{N,V} = k_B \frac{1}{E} \left( \frac{3N}{2} - 1 \right) \\ &\implies k_B T = \frac{E}{\frac{3N}{2} - 1} . \end{aligned}$$

This is to be compared with (1.121):

$$k_B T = \frac{E}{\frac{3N}{2}}.$$

For  $N \rightarrow \infty$  the expressions are equivalent! On the other hand, it obviously does not make sense to define a temperature for systems with only a few degrees of freedom.

## Section 1.4.5

### Solution 1.4.1

Hamilton function:

$$H(q, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2.$$

According to (1.136) it is to be calculated:

$$\begin{aligned} Z &= \frac{1}{h^1 1!} \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} dp e^{-\beta H(q, p)} \\ &= \frac{1}{h} \underbrace{\int_{-\infty}^{+\infty} q e^{-\frac{\beta}{2} m \omega^2 q^2} dq}_{\sqrt{\frac{2\pi}{\beta m \omega^2}}} \underbrace{\int_{-\infty}^{+\infty} dp e^{-\beta \frac{p^2}{2m}}}_{\sqrt{\frac{2\pi m}{\beta}}} \\ &= \frac{1}{h} \frac{2\pi}{\beta \omega} = \frac{k_B T}{\hbar \omega}. \end{aligned}$$

### Solution 1.4.2

Ideal gas in the gravitational field:

$$H = \sum_{i=1}^N \left( \frac{\mathbf{p}_i^2}{2m} + mgz_i \right).$$

1. Average kinetic energy:

$$\begin{aligned} \langle t \rangle &= \frac{\iint d^{3N} q d^{3N} p \frac{\mathbf{p}_1^2}{2m} e^{-\beta H(\mathbf{q}, \mathbf{p})}}{\iint d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})}} \\ &= \frac{1}{2m} \frac{\int d^3 p_1 \mathbf{p}_1^2 \exp\left(-\beta \frac{\mathbf{p}_1^2}{2m}\right)}{\int d^3 p_1 \exp\left(-\beta \frac{\mathbf{p}_1^2}{2m}\right)} = \frac{1}{2m} \frac{\int_0^\infty dp_1 p_1^4 \exp\left(-\beta \frac{p_1^2}{2m}\right)}{\int_0^\infty dp_1 p_1^2 \exp\left(-\beta \frac{p_1^2}{2m}\right)}. \end{aligned}$$

Formulary:

$$\int_0^\infty dx x^n e^{-\alpha x^2} = \frac{1}{2} \alpha^{-\frac{n+1}{2}} \Gamma\left(\frac{n+1}{2}\right)$$

$$\implies \langle t \rangle = \frac{1}{2m} \frac{\frac{1}{2} \left(\frac{2m}{\beta}\right)^{5/2} \Gamma\left(\frac{5}{2}\right)}{\frac{1}{2} \left(\frac{2m}{\beta}\right)^{3/2} \Gamma\left(\frac{3}{2}\right)},$$

$$\Gamma(x+1) = x\Gamma(x); \quad \Gamma(1) = 1; \quad \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}.$$

Average kinetic energy per particle:

$$\langle t \rangle = \frac{3}{2} k_B T.$$

We found the same result with the micro-canonical ensemble (1.113).

2.

$$\begin{aligned} \langle v \rangle &= \frac{\iint d^{3N} q d^{3N} p mgz_1 e^{-\beta H(\mathbf{q}, \mathbf{p})}}{\iint d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})}} = mg \frac{\int_0^\infty dz_1 z_1 e^{-\beta mgz_1}}{\int_0^\infty dz_1 e^{-\beta mgz_1}} \\ &= -\frac{d}{d\beta} \ln \int_0^\infty dz_1 e^{-\beta mgz_1} = -\frac{d}{d\beta} \ln \left( +\frac{1}{\beta mg} \right) = -\beta mg \left( -\frac{1}{mg\beta^2} \right). \end{aligned}$$

Average potential energy per particle:

$$\langle v \rangle = \frac{1}{\beta} = k_B T .$$

### Solution 1.4.3

1. No interactions between the molecules

$$Z_N(T, V) = \frac{1}{h^{6N}(2N)!} \left\{ \int \cdots \int d^3 p_1 d^3 p_2 d^3 r_1 d^3 r_2 e^{-\beta H_0} \right\}^N .$$

The momentum-integrations can be immediately performed (1.137):

$$\int d^3 p \exp\left(-\beta \frac{\mathbf{p}^2}{2m}\right) = (2\pi m k_B T)^{3/2} .$$

It remains to be calculated for the partition function:

$$Z_N(T, V) = \frac{(2\pi m k_B T)^{3N}}{h^{6N}(2N)!} Q_\alpha^N(T),$$

$$Q_\alpha(T) = \iint d^3 r_1 d^3 r_2 \exp\left(-\beta \frac{\alpha}{2} |\mathbf{r}_1 - \mathbf{r}_2|^2\right) .$$

Center of gravity coordinates and relative coordinates:

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) ; \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 ,$$

$$dr_x dR_x = \frac{\partial(r_x, R_x)}{\partial(r_{1x}, r_{2x})} dr_{1x} dr_{2x} = \begin{vmatrix} 1 & -1 \\ \frac{1}{2} & \frac{1}{2} \end{vmatrix} dr_{1x} dr_{2x} .$$

Analogously the other components:

$$d^3 r d^3 R = d^3 r_1 d^3 r_2$$

$$\implies Q_\alpha(T) = \iint d^3 R d^3 r \exp\left(-\beta \frac{\alpha}{2} r^2\right) = V 4\pi \int_0^\infty dr r^2 \exp\left(-\beta \frac{\alpha}{2} r^2\right)$$

$$= 4\pi V \left(\frac{2}{\beta\alpha}\right)^{3/2} \frac{1}{2} \Gamma\left(\frac{3}{2}\right) = V \left(\frac{2}{\beta\alpha}\right)^{3/2} \pi^{3/2} .$$

Partition function:

$$\begin{aligned} Z_N(T, V) &= \frac{(2\pi mk_B T)^{3N}}{h^{6N} (2N)!} V^N \left( \frac{2\pi k_B T}{\alpha} \right)^{3N/2} \\ &= c_N V^N (k_B T)^{9N/2} . \end{aligned}$$

2. Free energy:

$$\begin{aligned} F(T, V, N) &= -k_B T \ln Z_N(T, V) \\ &= -k_B T \left( \ln c_N + N \ln V + \frac{9N}{2} \ln k_B T \right) . \end{aligned}$$

Pressure:

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T, N} = k_B T \frac{N}{V} .$$

⇒ Equation of state of the ideal gas:

$$pV = Nk_B T .$$

3. Internal energy:

$$\begin{aligned} U &= - \frac{\partial}{\partial \beta} \ln Z_N(T, V) = - \frac{\partial}{\partial \beta} \left( \ln c_N + N \ln V - \frac{9N}{2} \ln \beta \right) \\ &= \frac{9N}{2} \frac{1}{\beta} = \frac{9N}{2} k_B T . \end{aligned}$$

Heat capacity:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V, N} = \frac{9}{2} N k_B .$$

4.

$$\langle |\mathbf{r}_1 - \mathbf{r}_2|^2 \rangle = \frac{\iint d^3 r_1 d^3 r_2 |\mathbf{r}_1 - \mathbf{r}_2|^2 \exp \left( -\beta \frac{\alpha}{2} |\mathbf{r}_1 - \mathbf{r}_2|^2 \right)}{\iint d^3 r_1 d^3 r_2 \exp \left( -\beta \frac{\alpha}{2} |\mathbf{r}_1 - \mathbf{r}_2|^2 \right)} .$$

All the other factors cancel each other:

$$\begin{aligned} \Rightarrow \langle r^2 \rangle &= -\frac{2}{\alpha} \frac{\partial}{\partial \beta} \ln \left[ \iiint d^3 r_1 d^3 r_2 \exp \left( -\beta \frac{\alpha}{2} |\mathbf{r}_1 - \mathbf{r}_2|^2 \right) \right] \stackrel{!}{=} -\frac{2}{\alpha} \frac{\partial}{\partial \beta} \ln Q_\alpha(T) \\ &= -\frac{2}{\alpha} \frac{\partial}{\partial \beta} \ln \left[ V \left( \frac{2}{\beta \alpha} \right)^{3/2} \pi^{3/2} \right] = -\frac{2}{\alpha} \left( -\frac{3}{2} \right) \frac{1}{\beta} \\ \Rightarrow \langle r^2 \rangle &= \frac{3}{\alpha} k_B T . \end{aligned}$$

### Solution 1.4.4

1. For the partition function of the ideal gas it holds according to (1.138):

$$\begin{aligned} Z_N(T, V) &= \frac{V^N}{\lambda^{3N}(T) N!} , \\ \lambda(T) &= \frac{h}{\sqrt{2\pi m k_B T}} . \end{aligned}$$

Free energy:

$$F(T, V, N) = -k_B T \left[ N \ln V - 3N \ln \lambda(T) - N (\ln N - 1) \right] .$$

We have thereby applied the Stirling formula:

$$\ln N! \approx N (\ln N - 1) .$$

2. Entropy:

$$\begin{aligned} S(T, V, N) &= - \left( \frac{\partial F}{\partial T} \right)_{V, N} \\ &= k_B N \left\{ \ln \left[ \frac{V}{N} \frac{(2\pi m k_B T)^{3/2}}{h^3} \right] + 1 \right\} - 3N k_B T \frac{1}{\lambda(T)} \frac{\lambda(T)}{dT} . \end{aligned}$$

with

$$\frac{1}{\lambda(T)} \frac{d\lambda(T)}{dT} = -\frac{1}{2} \frac{1}{T}$$

follows the Sackur-Tetrode equation:

$$S(T, V, N) = Nk_B \left\{ \ln \left[ \frac{V}{N} \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\},$$

if one inserts  $E = \frac{3}{2}Nk_B T$  (1.121) into (1.124).

3. Thermal equation of state:

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T, N} = Nk_B T \frac{1}{V}$$

$$\implies pV = Nk_B T.$$

### Solution 1.4.5

1. This is nothing else but the representation (1.138) of the partition function:

$$Z_N(T, V) = Z_0(T) \frac{1}{V^N} \int_V d^{3N} q e^{-\beta \widehat{V}(\mathbf{q})}.$$

$Z_0(T)$  is the partition function of the non-interacting system:

$$Z_0(T) = (N! \lambda^{3N}(T))^{-1} V^N,$$

$$\lambda(T) = \frac{h}{\sqrt{2\pi mk_B T}} \quad (\text{thermal de Broglie wave length}),$$

$$Z_N(T, V) = Z_0(T) \frac{1}{V^N} \int \cdots \int d^3 r_1 \cdots d^3 r_N \exp \left[ -\beta \sum_{i < j} \widehat{V}(|\mathbf{r}_i - \mathbf{r}_j|) \right].$$

2.  $\widehat{V}$  is a repulsive pair potential and therewith positive. This has the consequence:

$$0 \leq \exp \left( -\beta \widehat{V}(|\mathbf{r}_i - \mathbf{r}_j|) \right) \leq 1 \quad \forall i, j.$$

Therewith

$$f(|\mathbf{r}_i - \mathbf{r}_j|) \quad \text{negative with} \quad |f(|\mathbf{r}_i - \mathbf{r}_j|)| \leq 1.$$



An expansion in products of the functions  $f(|\mathbf{r}_i - \mathbf{r}_j|)$  thus appears reasonable, since the products become smaller with increasing order.

$$\begin{aligned} \exp\left(-\beta \sum_{i<j} \widehat{V}(|\mathbf{r}_i - \mathbf{r}_j|)\right) &= \prod_{i<j} \exp\left(-\beta \widehat{V}(|\mathbf{r}_i - \mathbf{r}_j|)\right) \\ &= \prod_{i<j} \left(1 + f(|\mathbf{r}_i - \mathbf{r}_j|)\right) \\ &= 1 + \sum_{i<j} f(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i<j} \sum_{k<l} f(|\mathbf{r}_i - \mathbf{r}_j|) f(|\mathbf{r}_k - \mathbf{r}_l|) + \dots \\ &\quad (i,j) \neq (k,l). \end{aligned}$$

3.

$$\begin{aligned} \int \dots \int d^3 r_1 \dots d^3 r_N f(|\mathbf{r}_i - \mathbf{r}_j|) &= \int \dots \int d^3 r_1 \dots d^3 r_{i-1} d^3 r_{i+1} \dots d^3 r_N A, \\ A &= \int d^3 r_i f(|\mathbf{r}_i - \mathbf{r}_j|) = \int d^3 r_i f(|\mathbf{r}_i|) = 2a_1(T). \end{aligned}$$

It follows:

$$\begin{aligned} \int \dots \int d^3 r_1 \dots d^3 r_N \sum_{i<j} f(|\mathbf{r}_i - \mathbf{r}_j|) &= 2a_1(T) \frac{1}{2} N(N-1) V^{N-1} \\ &\approx a_1(T) N^2 V^{N-1}, \quad \text{because } N \gg 1. \end{aligned}$$

As to the second term of the expansion we have to distinguish whether all the four indexes are pairwise different;  $i \neq j \neq k \neq l$ ,

$$\begin{aligned} \int \dots \int d^3 r_1 \dots d^3 r_N \sum_{i<j} \sum_{k<l} f(|\mathbf{r}_i - \mathbf{r}_j|) f(|\mathbf{r}_k - \mathbf{r}_l|) \\ &= V^{N-2} \frac{1}{2} N(N-1) \frac{1}{2} (N-2)(N-3) (2a_1(T))^2 \\ &\approx V^{N-2} N^4 (a_1(T))^2 = V^{N-2} N^4 a_2(T), \end{aligned}$$

or whether two of the indexes are the same;  $i = k, j \neq l$ :

$$\begin{aligned} \int \dots \int d^3 r_1 \dots d^3 r_N \sum_{i<j} \sum_{i<l} f(|\mathbf{r}_i - \mathbf{r}_j|) f(|\mathbf{r}_i - \mathbf{r}_l|) \\ &= V^{N-2} \frac{1}{3!} N(N-1)(N-2) (2a_1(T))^2 \sim \frac{2}{3} N^3 V^{N-2} a_2(T). \end{aligned}$$

This term is by the factor  $N$  smaller than the above summand, and can therefore, because of  $N \gg 1$ , confidently be neglected. It thus remains for the expansion of part 1.:

$$\begin{aligned} Z_N(T, V) &= \frac{Z_0(T)}{V^N} (V^N + a_1(T)N^2V^{N-1} + a_2(T)V^{N-2}N^4 + \dots) \\ &= Z_0(T) \left( 1 + \frac{N^2}{V} a_1(T) + \frac{N^4}{V^2} a_2(T) + \dots \right) \end{aligned}$$

4.

$$\begin{aligned} a_1(T) &= \frac{1}{2} \int d^3r f(r) = 2\pi \int_0^\infty dr r^2 \left[ \exp\left(-\frac{\beta\alpha}{r^n}\right) - 1 \right] \\ &= 2\pi \left\{ \frac{1}{3} r^3 \left[ \exp\left(-\frac{\beta\alpha}{r^n}\right) - 1 \right] \right\}_0^\infty - \frac{2\pi}{3} \int_0^\infty dr r^3 \left[ \frac{n\beta\alpha}{r^{n+1}} \exp\left(-\frac{\beta\alpha}{r^n}\right) \right] \\ &= -\frac{2\pi}{3} n\beta\alpha \int_0^\infty dr \frac{1}{r^{n-2}} \exp\left(-\frac{\beta\alpha}{r^n}\right). \end{aligned}$$

Substitution:

$$\begin{aligned} \frac{\beta\alpha}{r^n} = x &\iff r = \left(\frac{\beta\alpha}{x}\right)^{1/n}, \\ \frac{dx}{dr} &= -n \frac{\beta\alpha}{r^{n+1}} = -n \frac{x}{r} \\ \implies a_1(T) &= +\frac{2\pi}{3} \int_\infty^0 dx r^3 e^{-x} = -\frac{2\pi}{3} (\beta\alpha)^{3/n} \int_0^\infty dx x^{-3/n} e^{-x} \\ &= -\frac{2\pi}{3} (\beta\alpha)^{3/n} \int_0^\infty dx x^{[(n-3)/n-1]} e^{-x}. \end{aligned}$$

Gamma function:

$$\Gamma(t) = \int_0^{\infty} dx x^{t-1} e^{-x}$$

$$\implies a_1(T) = -\frac{2\pi}{3} (\beta\alpha)^{3/n} \Gamma\left(\frac{n-3}{n}\right),$$

$$a_2(T) = (a_1(T))^2.$$

### Solution 1.4.6

1. Energy of the magnetic dipole in the magnetic field ((3.52), Vol. 3):

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}$$

$$\implies H_1 = -\mu B \sum_{i=1}^N \cos \vartheta_i,$$

$\vartheta_i$ : angle between the field  $\mathbf{B}$  and the  
magnetic moment  $\boldsymbol{\mu}_i$  of the  $i$ -th atom.

2.

$$Z_N(T, B) = \frac{1}{h^{3N} N!} \iint d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})}$$

$$= \frac{Z_N^{(0)}(T)}{(4\pi)^N} (2\pi)^N \int_{-1}^{+1} \cdots \int_{-1}^{+1} d \cos \vartheta_1 \cdots d \cos \vartheta_N \exp\left(+\beta \mu B \sum_{i=1}^N \cos \vartheta_i\right)$$

$$= Z_N^{(0)}(T) \left[ \frac{1}{2} \int_{-1}^{+1} dx e^{\beta \mu B x} \right]^N$$

$$= Z_N^{(0)}(T) \left[ \frac{1}{2\beta \mu B} (e^{\beta \mu B} - e^{-\beta \mu B}) \right]^N,$$

$Z_N^{(0)}(T)$  : partition function without magnetic field,

$$Z_N(T, B) = Z_N^{(0)}(T) \left( \frac{\sinh \beta \mu B}{\beta \mu B} \right)^N.$$

3.

$$\mathbf{m} = \frac{\iint d^{3N}q d^{3N}p \left( \sum_{i=1}^N \boldsymbol{\mu}_i \right) e^{-\beta H(\mathbf{q}, \mathbf{p})}}{\iint d^{3N}q d^{3N}p e^{-\beta H(\mathbf{q}, \mathbf{p})}},$$

$$\boldsymbol{\mu}_i = \mu (\sin \vartheta_i \cos \varphi_i, \sin \vartheta_i \sin \varphi_i, \cos \vartheta_i).$$

Because of the  $\varphi_i$ -integration:

$$m_x = m_y = 0; \quad \mathbf{m} = m_z \mathbf{e}_z,$$

$$m_z = \frac{d}{d(\beta B)} \ln Z_N(T, B).$$

It follows with the partition function from 2.:

$$m_z = N \left( \frac{d}{dx} (\ln \sinh \mu x - \ln \mu x) \right) (x = \beta B)$$

$$= N \mu \left( \frac{\cosh \mu x}{\sinh \mu x} - \frac{1}{\mu x} \right) (x = \beta B)$$

$$\implies \mathbf{m} = N \mu \left( \coth(\beta \mu B) - \frac{1}{\beta \mu B} \right) \mathbf{e}_z$$

*(classical Langevin paramagnetism)*

4.  $\beta \mu B \gg 1$  Low temperatures, strong fields.

$$\coth(\beta \mu B) \rightarrow 1; \quad \frac{1}{\beta \mu B} \rightarrow 0 \quad \implies \mathbf{m} \approx N \mu \mathbf{e}_z$$

*saturation:* all moments parallel.

$\beta \mu B \ll 1$  High temperatures, weak fields.

$$\coth x = \frac{1}{x} + \frac{x}{3} + \mathcal{O}(x^3) \quad (x^2 < \pi^2)$$

$$\implies \mathbf{m} \approx N \mu \left( \frac{1}{3} \frac{\mu B}{k_B T} \right) \mathbf{e}_z \quad (\text{Curie law}).$$

**Solution 1.4.7**

$$\left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle = \frac{\int \dots \int \pi_i \frac{\partial H}{\partial \pi_j} e^{-\beta H(\mathbf{q}, \mathbf{p})} dq_1 \dots dp_{3N}}{\int \dots \int e^{-\beta H(\mathbf{q}, \mathbf{p})} dq_1 \dots dp_{3N}}.$$

We investigate the *partial integral*:

$$\begin{aligned} \int \pi_i \frac{\partial H}{\partial \pi_j} e^{-\beta H(\mathbf{q}, \mathbf{p})} d\pi_j &= -\frac{1}{\beta} \int \pi_i \frac{\partial}{\partial \pi_j} (e^{-\beta H(\mathbf{q}, \mathbf{p})}) d\pi_j \\ &= -\frac{1}{\beta} (\pi_i e^{-\beta H(\mathbf{q}, \mathbf{p})}) \Big|_{\dots}^{\dots} + \frac{1}{\beta} \int \frac{\partial \pi_i}{\partial \pi_j} e^{-\beta H(\mathbf{q}, \mathbf{p})} d\pi_j. \end{aligned}$$

The integrated part vanishes. If  $\pi_j$  is the Cartesian component of a particle momentum, then the limits of integration are  $\pm\infty$ , the kinetic energy thus becomes infinite and  $e^{-\beta H}$  vanishes. If  $\pi_j$  is a position coordinate, then the potential energy becomes infinite at the edges of the volume (*wall*):

$$\int \pi_i \frac{\partial H}{\partial \pi_j} e^{-\beta H(\mathbf{q}, \mathbf{p})} d\pi_j = \frac{\delta_{ij}}{\beta} \int e^{-\beta H(\mathbf{q}, \mathbf{p})} d\pi_j.$$

It follows therewith the equipartition theorem:

$$\left\langle \pi_i \frac{\partial H}{\partial \pi_j} \right\rangle = \delta_{ij} k_B T.$$

**Solution 1.4.8**

Hamilton function:

$$H = H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^N \frac{1}{2m} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) + \alpha \sum_{i=1}^N (q_{ix}^4 + q_{iy}^4 + q_{iz}^4)$$

**Canonical Partition Function**

$$Z_N(T, V) = \frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})} = P_N(T) \cdot Q_N(T)$$

with  $P_N(T)$ ,  $Q_N(T)$ : momentum integrations and space integrations, respectively:

$$\begin{aligned}
 P_N(T) &= \frac{1}{h^{3N}N!} \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} dp_1 \cdots dp_{3N} \exp\left(-\frac{\beta}{2m}(p_1^2 + \cdots + p_{3N}^2)\right) \\
 &= \frac{1}{h^{3N}N!} \left( \int_{-\infty}^{+\infty} dp_i \exp\left(-\frac{\beta}{2m}p_i^2\right) \right)^{3N} \\
 &= \frac{1}{h^{3N}N!} \left( \sqrt{\frac{2m\pi}{\beta}} \right)^{3N} \\
 &= \frac{1}{\lambda^{3N}(T)N!}
 \end{aligned}$$

with  $\lambda(T) = \frac{h}{\sqrt{2\pi mk_B T}}$ : *thermal de Broglie wave length*

Space integration ( $V \rightarrow \infty$ ):

$$\begin{aligned}
 Q_N(T) &= \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} dq_1 \cdots dq_{3N} \exp(-\beta\alpha(q_1^4 + \cdots + q_{3N}^4)) \\
 &= \left( \int_{-\infty}^{+\infty} dq_i \exp(-\beta\alpha q_i^4) \right)^{3N}
 \end{aligned}$$

We define

$$\begin{aligned}
 f(\beta\alpha) &= \int_{-\infty}^{+\infty} dq \exp(-\beta\alpha q^4) = \int_{-\infty}^{+\infty} \frac{dy}{2\sqrt{y}} e^{-\beta\alpha y^2} \\
 \implies (f(\beta\alpha))^2 &= \frac{1}{4} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{dx dy}{\sqrt{xy}} \exp(-\beta\alpha(x^2 + y^2))
 \end{aligned}$$

Plane polar coordinates:

$$x = r \cos \varphi ; y = r \sin \varphi$$

Therewith:

$$(f(\beta\alpha))^2 = \frac{1}{4} \int_0^\pi d\varphi \int_0^\infty r dr \frac{1}{r\sqrt{\cos\varphi \sin\varphi}} \exp(-\beta\alpha r^2)$$

The  $\varphi$ -integration yields a constant which is unimportant for the following:

$$C = \frac{1}{4} \int_0^\pi \frac{d\varphi}{\sqrt{\cos\varphi \sin\varphi}} \implies (f(\beta\alpha))^2 = C \int_0^\infty dr e^{-\beta\alpha r^2} = C \cdot \sqrt{\frac{\pi}{\beta\alpha}}$$

$$\implies Q_N(T) = C^{3N/2} \cdot \left(\frac{\pi}{\beta\alpha}\right)^{3N/4}$$

It follows for the partition function:

$$\begin{aligned} Z_N(T) &= \frac{1}{h^{3N} N!} \left(\frac{2m\pi}{\beta}\right)^{3N/2} C^{3N/2} \left(\frac{\pi}{\beta\alpha}\right)^{3N/4} \\ &= \frac{C^{3N/2}}{h^{3N} N!} \left(\frac{4m^2\pi^3}{\alpha}\right)^{3N/4} \cdot \beta^{-9N/4} \end{aligned}$$

### **Internal Energy**

$$\begin{aligned} U = \langle H \rangle &= \frac{\int \dots \int d^{3N}q d^{3N}p H(\mathbf{q}, \mathbf{p}) e^{-\beta H(\mathbf{q}, \mathbf{p})}}{\int \dots \int d^{3N}q d^{3N}p e^{-\beta H(\mathbf{q}, \mathbf{p})}} \\ &= -\frac{\partial}{\partial \beta} \ln Z_N(T) \end{aligned}$$

With the abbreviation

$$g_N(\alpha) = \frac{C^{3N/2}}{h^{3N} N!} \left(\frac{4m^2\pi^3}{\alpha}\right)^{3N/4}$$

it follows

$$\begin{aligned} \ln Z_N &= \ln g_N(\alpha) - \frac{9N}{4} \ln \beta \\ U &= \frac{9N}{4} \frac{1}{\beta} = \frac{9N}{4} k_B T. \end{aligned}$$

## Entropy

$$\begin{aligned}
 S &= - \left( \frac{\partial F}{\partial T} \right)_{N,V} \\
 F &= -k_B T \ln Z_N(T) \\
 &= -k_B T \ln g_N(\alpha) - \frac{9N}{4} k_B T \ln(k_B T) \\
 \implies S(T) &= k_B \ln g_N(\alpha) + \frac{9N}{4} k_B (\ln(k_B T) + 1) \\
 &= S_0 + \frac{9N}{4} k_B \ln T
 \end{aligned}$$

### Solution 1.4.9

1.  $H$ : Hamilton function of the particle system in the magnetic field  $\mathbf{B}$ :

$$\langle \mathbf{m} \rangle = \frac{\iint d^{3N} q d^{3N} p \mathbf{m} e^{-\beta H(\mathbf{q}, \mathbf{p})}}{\iint d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})}} = \frac{1}{\beta Z_N} \nabla_{\mathbf{B}} Z_N .$$

$\mathbf{B} = \text{curl} \mathbf{A}$ ;  $\mathbf{A} = \mathbf{A}(\mathbf{r})$ : vector potential.

Hamilton function of the charged particles in the magnetic field ((2.39), Vol. 2):

$$H = \sum_{j=1}^N \frac{1}{2m_j} (\mathbf{p}_j - \bar{q}_j \mathbf{A}(\mathbf{q}_j))^2 + H_1(\mathbf{q}) .$$

Partition function:

$$\begin{aligned}
 Z_N(T) &= \frac{1}{N! h^{3N}} \int \cdots \int d^3 q_1 \cdots d^3 q_N \exp(-\beta H_1(\mathbf{q})) \\
 &\quad \cdot \prod_{j=1}^N \int d^3 p_j \exp \left[ -\frac{\beta}{2m_j} (\mathbf{p}_j - \bar{q}_j \mathbf{A}(\mathbf{q}_j))^2 \right] .
 \end{aligned}$$

2. Substitution:

$$\mathbf{u}_j \equiv \mathbf{p}_j - \bar{q}_j \mathbf{A}(\mathbf{q}_j) .$$



The limits of integration do not change:

$$\int d^3 p_j \cdots = \iiint_{-\infty}^{+\infty} dp_{jx} dp_{jy} dp_{jz} \cdots = \iiint_{-\infty}^{+\infty} du_{jx} du_{jy} du_{jz} \cdots = \int d^3 u_j \cdots .$$

The partition function can thus also be written as follows:

$$Z_N(T, V) = \frac{1}{N! h^{3N}} \int \cdots \int d^3 q_1 \cdots d^3 q_N \exp(-\beta H_1(\mathbf{q})) \\ \cdot \prod_{j=1}^N \int d^3 u_j \exp\left(-\frac{\beta}{2m_j} \mathbf{u}_j^2\right) .$$

$Z_N$  is obviously field-independent in spite of  $\mathbf{B} \neq 0$ :

$$Z_N \neq Z_N(\mathbf{B}) \iff \nabla_{\mathbf{B}} Z_N \equiv 0 .$$

This means according to part 1.:

$$\langle \mathbf{m} \rangle \equiv 0 .$$

This result corresponds to the so-called *Bohr-van Leeuwen theorem*:

*Magnetism is a quantum-mechanical effect. Strictly classically the resulting magnetic moment is always zero!*

### Solution 1.4.10

Because of the absence of interactions the Hamilton function factorizes:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{j=1}^N H_j(\mathbf{q}_j, \mathbf{p}_j) = \sum_{j=1}^N \left( \frac{1}{2m_j} \mathbf{p}_j^2 + \widehat{V}(\mathbf{q}_j) \right) .$$

According to (1.134)

$$\rho(\mathbf{q}, \mathbf{p}) = \frac{\exp(-\beta H(\mathbf{q}, \mathbf{p}))}{\iint d^{3N} q d^{3N} p \exp(-\beta H(\mathbf{q}, \mathbf{p}))}$$

is the normalized probability that the total system is at the temperature  $T$  in the phase  $\pi = (\mathbf{q}, \mathbf{p})$ . We are only interested in the  $i$ -th particle:

$$\rho_i(\mathbf{q}_i, \mathbf{p}_i) = \int \cdots \int \prod_{j \neq i} d^3 q_j d^3 p_j \rho(\mathbf{q}, \mathbf{p}) = \frac{\exp(-\beta H_i(\mathbf{q}_i, \mathbf{p}_i))}{\iint d^3 q_i d^3 p_i \exp(-\beta H_i(\mathbf{q}_i, \mathbf{p}_i))}.$$

It is asked for the momentum distribution in the gas:

$$\bar{w}(\mathbf{p}_i) \equiv \int d^3 q_i \rho_i(\mathbf{q}_i, \mathbf{p}_i) = \frac{\exp\left(-\beta \frac{\mathbf{p}_i^2}{2m}\right)}{\int d^3 p_i \exp\left(-\beta \frac{\mathbf{p}_i^2}{2m}\right)}.$$

The normalization integral was already calculated for (1.137). The probability that a gas particle possesses a momentum in the element  $d^3 p$  at  $\mathbf{p}$ , reads, when we from now on suppress the index  $i$ :

$$\bar{w}(\mathbf{p}) d^3 p = (2\pi m k_B T)^{-\frac{3}{2}} \exp\left(-\frac{\mathbf{p}^2}{2m k_B T}\right) d^3 p.$$

Because of the one-to-one relationship between particle momentum and particle velocity it must hold:

$$\bar{w}(\mathbf{p}) d^3 p \stackrel{!}{=} w(\mathbf{v}) d^3 v$$

Maxwell's velocity distribution is therewith proven:

$$w(\mathbf{v}) d^3 v = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) d^3 v.$$

### **Solution 1.4.11**

1. Velocity distribution of the gas atoms according to Exercise 1.4.10:

$$w(\mathbf{v}) d^3 v = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m\mathbf{v}^2}{2k_B T}\right) d^3 v.$$

We need here the distribution of the  $z$ -components of the velocities:

$$\begin{aligned}
 & w(v_z)dv_z \\
 = & \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y w(\mathbf{v})dv_z \\
 = & \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv_z^2}{2k_B T}\right) dv_z \int_{-\infty}^{+\infty} dv_x \exp\left(-\frac{mv_x^2}{2k_B T}\right) \int_{-\infty}^{+\infty} dv_y \exp\left(-\frac{mv_y^2}{2k_B T}\right) \\
 = & \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_z^2}{2k_B T}\right) dv_z .
 \end{aligned}$$

Doppler effect: energy or frequency change by a moving radiation source:

$$E = E_0 \left(1 + \frac{v_z}{c}\right) , c = \text{velocity of light.}$$

Average energy of the observed light:

$$\langle E \rangle = E_0 \left(1 + \frac{\langle v_z \rangle}{c}\right) .$$

It holds:

$$\langle v_z \rangle = \int_{-\infty}^{+\infty} v_z w(v_z) dv_z \sim \int_{-\infty}^{+\infty} v_z \exp\left(-\frac{mv_z^2}{2k_B T}\right) dv_z = 0 \implies \langle E \rangle = E_0 .$$

2.

$$\begin{aligned}
 E - \langle E \rangle &= E_0 \left(1 + \frac{v_z}{c}\right) - E_0 = \frac{E_0}{c} v_z \\
 \implies \langle \Delta E \rangle &= \frac{E_0}{c} \sqrt{\langle v_z^2 \rangle} ,
 \end{aligned}$$

$$\begin{aligned}
 & \int_{-\infty}^{+\infty} dv_z v_z^2 \exp\left(-\frac{mv_z^2}{2k_B T}\right) = -2k_B T \frac{d}{dm} \int_{-\infty}^{+\infty} dv_z \exp\left(-\frac{mv_z^2}{2k_B T}\right) \\
 &= -2k_B T \frac{d}{dm} \left(\frac{2\pi k_B T}{m}\right)^{1/2} = (2\pi)^{1/2} (k_B T)^{3/2} m^{-3/2} \\
 \implies \langle v_z^2 \rangle &= \int_{-\infty}^{+\infty} dv_z v_z^2 w(v_z) = \frac{k_B T}{m} .
 \end{aligned}$$

This corresponds to the equipartition theorem (see Exercise 1.4.7)!

$$\overline{(\Delta E)} = \frac{E_0}{c} \sqrt{\frac{k_B T}{m}}.$$

3.  $I(E)dE$ : Probability to observe a light energy from the interval  $(E; E + dE)$ .  
Because of the bi-unique relation between  $E$  and  $v_z$  we have:

$$\begin{aligned} I(E)dE &\stackrel{!}{=} w(v_z)dv_z, \\ v_z &= \frac{c}{E_0}(E - E_0) \implies dv_z = \frac{c}{E_0}dE \\ \implies I(E)dE &= \left(\frac{m}{2k_B T}\right)^{1/2} \exp\left(-\frac{mc^2}{2k_B T} \frac{(E - E_0)^2}{E_0^2}\right) \frac{c}{E_0}dE. \end{aligned}$$

### Solution 1.4.12

1. The velocities of the gas atoms obey a Maxwell distribution at the temperature  $T$ . A particle of the velocity

$$\mathbf{v} = (v_x, v_y, v_z) \quad (v_z > 0)$$

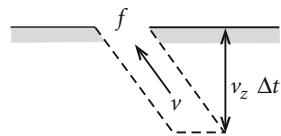
reaches within the time  $\Delta t$  the hole if it is at the beginning in the inclined cylinder sketched in Fig. A.6. This cylinder contains

$$\frac{N}{V}(fv_z\Delta t)$$

particles, each possesses with the probability  $w(\mathbf{v})d^3v$  the respective velocity. In the time  $\Delta t$

$$\frac{N}{V}(fv_z\Delta t)w(\mathbf{v})d^3v$$

Fig. A.6



particles with a velocity in the *volume element*  $d^3v$  at  $\mathbf{v}$  pass the hole. We obtain the total number of all atoms, which escape through the hole, by summing over all velocities which come into question:

$$\begin{aligned} -\frac{\Delta N}{\Delta t} &= \frac{N}{V} f \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_0^{+\infty} dv_z v_z w(\mathbf{v}) \\ &= \frac{N}{V} f \int_0^{\infty} dv_z A.6) v_z w(v_z) . \end{aligned}$$

Because of the finite dimensions of the container, this expression is of course not completely correct. As an example, the height  $v_z \Delta t$  of the inclined cylinder (Fig. A.6) can of course not be larger than  $L_z$ . Furthermore,  $|v_x|$  and  $|v_y|$  can actually not become arbitrarily large, if the cylinder has to completely fit into the container. However, since the velocity components  $v_x$ ,  $v_y$ ,  $v_z$  take care, in the form of  $\exp(-\alpha(v_x^2 + v_y^2 + v_z^2))$ , for a rapid decline of the Maxwell distribution  $w(\mathbf{v})$ , we make surely only an unimportant mistake, when we choose as limits of integration  $\pm\infty$  for  $v_x$  and  $v_y$ , and correspondingly permit arbitrarily large **positive**  $v_z$ -values. - We have calculated the Maxwell distribution  $w(v_z)$  in Exercise 1.4.11. With  $\Delta t \rightarrow dt$  it remains to be calculated:

$$\begin{aligned} -\frac{dN}{dt} &= \frac{N}{V} f \left( \frac{m}{2\pi k_B T} \right)^{1/2} \int_0^{\infty} dv_z v_z \exp\left(-\frac{mv_z^2}{2k_B T}\right) \\ &= -\frac{N}{V} f \left( \frac{m}{2\pi k_B T} \right)^{1/2} \frac{k_B T}{m} \int_0^{\infty} dv_z \frac{d}{dv_z} \exp\left(-\frac{mv_z^2}{2k_B T}\right) \\ \implies -\frac{dN}{dt} &= f \frac{N}{V} \left( \frac{k_B T}{2\pi m} \right)^{1/2} . \end{aligned}$$

2. Integration of the above differential equation:

$$\frac{N}{N_0} = \exp \left[ -\frac{f}{V} \left( \frac{k_B T}{2\pi m} \right)^{1/2} (t - t_0) \right] .$$

Ideal gas:  $pV = Nk_B T$

$$T, V \text{ fixed} \implies \frac{p}{p_0} = \frac{N}{N_0},$$

$$\frac{p}{p_0} = e^{-1} \implies t_e - t_0 = \frac{V}{f} \left( \frac{2\pi m}{k_B T} \right)^{1/2}.$$

3. We decompose the kinetic energy as follows:

$$\langle T \rangle = \langle T_x \rangle + \langle T_y \rangle + \langle T_z \rangle,$$

$$\langle T_{x,y,z} \rangle = \frac{1}{2} m \langle v_{x,y,z}^2 \rangle.$$

The  $x$ - and  $y$ -contributions inside and outside the container are the same, and it holds according to the equipartition theorem ((1.113) and Exercise 1.4.7):

$$\langle T_x \rangle_{out,in} = \langle T_y \rangle_{out,in} = \frac{1}{2} k_B T.$$

The  $z$ -contribution is, however, different. According to part 1. it holds outside:

$$\langle v_z^2 \rangle_{out} = \frac{\int_0^\infty dv_z v_z^2 w(v_z) \frac{1}{V} f v_z \Delta t}{\int_0^\infty dv_z w(v_z) \frac{1}{V} f v_z \Delta t} = \frac{\int_0^\infty dv_z v_z^3 \exp\left(-\frac{mv_z^2}{2k_B T}\right)}{\int_0^\infty dv_z v_z \exp\left(-\frac{mv_z^2}{2k_B T}\right)},$$

$$\int_0^\infty dv v^3 e^{-\alpha v^2} = -\frac{1}{2\alpha} \int_0^\infty dv v^2 \frac{d}{dv} e^{-\alpha v^2} = \frac{1}{\alpha} \int_0^\infty dv v e^{-\alpha v^2},$$

$$\implies \langle v_z^2 \rangle_{out} = \frac{2k_B T}{m} \implies \langle T_z \rangle_{out} = k_B T.$$

It is therefore:

$$\langle T \rangle_{out} = 2k_B T; \quad \langle T \rangle_{in} = \frac{3}{2} k_B T \iff \frac{\langle T \rangle_{out}}{\langle T \rangle_{in}} = \frac{4}{3}.$$

**Solution 1.4.13**

1. Particle density:  $n(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle$

$$\begin{aligned} n(\mathbf{r}) &= \frac{\int \cdots \int d^3 r_1 \cdots d^3 r_N d^3 p_1 \cdots d^3 p_N \left( \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right) e^{-\beta H}}{\int \cdots \int d^3 r_1 \cdots d^3 r_N d^3 p_1 \cdots d^3 p_N e^{-\beta H}} \\ &= \frac{\int \cdots \int d^3 r_1 \cdots d^3 r_N \left( \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right) \exp \left( -\beta \sum_{i=1}^N v(\mathbf{r}_i) \right)}{\int \cdots \int d^3 r_1 \cdots d^3 r_N \exp \left( -\beta \sum_{i=1}^N v(\mathbf{r}_i) \right)} \\ &= N \frac{\int d^3 r_1 \delta(\mathbf{r} - \mathbf{r}_1) \exp \left( -\beta v(\mathbf{r}_1) \right)}{\int d^3 r_1 \exp \left( -\beta v(\mathbf{r}_1) \right)} \end{aligned}$$

$\implies$  Barometric equation

$$n(\mathbf{r}) = N \frac{\exp \left( -\beta v(\mathbf{r}) \right)}{\int d^3 r_1 \exp \left( -\beta v(\mathbf{r}_1) \right)} .$$

2. Gravitational field:  $v(\mathbf{r}) = v(z) = mgz$  ( $z$ -axis vertically upwards!)

$$\implies n(\mathbf{r}) = n(z) = c \exp(-\beta mgz) = n(0) \exp(-\beta mgz) .$$

Pressure of the ideal gas:

$$p(z) = n(z) k_B T$$

$$\implies p(z) = p(0) \exp(-\beta mgz) .$$

**Solution 1.4.14**

1. Ideal gas:

$$H(\mathbf{q}, \mathbf{p}) = \sum_{i=1}^N T_i(\mathbf{p}_i) .$$

Relativistic one-particle energies ((2.63), Vol. 4):

$$T_i(\mathbf{p}_i) = \sqrt{c^2 \mathbf{p}_i^2 + m^2 c^2} \xrightarrow{m=0} cp_i .$$

Partition function:

$$\begin{aligned} Z_N(T, V) &= \frac{1}{N! h^{3N}} \iint d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})} = \frac{V^N}{N! h^{3N}} \left( \int d^3 p e^{-\beta cp} \right)^N , \\ \int d^3 p e^{-\beta cp} &= 4\pi \int_0^\infty dp p^2 e^{-\beta cp} = \frac{4\pi}{(\beta c)^3} \int_0^\infty dx x^2 e^{-x} = \frac{4\pi}{(\beta c)^3} \Gamma(3) = \frac{8\pi}{(\beta c)^3} \\ \implies Z_N(T, V) &= \frac{1}{N!} \left[ \frac{8\pi V}{(\beta ch)^3} \right]^N . \end{aligned}$$

2. Internal energy (1.141):

$$U = -\frac{\partial}{\partial \beta} \ln Z_N = 3N \frac{1}{\beta} \implies U(T, V, N) = 3Nk_B T .$$

3. Pressure  $p$  (1.142):

$$\begin{aligned} p &= \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z_N = \frac{1}{\beta} \frac{N}{V} \\ \implies p &= \frac{N}{V} k_B T = \frac{1}{3} \frac{U}{V} \end{aligned}$$

(Attention:  $\frac{1}{3} \frac{U}{V}$  instead of  $\frac{2}{3} \frac{U}{V}$  as in the non-relativistic case).

4. Free energy (1.144):

$$F(T, V, N) = -\frac{1}{\beta} \ln Z_N = -Nk_B T \left[ \ln \left( \frac{8\pi V}{(ch)^3} \right) + 3 \ln k_B T - \ln N + 1 \right] .$$

Thereby we have used the Stirling formula

$$\ln N! = N (\ln N - 1) .$$

We check:

$$-\left( \frac{\partial F}{\partial V} \right)_{T, N} = +Nk_B T \frac{1}{V} \stackrel{3.}{=} p .$$

5. Enthalpy:  $H = U + pV = 4Nk_B T$ .



6. Entropy:

$$S(T, V, N) = \frac{1}{T}(U - F) = Nk_B \left( \ln \frac{V}{N} + \ln \frac{8\pi}{(ch)^3} + 3 \ln k_B T + 4 \right) = - \left( \frac{\partial F}{\partial T} \right)_{V, N} .$$

7. Heat capacities:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_{p, N} = 4Nk_B ,$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V, N} = 3Nk_B .$$

### Solution 1.4.15

$$Z_N(T, V) = \frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p e^{-\beta H(\mathbf{q}, \mathbf{p})} = \exp(-\beta F(T, V, N))$$

$$H = H_0 + H_1$$

$$\implies \exp(-\beta F) = \frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p \exp(-\beta H_0) \left( 1 - \beta H_1 + \frac{1}{2!} \beta^2 H_1^2 + \dots \right) .$$

For the free system one has:

$$\exp(-\beta F_0) = \frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p e^{-\beta H_0} .$$

Averages in the free system:

$$\begin{aligned} \langle A \rangle^{(0)} &= \frac{\int \dots \int d^{3N} q d^{3N} p A(\mathbf{q}, \mathbf{p}) e^{-\beta H_0(\mathbf{q}, \mathbf{p})}}{\int \dots \int d^{3N} q d^{3N} p e^{-\beta H_0(\mathbf{q}, \mathbf{p})}} \\ &= e^{+\beta F_0} \frac{1}{h^{3N} N!} \int \dots \int d^{3N} q d^{3N} p A(\mathbf{q}, \mathbf{p}) e^{-\beta H_0} . \end{aligned}$$

This is used in  $e^{-\beta F}$ :

$$\begin{aligned} \exp(-\beta F) &= \exp(-\beta F_0) - \beta \langle H_1 \rangle^{(0)} e^{-\beta F_0} + \frac{1}{2} \beta^2 \langle H_1^2 \rangle^{(0)} e^{-\beta F_0} + \dots \\ &= \exp(-\beta F_0) \left\{ 1 - \beta \langle H_1 \rangle^{(0)} + \frac{1}{2} \beta^2 \langle H_1^2 \rangle^{(0)} + \dots \right\} . \end{aligned}$$

It thus holds ( $\ln(1 \pm x) \approx \pm x - (1/2)x^2$ ):

$$\begin{aligned} -\beta F &= -\beta F_0 + \ln \left\{ 1 - \beta \langle H_1 \rangle^{(0)} + \frac{1}{2} \beta^2 \langle H_1^2 \rangle^{(0)} + \dots \right\} \\ &\approx -\beta F_0 - \beta \langle H_1 \rangle^{(0)} + \frac{1}{2} \beta^2 \left( \langle H_1^2 \rangle^{(0)} - \langle H_1 \rangle^{(0)2} \right) \\ \implies F(T, V, N) &= F_0(T, V, N) + \langle H_1 \rangle^{(0)} - \frac{1}{2} \beta \left( \langle H_1^2 \rangle^{(0)} - \langle H_1 \rangle^{(0)2} \right). \end{aligned}$$

Compare this expression with the quantum-mechanical result (2.126).

## Section 1.5.4

### Solution 1.5.1

1. Canonical partition function for  $N$  noninteracting particles in the volume  $V$  according to (1.138):

$$\begin{aligned} Z_N^{(0)}(T, V) &= \frac{V^N}{\lambda^{3N}(T)N!}, \\ \lambda(T) &= \frac{h}{\sqrt{2\pi m k_B T}}. \end{aligned}$$

Grand-canonical partition function (1.159):

$$\Xi_\mu^{(0)}(T, V) = \sum_{N=0}^{\infty} z_0^N \frac{V^N}{\lambda^{3N}(T)N!} = \exp\left(z_0 \frac{V}{\lambda^3(T)}\right); \quad z_0 = e^{\beta\mu_0}.$$

2. Grand-canonical potential:

$$\begin{aligned} -pV &= \Omega(T, V, \mu_0) = -k_B T \ln \Xi_\mu^{(0)}(T, V) = -k_B T \left( z_0 \frac{V}{\lambda^3} \right) \\ &= -k_B T \frac{1}{\beta} \frac{\partial}{\partial \mu_0} \left( z_0 \frac{V}{\lambda^3} \right) = -k_B T \frac{1}{\beta} \left( \frac{\partial}{\partial \mu_0} \ln \Xi_\mu^{(0)}(T, V) \right)_{T, V} \\ &\stackrel{(1.168)}{=} -k_B T \langle N \rangle \\ \implies pV &= \langle N \rangle k_B T. \end{aligned}$$

## 3. Fugacity, chemical potential

$$\begin{aligned}
 z_0 \frac{V}{\lambda^3} &= \ln \Xi_{\mu}^{(0)} \stackrel{2}{=} \langle N \rangle, \\
 \beta \mu_0 &= \ln z_0 = \ln \left( \frac{\langle N \rangle \lambda^3}{V} \right), \\
 \mu_0 &= k_B T \ln \left( \langle N \rangle h^3 / V (2\pi m k_B T)^{3/2} \right) \\
 &= k_B T \ln \left( \frac{p h^3}{(k_B T)^{5/2} (2\pi m)^{3/2}} \right) = \mu_0(T, p).
 \end{aligned}$$

## 4. According to (1.167):

$$\begin{aligned}
 w_N(T, V) &= \frac{z_0^N Z_N^{(0)}(T, V)}{\Xi_{\mu_0}(T, V)}; \quad \Xi_{\mu}^{(0)}(T, V) \stackrel{1,3}{=} \exp(\langle N \rangle) \\
 \Rightarrow w_N(T, V) &= e^{-\langle N \rangle} \left( \langle N \rangle^N \frac{\lambda^{3N}}{V^N} \right) \frac{V^N}{\lambda^{3N} N!} \\
 &= e^{-\langle N \rangle} \frac{\langle N \rangle^N}{N!} \\
 &\quad \text{Poisson distribution.}
 \end{aligned}$$

**Solution 1.5.2**

Free energy according to (1.181):

$$\begin{aligned}
 F(T, V, \langle N \rangle) &= \mu \langle N \rangle - k_B T \ln \Xi_{\mu}(T, V) \\
 \text{with } \mu &= \mu(T, V, \langle N \rangle).
 \end{aligned}$$

It follows:

$$\begin{aligned}
 \left( \frac{\partial F}{\partial \langle N \rangle} \right)_{T, V} &= \mu + \left( \frac{\partial \mu}{\partial \langle N \rangle} \right)_{T, V} \langle N \rangle - k_B T \left( \frac{\partial}{\partial \mu} \ln \Xi_{\mu}(T, V) \right)_{T, V} \left( \frac{\partial \mu}{\partial \langle N \rangle} \right)_{T, V} \\
 &\stackrel{(1.168)}{=} \mu + \left( \frac{\partial \mu}{\partial \langle N \rangle} \right)_{T, V} \langle N \rangle - \langle N \rangle \left( \frac{\partial \mu}{\partial \langle N \rangle} \right)_{T, V} = \mu(T, V, \langle N \rangle)
 \end{aligned}$$

**Solution 1.5.3**

Entropy as a function of  $T, V, \mu$ :

$$S(T, V, \mu) \stackrel{(1.177)}{=} - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} \stackrel{(1.178)}{=} k_B \left[ \ln \Xi_\mu(T, V) + T \left( \frac{\partial}{\partial T} \ln \Xi_\mu \right)_{V, \mu} \right].$$

Exercise 1.5.1  $\implies$

$$\Xi_\mu(T, V) = \exp \left( z \frac{V}{\lambda^3} \right); \quad z = e^{\beta \mu}.$$

With

$$\frac{\partial \lambda}{\partial T} = -\frac{1}{2} \frac{\lambda}{T}; \quad \frac{\partial z}{\partial T} = \mu z \left( -\frac{\beta}{T} \right)$$

it follows:

$$S(T, V, \mu) = k_B \left( z \frac{V}{\lambda^3} + \frac{1}{2} T z \frac{3V}{\lambda^4} \frac{\lambda}{T} - T \frac{V}{\lambda^3} \mu z \frac{\beta}{T} \right) = k_B \frac{zV}{\lambda^3} \left[ \frac{5}{2} - \beta \mu \right].$$

We take from Exercise 1.5.1

$$\mu(T, V, \langle N \rangle) = k_B T \ln \left( \frac{\langle N \rangle \lambda^3}{V} \right)$$

and insert it into the above equation:

$$S(T, V, \langle N \rangle) = k_B \langle N \rangle \left[ \frac{5}{2} + \ln \left( \frac{V}{\langle N \rangle \lambda^3} \right) \right].$$

That exactly agrees with the Sackur-Tetrode equation, if one identifies the ensemble average  $\langle N \rangle$  with the thermodynamic state variable 'particle number'.

**Solution 1.5.4**

1. Hamilton function:

$$H_{\sum N_i}(\mathbf{q}, \mathbf{p}) \equiv H_{\sum N_i}(\boldsymbol{\pi}_1, \boldsymbol{\pi}_2, \dots, \boldsymbol{\pi}_n) \quad \boldsymbol{\pi}_i = (\mathbf{q}_i, \mathbf{p}_i).$$

We have to take into consideration that only the interchange of particles of one and the same component **does not lead** to a new state. That modifies the factor of

the *correct Boltzmann counting* as for the phase volume  $\Gamma(E)$  in (1.130). It thus holds for the expectation value (1.162) of a phase-space observable:

$$\langle F \rangle = \frac{1}{\Xi_{\{\mu_l\}}(T, V)} \sum_{N_1=0}^{\infty} \cdots \sum_{N_n=0}^{\infty} \frac{1}{\prod_{i=1}^n h^{3N_i} N_i!} \\ \cdot \int \cdots \int \prod_{i=1}^n d^{3N_i} q_i d^{3N_i} p_i \exp \left[ -\beta \left( H_{\Sigma N_l}(\mathbf{q}, \mathbf{p}) - \sum_l \mu_l N_l \right) \right] F_{\Sigma N_l}(\mathbf{q}, \mathbf{p}).$$

If one uses this formula especially for  $F = \mathbb{1}$ , then it follows:

$$\Xi_{\{\mu_l\}}(T, V) = \sum_{N_1=0}^{\infty} \cdots \sum_{N_n=0}^{\infty} \frac{1}{\prod_{i=1}^n h^{3N_i} N_i!} \int \cdots \int \prod_{i=1}^n d^{3N_i} q_i d^{3N_i} p_i \\ \cdot \exp \left[ \beta \left( H_{\Sigma N_l}(\mathbf{q}, \mathbf{p}) - \sum_{l=1}^n \mu_l N_l \right) \right].$$

2. In the case of missing interaction between the components:

$$H_{\Sigma N_l}(\mathbf{q}, \mathbf{p}) = \sum_{l=1}^n H_{N_l}(\mathbf{q}_l, \mathbf{p}_l).$$

It is clear therewith that the partition function factorizes:

$$\Xi_{\{\mu_l\}}(T, V) = \prod_{l=1}^n \Xi_{\mu_l}(T, V), \\ \Xi_{\mu_l}(T, V) = \sum_{N_l=0}^{\infty} \frac{1}{h^{3N_l} N_l!} \iint d^{3N_l} q_l d^{3N_l} p_l \exp \left[ -\beta (H_{N_l}(\mathbf{q}_l, \mathbf{p}_l) - \mu_l N_l) \right].$$

3. Partial results can be taken from Exercise 1.5.1:

$$\Xi_{\mu_r}^{(0)}(T, V) = \exp \left( z_r \frac{V}{\lambda_r^3(T)} \right), \\ \lambda_r(T) = \frac{h}{\sqrt{2\pi m_r k_B T}}; \quad z_r = e^{\beta \mu_r}.$$

This means:

$$\Xi_{\{\mu_r\}}^{(0)}(T, V) = \exp \left[ V \sum_{r=1}^n \frac{e^{\beta \mu_r}}{\lambda_r^3(T)} \right] = \exp \left[ \sum_{r=1}^n \langle N_r \rangle \right].$$

4.

$$\frac{pV}{k_B T} = \ln \Xi_{\{\mu_r\}}^{(0)}(T, V) = \sum_{r=1}^N \langle N_r \rangle, \quad pV = k_B T \sum_{r=1}^n \langle N_r \rangle .$$

**Solution 1.5.6**

At first it follows with the *chain rule* ((1.237), Vol. 1):

$$\begin{aligned} \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} &= - \left( \frac{\partial V}{\partial \mu} \right)_{T,\langle N \rangle} \left( \frac{\partial \langle N \rangle}{\partial V} \right)_{T,\mu} \\ &= - \left( \frac{\partial V}{\partial p} \right)_{T,\langle N \rangle} \left( \frac{\partial p}{\partial \mu} \right)_{T,\langle N \rangle} \left( \frac{\partial \langle N \rangle}{\partial V} \right)_{T,\mu} . \end{aligned}$$

From (1.177) one reads off the following Maxwell relation of the grand-canonical potential:

$$\left( \frac{\partial \langle N \rangle}{\partial V} \right)_{T,\mu} = \left( \frac{\partial p}{\partial \mu} \right)_{T,V} .$$

Intermediate result:

$$\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = - \left( \frac{\partial V}{\partial p} \right)_{T,\langle N \rangle} \left( \frac{\partial p}{\partial \mu} \right)_{T,\langle N \rangle} \left( \frac{\partial p}{\partial \mu} \right)_{T,V} .$$

For the grand-canonical potential a *homogeneity relation* is valid as for the other thermodynamic potentials (see section 3.3, Vol. 4):

$$\Omega(T, \lambda V, \mu) = \lambda \Omega(T, V, \mu) \quad \lambda \in \mathbb{R} .$$

This also means:

$$p(T, \lambda V, \mu)(\lambda V) = \lambda p(T, V, \mu)V .$$

Hence it must be for arbitrary real  $\lambda$

$$p(T, \lambda V, \mu) = p(T, V, \mu) .$$

$p$  is therefore only dependent on  $T$  and  $\mu$ :

$$p = p(T, \mu)$$

(see (1.193) for the special case of the ideal gas). Therewith it is formally of course also valid

$$\left(\frac{\partial p}{\partial \mu}\right)_{T, \langle N \rangle} = \left(\frac{\partial p}{\partial \mu}\right)_{T, V}.$$

The indexings  $\langle N \rangle$  and  $V$  are redundant. The above *intermediate result* therewith yields already the assertion addressed by the exercise.

### Solution 1.5.6

1. Grand-canonical partition function according to (1.159):

$$\Xi_z(T, V) = \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} \iint d^{3N} q d^{3N} p e^{-\beta H_N(\mathbf{q}, \mathbf{p})}.$$

It then holds obviously according to (1.162):

$$\begin{aligned} \langle H \rangle &= -\frac{1}{\Xi_z} \left( \frac{\partial}{\partial \beta} \Xi_z(T, V) \right)_{z, V} = - \left( \frac{\partial}{\partial \beta} \ln \Xi_z(T, V) \right)_{z, V}, \\ \langle H^2 \rangle &= \frac{1}{\Xi_z} \left( \frac{\partial^2}{\partial \beta^2} \Xi_z(T, V) \right)_{z, V}. \end{aligned}$$

It results the energy fluctuation:

$$\begin{aligned} \langle (H - \langle H \rangle)^2 \rangle &= \langle H^2 \rangle - \langle H \rangle^2 \\ &= \frac{1}{\Xi_z} \left( \frac{\partial^2}{\partial \beta^2} \Xi_z(T, V) \right)_{z, V} - \frac{1}{\Xi_z^2} \left( \frac{\partial}{\partial \beta} \Xi_z(T, V) \right)_{z, V}^2 \\ &= \left( \frac{\partial^2}{\partial \beta^2} \ln \Xi_z(T, V) \right)_{z, V}. \end{aligned}$$

It thus holds:

$$\langle (\Delta E)_r \rangle = \left( \frac{\left( \frac{\partial^2}{\partial \beta^2} \ln \Xi_z(T, V) \right)_{z, V}}{\left[ \left( \frac{\partial}{\partial \beta} \ln \Xi_z(T, V) \right)_{z, V} \right]^2} \right)^{1/2}.$$

2. Ideal gas (see solution of Exercise 1.5.1):

$$\ln \Xi_z(T, V) = \frac{zV}{\lambda^3(T)} = \langle N \rangle, \quad (1.137): \quad \lambda = \alpha\beta^{1/2}$$

$$\implies \langle H \rangle = \frac{3}{2} \langle N \rangle k_B T = \frac{3}{2} \langle N \rangle \frac{1}{\beta}.$$

Furthermore:

$$\left( \frac{\partial^2}{\partial \beta^2} \ln \Xi_z(T, V) \right)_{z, V} = \frac{15}{4} \frac{zV}{\lambda^3} \frac{1}{\beta^2} = \frac{15}{4} \langle N \rangle \frac{1}{\beta^2}$$

$$\implies (\overline{\Delta E})_r = \left( \frac{5}{3} \frac{1}{\langle N \rangle} \right)^{1/2}.$$

## Section 2.1.3

### Solution 2.1.1

1.  $\{|\varphi_n\rangle\}$ : CON-system

$$\text{Tr} \widehat{F}^+ = \sum_n \langle \varphi_n | \widehat{F}^+ | \varphi_n \rangle = \sum_n (\langle \varphi_n | \widehat{F} | \varphi_n \rangle)^* = (\text{Tr} \widehat{F})^*.$$

2. That follows directly from:

$$\langle \varphi_n | (\alpha \widehat{F} + \beta \widehat{G}) | \varphi_n \rangle = \alpha \langle \varphi_n | \widehat{F} | \varphi_n \rangle + \beta \langle \varphi_n | \widehat{G} | \varphi_n \rangle.$$

3.

$$\begin{aligned} \text{Tr}(\widehat{F}^+ \widehat{F}) &= \sum_n \langle \varphi_n | \widehat{F}^+ \widehat{F} | \varphi_n \rangle = \sum_{n,m} \langle \varphi_n | \widehat{F}^+ | \varphi_m \rangle \langle \varphi_m | \widehat{F} | \varphi_n \rangle \\ &= \sum_{n,m} |\langle \varphi_m | \widehat{F} | \varphi_n \rangle|^2 \geq 0. \end{aligned}$$

4. It holds for two operators:

$$\begin{aligned} \text{Tr}(\widehat{F} \widehat{G}) &= \sum_n \langle \varphi_n | \widehat{F} \widehat{G} | \varphi_n \rangle = \sum_{n,m} \langle \varphi_n | \widehat{F} | \varphi_m \rangle \langle \varphi_m | \widehat{G} | \varphi_n \rangle \\ &= \sum_{n,m} \langle \varphi_m | \widehat{G} | \varphi_n \rangle \langle \varphi_n | \widehat{F} | \varphi_m \rangle = \sum_m \langle \varphi_m | \widehat{G} \widehat{F} | \varphi_m \rangle = \text{Tr}(\widehat{G} \widehat{F}). \end{aligned}$$



The assertion follows immediately from this cyclic invariance, for instance:

$$\text{Tr}(\widehat{F}(\widehat{G}\widehat{H})) = \text{Tr}((\widehat{G}\widehat{H})\widehat{F}) .$$

$$5. \widehat{U}\widehat{U}^+ = \widehat{U}^+\widehat{U} = \mathbf{1} .$$

We use the *cyclic invariance* of the trace, proven in part 4.:

$$\text{Tr}(\widehat{U}^+\widehat{F}\widehat{U}) = \text{Tr}(\widehat{F}\widehat{U}\widehat{U}^+) = \text{Tr}(\widehat{F}\mathbb{1}) = \text{Tr}\widehat{F} .$$

### Solution 2.1.2

$$\hat{\rho} = \sum_m p_m |\psi_m\rangle\langle\psi_m|; \quad \langle\psi_m | \psi_m\rangle = 1 ,$$

$$\{|\psi_m\rangle\} \text{ not orthogonal}; \quad \sum_m p_m = 1 .$$

1.  $\hat{\rho}$  Hermitian, because the projector  $|\psi_m\rangle\langle\psi_m|$  is Hermitian, and all the  $p_m$  are real.
2.  $\{|\bar{\varphi}_i\rangle\}$  basis of the Hilbert space:

$$\text{Tr}\hat{\rho} = \sum_m p_m \sum_i \langle\bar{\varphi}_i | \psi_m\rangle\langle\psi_m | \bar{\varphi}_i\rangle = \sum_m p_m \langle\psi_m | \psi_m\rangle = \sum_m p_m = 1 .$$

3.  $\hat{\rho}$  is also now non-negative:

$$\langle\varphi | \hat{\rho} | \varphi\rangle = \sum_m p_m |\langle\varphi | \psi_m\rangle|^2 \geq 0$$

for arbitrary  $|\varphi\rangle$ .

- 4.

$$\hat{\rho}|\rho_n\rangle = \rho_n|\rho_n\rangle .$$

Because of 1. the  $|\rho_n\rangle$  are orthonormal. The eigen-values  $\rho_n$  are real, and according to 3., even non-negative. Furthermore, because of 2.:

$$\sum_n \rho_n = 1 .$$

Spectral decomposition:

$$\hat{\rho} = \sum_n \rho_n |\rho_n\rangle\langle\rho_n| .$$

The presumption (2.2) for the statistical operator is actually redundant.

**Solution 2.1.3**

$$\rho^2 = \alpha^2 \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 3 \\ 1 & 2 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 2 & 1 \\ 0 & 0 & 3 \\ 1 & 2 & 1 \end{pmatrix} = \alpha^2 \begin{pmatrix} 2 & \dots & \dots \\ \dots & 6 & \dots \\ \dots & \dots & 8 \end{pmatrix}$$

This means:

$$\text{Sp } \rho^2 = \alpha^2 \cdot 16$$

For  $\alpha = 1/4$   $\rho$  thus describes a pure state!

**Section 2.2.3****Solution 2.2.1**

Micro-canonical ensemble (2.17):

$$p_m = \begin{cases} \frac{1}{\Gamma(E)}, & \text{if } E < E_m < E + \Delta \\ 0, & \text{otherwise.} \end{cases}$$

Phase volume, partition function:

$$\Gamma(E) = \sum_{m}^{E < E_m < E + \Delta} 1.$$

Entropy and phase volume (2.20):

$$S(E) = k_B \ln \Gamma(E) \quad \curvearrowright \quad \Gamma(E) = \exp\left(\frac{S}{k_B}\right).$$

Free energy in the micro-canonical ensemble:

$$F = U - TS = E - TS \quad \curvearrowright \quad \Gamma(E) = \exp\left(-\frac{F - E}{k_B T}\right).$$

It thus remains:

$$p_m = \begin{cases} \exp\left(-\frac{S}{k_B}\right) = \exp(\beta(F - E)), & \text{if } E < E_m < E + \Delta \\ 0, & \text{otherwise.} \end{cases}$$

**Solution 2.2.2**

1.  $\{|\varphi_i\rangle\}$ : CON-system

$$\begin{aligned}
 |E_m\rangle &= \sum_i |\varphi_i\rangle \langle \varphi_i | E_m\rangle \\
 \implies \hat{\rho} &= \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} \sum_{i,j} |\varphi_i\rangle \langle \varphi_i | E_m\rangle \langle E_m | \varphi_j\rangle \langle \varphi_j| \\
 &= \frac{1}{\Gamma(E)} \sum_{i,j} \alpha_{ij}(E) |\varphi_i\rangle \langle \varphi_j|, \\
 \alpha_{ij}(E) &= \sum_m^{E < E_m < E + \Delta} \langle \varphi_i | E_m\rangle \langle E_m | \varphi_j\rangle.
 \end{aligned}$$

Matrix elements of  $\hat{\rho}$  in the basis  $\{|\varphi_i\rangle\}$ :

$$(\hat{\rho}(\varphi))_{rt} = \frac{1}{\Gamma(E)} \alpha_{rt}(E).$$

Phase volume:

$$\begin{aligned}
 \Gamma(\varphi) &= \text{Tr} \left( \sum_{i,j} \alpha_{ij}(E) |\varphi_i\rangle \langle \varphi_j| \right) \\
 &= \sum_n \alpha_{nn}(E) = \sum_n \sum_m^{E < E_m < E + \Delta} \langle \varphi_n | E_m\rangle \langle E_m | \varphi_n\rangle \\
 &= \sum_m^{E < E_m < E + \Delta} \langle E_m | \left( \sum_n |\varphi_n\rangle \langle \varphi_n| \right) | E_m\rangle = \sum_m^{E < E_m < E + \Delta} 1 = \Gamma(E).
 \end{aligned}$$

The phase volume is of course representation-independent.

2.

$$\begin{aligned}
 \hat{A}|a_n\rangle &= a_n|a_n\rangle, \\
 |a_n\rangle &= \sum_m |E_m\rangle \langle E_m | a_n\rangle \\
 \implies \hat{\rho}\hat{A} &= \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} |E_m\rangle \langle E_m | \hat{A},
 \end{aligned}$$

$$\begin{aligned}
 (\widehat{\rho A})_{ij} &= \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} \langle a_i | E_m \rangle \langle E_m | \widehat{A} | a_j \rangle \\
 &= \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} a_j \langle a_i | E_m \rangle \langle E_m | a_j \rangle .
 \end{aligned}$$

The trace is independent of the representation:

$$\langle \widehat{A} \rangle = \text{Tr}(\widehat{\rho A}) = \sum_i (\widehat{\rho A})_{ii} = \frac{1}{\Gamma(E)} \sum_m^{E < E_m < E + \Delta} \sum_i a_i |\langle a_i | E_m \rangle|^2 .$$

The interpretation of the result is evident.

### Solution 2.2.3

1.

$\Gamma(E)$  = number of the possible states with the energy  $E$   
 = number of the different possibilities to distribute the spins  
 for a given energy, determined by  $M = N_\uparrow - N_\downarrow$ , over  $N$  sites  
 $\cong$  degree of degeneracy of the energy  $E$ .

$$\Gamma(E) = \frac{N!}{N_\uparrow! N_\downarrow!} .$$

Entropy:  $S = k_B \ln \Gamma(E)$ .

Stirling formula for  $N \gg 1$ :  $\ln N! \approx N (\ln N - 1)$

$$\implies S(E, N) \approx k_B \left\{ N (\ln N - 1) - N_\uparrow (\ln N_\uparrow - 1) - N_\downarrow (\ln N_\downarrow - 1) \right\} ,$$

$$N = N_\uparrow + N_\downarrow ,$$

$$S(E, N) = k_B \left\{ N_\uparrow \ln \frac{N}{N_\uparrow} + N_\downarrow \ln \frac{N}{N_\downarrow} \right\} ,$$

$$N_\uparrow = \frac{1}{2}(N + M) ; \quad N_\downarrow = \frac{1}{2}(N - M)$$

$$\implies S(M, N) = \frac{1}{2} k_B \left\{ (N + M) \ln \frac{2N}{N + M} + (N - M) \ln \frac{2N}{N - M} \right\} .$$

## 2. Temperature:

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial S}{\partial E} \right)_N = \left( \frac{\partial S}{\partial M} \right)_N \left( \frac{\partial M}{\partial E} \right)_N = -\frac{1}{\mu_B B} \left( \frac{\partial S}{\partial M} \right)_N, \\ \left( \frac{\partial S}{\partial M} \right)_N &= \frac{1}{2} k_B \left\{ \ln \frac{2N}{N+M} + (N+M) \left( -\frac{1}{N+M} \right) \right. \\ &\quad \left. + (N-M) \left( +\frac{1}{N-M} \right) - \ln \frac{2N}{N-M} \right\} \\ &= \frac{1}{2} k_B \ln \frac{N-M}{N+M} \\ \implies \frac{1}{T} &= \frac{k_B}{2\mu_B B} \ln \frac{N+M}{N-M}. \end{aligned}$$

The temperature can thus become even **negative**, if namely  $N - M > N + M$ , i.e.  $N_\downarrow > N_\uparrow$ . In this case the majority of the spins is oriented antiparallel to the field. Parallel orientation means for a spin the energy level  $-\mu_B B$ , antiparallel orientation  $+\mu_B B$ . *Negative temperatures* appear when the energetically higher level is more (!) occupied.

## 3. Internal energy:

$$\begin{aligned} \frac{N_\uparrow}{N_\downarrow} &= \exp(\beta 2\mu_B B), \\ M &= N \frac{M}{N} = N \frac{\frac{N_\uparrow}{N_\downarrow} - 1}{\frac{N_\uparrow}{N_\downarrow} + 1} \\ \implies E &= -M\mu_B B = N\mu_B B \frac{1 - \exp(2\beta\mu_B B)}{1 + \exp(2\beta\mu_B B)} = \\ &= -N\mu_B B \tanh(\beta\mu_B B) \equiv U(T, N, B). \end{aligned}$$

## 4. Heat capacities:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_N = -N\mu_B B \frac{\partial}{\partial T} \tanh(\beta\mu_B B) = N \frac{\mu_B^2 B^2}{k_B T^2} \frac{1}{\cosh^2(\beta\mu_B B)}.$$

**Solution 2.2.4**

1.

$N_r =$  occupation number of the level  $\varepsilon_r$ ,

$$E = \sum_r \varepsilon_r N_r .$$

The energy is thus determined by the distribution  $\{N_r\}$  of the occupation numbers. Let us assume that at first this distribution is given:

$$\Gamma(\{N_r\}) = \frac{N!}{\prod_r N_r!} ,$$

$$S(E) = S(\{N_r\}) = k_B \ln \Gamma(\{N_r\}) = k_B \left[ N (\ln N - 1) - \sum_r N_r (\ln N_r - 1) \right] ,$$

2. The most probable distribution of the  $N$  particles over the various levels is that with the highest number of possibilities of realization. We thus have to find the maximum of  $\Gamma(\{N_r\})$ , which of course agrees with that of  $\ln \Gamma$ . Thereby the following constraints are to be fulfilled:

$$N = \sum_r N_r; \quad E = \sum_r \varepsilon_r N_r$$

These we couple, according to *Lagrange's variational principle*, with at first still undetermined *multipliers*  $\alpha_1, \alpha_2$  to the extremal condition:

$$\begin{aligned} & \delta \left( \ln \Gamma + \alpha_1 \sum_r N_r + \alpha_2 \sum_r \varepsilon_r N_r \right) \stackrel{!}{=} 0 \\ \iff & - \sum_r \delta N_r (\ln N_r - 1) - \sum_r \delta N_r + \alpha_1 \sum_r \delta N_r + \alpha_2 \sum_r \varepsilon_r \delta N_r \stackrel{!}{=} 0 \\ & \iff \sum_r (\ln N_r - \alpha_1 - \alpha_2 \varepsilon_r) \delta N_r \stackrel{!}{=} 0 . \end{aligned}$$

By the introduction of the Lagrange multiplier the variation is now free. We can choose the  $\delta N_r$  arbitrarily, for instance such that only one  $\delta N_r \neq 0$ , while the others are all equal to zero. This means:

$$\ln N_r = \alpha_1 + \alpha_2 \varepsilon_r \iff N_r = \exp(\alpha_1 + \alpha_2 \varepsilon_r) .$$

3. The extremal condition can obviously be written as follows:

$$\delta S + k_B \alpha_1 \delta N + k_B \alpha_2 \delta E \stackrel{!}{=} 0 .$$

Therewith:

$$\left( \frac{\partial S}{\partial N} \right)_E = -k_B \alpha_1 \stackrel{(1.96)}{=} -\frac{\mu}{T} ,$$

$$\left( \frac{\partial S}{\partial E} \right)_N = -k_B \alpha_2 \stackrel{(1.89)}{=} \frac{1}{T}$$

$$\implies \alpha_1 = \frac{\mu}{k_B T} = \beta \mu ; \quad \alpha_2 = -\frac{1}{k_B T} = -\beta .$$

Distribution:

$$N_r = \exp [ -\beta (\varepsilon_r - \mu) ] .$$

The chemical potential  $\mu$  is eventually determined by the condition:

$$N \stackrel{!}{=} \sum_r \exp [ -\beta (\varepsilon_r - \mu) ] .$$

The  $\varepsilon_r$  are known!

Essential parts of this derivation will appear once more in subsection 2.3.4 in connection with the *canonical ensemble*.

## Solution 2.2.5

*Two-dimensional harmonic oscillator:*

Known eigen-values of the harmonic oscillator:

$$E_{n_x n_y} = \hbar \omega (n + 1) = \hbar \omega (n_x + n_y + 1) = \hbar \omega [n_x + (n - n_x) + 1] \equiv E_n ,$$

$$0 \leq n_x \leq n .$$

Eigen-states are product states (subsection 4.4.6, Vol. 6):

$$|n_x, n - n_x\rangle \equiv |n_x\rangle |n - n_x\rangle ,$$

$|n_x\rangle$ :  $|n_x\rangle$ -th eigen-state of the oscillator in  $x$ -direction,

$|n - n_x\rangle$ :  $(n - n_x)$ -th eigen-state of the oscillator in  $y$ -direction.

*Quantum-mechanical phase volume:*

$\Gamma(E_n)$ : number of states  $|n_x, n - n_x\rangle$  of the energy  $E_n$  (degree of degeneracy!).

$n_x$  can take the  $n + 1$  values  $0, 1, 2, \dots, n$ ,  $n_y = n - n_x$  is then already fixed:

$$\implies \Gamma(E_n) = n + 1 .$$

*Statistical operator:*

$$\hat{\rho}(E_n) \equiv \frac{1}{n+1} \sum_{n_x=0}^n |n_x, n - n_x\rangle \langle n_x, n - n_x| .$$

*Expectation values for  $\hat{A} = \hat{p}_x, \hat{q}_x$ :*

$$\langle \hat{A}^2 \rangle = \text{Tr}(\hat{\rho} \hat{A}^2) = \frac{1}{n+1} \sum_{\mu, \nu} \sum_{n_x=0}^n \langle \mu, \nu | n_x, n - n_x \rangle \langle n_x, n - n_x | \hat{A}^2 | \mu, \nu \rangle .$$

$\hat{A} = \hat{A}^+$  acts only on the  $x$ -component:

$$\begin{aligned} \langle \hat{A}^2 \rangle &= \frac{1}{n+1} \sum_{\mu, \nu} \sum_{n_x=0}^n \delta_{\mu, n_x} \delta_{\nu, n - n_x} \delta_{n - n_x, \nu} \langle n_x | \hat{A}^+ \hat{A} | \mu \rangle \\ &= \frac{1}{n+1} \sum_{n_x=0}^n \langle n_x | \hat{A}^+ \hat{A} | n_x \rangle . \end{aligned}$$

According to (4.127), (4.128) in Vol. 6:

$$\begin{aligned} \hat{q}_x &= \sqrt{\frac{\hbar}{2m\omega}} (a + a^+) ; & \hat{p}_x &= -i \sqrt{\frac{\hbar m \omega}{2}} (a - a^+) \\ \implies \hat{q}_x |n_x\rangle &= \sqrt{\frac{\hbar}{2m\omega}} (a |n_x\rangle + a^+ |n_x\rangle) \\ &= \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n_x} |n_x - 1\rangle + \sqrt{n_x + 1} |n_x + 1\rangle) , \\ \hat{p}_x |n_x\rangle &= -i \sqrt{\frac{\hbar m \omega}{2}} (a |n_x\rangle - a^+ |n_x\rangle) \\ &= -i \sqrt{\frac{\hbar m \omega}{2}} (\sqrt{n_x} |n_x - 1\rangle - \sqrt{n_x + 1} |n_x + 1\rangle) \end{aligned}$$



$$\begin{aligned} \Rightarrow \langle n_x | \hat{q}_x^+ \hat{q}_x | n_x \rangle &= \frac{\hbar}{2m\omega} (n_x + n_x + 1) , \\ \langle n_x | \hat{p}_x^+ \hat{p}_x | n_x \rangle &= \frac{\hbar m\omega}{2} (n_x + n_x + 1) , \\ \sum_{n_x=0}^n (2n_x + 1) &= \frac{1}{2} (n + 1)(2n + 2) = (n + 1)^2 . \end{aligned}$$

We have therewith found:

$$\langle p_x^2 \rangle = \frac{1}{2} \hbar m\omega (n + 1) ; \quad \langle \hat{q}_x^2 \rangle = \frac{\hbar}{2m\omega} (n + 1) .$$

Expectation values for  $\hat{B} = \hat{p}_y, \hat{q}_y$ : The analogous derivation yields:

$$\langle \hat{p}_y^2 \rangle = \langle \hat{p}_x^2 \rangle ; \quad \langle \hat{q}_y^2 \rangle = \langle \hat{q}_x^2 \rangle .$$

Kinetic energy:

$$\langle \hat{T} \rangle = \frac{1}{2m} \langle \hat{p}_x^2 + \hat{p}_y^2 \rangle = \frac{1}{2} \hbar \omega (n + 1) = \frac{1}{2} E_n .$$

Potential energy:

$$\langle \hat{V} \rangle = \frac{1}{2} m\omega^2 \langle \hat{q}_x^2 + \hat{q}_y^2 \rangle = \frac{1}{2} \hbar \omega (n + 1) = \frac{1}{2} E_n .$$

### Solution 2.2.6

1.  $\Gamma_N(E)$  is the number of the *conceivable* states of the energy  $E$  and therewith equal to the number of possibilities to assign  $N_0$  oscillator quanta to  $N$  oscillators.  $E_0 = 1/2N\hbar\omega$  is just the *zero-point energy* of the total system.

Let us mark the  $N_0$  oscillator quanta by crosses ( $\times \times \times \times$ ) and the  $N$  oscillators by full circles ( $\bullet \bullet \bullet \bullet$ ), so that we can, for the counting, schematically ascribe to each oscillator *vertically* all the quanta which belong to it:

$$\begin{array}{ccccccc} & & & & \times & & \\ & & & & \times & \times & \times \\ & & & \times & \times & \times & \times \\ & & \bullet & \bullet & \bullet & \bullet & \bullet & \bullet \end{array}$$

This can also be brought into a *horizontal* version by arranging the oscillator quanta adjacent to the respective oscillator bringing:

$$\bullet \times \times \bullet \bullet \bullet \times \times \times \bullet \times \times \bullet \bullet \times$$

$\Gamma_N(E)$  is then obviously equal to the number of different possibilities to collocate the  $N_0 + N$  symbols.  $(N_0 + N)!$  is the total number of possibilities of arrangement. The  $N_0!$  possibilities to interchange the oscillator quanta (crosses) among themselves does not lead to a new arrangement (to a new state). The same holds for the  $N!$  interchanges of the oscillators (full circles) among themselves. That means:

$$\Gamma_N(E) = \frac{(N_0 + N)!}{N_0!N!}.$$

2. Using the Stirling formula one gets for the entropy:

$$\begin{aligned} S_N(E) &= k_B \left\{ (N_0 + N) (\ln(N_0 + N) - 1) \right. \\ &\quad \left. - N_0 (\ln N_0 - 1) - N (\ln N - 1) \right\} \\ &= k_B \left\{ (N_0 + N) \ln(N_0 + N) - N_0 \ln N_0 - N \ln N \right\}. \end{aligned}$$

$N$  is fixed. The energy-dependence is therefore due to  $N_0$ :

$$N_0 = \frac{E}{\hbar\omega} - \frac{1}{2}N.$$

Temperature:

$$\begin{aligned} \frac{1}{T} &= \left( \frac{\partial S}{\partial E} \right)_N = \left( \frac{\partial S}{\partial N_0} \right)_N \left( \frac{\partial N_0}{\partial E} \right)_N \\ &= \frac{k_B}{\hbar\omega} \left\{ \ln(N_0 + N) + 1 - \ln N_0 - 1 \right\} \\ \leadsto \frac{1}{T} &= \frac{k_B}{\hbar\omega} \ln \frac{N_0 + N}{N_0}. \end{aligned}$$

3.

$$\exp(\beta\hbar\omega) = \frac{N_0 + N}{N_0} \quad \leadsto \quad N_0(T) = \frac{N}{\exp(\beta\hbar\omega) - 1}$$

## Section 2.3.5

### Solution 2.3.1

$$\begin{aligned}
 \langle \hat{H} \rangle &= -\frac{1}{Z} \frac{\partial}{\partial \beta} Z; & \langle \hat{H}^2 \rangle &= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z \\
 \implies \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 &= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z - \frac{1}{Z^2} \left( \frac{\partial}{\partial \beta} Z \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial}{\partial \beta} Z \right) \\
 &= \frac{\partial}{\partial \beta} \left( \frac{\partial}{\partial \beta} \ln Z \right) \stackrel{2.30}{=} -\frac{\partial}{\partial \beta} U = k_B T^2 \frac{\partial U}{\partial T} \\
 &= C_V k_B T^2 \\
 \implies \sqrt{\frac{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2}{\langle \hat{H} \rangle^2}} &= \frac{\sqrt{C_V k_B T^2}}{U}.
 \end{aligned}$$

### Solution 2.3.2

1. Statistical operator in the canonical ensemble:

$$\hat{\rho} = \frac{1}{Z} \sum_m e^{-\beta E_m} |E_m\rangle \langle E_m|.$$

has to be investigated for the linear harmonic oscillator:

$$\hat{H}|E_m\rangle = E_m|E_m\rangle.$$

Position representation:

$$\rho(q) = \frac{1}{Z} \sum_m e^{-\beta E_m} |\langle q | E_m \rangle|^2;$$

$\langle q | E_m \rangle \equiv \varphi_m(q)$  : real eigen-function of the harmonic oscillator.

Differentiation with respect to  $q$ :

$$\frac{d}{dq} \rho(q) = \frac{2}{Z} \sum_m e^{-\beta E_m} \varphi_m(q) \frac{d}{dq} \varphi_m(q).$$

Reminder of Quantum Mechanics:

$$\frac{d}{dq} = \sqrt{\frac{m\omega}{2\hbar}}(a - a^+); \quad q = \sqrt{\frac{\hbar}{2m\omega}}(a + a^+).$$

The above differential equation therewith reads:

$$\frac{d}{dq}\rho(q) = \frac{1}{Z} \sqrt{\frac{2m\omega}{\hbar}} \sum_m e^{-\beta E_m} \varphi_m(q)(a - a^+)\varphi_m(q).$$

With

$$a\varphi_m = \sqrt{m}\varphi_{m-1}; \quad a^+\varphi_m = \sqrt{m+1}\varphi_{m+1}$$

it follows:

$$\frac{d}{dq}\rho(q) = \frac{1}{Z} \sqrt{\frac{2m\omega}{\hbar}} \sum_m e^{-\beta E_m} \varphi_m(q) \left( \sqrt{m}\varphi_{m-1}(q) - \sqrt{m+1}\varphi_{m+1}(q) \right).$$

In the first summand we use  $E_{m+1} = E_m + \hbar\omega$  and  $m \rightarrow m+1$ :

$$\frac{d}{dq}\rho(q) = \frac{1}{Z} \sqrt{\frac{2m\omega}{\hbar}} \sum_m e^{-\beta E_m} \sqrt{m+1} \left( \varphi_{m+1}(q)\varphi_m(q)e^{-\beta\hbar\omega} - \varphi_m(q)\varphi_{m+1}(q) \right).$$

It thus remains:

$$\frac{d}{dq}\rho(q) = \frac{1}{Z} \sqrt{\frac{2m\omega}{\hbar}} (e^{-\beta\hbar\omega} - 1) \sum_m \sqrt{m+1} \varphi_{m+1}(q)\varphi_m(q)e^{-\beta E_m}.$$

We now exploit the recursion formula ((4.168), Vol. 6):

$$\sqrt{\frac{2m\omega}{\hbar}} q\varphi_m(q) = \sqrt{m+1}\varphi_{m+1}(q) + \sqrt{m}\varphi_{m-1}(q).$$

Therewith:

$$\begin{aligned} q\rho(q) &= \frac{1}{Z} \sum_m e^{-\beta E_m} q\varphi_m^2(q) \\ &= \sqrt{\frac{\hbar}{2m\omega}} \frac{1}{Z} \sum_m e^{-\beta E_m} \left( \sqrt{m+1}\varphi_{m+1}(q) + \sqrt{m}\varphi_{m-1}(q) \right) \varphi_m(q) \\ &= \sqrt{\frac{\hbar}{2m\omega}} \frac{1}{Z} \sum_m e^{-\beta E_m} \sqrt{m+1} \varphi_{m+1}(q) \varphi_m(q) (1 + e^{-\beta\hbar\omega}). \end{aligned}$$

By comparison we find:

$$\frac{d}{dq}\rho(q) = \frac{2m\omega}{\hbar} \frac{e^{-\beta\hbar\omega} - 1}{1 + e^{-\beta\hbar\omega}} \rho(q)q .$$

It remains eventually:

$$\frac{d}{dq}\rho(q) = \left( -\frac{2m\omega}{\hbar} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) \right) q\rho(q) .$$

2.

$\langle q | \hat{\rho} | q \rangle$ : part with which the mixed state, described by  $\hat{\rho}$ , is contained in  $|q\rangle$ .

The temperature-dependent position probability should be normalized:

$$\int_{-\infty}^{+\infty} dq \rho(q) = 1 .$$

Solution of the differential equation:

$$\rho(q) = A e^{-\alpha q^2} ; \quad \alpha = \frac{m\omega}{\hbar} \tanh\left(\frac{1}{2}\beta\hbar\omega\right) .$$

Normalization condition:

$$\int_{-\infty}^{+\infty} dq \rho(q) = A \sqrt{\frac{\pi}{\alpha}} \stackrel{!}{=} 1 .$$

It follows:

$$A = \sqrt{\frac{m\omega}{\pi\hbar} \tanh\left(\frac{1}{2}\beta\hbar\omega\right)} .$$

The *'thermal'* position probability extends more and more with increasing temperature!

**Solution 2.3.3**

The energy eigen-values of the 2d-oscillator are known:

$$\begin{aligned} E_n &= \hbar\omega\left(n_1 + \frac{1}{2} + n_2 + \frac{1}{2}\right) \\ &= \hbar\omega(n + 1) \\ n &= n_1 + n_2 = 0, 1, 2, \dots \end{aligned}$$

For a given  $n$ ,  $n_1$  goes through the values  $0, 1, 2, \dots, n$  and  $n_2$  through the values  $n - n_1$ . The degree of degeneracy therefore amounts to  $g_n = n + 1$ . Therewith the partition function of the oscillator reads:

$$Z_2 = \sum_{n=0}^{\infty} (n + 1) e^{-\beta\hbar\omega(n+1)}$$

That can further be reformulated:

$$\begin{aligned} Z_2 &= -\frac{\partial}{\partial(\beta\hbar\omega)} e^{-\beta\hbar\omega} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n \\ &= -\frac{\partial}{\partial(\beta\hbar\omega)} \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \\ &= \frac{+e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \\ &= \left[ e^{-\frac{1}{2}\beta\hbar\omega} \frac{1}{1 - e^{-\beta\hbar\omega}} \right]^2 \\ &= \left[ e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} (e^{-\beta\hbar\omega})^n \right]^2 \\ &= \left[ \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} \right]^2 \end{aligned}$$

The bracket contains the partition function of the one-dimensional oscillator. Therefore:

$$Z_2 = Z_1^2$$

**Solution 2.3.4**

1. Because there are no interactions in the ideal gas, it holds:

$$Z_N(T, V) = (Z_1(T, V))^N,$$

$$Z_1(T, V) = \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp \left[ -\beta \frac{\hbar^2}{2m} 4\pi^2 \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \right] \equiv Z_x \cdot Z_y \cdot Z_z,$$

$$Z_x = \sum_{n_x} \exp \left( -\beta \frac{2\pi^2 \hbar^2}{m} \frac{n_x^2}{L_x^2} \right),$$

$Z_y, Z_z$  : analogously .

2.

$$Z_x = \int_{-\infty}^{+\infty} \ddot{x} \exp \left( -\beta \frac{2\pi^2 \hbar^2}{m} \frac{x^2}{L_x^2} \right) = \frac{L_x}{\pi \hbar} \sqrt{\frac{m}{2\beta}} \int_{-\infty}^{+\infty} \ddot{y} e^{-y^2} = \frac{L_x}{\pi \hbar} \sqrt{\frac{m\pi}{2\beta}}$$

$$\Rightarrow Z_N(T, V) = \left[ L_x L_y L_z \left( \frac{m}{2\pi \hbar^2} \right)^{3/2} \beta^{-3/2} \right]^N = V^N \beta^{-3N/2} \alpha^{3N/2}; \quad \alpha = \frac{m}{2\pi \hbar^2}.$$

3. Internal energy:

$$U = -\frac{\partial}{\partial \beta} \ln Z_N,$$

$$\ln Z_N(T, V) = N \ln V - \frac{3}{2} N \ln \beta + \frac{3}{2} N \ln \alpha$$

$$\Rightarrow U = \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T.$$

**Solution 2.3.5**

Eigen-states in the occupation-number representation:

$$|N\rangle = |n_1\rangle |n_2\rangle \cdots |n_N\rangle \equiv |n_1 n_2 \cdots n_N\rangle.$$

Eigen-energies of the single oscillator:

$$\varepsilon_{n_i} = \hbar \omega \left( n_i + \frac{1}{2} \right).$$

Total energy:

$$E_{|N\rangle} \equiv E(\{n_i\}) = \hbar \omega \sum_{i=1}^N \left( n_i + \frac{1}{2} \right).$$

Partition function:

$$\begin{aligned} Z_N(T) &= \text{Tr} e^{-\beta \hat{H}} = \sum_{|N\rangle} \langle N | e^{-\beta \hat{H}} | N \rangle \\ &= \sum_{\{n_i\}} \exp \left[ -\beta \hbar \omega \sum_{j=1}^N \left( n_j + \frac{1}{2} \right) \right] \\ &= \exp \left( -\beta N \frac{\hbar \omega}{2} \right) \sum_{n_1} e^{-\beta \hbar \omega n_1} \dots \sum_{n_N} e^{-\beta \hbar \omega n_N} \\ &= \exp \left( -\beta N \frac{\hbar \omega}{2} \right) \prod_{i=1}^N \left( \sum_{n_i=0}^{\infty} e^{-\beta \hbar \omega n_i} \right) \\ &= \exp \left( -\beta N \frac{\hbar \omega}{2} \right) \left[ \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n \right]^N \\ &= \exp \left( -\beta N \frac{\hbar \omega}{2} \right) \left[ \frac{1}{1 - e^{-\beta \hbar \omega}} \right]^N \\ &= \exp \left( -\beta N \frac{\hbar \omega}{2} \right) \left[ \frac{\exp(\frac{1}{2} \beta \hbar \omega)}{\exp(\frac{1}{2} \beta \hbar \omega) - \exp(-\frac{1}{2} \beta \hbar \omega)} \right]^N \\ \implies Z_N(T) &= \left[ \frac{1}{2 \sinh(\frac{1}{2} \beta \hbar \omega)} \right]^N. \end{aligned}$$

### Solution 2.3.6

1. Internal energy, Eq. (2.30):

$$\begin{aligned} U &= -\frac{\partial}{\partial \beta} \ln Z_N(T, V) = k_B T^2 \frac{\partial}{\partial T} \ln Z_N(T, V) \\ \ln Z_N(T, V) &= N(\ln \gamma + \ln V - \ln N + 3 \ln T) \end{aligned}$$



$$\begin{aligned}\Rightarrow \frac{\partial}{\partial T} \ln Z_N(T, V) &= \frac{3N}{T} \\ \Rightarrow U &= 3Nk_B T\end{aligned}$$

Entropy:

$$\begin{aligned}S(T, V, N) &= - \left( \frac{\partial F}{\partial T} \right)_{V, N} \\ F &= -k_B T \ln Z_N(T, V) \\ \Rightarrow S(T, V, N) &= k_B \frac{\partial}{\partial T} (T \ln Z_N(T, V)) \\ &= k_B \ln Z_N(T, V) + k_B T \frac{\partial}{\partial T} \ln Z_N(T, V) \\ &= k_B \left( N \ln \left( \gamma \frac{V}{N} T^3 \right) + 3N \right) \\ &= Nk_B \ln \left( e^3 \gamma \frac{V}{N} T^3 \right)\end{aligned}$$

2. In general it holds:  $S > 0$  (see (2.20)). It is therefore to be required for the  $S$  in part 1.:

$$e^3 \gamma \frac{V}{N} T^3 > 1 .$$

The  $S$ -formula is thus useful only for  $T > T^*$ , where

$$T^* = \frac{1}{e} \left( \frac{N}{\gamma V} \right)^{1/3}$$

3. Thermal equation of state

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T, N} = k_B T \left( \frac{\partial}{\partial V} \ln Z_N \right) = k_B T \cdot \frac{N}{V} \quad (\text{see 1.})$$

Hence:

$$pV = Nk_B T$$

as for the ideal gas, but

$$pV = \frac{1}{3} U ,$$

i.e.,  $x = 1/3$  (in contrast,  $x = 2/3$  for the classical ideal gas).  $x = 1/3$  is typical for relativistic particles!

#### 4. Chemical potential

$$\begin{aligned}\mu(T, V, N) &= \left( \frac{\partial F}{\partial N} \right)_{T, V} \\ &= -k_B T \left( \frac{\partial}{\partial N} \ln Z_N \right)_{T, V} \\ &= -k_B T \ln \left( \gamma \frac{V}{N} T^3 \right) + k_B T \\ &= k_B T \left( 1 - \ln \left( \gamma \frac{V}{N} T^3 \right) \right)\end{aligned}$$

$$\text{for } T = T^* : \ln \left( \gamma \frac{V}{N} T^3 \right) = -3 \Rightarrow \mu = 4k_B T$$

$$\text{for } T \rightarrow \infty : \mu \approx -3k_B T \ln T$$

### Solution 2.3.7

- The oscillations in the three space-directions are uncoupled. The partition function thus factorizes:

$$Z = (Z_x Z_y Z_z)^N .$$

As in Exercise 2.3.5:

$$Z_{x,y,z} = \sum_n \exp \left[ -\frac{\hbar \omega_{x,y,z}}{k_B T} \left( n + \frac{1}{2} \right) \right] = \frac{1}{2 \sinh \left( \frac{1}{2} \beta \hbar \omega_{x,y,z} \right)} .$$

- 

$$U = -\frac{\partial}{\partial \beta} \ln Z = N(U_x + U_y + U_z) ,$$

$$U_{x,y,z} = -\frac{\partial}{\partial \beta} \ln Z_{x,y,z} = \frac{\hbar \omega_{x,y,z}}{2} \coth \left( \frac{1}{2} \beta \hbar \omega_{x,y,z} \right) .$$

3. Heat capacity:

$$C_V = N(C_{Vx} + C_{Vy} + C_{Vz}) ,$$

$$\frac{d}{dx} \coth x = -\frac{1}{\sinh^2 x} ,$$

$$C_{Vx} = \frac{\partial U_x}{\partial T} = \frac{1}{2} \hbar \omega_x \frac{-1}{\sinh^2 \frac{1}{2} \beta \hbar \omega_x} \frac{1}{2} \hbar \omega_x \left( -\frac{1}{k_B T^2} \right)$$

$$\Rightarrow C_{V_{x,y,z}} = k_B \left( \frac{\beta \hbar \omega_{x,y,z}}{2 \sinh \frac{1}{2} \beta \hbar \omega_{x,y,z}} \right)^2 ,$$

$$\sinh x \approx \begin{cases} x & \text{for } x \ll 1, \\ \frac{1}{2} e^x & \text{for } x \gg 1. \end{cases}$$

It follows therewith for  $\hbar \omega_x = \hbar \omega_y \gg k_B T$ ;  $\hbar \omega_z \ll k_B T$ :

$$C_V \approx N k_B \left[ 2 \left( \frac{\hbar \omega_x}{k_B T} \right)^2 \exp \left( -\frac{\hbar \omega_x}{k_B T} \right) + 1 \right] .$$

### Solution 2.3.8

1. Each spin  $S_i$  has two possibilities of orientation  $\Rightarrow 2^n$  different spin states.

Canonical partition function:

$$Z_N(T) = \text{Tr} e^{-\beta \hat{H}} = \sum_{\sigma_1}^{\pm \frac{1}{2}} \cdots \sum_{\sigma_N}^{\pm \frac{1}{2}} \exp \left( \beta \sum_{i=1}^{N-1} J_i \sigma_i \sigma_{i+1} \right) .$$

$$Z_{N+1} = \underbrace{\sum_{\sigma_1} \cdots \sum_{\sigma_N} \exp \left( \beta \sum_{i=1}^{N-1} J_i \sigma_i \sigma_{i+1} \right)}_{Z_N(T)} \underbrace{\sum_{\sigma_{N+1}}^{\pm \frac{1}{2}} \exp \left( \beta J_N \overbrace{\sigma_N \sigma_{N+1}}^{\pm \frac{1}{4}} \right)}_{2 \cosh \left( \frac{1}{4} \beta J_N \right)}$$

$$= 2 Z_N(T) \cosh \left( \frac{1}{4} \beta J_N \right) .$$

2. Recursion formula from part 1.:

$$\begin{aligned} Z_N(T) &= 2Z_{N-1}(T) \cosh\left(\frac{1}{4}\beta J_{N-1}\right) \\ &= 2^2 Z_{N-2}(T) \cosh\left(\frac{1}{4}\beta J_{N-1}\right) \cosh\left(\frac{1}{4}\beta J_{N-2}\right) = \dots = \\ &= 2^N \prod_{i=1}^{N-1} \cosh\left(\frac{1}{4}\beta J_i\right) . \end{aligned}$$

3. The single spin does not interact, but has two possibilities of orientation:

$$Z_1(T) = \sum_{\sigma_1}^{\pm\frac{1}{2}} e^0 = 2 .$$

4.

$$\langle S_i^z S_{i+1}^z \rangle = \frac{1}{Z_N} \text{Tr}(S_i^z S_{i+1}^z e^{-\beta \hat{H}}) = \frac{1}{Z_N} \frac{1}{\beta} \frac{\partial}{\partial J_i} \text{Tr}(e^{-\beta \hat{H}}) = \frac{1}{\beta} \frac{\partial}{\partial J_i} \ln Z_N .$$

It follows with the above result for  $Z_N(T)$ :

$$\begin{aligned} \langle S_i^z S_{i+1}^z \rangle &= \frac{1}{\beta} \frac{1}{4} \beta \frac{\left[ \prod_{m=1}^{i-1} \cosh\left(\frac{1}{4}\beta J_m\right) \right] \sinh\left(\frac{1}{4}\beta J_i\right) \left[ \prod_{m=i+1}^{N-1} \cosh\left(\frac{1}{4}\beta J_m\right) \right]}{2^N \prod_{m=1}^{N-1} \cosh\left(\frac{1}{4}\beta J_m\right)} \\ &= \frac{1}{4} \tanh\left(\frac{1}{4}\beta J_i\right) . \end{aligned}$$

### Solution 2.3.9

1. Eigen-values:

$$E_\sigma = -2\mu_B B \sum_{i=1}^N \sigma_i ; \quad |\sigma\rangle \equiv |\sigma_1 \sigma_2 \dots \sigma_N\rangle .$$

Each  $\sigma_i$  can adopt two values. Hence there are altogether  $2^N$  possibilities for the spin state  $|\sigma\rangle$ . Two states have always then the same energy when the number of field-parallel spins (and therewith also the number of field-antiparallel spins) is same. The two extremal values of  $E_\sigma$  are those for which all spins are oriented parallel and antiparallel, respectively, to the field. All in all the following energies are possible:

$$E_n = -\mu_B B(2n - N); \quad n = 0, 1, \dots, N .$$

Degree of degeneracy  $g_n$ : number of possibilities to sort out  $n$  from  $N$  lattice sites.

$$g_n = \frac{N!}{n!(N-n)!} = \binom{N}{n}.$$

2.  $Z(T, B) = \text{Tr} e^{-\beta \hat{H}}$  energy representation:

$$\begin{aligned} Z(T, B) &= \sum_{n=0}^N g_n e^{-\beta E_n} = \sum_{n=0}^N \binom{N}{n} (e^{+\beta \mu_B B})^n (e^{-\beta \mu_B B})^{N-n} \\ &= (e^{+\beta \mu_B B} + e^{-\beta \mu_B B})^N = [2 \cosh(\beta \mu_B B)]^N. \end{aligned}$$

3. Free energy:

$$F(T, B) = -k_B T \ln Z(T, B) = -Nk_B T \ln [2 \cosh(\beta \mu_B B)].$$

Internal energy:

$$U(T, B) = -\frac{\partial}{\partial \beta} \ln Z = -N\mu_B B \tanh(\beta \mu_B B).$$

4. Entropy (Fig. A.7):

$$S(T, B) = -\left(\frac{\partial F}{\partial T}\right)_B = +Nk_B [\ln(2 \cosh \beta \mu_B B) - \beta \mu_B B \tanh(\beta \mu_B B)].$$

5. Heat capacity (Fig. A.7):

$$\begin{aligned} C_B &= T \left(\frac{\partial S}{\partial T}\right)_B = -\frac{N}{T} \mu_B B \left( \tanh \beta \mu_B B - \beta \mu_B B \frac{1}{\cosh^2 \beta \mu_B B} - \tanh \beta \mu_B B \right) \\ &\implies C_B = k_B N \left[ \frac{\beta \mu_B B}{\cosh \beta \mu_B B} \right]^2. \end{aligned}$$

6. Average magnetic moment

$$\begin{aligned} M &= \text{Tr} \left( \hat{\rho} \sum_{i=1}^N 2\mu_B \hat{S}_i^z \right) \\ &= \frac{1}{Z} \sum_n g_n e^{-\beta E_n} \left( -\frac{1}{B} E_n \right) = \quad (\text{energy representation}) \end{aligned}$$

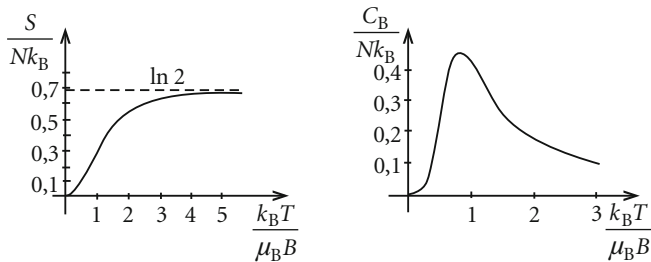


Fig. A.7

$$\begin{aligned}
 &= \frac{1}{B} \frac{\partial}{\partial \beta} \ln Z \\
 \implies M(T, B) &= N\mu_B \tanh(\beta\mu_B B) .
 \end{aligned}$$

7.  $\beta\mu_B B \ll 1$ :

$$\tanh(\beta\mu_B B) \approx \beta\mu_B B \implies M(T, B) \approx N\mu_B \frac{\mu_B B}{k_B T} \quad (\text{Curie law}) .$$

This agrees, except for the factor  $\frac{1}{3}$  with the classical result!  
 $\beta\mu_B B \gg 1$ :

$$\tanh(\beta\mu_B B) \approx 1 \implies M(T, B) \approx N\mu_B \quad (\text{saturation}) .$$

This agrees with the classical result! All spins (moments) are oriented field-parallel.

8. The third law of Thermodynamics is fulfilled:

$$\begin{aligned}
 S(T \rightarrow 0, B) &\approx Nk_B [\ln(e^{\beta\mu_B B}) - \beta\mu_B B] = 0 \quad (\text{independent of } B!) , \\
 C_B &\xrightarrow{T \rightarrow 0} 0 .
 \end{aligned}$$

### Solution 2.3.10

1. Noninteracting moments:

$$\begin{aligned}
 Z(T, B) &= (Z_1(T, B))^N , \\
 Z_1(T, B) &= \text{Tr}[\exp(+\beta\hat{\mu} \cdot \mathbf{B})] ,
 \end{aligned}$$

$$\boldsymbol{\mu} \cdot \mathbf{B} = g_J \mu_B M_J B \quad (\text{eigen-values!}),$$

$M_J$  = magnetic quantum number going through the values  $J, J-1, \dots, -J$

$$\begin{aligned} \Rightarrow Z_1(T, B) &= \sum_{M_J=-J}^{+J} \exp(+\beta g_J \mu_B M_J B) \\ &= \exp(\beta g_J \mu_B J B) \sum_{n=0}^{2J} [\exp(-\beta g_J \mu_B B)]^n \\ &= \exp(\beta g_J \mu_B J B) \frac{1 - \exp[-\beta g_J \mu_B B (2J + 1)]}{1 - \exp(-\beta g_J \mu_B B)} \\ &= \frac{\exp[\beta g_J \mu_B B (J + \frac{1}{2})] - \exp[-\beta g_J \mu_B B (J + \frac{1}{2})]}{\exp[\frac{1}{2}\beta g_J \mu_B B] - \exp[-\frac{1}{2}\beta g_J \mu_B B]} \\ Z_1(T, B) &= \frac{\sinh[\beta g_J \mu_B B (J + \frac{1}{2})]}{\sinh(\frac{1}{2}\beta g_J \mu_B B)}. \end{aligned}$$

2. Magnetic moment:

$$\begin{aligned} M &= N \langle g_J \mu_B \widehat{J}_z \rangle = \frac{1}{B} N \frac{\partial}{\partial \beta} \ln Z_1(T, B) = \frac{N}{B} \frac{1}{Z_1(T, B)} \frac{\partial Z_1(T, B)}{\partial \beta}, \\ \frac{d}{dx} \frac{\sinh[x(J + \frac{1}{2})]}{\sinh(\frac{1}{2}x)} &= \frac{1}{\sinh \frac{1}{2}x} \left( J + \frac{1}{2} \right) \cosh \left[ x \left( J + \frac{1}{2} \right) \right] \\ &\quad - \frac{1}{2} \frac{\sinh[x(J + \frac{1}{2})]}{\sinh^2(\frac{1}{2}x)} \cosh \left( \frac{1}{2}x \right) \end{aligned}$$

$$\begin{aligned} M &= N g_J \mu_B \left\{ \left( J + \frac{1}{2} \right) \coth \left[ \beta g_J \mu_B B \left( J + \frac{1}{2} \right) \right] - \frac{1}{2} \coth \left( \frac{1}{2} \beta g_J \mu_B B \right) \right\} \\ &= M_0 B_J (\beta g_J \mu_B B). \end{aligned}$$

3a)  $J = 1/2$ :

$$B_{1/2}(x) = 2 \coth(2x) - \coth x = 2 \frac{\coth^2 x + 1}{2 \coth x} - \coth x = \frac{1}{\coth x} = \tanh x.$$

For  $J = \frac{1}{2}$  the result of the last exercise is reproduced, as it should be, where, for  $J = S = \frac{1}{2}$ ,  $g_J = 2$  is still to be included.

3b)  $J \rightarrow \infty$  (classical limiting case):

$$B_\infty(x) = \coth x - \frac{1}{x}.$$

Thereby we use in the second summand, because the argument tends to zero, the series expansion

$$\coth z = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \mathcal{O}(z^5)$$

$B_\infty(x)$  is the classical *Langevin function*. As we have calculated in the solution of Exercise 1.4.6, the Langevin function fixes the magnetic moment in a classical treatment of the problem, when the directional quantization is disregarded.

3c)  $\beta\mu_B B \gg 1$ : Low temperatures, high fields:

$$B_J \rightarrow 1 \implies M \rightarrow M_0 \quad \text{saturation.}$$

All magnetic moments are oriented parallel to the field!

3d)  $\beta\mu_B B \ll 1$ : We terminate the above series expansion after the linear term:

$$\begin{aligned} B_J(x) &= \frac{1}{3} \left[ \left( \frac{2J+1}{2J} \right)^2 x - \frac{1}{(2J)^2} x \right] + \mathcal{O}(x^3) \approx \frac{J+1}{3J} x \\ \implies M &= N g_J J \mu_B \frac{J+1}{3J} \beta g_J J \mu_B B = \frac{C}{T}, \\ C &= N \left[ g_J^2 J (J+1) \right] \frac{\mu_B^2}{3k_B}: \quad \text{Curie constant.} \end{aligned}$$

This is the well-known *Curie law* for the *Langevin paramagnet* (see (1.25), Vol. 5) for  $B = \mu_0 H$ . Sometimes one puts  $\mu_0$  into the Curie constant  $C$ , as well as the volume  $V$ , when the *magnetization*  $M/V$  is discussed (see (4.136)).  $V$  is in such a case only a parameter, and not at all a thermodynamic variable!

### Solution 2.3.11

1. Classical equipartition theorem (1.110):

$$\begin{aligned} \left\langle p_j \frac{\partial H}{\partial p_j} \right\rangle &= \left\langle q_j \frac{\partial H}{\partial q_j} \right\rangle = k_B T, \\ \left\langle p_j \frac{\partial H}{\partial p_j} \right\rangle &= \frac{1}{m} \langle p_j^2 \rangle; \quad \left\langle q_j \frac{\partial H}{\partial q_j} \right\rangle = m \omega_j^2 \langle q_j^2 \rangle \end{aligned}$$



$$\begin{aligned} \Rightarrow U = \langle H \rangle &= \sum_{j=1}^{3N} \left( \frac{1}{2m} \langle p_j^2 \rangle + \frac{1}{2} m \omega_j^2 \langle q_j^2 \rangle \right) \\ &= \sum_{j=1}^{3N} \left( \frac{1}{2} k_B T + \frac{1}{2} k_B T \right) = 3N k_B T . \end{aligned}$$

Heat capacity:

$$C = \frac{\partial U}{\partial T} = 3N k_B \quad (\text{Dulong-Petit law}).$$

2. *Einstein assumption:*  $\omega_j \equiv \omega_E \quad \forall j$ :

Quantum-mechanical canonical partition function according to the solution of Exercise 2.3.5:

$$Z_N(T) = \left[ \frac{1}{2 \sinh \left( \frac{\hbar \omega_E}{2 k_B T} \right)} \right]^{3N} .$$

Internal energy:

$$\begin{aligned} U(T, N) &= -\frac{\partial}{\partial \beta} \ln Z_N(T) = 3N \frac{\partial}{\partial \beta} \ln \left[ 2 \sinh \left( \frac{1}{2} \beta \hbar \omega_E \right) \right] \\ &= \frac{3}{2} N \hbar \omega_E \coth \left( \frac{1}{2} \beta \hbar \omega_E \right) \xrightarrow{T \rightarrow 0} \frac{3N}{2} \hbar \omega_E . \end{aligned}$$

Heat capacity:

$$C = \frac{\partial U}{\partial T} = \frac{3}{4} N k_B \left( \frac{\hbar \omega_E}{k_B T} \right)^2 \frac{1}{\sinh^2 \frac{1}{2} \frac{\hbar \omega_E}{k_B T}} = 3N k_B \left( \frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2} .$$

High temperatures:  $T \gg \Theta_E$ :

$$\frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \approx \frac{1}{(1 + (\Theta_E/T) - 1)^2} \quad \Rightarrow \quad C = 3N k_B .$$

For high temperatures the quantum-mechanical result approaches the classical one. The latter violates the third law of Thermodynamics, **must** therefore fail for low temperatures.

Low temperatures:  $T \ll \Theta_E$ :

$$C \approx 3N k_B \left( \frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T} \xrightarrow{T \rightarrow 0} 0 .$$



Fig. A.8

The Einstein theory of the crystal lattice obviously fulfills the third law of Thermodynamics.

The classical equipartition theorem is acceptable only in the limit of high temperatures (Fig. A.8).

### Solution 2.3.12

The partition function for a single oscillator is the same as in the preceding exercise:

$$Z_1^{(j)}(T) = \frac{1}{2 \sinh\left(\frac{1}{2}\beta\hbar\omega_j\right)}.$$

Since the oscillators are uncoupled, the total partition function reads:

$$Z_N(T) = \prod_{j=1}^{3N} Z_1^{(j)}(T).$$

It follows for the internal energy:

$$\begin{aligned} U(T, N) &= -\frac{\partial}{\partial\beta} \ln Z_N(T) = +\frac{\partial}{\partial\beta} \sum_{j=1}^{3N} \ln \left[ 2 \sinh\left(\frac{1}{2}\beta\hbar\omega_j\right) \right] \\ &= \sum_{j=1}^{3N} \frac{1}{2}\hbar\omega_j \coth\left(\frac{1}{2}\beta\hbar\omega_j\right). \end{aligned}$$

That we express by the density of states:

$$U(T, N) = \int_0^{\infty} d\omega D(\omega) \left(\frac{1}{2}\hbar\omega\right) \coth\left(\frac{1}{2}\beta\hbar\omega\right).$$

Heat capacity:

$$\begin{aligned}
 C &= \frac{\partial U}{\partial T} = \frac{k_B}{4} \int_0^\infty d\omega D(\omega) \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{1}{\sinh^2 \left( \frac{1}{2} \beta \hbar \omega \right)} \\
 &= \frac{9Nk_B}{\omega_D^3} \int_0^{\omega_D} \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \omega^2 d\omega .
 \end{aligned}$$

Substitution of variables:

$$\begin{aligned}
 x &= \beta \hbar \omega; & \Theta_D &= \frac{\hbar \omega_D}{k_B} & \text{Debye temperature} \\
 \Rightarrow C &= 9Nk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} dx x^4 \frac{e^x}{(e^x - 1)^2} .
 \end{aligned}$$

High temperatures:  $\Theta_D/T \ll 1$ :  $x$  is then in the integrand of course also small compared to 1:

$$\begin{aligned}
 \frac{x^4 e^x}{(e^x - 1)^2} &= \frac{x^4 (1 + x + \dots)}{(1 + x + \dots - 1)^2} \approx x^2 \\
 \Rightarrow C &\approx 3Nk_B .
 \end{aligned}$$

This is just the classical Dulong-Petit result!

Low temperatures:  $\Theta_D/T \gg 1$ : The upper limit of the integration can then be approximately chosen to be  $+\infty$ :

$$C \approx 9Nk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^\infty dx x^4 \frac{e^x}{(e^x - 1)^2} = \alpha T^3, \quad \alpha = \frac{12}{5} \pi^4 \frac{Nk_B}{\Theta_D^3} .$$

This is the famous *Debye's  $T^3$ -law*. The third law of Thermodynamics is obviously fulfilled.

### Solution 2.3.13

Ortho- $H_2$ : parallel nuclear spins

$\Rightarrow$  triplet-spin state:

$$|1, 1\rangle = |\uparrow\rangle|\uparrow\rangle ,$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle),$$

$$|1, -1\rangle = |\downarrow\rangle|\downarrow\rangle$$

$\implies$  space-part of the wave function antisymmetric

$\implies l = 1, 3, 5, \dots$

Para- $H_2$ : antiparallel nuclear spins

$\implies$  singlet-spin state:

$$|0, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

$\implies$  space-part of the wave function symmetric

$\implies l = 0, 2, 4, 6, \dots$

### 1. Partition functions:

$$Z = \sum_l g_l \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right], \quad g_l: \text{degree of degeneracy},$$

$$g_l^{\text{ortho}} = 3(2l+1) \quad ((2l+1): \text{due to } \widehat{L}_z, \quad 3: \text{due to the triplet}),$$

$$g_l^{\text{para}} = 2l+1.$$

$$\begin{aligned} Z_{\text{ortho}}(T) &= \sum_l^{1,3,5,\dots} 3(2l+1) \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right] \\ &= 3 \sum_{n=0}^{\infty} (4n+3) \exp\left[-\beta \frac{\hbar^2}{2J} (2n+1)(2n+2)\right], \end{aligned}$$

$$\begin{aligned} Z_{\text{para}}(T) &= \sum_l^{0,2,4,\dots} (2l+1) \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right] \\ &= \sum_{n=0}^{\infty} (4n+1) \exp\left[-\beta \frac{\hbar^2}{2J} 2n(2n+1)\right]. \end{aligned}$$

**Internal energies:**

$$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{Z} \frac{\partial Z}{\partial \beta},$$

$$U_{\text{ortho}}(T) = \frac{1}{Z_{\text{ortho}}} \sum_l^{1,3,5,\dots} 3 \frac{\hbar^2}{2J} (2l+1)l(l+1) \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right],$$

$$U_{\text{para}}(T) = \frac{1}{Z_{\text{para}}} \sum_l^{0,2,4,\dots} \frac{\hbar^2}{2J} (2l+1)l(l+1) \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right].$$

**Heat capacities:**

$$C = \frac{\partial U}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} U,$$

$$C_{\text{ortho}} = -\frac{1}{k_B T^2} \left\{ U_{\text{ortho}}^2(T) - \frac{1}{Z_{\text{ortho}}} \sum_l^{1,3,\dots} 3(2l+1) \left[ \frac{\hbar^2}{2J} l(l+1) \right]^2 \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right] \right\},$$

$$C_{\text{para}} = -\frac{1}{k_B T^2} \left\{ U_{\text{para}}^2(T) - \frac{1}{Z_{\text{para}}} \sum_l^{0,2,\dots} (2l+1) \left[ \frac{\hbar^2}{2J} l(l+1) \right]^2 \exp\left[-\beta \frac{\hbar^2}{2J} l(l+1)\right] \right\}.$$

**2. Low temperatures:  $\beta(\hbar^2/2J) \gg 1$ :**

$$Z_{\text{ortho}}(T) \approx 9 \exp\left(-\beta \frac{\hbar^2}{2J} 2\right) + 21 \exp\left(-\beta \frac{\hbar^2}{2J} 12\right),$$

$$Z_{\text{para}}(T) \approx 1 + 5 \exp\left(-\beta \frac{\hbar^2}{2J} 6\right),$$

$$\begin{aligned} U_{\text{ortho}}(T) &\approx \frac{18 \exp\left(-\beta \frac{\hbar^2}{2J} 2\right) + 252 \exp\left(-\beta \frac{\hbar^2}{2J} 12\right)}{9 \exp\left(-\beta \frac{\hbar^2}{2J} 2\right) + 21 \exp\left(-\beta \frac{\hbar^2}{2J} 12\right)} \frac{\hbar^2}{2J} \\ &= \frac{\hbar^2}{2J} \frac{2 + 28 \exp\left(-5\beta \frac{\hbar^2}{J}\right)}{1 + \frac{7}{3} \exp\left(-5\beta \frac{\hbar^2}{J}\right)} \approx \frac{\hbar^2}{J} \left[ 1 + \frac{35}{3} \exp\left(-5\beta \frac{\hbar^2}{J}\right) \right], \end{aligned}$$

$$U_{\text{para}}(T) \approx \frac{\hbar^2}{2J} \frac{30 \exp\left(-\beta \frac{\hbar^2}{2J} 6\right)}{1 + 5 \exp\left(-\beta \frac{\hbar^2}{2J} 6\right)} \approx 15 \frac{\hbar^2}{J} \exp\left(-3\beta \frac{\hbar^2}{J}\right),$$

$$C_{\text{ortho}} = -k_B \beta^2 \frac{\partial}{\partial \beta} U_{\text{ortho}} \approx k_B \frac{175}{3} \left( \beta \frac{\hbar^2}{J} \right)^2 \exp \left( -5\beta \frac{\hbar^2}{J} \right) \xrightarrow{T \rightarrow 0} 0,$$

$$C_{\text{para}} \approx k_B 45 \left( \beta \frac{\hbar^2}{J} \right)^2 \exp \left( -3\beta \frac{\hbar^2}{J} \right) \xrightarrow{T \rightarrow 0} 0.$$

**High temperatures:**  $\beta(\hbar^2/2J) \ll 1$ :

The discrete energy-eigen values of the partition function move closer together, practically building a continuum, so that the sums can be replaced by integrals:

$$\begin{aligned} Z_{\text{ortho}} &\approx 3 \int_0^{\infty} (4x+3) \exp \left[ -\beta \frac{\hbar^2}{2J} (2x+1)(2x+2) \right] dx \\ &= 3 \int_0^{\infty} (4x+3) \exp \left\{ -\beta \frac{\hbar^2}{2J} \left[ 4 \left( x + \frac{3}{4} \right)^2 - \frac{1}{4} \right] \right\} dx. \end{aligned}$$

Substitution:  $y = x + 3/4$ :

$$\begin{aligned} Z_{\text{ortho}} &= 12 \exp \left( \beta \frac{\hbar^2}{8J} \right) \int_0^{\infty} dy y \exp \left( -\beta \frac{\hbar^2}{2J} 4y^2 \right) \\ &= 12 \exp \left( \beta \frac{\hbar^2}{8J} \right) \int_0^{\infty} dy \left[ \frac{d}{dy} \exp \left( -\beta \frac{2\hbar^2}{J} y^2 \right) \right] \left( -\frac{J}{4\hbar^2 \beta} \right) \\ &= \frac{3J}{\hbar^2 \beta} \exp \left( \beta \frac{\hbar^2}{8J} \right) \approx \frac{3J}{\hbar^2 \beta}, \\ Z_{\text{para}} &\approx \int_0^{\infty} (4x+1) \exp \left[ -\beta \frac{\hbar^2}{2J} 2x(2x+1) \right] dx \\ &= \exp \left( \beta \frac{\hbar^2}{8J} \right) \int_0^{\infty} (4x+1) \exp \left[ -\beta \frac{2\hbar^2}{J} \left( x + \frac{1}{4} \right)^2 \right] dx \\ &= 4 \exp \left( \beta \frac{\hbar^2}{8J} \right) \int_0^{\infty} dy y \exp \left( -\beta \frac{2\hbar^2}{J} y^2 \right) \end{aligned}$$

$$\begin{aligned}
 &= -\frac{J}{\beta\hbar^2} \exp\left(\beta\frac{\hbar^2}{8J}\right) \int_0^\infty dy \frac{d}{dy} \exp\left(-\beta\frac{2\hbar^2}{J}y^2\right) \\
 &= \frac{J}{\beta\hbar^2} \exp\left(\beta\frac{\hbar^2}{8J}\right) \approx \frac{J}{\hbar^2\beta},
 \end{aligned}$$

$$U_{\text{ortho}} = -\frac{\partial}{\partial\beta} \ln Z_{\text{ortho}} = \frac{1}{\beta} = k_{\text{B}}T,$$

$$U_{\text{para}} = k_{\text{B}}T$$

$$\implies C_{\text{ortho}} = C_{\text{para}} = k_{\text{B}}.$$

3. Mixture at thermal equilibrium: **All** states are now available for the system. Therefore:

$$Z(T) = Z_{\text{ortho}}(T) + Z_{\text{para}}(T).$$

**Low temperatures:**

$$Z(T) \approx 1 + 9 \exp\left(-\beta\frac{\hbar^2}{J}\right),$$

$$U(T) \approx 9\frac{\hbar^2}{J} \frac{\exp\left(-\beta\frac{\hbar^2}{J}\right)}{1 + 9 \exp\left(-\beta\frac{\hbar^2}{J}\right)} \approx 9\frac{\hbar^2}{J} \exp\left(-\beta\frac{\hbar^2}{J}\right),$$

$$C(T) \approx 9k_{\text{B}} \left(\frac{\hbar^2}{Jk_{\text{B}}T}\right)^2 \exp\left(-\frac{\hbar^2}{Jk_{\text{B}}T}\right) \xrightarrow{T \rightarrow 0} 0.$$

The third law of Thermodynamics is fulfilled!

Ratio at equilibrium:

$$\alpha(T) \approx \frac{9 \exp\left(-\beta\frac{\hbar^2}{J}\right)}{1 + 5 \exp\left(-3\beta\frac{\hbar^2}{J}\right)} \xrightarrow{T \rightarrow 0} 0.$$

For  $T \rightarrow 0$  the particle is in the para-state. The ground state of the system ( $l = 0$ ) is of para-type.

**High temperatures:**

$$Z(T) \approx \frac{4J}{\hbar^2\beta}, \quad U(T) \approx k_{\text{B}}T, \quad C(T) \approx k_{\text{B}}, \quad \alpha(T) = \frac{3J/\hbar^2\beta}{J/\hbar^2\beta} = 3.$$

All levels are equiprobable at high temperatures. Ortho-states are weighted by a factor 3.

### **Solution 2.3.14**

We have the relations:

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T,N} ; \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} .$$

Gibbs-Duhem relation ((3.35), Vol. 5):

$$F + pV = \mu N .$$

It follows therewith:

$$-k_B T \ln Z_N(T, V) + k_B T V \left( \frac{\partial \ln Z_N}{\partial V} \right)_{T,N} = -k_B T N \left( \frac{\partial \ln Z_N}{\partial N} \right)_{T,V} .$$

This means:

$$\ln Z_N(T, V) = V \left( \frac{\partial \ln Z_N}{\partial V} \right)_{T,N} + N \left( \frac{\partial \ln Z_N}{\partial N} \right)_{T,V} .$$

### **Solution 2.3.15**

Choose:

$$x = Nz .$$

Then it holds:

$$\Gamma(N + 1) = N^{N+1} \int_0^{\infty} e^{-Nz} z^N dz = N^{N+1} \int_0^{\infty} \exp[N(\ln z - z)] dz .$$



The integral has the structure of (2.35) with:

$$g(z) = \ln z - z$$

$$\implies g'(z) = \frac{1}{z} - 1 \implies z_0 = 1 ,$$

$$g''(z) = -\frac{1}{z^2} \implies g''(z_0) = -1 \quad (\text{maximum at } z_0).$$

Insertion into the *saddle point formula* (2.37):

$$\Gamma(N+1) = N^{N+1} \sqrt{\frac{2\pi}{N}} e^{-N} = \sqrt{2\pi N} N^N e^{-N} = N!$$

### Solution 2.3.16

1. Taylor expansion (Lagrange-remainder term)

$$F(E) = F(\langle E \rangle) + (E - \langle E \rangle)F'(\langle E \rangle) + \frac{1}{2}(E - \langle E \rangle)^2 F''(E^*) ,$$

$E^*$ : any fixed real number. We *average* the above equation:

$$\langle F(E) \rangle = F(\langle E \rangle) + \frac{1}{2} \langle (E - \langle E \rangle)^2 \rangle F''(E^*) ,$$

$$F''(E^*) \geq 0 \implies \langle F(E) \rangle \geq F(\langle E \rangle)$$

2. We discuss at first the corresponding inequality for the partition function.

Assertion:

$$Z \geq \widehat{Z} = \sum_n e^{-\beta \langle \varphi_n | \widehat{H} | \varphi_n \rangle} .$$

For the proof we can assume that  $\{|\varphi_n\rangle\}$  is a complete set. In the case of *incompleteness* there would be absence of some positive terms on the right-hand side of the inequality so that the inequality would more than ever be valid.

Eigen-states of  $\widehat{H}$  represent in any case a complete system:

$$|\varphi_n\rangle = \sum_m c_{nm} |E_m\rangle ; \quad \sum_m |c_{nm}|^2 = 1 ,$$

$$\langle \varphi_n | H | \varphi_n \rangle = \sum_{m,m'} c_{nm}^* c_{nm'} \langle E_m | H | E_{m'} \rangle = \sum_m |c_{nm}|^2 E_m .$$

Canonical partition function  $Z$ :

$$\begin{aligned} Z &= \text{Tr}(e^{-\beta\widehat{H}}) = \sum_n \langle \varphi_n | e^{-\beta\widehat{H}} | \varphi_n \rangle \\ &= \sum_n \sum_{m,m'} c_{nm}^* c_{nm'} \langle E_m | e^{-\beta\widehat{H}} | E_{m'} \rangle = \sum_n \left( \sum_m |c_{nm}|^2 e^{-\beta E_m} \right). \end{aligned}$$

For  $\widehat{Z}$  it holds:

$$\widehat{Z} = \sum_n e^{-\beta \langle \varphi_n | \widehat{H} | \varphi_n \rangle} = \sum_n e^{-\beta \sum_m |c_{nm}|^2 E_m}.$$

Let it be now:

$$F(E) = e^{-\beta E} \implies F''(E) \geq 0,$$

$$d_m \longleftrightarrow |c_{nm}|^2$$

$$\langle E \rangle = \sum_m |c_{nm}|^2 E_m$$

$$\langle F(E) \rangle = \sum_m |c_{nm}|^2 e^{-\beta E_m}.$$

The preconditions of part 1. are fulfilled:

$$\langle F(E) \rangle \geq F(\langle E \rangle)$$

$$\implies \sum_m |c_{nm}|^2 e^{-\beta E_m} \geq e^{-\beta \sum_m |c_{nm}|^2 E_m}$$

$$\implies \sum_n \sum_m |c_{nm}|^2 e^{-\beta E_m} \geq \sum_n e^{-\beta \sum_m |c_{nm}|^2 E_m}$$

$$\implies Z \geq \widehat{Z}$$

$$\implies F = -k_B T \ln Z \leq -k_B T \ln \left( \sum_n e^{-\beta \langle \varphi_n | \widehat{H} | \varphi_n \rangle} \right)$$

That was to be proven. The equality sign holds then and only then when the  $|\varphi_n\rangle$  are the eigen-states of  $\widehat{H}$ .

### Solution 2.3.17

1. Reformulation of the Airy-function:

$$Ai(\eta) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} ds e^{i(\frac{s^3}{3} + \eta s)} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} ds e^{\eta g(s)} .$$

Here we have defined:

$$g(s) = is + i\frac{s^3}{3\eta} .$$

We investigate

$$\begin{aligned} g(z) &= g(x + iy) = i(x + iy) + i\frac{(x + iy)^3}{3\eta} = \\ &= u(x, y) + iv(x, y) \end{aligned}$$

with

$$u(x, y) = \frac{y^3}{3\eta} - \frac{x^2y}{\eta} - y ; \quad v(x, y) = \frac{x^3}{3\eta} - \frac{xy^2}{\eta} + x .$$

Because of

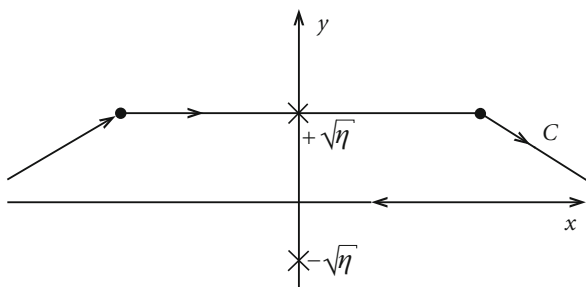
$$g'(z) = i + i\frac{z^2}{\eta} \quad \text{and} \quad g'(z_0) \stackrel{!}{=} 0 = i \left( 1 + \frac{z_0^2}{\eta} \right)$$

there is a saddle point at

$$z_0^{(\pm)} = \pm i\sqrt{\eta} .$$

The path  $C$  (Fig. A.9) is chosen such that it runs, for a finite  $x$ -interval, parallel to the  $x$ -axis ( $z = x + i\sqrt{\eta}$ ), but apart from that leading at  $\pm\infty$  into the real axis.

Fig. A.9



According to Cauchy's integral theorem ((4.413), Vol. 3) the integration along the real axis can be replaced by that along  $C$ . One easily recognizes that  $u(x, y)$  becomes maximal at  $z_0^{(+)} = i\sqrt{\eta}$ .

$$\begin{aligned}\frac{d}{dx}u(x, \sqrt{\eta}) &= -\frac{2x}{\sqrt{\eta}} \longrightarrow \frac{d}{dx}u(x, \sqrt{\eta})\Big|_{x=0} = 0, \\ \frac{d^2}{dx^2}u(x, \sqrt{\eta}) &= -\frac{2}{\sqrt{\eta}} < 0 \quad (\text{maximum}).\end{aligned}$$

In order to exploit the integral-estimation (2.37) we need:

$$\begin{aligned}g(z_0^{(+)}) &= -\frac{2}{3}\sqrt{\eta} \\ g''(z) &= 2i\frac{z}{\eta} \implies g''(z_0^{(+)}) = -\frac{2}{\sqrt{\eta}}.\end{aligned}$$

This eventually yields the assertion:

$$\begin{aligned}Ai(\eta) &\simeq \frac{1}{2\pi} \sqrt{\frac{2\pi}{-\eta g''(z_0^{(+)})}} e^{\eta g(z_0)} = \frac{1}{2\pi} \sqrt{\frac{2\pi}{-\eta \left(-\frac{2}{\sqrt{\eta}}\right)}} e^{-\eta \frac{2}{3}\sqrt{\eta}} \\ &= \frac{1}{2\sqrt{\pi}} \eta^{-\frac{1}{4}} e^{-\frac{2}{3}\eta^{3/2}}.\end{aligned}$$

2. The saddle-point method presumes for its applicability that only the immediate neighborhood of the saddle point on the path  $C$  contributes to the integral. This requires in particular that the integrand must not diverge at infinity.

Investigation of the integrand  $e^{\eta g(z)}$  at infinity:

$$z = Re^{i\varphi} = R(\cos \varphi + i \sin \varphi).$$

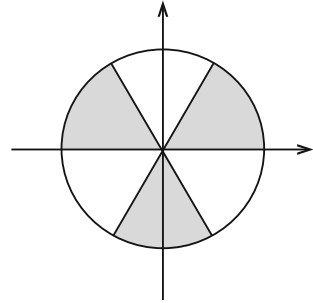
Integrand:

$$\begin{aligned}e^{\eta g(z)} &= \exp\left(i\frac{R^3}{3}e^{3i\varphi} + i\eta R e^{i\varphi}\right) \\ &= \exp\left[-\frac{1}{3}R^3 \sin(3\varphi) - \eta R \sin \varphi\right] \exp\left[i\left(\frac{1}{3}R^3 \cos(3\varphi) + \eta R \cos \varphi\right)\right].\end{aligned}$$

The asymptotic behavior ( $R \rightarrow \infty$ ) is determined by the term  $\exp\left(-\frac{1}{3}R^3 \sin(3\varphi)\right)$ .

$$\sin(3\varphi) \geq 0 \quad \text{for} \quad 0 \leq \varphi \leq \frac{\pi}{3}, \quad \frac{2\pi}{3} \leq \varphi \leq \pi, \quad \frac{4\pi}{3} \leq \varphi \leq \frac{5\pi}{3}.$$

Fig. A.10



In the other sectors:  $\sin(3\varphi) \leq 0$ . Only in the (hatched) regions (Fig. A.10) with  $\sin(3\varphi) \geq 0$  the integrand vanishes at infinity, in the other regions with  $\sin(3\varphi) \leq 0$  it diverges. When we would put the path  $C$  through the lower saddle point  $z_0^{(-)} = -i\sqrt{\eta}$ , then the integrand would grow beyond all limits at infinity.

### Solution 2.3.18

1.

$$g'(z) = g'(z) \frac{\partial z}{\partial x} = \frac{\partial g}{\partial x} = \frac{\partial u}{\partial x} + i \frac{\partial v}{\partial x}$$

$$g'(z) = g'(z) \frac{\partial z}{\partial y} (-i) = -i \frac{\partial g}{\partial y} = -i \frac{\partial u}{\partial y} + \frac{\partial v}{\partial y}.$$

The two equations must agree with respect to the real part as well as the imaginary part:

$$\frac{\partial u}{\partial x} \stackrel{!}{=} \frac{\partial v}{\partial y}; \quad \frac{\partial v}{\partial x} \stackrel{!}{=} -\frac{\partial u}{\partial y}.$$

$u$  and  $v$  are both at least twofold continuously differentiable because  $g(z)$  is analytic:

$$\frac{\partial^2 u}{\partial x^2} = \frac{\partial^2 v}{\partial x \partial y} = \frac{\partial^2 v}{\partial y \partial x} = -\frac{\partial^2 u}{\partial y^2}$$

This means:

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} = 0$$

Analogously one finds:

$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = 0 .$$

2.

$$\left. \frac{dg}{dz} \right|_{z=z_0} = 0 .$$

According to part 1. it must then hold:

$$\begin{aligned} \left( \frac{\partial u}{\partial x} + i \frac{\partial v}{\partial x} \right) \Big|_{z_0} = 0 &\quad \curvearrowright \quad \frac{\partial u}{\partial x} \Big|_{z_0} = \frac{\partial v}{\partial x} \Big|_{z_0} = 0 \\ \left( -i \frac{\partial u}{\partial y} + \frac{\partial v}{\partial y} \right) \Big|_{z_0} = 0 &\quad \curvearrowright \quad \frac{\partial u}{\partial y} \Big|_{z_0} = \frac{\partial v}{\partial y} \Big|_{z_0} = 0 . \end{aligned}$$

### **Solution 2.3.19**

1. Take

$$\sqrt{-g''(z_0)} \equiv a + ib \quad (a, b \text{ known}) .$$

Then we have on  $C$ :

$$\begin{aligned} z = x + iy &= \frac{t}{a + ib} + z_0 \\ &= \left( \frac{a}{a^2 + b^2} t + x_0 \right) + i \left( \frac{-b}{a^2 + b^2} t + y_0 \right) . \end{aligned}$$

We have therefore to choose  $C$  such that for  $z = x + iy$ :

$$x = \frac{a}{a^2 + b^2} t + x_0 ; \quad y = \frac{-b}{a^2 + b^2} t + y_0 .$$

With a real  $t$  that is obviously always satisfiable!

2. (a)

$$z_0 = x_0 \in \mathbb{R} ; \quad g''(z_0) > 0 .$$

This means

$$y_0 = 0 ; \quad a = 0 ; \quad b = \sqrt{g''(x_0)}$$

and therewith on  $C$ :

$$z = x + iy = x_0 - i\frac{1}{b}t .$$

It is thus a line parallel to the imaginary axis through the point  $x_0$  on the real axis (see Darwin-Fowler method in subsection 2.3.3)!

(b)

$$z_0 = i\eta, \eta \in \mathbb{R}; \quad g''(z_0) < 0 .$$

This means

$$y_0 = \eta; \quad x_0 = 0 \quad b = 0; \quad a = \sqrt{-g''(y_0)}$$

and therewith on  $C$ :

$$z = x + iy = \frac{1}{a}t + i\eta .$$

This is a line parallel to the real axis through the point  $z = i\eta$  (see Exercise 2.3.16).

## Section 2.4.2

### Solution 2.4.1

1. Possibilities of realization:

$$W(\{n_m(N)\}) = \frac{M!}{\prod_{m,N} n_m(N)!} .$$

Boundary conditions:

$$\begin{aligned} \sum_{m,N} n_m(N) &= M , \\ \sum_{m,N} E_m(N)n_m(N) &= E_t , \\ \sum_{m,N} Nn_m(N) &= N_t . \end{aligned}$$

2.

$$\ln W(\{n_m(N)\}) \approx M (\ln M - 1) - \sum_{m,N} n_m(N) (\ln n_m(N) - 1) .$$

$\lambda_1, \lambda_2, \lambda_3$ : Lagrange multipliers.

$$\begin{aligned} 0 &\stackrel{!}{=} \delta \left[ \ln W(\{n_m^{(0)}(N)\}) - \lambda_1 \sum_{m,N} n_m^{(0)}(N) \right. \\ &\quad \left. - \lambda_2 \sum_{m,N} E_m(N) n_m^{(0)}(N) - \lambda_3 \sum_{m,N} N n_m^{(0)}(N) \right] \\ &= \sum_{m,N} \delta n_m^{(0)}(N) \left[ \ln n_m^{(0)}(N) - 1 + 1 + \lambda_1 + \lambda_2 E_m(N) + \lambda_3 N \right] , \end{aligned}$$

Free variation  $\implies$  each summand by itself must already be zero.

$$\implies n_m^{(0)}(N) = \exp(-\lambda_1 - \lambda_2 E_m(N) - \lambda_3 N) .$$

3.

$$\begin{aligned} \ln W_{\max} &\approx M \ln M - \sum_{m,N} n_m^{(0)}(N) \ln n_m^{(0)}(N) \\ &= M \ln M - \sum_{m,N} n_m^{(0)}(N) (-\lambda_1 - \lambda_2 E_m(N) - \lambda_3 N) \\ &= M \ln M + \lambda_1 M + \lambda_2 E_t + \lambda_3 N_t , \\ \frac{1}{T} &\approx \frac{\partial}{\partial E_t} k_B \ln W_{\max} = k_B \lambda_2 , \\ -\frac{\mu}{T} &\approx \frac{\partial}{\partial N_t} k_B \ln W_{\max} = k_B \lambda_3 . \end{aligned}$$

Intermediate result:

$$n_m^{(0)}(N) = e^{-\lambda_1} e^{-\beta(E_m(N) - \mu N)} .$$



The parameter  $\lambda_1$  is fixed by the boundary condition:

$$M = \sum_{m,N} n_m^{(0)}(N) = e^{-\lambda_1} \sum_{m,N} e^{-\beta(E_m(N) - \mu N)}$$

$$\implies n_m^{(0)}(N) = M \frac{e^{-\beta(E_m(N) - \mu N)}}{\sum_{m,N} e^{-\beta(E_m(N) - \mu N)}} .$$

4.

$$p_m(N) \equiv \frac{n_m^{(0)}(N)}{M} : \text{probability to find one of the } M \text{ single systems}$$

$$\text{in the state } |E_m(N)\rangle .$$

It follows therewith for the statistical operator:

$$\hat{\rho} = \sum_{m,N} p_m(N) |E_m(N)\rangle \langle E_m(N)|$$

$$= \frac{\sum_{m,N} e^{-\beta(E_m(N) - \mu N)} |E_m(N)\rangle \langle E_m(N)|}{\sum_{m,N} e^{-\beta(E_m(N) - \mu N)}}$$

$$= \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\sum_{m,N} e^{-\beta(E_m(N) - \mu N)}} \underbrace{\sum_{m,N} |E_m(N)\rangle \langle E_m(N)|}_{\mathbb{1}}$$

$$= \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\sum_{m,N} e^{-\beta(E_m(N) - \mu N)}} = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\text{Tre}^{-\beta(\hat{H} - \mu \hat{N})}} \iff (2.71) .$$

### Solution 2.4.2

$$\Xi_z(T, V) = \sum_{\hat{N}} z^{\hat{N}} Z_{\hat{N}}(T, V) .$$

We consider  $z$  as complex variable.  $Z_N$  is then the residue of the complex function:  $\Xi_z/z^{N+1}$ . According to the residue theorem we thus have:

$$Z_N = \frac{1}{2\pi i} \oint_C \frac{\Xi_z}{z^{N+1}} dz ,$$

$C$ : closed path around the singularity  $z = 0$  in the complex plane.

**Solution 2.4.3**

We use the Eq. (2.87):

$$\Xi_z(T, V) = \exp(-\beta\Omega(T, V, z)) ,$$

where the  $T, V$ -dependences do not play a role here, so that these variables can be suppressed. With

$$\frac{\Xi_z}{z^{N+1}} \equiv \exp(Ng(z)) \rightsquigarrow g(z) = -\frac{1}{N}\beta\Omega - \left(1 + \frac{1}{N}\right) \ln z \approx -\left(\frac{1}{N}\beta\Omega + \ln z\right)$$

the integral

$$Z_N = \frac{1}{2\pi i} \oint_C \frac{\Xi_z}{z^{N+1}} dz$$

has, except for the factor  $1/2\pi i$ , the form of the integral in (2.35). It can therefore be evaluated according to the saddle-point method.

Saddle-point condition (2.36)

$$\left. \frac{dg}{dz} \right|_{z_0} \stackrel{!}{=} 0 = -\left. \left( \frac{1}{N}\beta \frac{d\Omega}{dz} + \frac{1}{z} \right) \right|_{z_0} .$$

According to (2.80):

$$\langle \widehat{N} \rangle = z \left( \frac{\partial}{\partial z} \ln \Xi_z(T, V) \right)_{T, V} = -\frac{z}{k_B T} \left( \frac{\partial \Omega}{\partial z} \right)_{T, V} .$$

The saddle-point condition thus reads:

$$\frac{1}{z_0} \stackrel{!}{=} \frac{1}{N} \frac{\langle \widehat{N} \rangle}{z_0} \iff \langle \widehat{N} \rangle \stackrel{!}{=} N ; \quad z_0 = e^{\beta\mu} .$$

$\mu$  is thereby the chemical potential for  $N = \langle \widehat{N} \rangle$ .

The saddle point  $z_0 = e^{\beta\mu}$  is real.

$$g(z_0) = \left( \frac{1}{\langle \widehat{N} \rangle} \beta\Omega + \beta\mu \right)$$

$$g''(z_0) = -\left. \left( \frac{1}{N} \beta \frac{d^2\Omega}{dz^2} - \frac{1}{z^2} \right) \right|_{z_0} .$$

The grand-canonical potential is extensive ( $\propto N$ ). Therefore:

$$\ln N g''(z_0) = \mathcal{O}(\ln N) .$$

When we now exploit the saddle-point approximation (2.37),

$$\ln Z_N \approx \ln \frac{1}{2\pi} + \ln \sqrt{\frac{2\pi}{N(z_0)g''(z_0)}} + N(z_0)g(z_0) ; \quad N(z_0) = \langle \widehat{N} \rangle ,$$

then we can confidently neglect for large particle numbers the first two summands compared to the third term:

$$\ln Z_N \approx \langle \widehat{N} \rangle g(z_0) = -\beta \left( \Omega + \mu \langle \widehat{N} \rangle \right) .$$

This yields:

$$F = -k_B T \ln Z_N = \Omega + \mu \langle \widehat{N} \rangle .$$

### Solution 2.4.4

$$\begin{aligned} \frac{\partial}{\partial z} \left( z \frac{\partial \ln \Xi_z}{\partial z} \right) &= \frac{\partial}{\partial z} \ln \Xi_z + z \frac{\partial^2}{\partial z^2} \ln \Xi_z = \\ &= \frac{1}{\Xi_z} \frac{\partial \Xi_z}{\partial z} - z \frac{1}{\Xi_z^2} \left( \frac{\partial \Xi_z}{\partial z} \right)^2 + z \frac{1}{\Xi_z} \frac{\partial^2 \Xi_z}{\partial z^2} , \\ \frac{1}{\Xi_z} \frac{\partial}{\partial z} \Xi_z &= \frac{1}{\Xi_z} \sum_N N z^{N-1} Z_N = \frac{1}{z} \langle \widehat{N} \rangle , \\ -z \frac{1}{\Xi_z^2} \left( \frac{\partial \Xi_z}{\partial z} \right)^2 &= -\frac{1}{z} \langle \widehat{N} \rangle^2 , \\ z \frac{1}{\Xi_z} \frac{\partial^2 \Xi_z}{\partial z^2} &= z \frac{1}{\Xi_z} \sum_N N(N-1) z^{N-2} Z_N = \frac{1}{z} (\langle \widehat{N}^2 \rangle - \langle \widehat{N} \rangle) \\ \implies \frac{\partial}{\partial z} \left( z \frac{\partial}{\partial z} \ln \Xi_z \right) &= \frac{1}{z} (\langle \widehat{N} \rangle - \langle \widehat{N} \rangle^2 + \langle \widehat{N}^2 \rangle - \langle \widehat{N} \rangle) \\ &= \frac{1}{z} \langle (\widehat{N} - \langle \widehat{N} \rangle)^2 \rangle \geq 0, \quad \text{since } z > 0 . \end{aligned}$$

## Section 2.6.4

### Solution 2.6.1

$$H = H_0 + H_1 ;$$

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 , \quad H_1 = \alpha \frac{1}{2}m\omega^2 q^2 ; \quad |\alpha| < 1 .$$

1. Introduction of creation and annihilation operators ((4.125) and (4.126), Vol. 6):

$$a = \frac{1}{\sqrt{2\hbar}} \left( \sqrt{m\omega} q + i \frac{p}{\sqrt{m\omega}} \right) , \quad a^+ = \frac{1}{\sqrt{2\hbar}} \left( \sqrt{m\omega} q - i \frac{p}{\sqrt{m\omega}} \right) .$$

The reversal yields

$$q = \sqrt{\frac{\hbar}{2m\omega}} (a + a^+) , \quad p = -i \sqrt{\frac{1}{2}\hbar m\omega} (a - a^+)$$

and leads to:

$$H_0 = \hbar \omega \left( a^+ a + \frac{1}{2} \right) .$$

The solution of the eigen-value problem is known:

$$H_0 |n\rangle = E_n |n\rangle , \quad E_n = \hbar \omega \left( n + \frac{1}{2} \right) ; \quad n = 0, 1, 2, \dots$$

Free energy:

a) 'unperturbed' system:

$$\begin{aligned} F_0 &= -k_B T \ln Z_0(T) , \\ Z_0 &= \text{Tr} e^{-\beta H_0} = \sum_n \langle n | e^{-\beta H_0} | n \rangle \\ &= \sum_n e^{-\beta \hbar \omega (n + \frac{1}{2})} = e^{-\frac{1}{2} \beta \hbar \omega} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n \\ \implies Z_0(T) &= e^{-\frac{1}{2} \beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}} = \frac{1}{2 \sinh \frac{1}{2} \beta \hbar \omega} \end{aligned}$$

$$\begin{aligned} \implies F_0(T) &= k_B T \ln \left( 2 \sinh \left( \frac{1}{2} \beta \hbar \omega \right) \right) \\ &= \frac{1}{2} \hbar \omega + k_B T \ln(1 - e^{-\beta \hbar \omega}) . \end{aligned}$$

b) Perturbation theory of first order:

$$F \approx F_0 + \langle H_1 \rangle^{(0)} .$$

Thereby

$$\begin{aligned} \langle H_1 \rangle^{(0)} &= \frac{1}{Z_0} \text{Tr}(e^{-\beta H_0} H_1) = \frac{1}{Z_0} \sum_n \langle n | e^{-\beta H_0} H_1 | n \rangle \\ &= \frac{1}{Z_0} \sum_n e^{-\beta \hbar \omega (n + \frac{1}{2})} \langle n | H_1 | n \rangle . \end{aligned}$$

It remains to be calculated:

$$\begin{aligned} \langle n | H_1 | n \rangle &= \alpha \frac{1}{2} m \omega^2 \langle n | q^2 | n \rangle \\ &= \alpha \frac{1}{2} m \omega^2 \frac{\hbar}{2m\omega} \langle n | a^{+2} + a^2 + aa^+ + a^+a | n \rangle \\ &= \frac{1}{4} \alpha \hbar \omega \langle n | (2a^+a + 1) | n \rangle \\ &= \frac{1}{4} \alpha \hbar \omega (2n + 1) = \frac{1}{2} \alpha \hbar \omega \left( n + \frac{1}{2} \right) . \end{aligned}$$

It follows therewith:

$$\begin{aligned} \langle H_1 \rangle^{(0)} &= \frac{1}{2} \alpha \hbar \omega \frac{1}{Z_0} \sum_{n=0}^{\infty} \left( n + \frac{1}{2} \right) e^{-\beta \hbar \omega (n + \frac{1}{2})} = -\frac{1}{Z_0} \frac{\alpha}{2} \frac{\partial}{\partial \beta} Z_0(T) \\ &= -\frac{\alpha}{2} \frac{\partial}{\partial \beta} \ln Z_0(T) = \frac{\alpha}{2} \frac{1}{2} \hbar \omega \coth \left( \frac{1}{2} \beta \hbar \omega \right) . \end{aligned}$$

Free energy:

$$F(T) \approx k_B T \ln \left( 2 \sinh \left( \frac{1}{2} \beta \hbar \omega \right) \right) + \frac{\alpha}{4} \hbar \omega \coth \left( \frac{1}{2} \beta \hbar \omega \right) .$$

2. The problem is of course exactly solvable:

$$\omega \rightarrow \bar{\omega} = \omega \sqrt{1 + \alpha} .$$

Partition function:

$$\begin{aligned}
 Z &= Z_0(\omega\sqrt{1+\alpha}) = Z_0\left(\omega\left(1 + \frac{1}{2}\alpha + \dots\right)\right) \\
 &= Z_0(\omega) + \frac{1}{2}\alpha\omega\frac{d}{d\omega}Z_0(\omega) + \dots \\
 &= Z_0(\omega) + \frac{1}{2}\alpha\beta\frac{d}{d\beta}Z_0 + \dots \\
 &= Z_0 - \beta Z_0\langle H_1 \rangle^{(0)} = Z_0(1 - \beta\langle H_1 \rangle^{(0)}) .
 \end{aligned}$$

Free energy:

$$\begin{aligned}
 F &= -k_B T \ln Z = F_0 - k_B T \ln(1 - \beta\langle H_1 \rangle^{(0)}) \approx \\
 &\approx F_0 + k_B T \beta\langle H_1 \rangle^{(0)} = F_0 + \langle H_1 \rangle^{(0)} \quad \text{q. e. d.}
 \end{aligned}$$

### Solution 2.6.2

1. Upper limit for the free energy (2.139):

$$F \leq F^* + \langle H - H^* \rangle^* .$$

It holds thereby:

$$H - H^* = \frac{1}{2}m(\omega^2 - \omega^{*2})q^2 + \alpha\frac{m^2\omega^2}{\hbar}q^4 .$$

The free energy  $F^*$  of the test-system corresponds to the  $F_0$  in Exercise 2.6.1:

$$F^* = \frac{1}{2}\hbar\omega^* + k_B T \ln(1 - e^{-\beta\hbar\omega^*}) .$$

With

$$f_+(\omega^*) = \frac{1}{e^{\beta\hbar\omega^*} - 1} \quad (\text{'Bose function'})$$

$F^*$  can also be written as follows:

$$F^* = -\frac{1}{2}\hbar\omega^* - k_B T \ln f_+(\omega^*) .$$

The test-Hamilton operator is that of the harmonic oscillator. The solution of the respective problem is known:

$$H^*|n\rangle^* = \hbar\omega^* \left( n + \frac{1}{2} \right) |n\rangle^* ; \quad n = 0, 1, 2, \dots$$

It thus remains to be calculated:

$$\langle q^2 \rangle^* = \frac{1}{Z^*} \sum_n e^{-\beta\hbar\omega^*(n+\frac{1}{2})} \langle n | q^2 | n \rangle^* ,$$

$$\langle q^4 \rangle^* = \frac{1}{Z^*} \sum_n e^{-\beta\hbar\omega^*(n+\frac{1}{2})} \langle n | q^4 | n \rangle^* .$$

Because of

$$q^2 = \frac{\hbar}{2m\omega^*} (a^2 + aa^+ + a^+a + a^{+2}) \quad \text{and} \quad [a, a^+]_- = 1$$

one finds:

$$\langle n | q^2 | n \rangle^* = \frac{\hbar}{2m\omega^*} \langle n | (2a^+a + 1) | n \rangle^* = \frac{\hbar}{2m\omega^*} (2n + 1) .$$

Analogously:

$$\begin{aligned} & \langle n | q^4 | n \rangle^* \\ &= \frac{\hbar^2}{4m^2\omega^{*2}} \langle n | (a^4 + a^3a^+ + a^2a^+a + a^2a^{+2} + aa^+a^2 + aa^+aa^+ + aa^{+2}a \\ & \quad + aa^{+3} + a^+a^3 + a^+a^2a^+ + a^+aa^+a + a^+aa^{+2} + a^{+2}a^2 \\ & \quad + a^{+2}aa^+ + a^{+3}a + a^{+4}) | n \rangle^* \\ &= \frac{\hbar^2}{4m^2\omega^{*2}} \langle n | (a^2a^{+2} + aa^+aa^+ + aa^{+2}a + a^+a^2a^+ + a^+aa^+a + a^{+2}a^2) | n \rangle^* \\ &= \frac{\hbar^2}{4m^2\omega^{*2}} \left( (n+1)(n+2) + (n+1)^2 + n(n+1) + n(n+1) + n^2 + n(n-1) \right) \\ &= \frac{\hbar^2}{4m^2\omega^{*2}} (6n^2 + 6n + 3) . \end{aligned}$$

It was used:

$$a^+|n\rangle^* = \sqrt{n+1}|n+1\rangle^* , \quad a|n\rangle^* = \sqrt{n}|n-1\rangle^* .$$

The partition function  $Z^*$  was calculated as  $Z_0$  in Exercise 2.6.1:

$$Z^* = \frac{1}{2 \sinh\left(\frac{1}{2}\beta\hbar\omega^*\right)}.$$

Therewith we determine:

$$\begin{aligned} \langle q^2 \rangle^* &= \frac{\hbar}{2m\omega^*} \frac{1}{Z^*} \sum_n e^{-\beta\hbar\omega^*(n+\frac{1}{2})} (2n+1) \\ &= \frac{\hbar}{m\omega^*} \frac{1}{Z^*} \left( -\frac{\partial}{\partial\beta} \sum_n e^{-\beta\hbar\omega^*(n+\frac{1}{2})} \right) \frac{1}{\hbar\omega^*} = -\frac{1}{m\omega^{*2}} \frac{1}{Z^*} \frac{\partial}{\partial\beta} Z^* \\ &= \frac{1}{m\omega^{*2}} \frac{\partial}{\partial\beta} \ln [2 \sinh\left(\frac{1}{2}\beta\hbar\omega^*\right)] = \frac{\hbar}{2m\omega^*} \coth\left(\frac{1}{2}\beta\hbar\omega^*\right). \end{aligned}$$

We still use

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} = \frac{e^{2x} + 1}{e^{2x} - 1} = \frac{2}{e^{2x} - 1} + 1.$$

getting therewith the first intermediate result:

$$\frac{1}{2}m(\omega^2 - \omega^{*2})\langle q^2 \rangle^* = \frac{\hbar}{4\omega^*}(\omega^2 - \omega^{*2})(2f_+(\omega^*) + 1).$$

We still need

$$\begin{aligned} \langle q^4 \rangle^* &= \frac{3\hbar^2}{4m^2\omega^{*2}} \frac{1}{Z^*} \sum_n e^{-\beta\hbar\omega^*(n+\frac{1}{2})} [2n^2 + (2n+1)] \\ &= \frac{3\hbar^2}{2m^2\omega^{*2}} \frac{1}{Z^*} \sum_n e^{-\beta\hbar\omega^*(n+\frac{1}{2})} \left( n + \frac{1}{2} \right) \\ &\quad + \frac{3\hbar^2}{2m^2\omega^{*2}} \frac{1}{Z^*} \sum_n e^{-\beta\hbar\omega^*n} n^2 e^{-\frac{1}{2}\beta\hbar\omega^*} \\ &= \frac{3\hbar^2}{2m^2\omega^{*2}} \frac{1}{2} \coth\left(\frac{1}{2}\beta\hbar\omega^*\right) \\ &\quad + \frac{3\hbar^2}{2m^2\omega^{*2}} e^{-\frac{1}{2}\beta\hbar\omega^*} \frac{1}{(\hbar\omega^*)^2} \frac{1}{Z^*} \frac{\partial^2}{\partial\beta^2} \frac{1}{1 - e^{-\beta\hbar\omega^*}} \end{aligned}$$



$$\begin{aligned}
&= \frac{3\hbar^2}{4m^2\omega^{*2}} \coth\left(\frac{1}{2}\beta\hbar\omega^*\right) \\
&\quad + \frac{3\hbar^2}{2m^2\omega^{*2}} e^{-\frac{1}{2}\beta\hbar\omega^*} \frac{1}{\hbar\omega^*} \frac{1}{Z^*} \frac{\partial}{\partial\beta} \frac{-e^{-\beta\hbar\omega^*}}{(1-e^{-\beta\hbar\omega^*})^2} \\
&= \frac{3\hbar^2}{4m^2\omega^{*2}} \left[ \coth\left(\frac{1}{2}\beta\hbar\omega^*\right) \right. \\
&\quad \left. + 2 \frac{e^{-\frac{1}{2}\beta\hbar\omega^*}}{Z^*} \frac{e^{-\beta\hbar\omega^*}}{(1-e^{-\beta\hbar\omega^*})^2} \left(1 + \frac{2e^{-\beta\hbar\omega^*}}{1-e^{-\beta\hbar\omega^*}}\right) \right] \\
&= \frac{3\hbar^2}{4m^2\omega^{*2}} \coth\left(\frac{1}{2}\beta\hbar\omega^*\right) \left[1 + 2 \frac{e^{-\beta\hbar\omega^*}(1-e^{-\beta\hbar\omega^*})}{(1-e^{-\beta\hbar\omega^*})^2}\right] \\
&= \frac{3\hbar^2}{4m^2\omega^{*2}} \left[\coth\left(\frac{1}{2}\beta\hbar\omega^*\right)\right]^2.
\end{aligned}$$

It remains therewith

$$\alpha \frac{m^2\omega^2}{\hbar} \langle q^4 \rangle^* = \alpha \frac{3\hbar\omega^2}{4\omega^{*2}} (2f_+(\omega^*) + 1)^2.$$

For the free energy of the anharmonic oscillator we have found the following estimation:

$$\begin{aligned}
F \leq F^* + \langle H - H^* \rangle^* &= -k_B T \ln f_+(\omega^*) - \frac{1}{2}\hbar\omega^* \left(f_+(\omega^*) + \frac{3}{2}\right) \\
&\quad + \frac{1}{2}\hbar \frac{\omega^2}{\omega^*} \left(f_+(\omega^*) + \frac{1}{2}\right) + \frac{3}{4}\hbar\alpha \frac{\omega^2}{\omega^{*2}} (2f_+(\omega^*) + 1)^2.
\end{aligned}$$

$\omega^*$  remains at first a free variational parameter, which can be adjusted in such a manner that the right-hand side of the inequality becomes minimal.

2. We look for the minimum of the upper bound of  $F$ , in order to achieve in this way an optimal estimation for  $F$ .

$$\begin{aligned}
&\frac{\partial}{\partial\omega^*} (F^* + \langle H - H^* \rangle^*) \\
&= -k_B T \frac{f'_+}{f_+} - \frac{\hbar}{2} \left(f_+ + \frac{3}{2}\right) - \frac{1}{2}\hbar\omega^* f'_+ - \frac{1}{2}\hbar \frac{\omega^2}{\omega^{*2}} \left(f_+ + \frac{1}{2}\right) \\
&\quad + \frac{1}{2}\hbar \frac{\omega^2}{\omega^{*2}} f'_+ - \frac{3}{2}\hbar\alpha \frac{\omega^2}{\omega^{*3}} (2f_+ + 1)^2 + 3\hbar\alpha \frac{\omega^2}{\omega^{*2}} f'_+ (2f_+ + 1).
\end{aligned}$$

For the derivative  $f'_+$  we get:

$$\begin{aligned} f'_+ &\equiv \frac{d}{d\omega^*} f_+(\omega^*) = -\beta\hbar \frac{e^{\beta\hbar\omega^*}}{(e^{\beta\hbar\omega^*} - 1)^2} \\ &= -\beta\hbar \left[ \frac{1}{(e^{\beta\hbar\omega^*} - 1)} + \frac{1}{(e^{\beta\hbar\omega^*} - 1)^2} \right] \\ &= -\beta\hbar f_+(\omega^*) (1 + f_+(\omega^*)). \end{aligned}$$

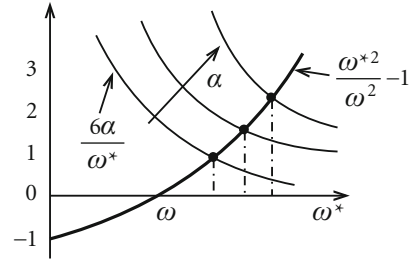
Therewith the extremal condition can be written as follows:

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{\partial}{\partial\omega^*} (F^* + \langle H - H^* \rangle) \\ &= \hbar (1 + f_+) - \frac{\hbar}{2} \left( f_+ + \frac{3}{2} \right) + \frac{\hbar^2 \omega^*}{2k_B T} f_+ (1 + f_+) \\ &\quad - \frac{1}{2} \hbar \frac{\omega^2}{\omega^{*2}} \left( f_+ + \frac{1}{2} \right) - \frac{1}{2} \frac{\hbar^2 \omega^2}{k_B T \omega^*} f_+ (1 + f_+) \\ &\quad - \frac{3}{2} \hbar \alpha \frac{\omega^2}{\omega^{*3}} (2f_+ + 1)^2 - \frac{3\hbar^2 \alpha}{k_B T} \frac{\omega^2}{\omega^{*2}} f_+ (1 + f_+) (2f_+ + 1) \\ &= \frac{\hbar}{2} \left( f_+ + \frac{1}{2} \right) \left( 1 - \frac{\omega^2}{\omega^{*2}} \right) + \frac{\hbar^2}{2k_B T} f_+ (1 + f_+) \left( \omega^* - \frac{\omega^2}{\omega^*} \right) \\ &\quad - 6\hbar \alpha \frac{\omega^2}{\omega^{*3}} \left( f_+ + \frac{1}{2} \right)^2 - 6 \frac{\hbar^2 \alpha}{k_B T} f_+ (1 + f_+) \left( f_+ + \frac{1}{2} \right) \frac{\omega^2}{\omega^{*2}} \\ &= \frac{\hbar}{2} \left( f_+ + \frac{1}{2} \right) \left[ 1 - \frac{\omega^2}{\omega^{*2}} - 12\alpha \frac{\omega^2}{\omega^{*3}} \left( f_+ + \frac{1}{2} \right) \right] \\ &\quad + \frac{\hbar^2 \omega^*}{2k_B T} f_+ (1 + f_+) \left[ 1 - \frac{\omega^2}{\omega^{*2}} - 12\alpha \frac{\omega^2}{\omega^{*3}} \left( f_+ + \frac{1}{2} \right) \right]. \end{aligned}$$

This can be compressed as follows:

$$0 \stackrel{!}{=} \left[ \frac{\hbar}{2} \left( f_+ + \frac{1}{2} \right) + \frac{\hbar^2 \omega^*}{2k_B T} f_+ (1 + f_+) \right] \left[ 1 - \frac{\omega^2}{\omega^{*2}} - 12\alpha \frac{\omega^2}{\omega^{*3}} \left( f_+ + \frac{1}{2} \right) \right].$$

Fig. A.11



The first bracket is in any case unequal zero, so that we are left with a transcendental conditional equation for the ‘optimal’ parameter  $\omega^*$ :

$$12\alpha \left( f_+ + \frac{1}{2} \right) = \omega^* \left( \frac{\omega^{*2}}{\omega^2} - 1 \right) .$$

Special case:  $T = 0 \implies f_+ \equiv 0$ .

It then only remains to solve:  $\omega^{*2}/\omega^2 - 1 = 6\alpha/\omega^*$  (Fig. A.11).

- (1)  $\alpha = 0 \implies \omega^* = \omega$ : plausible
- (2)  $\alpha$  small  $\implies \omega^* = \omega + x \implies \frac{2x}{\omega} \approx \frac{6\alpha}{\omega} \left( 1 - \frac{x}{\omega} \right)$   
 $\implies x \approx 3\alpha \implies \omega^* \approx \omega + 3\alpha$
- (3)  $\alpha$  very large:  $\implies \omega^* \approx (6\alpha\omega^2)^{1/3}$ .

**Solution 2.6.3**

Consider at first:  $n \in \mathbf{N}$ ;  $[A, B]_- \neq 0$ .

$$\begin{aligned} \frac{d}{dx} \text{Tr}(xA + B)^n &= \text{Tr} \left( \frac{d}{dx} (xA + B)^n \right) = \text{Tr} \left[ \frac{d}{dx} (xA + B) \cdots (xA + B) \right] \\ &= \sum_{i=1}^n \text{Tr} \left[ (xA + B) \cdots \frac{d}{dx} \underbrace{(xA + B)}_{i\text{-th position}} \cdots (xA + B) \right] \\ &= \sum_{i=1}^n \text{Tr} \left[ (xA + B) \cdots \underbrace{A}_{i\text{-th position}} \cdots (xA + B) \right] \\ &= \sum_{i=1}^n \text{Tr} [A (xA + B)^{n-1}] \quad (\text{cyclic invariance}) \\ &= n \text{Tr} [A (xA + B)^{n-1}] . \end{aligned}$$

It follows therewith:

$$\begin{aligned} \frac{d}{dx} \text{Tr}(e^{xA+B}) &= \frac{d}{dx} \text{Tr} \left( \sum_{n=0}^{\infty} \frac{1}{n!} (xA+B)^n \right) = \text{Tr} \left( \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d}{dx} (xA+B)^n \right) \\ &= \text{Tr} \left( \sum_{n=0}^{\infty} \frac{1}{n!} nA (xA+B)^{n-1} \right) = \text{Tr} \left( \sum_{n'=0}^{\infty} A \frac{1}{n'!} (xA+B)^{n'} \right) \\ &= \text{Tr}(Ae^{xA+B}) . \end{aligned}$$

### Section 3.1.3

#### Solution 3.1.1

1. Canonical partition function of the ideal quantum gases:

$$Z_N(T, V) = \sum_{\{n_r\}}^{\sum_r n_r = N} \exp \left( -\beta \sum_r n_r \varepsilon_r \right) .$$

Average occupation number:

$$\begin{aligned} \langle \hat{n}_j \rangle &= \text{Tr}(\hat{\rho} \hat{n}_j) = \frac{1}{Z_N} \sum_{\{n_r\}}^{\sum_r n_r = N} n_j \exp \left( -\beta \sum_r n_r \varepsilon_r \right) \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_j} \ln Z_N(T, V) . \end{aligned}$$

2. We define:

$$Q(z) = \sum_{N=0}^{\infty} z^N Z_N .$$

Exactly the same justification as that after (3.18) leads to:

$$Q(z) = \prod_r \left[ \sum_{n_r} (ze^{-\beta \varepsilon_r})^{n_r} \right] = \begin{cases} \prod_r (1 + ze^{-\beta \varepsilon_r}) : & \text{fermions,} \\ \prod_r \frac{1}{1 - ze^{-\beta \varepsilon_r}} : & \text{bosons.} \end{cases}$$

In addition it holds:

$$Z_N(T, V) = \frac{1}{2\pi i} \oint_c \frac{Q(z)}{z^{N+1}} dz.$$

C: closed path in the complex plane around  $z = 0$ . It holds also:

$$Z_N(T, V) = \frac{1}{2\pi i} \oint_c e^{Ng(z)} z,$$

$$g(z) = \frac{1}{N} \ln Q(z) - \frac{N+1}{N} \ln z \approx \frac{1}{N} \ln Q(z) - \ln z.$$

Saddle point:

$$\begin{aligned} \left. \frac{d}{dz} g(z) \right|_{z_0} &\stackrel{!}{=} 0 = \left. \frac{1}{N} \frac{\partial}{\partial z} \ln Q(z) \right|_{z_0} - \frac{1}{z_0} \\ \implies \frac{N}{z_0} &= \begin{cases} \sum_r \frac{1}{e^{\beta \varepsilon_r} + z_0} &: \text{ fermions,} \\ \sum_r \frac{1}{e^{\beta \varepsilon_r} - z_0} &: \text{ bosons.} \end{cases} \end{aligned}$$

$z_0$  is therewith implicitly determined!

Saddle-point method:

$$\begin{aligned} \ln Z_N(T, V) &\approx Ng(z_0) \approx \ln Q(z_0) - N \ln z_0 \\ &= \begin{cases} \sum_r \ln(1 + z_0 e^{-\beta \varepsilon_r}) - N \ln z_0 &: \text{ fermions,} \\ -\sum_r \ln(1 - z_0 e^{-\beta \varepsilon_r}) - N \ln z_0 &: \text{ bosons.} \end{cases} \end{aligned}$$

3.

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{N, V} = -k_B T \left( \frac{\partial}{\partial N} \ln Z_N(T, V) \right)_{T, V} = +k_B T \ln z_0$$

$$\implies z_0 = e^{\beta \mu},$$

$$\implies N = \begin{cases} \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1} &: \text{ fermions,} \\ \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1} &: \text{ bosons.} \end{cases}$$

Average occupation numbers:

Fermions:

$$\langle \hat{n}_j \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_j} \ln Z_N(T, V) = -\frac{1}{\beta} \frac{-\beta e^{-\beta(\varepsilon_j - \mu)}}{1 + e^{-\beta(\varepsilon_j - \mu)}} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} + 1} .$$

Bosons:

$$\langle \hat{n}_j \rangle = +\frac{1 + \beta e^{-\beta(\varepsilon_j - \mu)}}{\beta} \frac{1}{1 - e^{-\beta(\varepsilon_j - \mu)}} = \frac{1}{e^{\beta(\varepsilon_j - \mu)} - 1} .$$

These are exactly the expressions (3.29) and (3.30).

### Solution 3.1.2

1. Because of the Pauli principle each energy level can be occupied by at most two fermions with opposite spin projections ( $m_s = +\frac{1}{2}$  and  $-\frac{1}{2}$ ). This means:

$$\langle \hat{N} \rangle \leq 2M .$$

2. For the grand-canonical partition function we have (3.20), where  $\prod_r$  is to be built over all *states*. Degenerate energy levels appear as factors so often as given by their degree of degeneracy:

$$\Xi_{\mu}^{(-)}(T, V) = \prod_{r=1}^M [1 + e^{-\beta(\varepsilon_r - \mu)}]^2 .$$

- 3.

$$\begin{aligned} F(\langle \hat{N} \rangle \text{ particles}, \mu) &= \langle \hat{N} \rangle \mu - k_B T \ln \Xi_{\mu} \\ &= \langle \hat{N} \rangle \mu - 2k_B T \sum_{r=1}^M \ln [1 + e^{-\beta(\varepsilon_r - \mu)}] \\ &= \langle \hat{N} \rangle \mu - 2k_B T \sum_{r=1}^M \ln \frac{1 + e^{\beta(\varepsilon_r - \mu)}}{e^{\beta(\varepsilon_r - \mu)}} \\ &= \langle \hat{N} \rangle \mu - 2k_B T \sum_{r=1}^M \ln [1 + e^{\beta(\varepsilon_r - \mu)}] + 2k_B T \sum_{r=1}^M \beta(\varepsilon_r - \mu) \end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{r=1}^M \varepsilon_r + (2M - \langle \hat{N} \rangle)(-\mu) \\
&\quad - k_B T \ln \prod_{r=1}^M \{1 + e^{-\beta [(-\varepsilon_r) - (-\mu)]}\}^2.
\end{aligned}$$

On the other hand:

$$\begin{aligned}
&F \left[ (2M - \langle \hat{N} \rangle) \text{ holes}, -\mu \right] \\
&= (2M - \langle \hat{N} \rangle)(-\mu) - k_B T \ln \prod_{r=1}^M \{1 + e^{-\beta [(-\varepsilon_r) - (-\mu)]}\}^2.
\end{aligned}$$

The difference thus lies only in the constant term  $2 \sum_{r=1}^M \varepsilon_r$ , which does **not** influence the thermodynamic properties of the system. (Free choice of the energy-zero!)

$\implies$  *particle-hole symmetry*.

### Solution 3.1.3

$$\langle \hat{n}_r \rangle^{(\pm)} = \frac{1}{\Xi_\mu^{(\pm)}} \sum_N \sum_{\{n_p\}}^{\sum_p n_p = N} n_r \exp \left[ -\beta \sum_p n_p (\varepsilon_p - \mu) \right].$$

This we use to calculate:

$$\begin{aligned}
&\frac{\partial}{\partial(\beta \varepsilon_r)} \langle \hat{n}_r \rangle^{(\pm)} \\
&= \frac{-1}{\Xi_\mu^{(\pm)}} \sum_N \sum_{\{n_p\}}^{\sum_p n_p = N} n_r^2 \exp \left[ -\beta \sum_p n_p (\varepsilon_p - \mu) \right] \\
&\quad + \frac{1}{\Xi_\mu^{(\pm)2}} \left\{ \sum_N \sum_{\{n_p\}}^{\sum_p n_p = N} n_r \exp \left[ -\beta \sum_p n_p (\varepsilon_p - \mu) \right] \right\}^2 \\
&= -\langle \hat{n}_r^2 \rangle^{(\pm)} + \langle \hat{n}_r \rangle^{(\pm)2}.
\end{aligned}$$

Therefore:

$$(\overline{\Delta n_r})^2 = \frac{-1}{\langle \hat{n}_r \rangle^{(\pm)2}} \frac{\partial}{\partial (\beta \varepsilon_r)} \langle \hat{n}_r \rangle^{(\pm)} .$$

With

$$\langle \hat{n}_r \rangle^{(\pm)} = \frac{1}{e^{\beta(\varepsilon_r - \mu)} \mp 1}$$

it further follows:

$$\begin{aligned} (\overline{\Delta n_r})^2 &= \frac{-1}{\langle \hat{n}_r \rangle^{(\pm)2}} \frac{-e^{\beta(\varepsilon_r - \mu)}}{[e^{\beta(\varepsilon_r - \mu)} \mp 1]^2} = e^{\beta(\varepsilon_r - \mu)} \\ &\implies (\overline{\Delta n_r})^2 = \frac{1}{\langle \hat{n}_r \rangle^{(\pm)}} \pm 1 . \end{aligned}$$

( $\pm$ : upper sign for bosons, lower sign for fermions.)

For fermions there exists of course, because of  $\hat{n}_r^2 = \hat{n}_r$ , a more direct way of solution!

### Solution 3.1.4

If the particle is composed by an even (odd) number of fermions, it is a boson (fermion):

$H_2$ -molecule:	2 protons + 2 electrons	→ boson ,
${}^4He^+$ -ion:	2 protons + 2 neutrons + 1 electron	→ fermion ,
${}^7Li^+$ -ion:	3 protons + 3 neutrons + 2 electrons	→ boson ,
${}^3He$ -atom:	2 protons + 1 neutrons + 2 electrons	→ fermion .

### Solution 3.1.5

$D(E) dE$ : number of states with energies between  $E$  and  $dE$ ; in the  $d$ -dimensional space:

$$D(E) dE = \frac{2S+1}{\Delta_d k} \int_{E \leq \varepsilon(\mathbf{k}) \leq E+dE} d^d k$$



with

$$\Delta_d k = \frac{(2\pi)^d}{V_d}.$$

$\varepsilon(\mathbf{k}) = \hbar^2 k^2 / 2m$  isotropic in the  $k$ -space  $\Rightarrow$  phase volume  $\varphi(E)$  is a  $d$ -dimensional sphere in the phase space:

$$\varphi(E) = \int_{\varepsilon(\mathbf{k}) \leq E} d^d k$$

Relation to the density of states:

$$D(E) = (2S + 1) \frac{V_d}{(2\pi)^d} \left( \frac{d}{dE} \varphi(E) \right) \Theta(E),$$

The factor  $(2S + 1)$  describes the spin degeneracy, and  $\Theta(E)$  guarantees  $\varepsilon(\mathbf{k}) \geq 0$ .

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \Leftrightarrow k_E = \sqrt{\frac{2m}{\hbar^2}} E^{1/2}$$

Therewith:

$$\varphi(E) = \Omega_d \int_0^{k_E} dk \cdot k^{d-1} = \Omega_d \frac{k_E^d}{d},$$

$\Omega_d$ : surface of the  $d$ -dimensional unit sphere (see below).

$$\Rightarrow D(E) = \left( (2S + 1) \frac{V_d}{(2\pi)^d} \Omega_d \left( \frac{2m}{\hbar^2} \right)^{d/2} \cdot 1/2 \right) E^{d/2-1} \cdot \Theta(E).$$

Calculation of the surface of the  $d$ -dimensional unit sphere by means of the Gaussian integral in the  $d$ -dimensional space

$$G_d = \int d^d p e^{-p^2}.$$

Cartesian coordinates:

$$G_d = \prod_{i=1}^d \int_{-\infty}^{+\infty} dp_i \cdot e^{-p_i^2} = (\sqrt{\pi})^d.$$

Spherical coordinates:

$$G_d = \Omega_d \int_0^\infty dp \cdot p^{d-1} e^{-p^2}.$$

Substitution:  $y = p^2 \Rightarrow dp = \frac{1}{2\sqrt{y}} dy$ , yields

$$\begin{aligned} G_d &= \Omega_d \int_0^\infty \frac{1}{2\sqrt{y}} dy \cdot y^{(d-1)/2} e^{-y} \\ &= \frac{1}{2} \Omega_d \int_0^\infty dy y^{d/2-1} e^{-y} \\ &= \frac{1}{2} \Omega_d \Gamma(d/2). \end{aligned}$$

Comparison with the Cartesian result  $\Rightarrow$

$$\Omega_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}.$$

Explicit evaluation for  $d = 1, 2, 3$ :

$$\begin{aligned} d = 1: \Gamma\left(\frac{1}{2}\right) &= \sqrt{\pi} \Rightarrow \Omega_1 = 2 \\ d = 2: \Gamma(1) &= 1 \Rightarrow \Omega_2 = 2\pi \\ d = 3: \Gamma\left(\frac{3}{2}\right) &= \frac{1}{2}\sqrt{\pi} \Rightarrow \Omega_3 = 4\pi \end{aligned}$$

It follows with  $V_1 = L$ ,  $V_2 = L^2$ ,  $V_3 = L^3$ :

(i)  $d = 1$ :

$$\begin{aligned} D(E) &= d_1 \cdot \frac{1}{\sqrt{E}} \cdot \Theta(E) \\ d_1 &= (2S + 1) \frac{L}{2\pi} \sqrt{\frac{2m}{\hbar^2}} \end{aligned}$$

(ii)  $d = 2$ :

$$\begin{aligned} D(E) &= d_2 \cdot \Theta(E) \\ d_2 &= (2S + 1) \frac{L^2}{4\pi} \cdot \frac{2m}{\hbar^2} \end{aligned}$$

(iii)  $d = 3$ :

$$D(E) = d_3 \cdot \sqrt{E} \cdot \Theta(E)$$

$$d_3 = (2S + 1) \frac{L^3}{4\pi^2} \cdot \left(\frac{2m}{\hbar^2}\right)^{3/2}.$$

### Solution 3.1.6

1. It holds according to (3.10)

$$\mathbf{P} \longrightarrow \sum_{\mathbf{k}, \mathbf{k}'} \sum_{\sigma, \sigma'} \langle \mathbf{k}\sigma | \mathbf{p} | \mathbf{k}'\sigma' \rangle a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}'\sigma'}$$

Calculation of the matrix element:

$$\begin{aligned} \langle \mathbf{k}\sigma | \mathbf{p} | \mathbf{k}'\sigma' \rangle &= \langle \mathbf{k}\sigma | \hbar \hat{\mathbf{k}} | \mathbf{k}'\sigma' \rangle \\ &= \langle \mathbf{k} | \hbar \hat{\mathbf{k}} | \mathbf{k}' \rangle \langle \sigma | \sigma' \rangle \\ &= \delta_{\sigma, \sigma'} \hbar \mathbf{k}' \langle \mathbf{k} | \mathbf{k}' \rangle \\ &= \hbar \mathbf{k} \delta_{\mathbf{k}, \mathbf{k}'} \delta_{\sigma, \sigma'} \end{aligned}$$

It therewith results:

$$\mathbf{P} = \sum_{\mathbf{k}\sigma} \hbar \mathbf{k} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma}$$

2.  $x$ -component of the total spin:

$$S^x \longrightarrow \sum_{\mathbf{k}, \mathbf{k}'} \sum_{\sigma, \sigma'} \langle \mathbf{k}\sigma | \sigma_x | \mathbf{k}'\sigma' \rangle a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}'\sigma'}$$

Pauli-spin matrix:

$$\sigma_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

Matrix element:

$$\begin{aligned} \langle \mathbf{k}\sigma | \sigma_x | \mathbf{k}'\sigma' \rangle &= \langle \mathbf{k} | \mathbf{k}' \rangle \langle \sigma | \sigma_x | \sigma' \rangle \\ &= \delta_{\mathbf{k}\mathbf{k}'} \frac{\hbar}{2} \left[ \delta_{\sigma'\uparrow} \langle \sigma | \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \delta_{\sigma'\downarrow} \langle \sigma | \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] \end{aligned}$$

$$\begin{aligned}
&= \delta_{\mathbf{k}\mathbf{k}'} \frac{\hbar}{2} [\delta_{\sigma'\uparrow} \langle \sigma | \downarrow \rangle + \delta_{\sigma'\downarrow} \langle \sigma | \uparrow \rangle] \\
&= \delta_{\mathbf{k}\mathbf{k}'} \frac{\hbar}{2} [\delta_{\sigma'\uparrow} \delta_{\sigma\downarrow} + \delta_{\sigma'\downarrow} \delta_{\sigma\uparrow}]
\end{aligned}$$

This means for the spin operator in second quantization:

$$S^x = \frac{\hbar}{2} \sum_{\mathbf{k}} \left( a_{\mathbf{k}\downarrow}^+ a_{\mathbf{k}\uparrow} + a_{\mathbf{k}\uparrow}^+ a_{\mathbf{k}\downarrow} \right)$$

3. We suppose that  $S^x$  commutes with  $\mathbf{P}$ :

$$\begin{aligned}
[S^x, \mathbf{P}]_- &= \frac{\hbar}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'\sigma} \hbar \mathbf{k}' \left[ a_{\mathbf{k}\downarrow}^+ a_{\mathbf{k}\uparrow} + a_{\mathbf{k}\uparrow}^+ a_{\mathbf{k}\downarrow}, a_{\mathbf{k}'\sigma}^+ a_{\mathbf{k}'\sigma} \right]_- \\
&= \frac{\hbar}{2} \sum_{\mathbf{k}} \sum_{\mathbf{k}'\sigma} \hbar \mathbf{k}' \left( \left[ a_{\mathbf{k}\downarrow}^+ a_{\mathbf{k}\uparrow}, a_{\mathbf{k}'\sigma}^+ a_{\mathbf{k}'\sigma} \right]_- + \left[ a_{\mathbf{k}\uparrow}^+ a_{\mathbf{k}\downarrow}, a_{\mathbf{k}'\sigma}^+ a_{\mathbf{k}'\sigma} \right]_- \right) \\
&= \frac{\hbar}{2} \sum_{\mathbf{k}\sigma} \hbar \mathbf{k} \left( \delta_{\sigma\uparrow} a_{\mathbf{k}\downarrow}^+ a_{\mathbf{k}\sigma} - \delta_{\sigma\downarrow} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\uparrow} + \delta_{\sigma\downarrow} a_{\mathbf{k}\uparrow}^+ a_{\mathbf{k}\sigma} - \delta_{\sigma\uparrow} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\downarrow} \right) \\
&= \frac{\hbar}{2} \sum_{\mathbf{k}} \hbar \mathbf{k} \left( a_{\mathbf{k}\downarrow}^+ a_{\mathbf{k}\uparrow} - a_{\mathbf{k}\downarrow}^+ a_{\mathbf{k}\uparrow} + a_{\mathbf{k}\uparrow}^+ a_{\mathbf{k}\downarrow} - a_{\mathbf{k}\uparrow}^+ a_{\mathbf{k}\downarrow} \right) \\
&= 0
\end{aligned}$$

## Section 3.2.11

### Solution 3.2.1

Equation (3.44):

$$n\lambda^3(T) = (2S + 1)f_{3/2}(z), \quad \lambda(T) \xrightarrow{T \rightarrow \infty} 0.$$

Therefore it must hold

$$f_{3/2}(z) \xrightarrow{T \rightarrow \infty} 0,$$

since  $n$  is to be considered as fixed.

$$\begin{aligned} f_{3/2}(z) &= z \frac{d}{dz} f_{5/2}(z) = z \frac{d}{dz} \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx x^2 \ln(1 + ze^{-x^2}) \\ &= \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx \frac{zx^2 e^{-x^2}}{1 + ze^{-x^2}} = \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx \frac{x^2}{\frac{e^{x^2}}{z} + 1} . \end{aligned}$$

$f_{3/2}(z) \rightarrow 0$  obviously means  $z \rightarrow 0$ . This in turn can be valid only if

$$\beta\mu \xrightarrow{T \rightarrow \infty} -\infty .$$

Eventually, this has the consequence

$$\mu \xrightarrow{T \rightarrow \infty} -\infty .$$

### Solution 3.2.2

Substitution:

$$p = mc \sinh \alpha$$

$$\implies \varepsilon(p) = \sqrt{c^2 p^2 + m^2 c^4} = mc^2 \sqrt{\sinh^2 \alpha + 1} = mc^2 \cosh \alpha .$$

For the average particle number we have according to (3.24):

$$\langle \widehat{N} \rangle = \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1} \stackrel{(3.37)}{=} (2S + 1) \frac{4\pi V}{h^3} \int_0^{\infty} \frac{p^2 dp}{e^{\beta(\varepsilon(p) - \mu)} + 1} ,$$

$$p^2 dp = (mc)^3 \sinh^2 \alpha \cosh \alpha d\alpha$$

$$\implies \langle \widehat{N} \rangle = (2S + 1) \frac{m^3 c^3}{2\pi^2 \hbar^3} V \int_0^{\infty} \frac{\sinh^2 \alpha \cosh \alpha d\alpha}{\exp(-\beta\mu + \beta mc^2 \cosh \alpha) + 1}$$

In an analogous manner the internal energy is derived from (3.28):

$$\begin{aligned} U &= \sum_r \frac{\varepsilon_r}{e^{\beta(\varepsilon_r - \mu)} + 1} \\ &= (2S + 1) \frac{m^4 c^5}{2\pi^2 \hbar^3} V \int_0^{\infty} \frac{\sinh^2 \alpha \cosh^2 \alpha d\alpha}{\exp(-\beta\mu + \beta mc^2 \cosh \alpha) + 1} . \end{aligned}$$

Low temperatures:

$$\frac{1}{\exp(-\beta\mu + \beta mc^2 \cosh \alpha) + 1} \xrightarrow{T \rightarrow 0} \begin{cases} 1, & \text{if } \mu > mc^2 \cosh \alpha, \\ 0, & \text{if } \mu < mc^2 \cosh \alpha. \end{cases}$$

Let  $\alpha_F$  be defined by

$$\varepsilon_F = \mu(T = 0) = mc^2 \cosh \alpha_F.$$

*Fermi momentum:*

$$p_F = mc \sinh \alpha_F.$$

Average number of particles:

$$\begin{aligned} \langle \widehat{N} \rangle &\approx (2S + 1) \frac{m^3 c^3}{2\pi^2 \hbar^3} V \int_0^{\alpha_F} \sinh^2 \alpha \cosh \alpha d\alpha \\ &= (2S + 1) \frac{m^3 c^3}{2\pi^2 \hbar^3} V \frac{1}{3} \int_0^{\alpha_F} \frac{d}{d\alpha} \sinh^3 \alpha d\alpha \\ &= (2S + 1) \frac{m^3 c^3}{6\pi^2 \hbar^3} V \sinh^3 \alpha_F. \end{aligned}$$

The same relation with the *Fermi momentum* is obtained as in the non-relativistic case:

$$\frac{\langle \widehat{N} \rangle}{V} = \frac{2S + 1}{6\pi^2 \hbar^3} p_F^3.$$

Internal energy:

$$\begin{aligned} U &\approx (2S + 1) \frac{m^4 c^5}{2\pi^2 \hbar^3} V \int_0^{\alpha_F} \sinh^2 \alpha \cosh^2 \alpha d\alpha, \\ \sinh^2 \alpha \cosh^2 \alpha &= \frac{1}{16} (e^{2\alpha} + e^{-2\alpha} - 2)(e^{2\alpha} + e^{-2\alpha} + 2) \\ &= \frac{1}{16} (e^{4\alpha} + e^{-4\alpha} - 2) = \frac{1}{8} (\cosh 4\alpha - 1) \\ \implies U &\approx (2S + 1) \frac{m^4 c^5}{16\pi^2 \hbar^3} V \left[ \frac{1}{4} \sinh(4\alpha_F) - \alpha_F \right]. \end{aligned}$$

**Solution 3.2.3**

1.

$$\begin{aligned}
 U(T=0) &= \sum_{\mathbf{k}}^{k \leq k_F} \frac{\hbar^2 k^2}{2m} = (2S+1) \frac{V}{8\pi^3} 4\pi \int_0^{k_F} dk k^4 \frac{\hbar^2}{2m} \\
 &= (2S+1) \frac{V}{2\pi^2} \frac{k_F^3}{5} \frac{\hbar^2 k_F^2}{2m} \stackrel{(3.61)}{=} E_F (2S+1) \frac{V}{10\pi^2} \frac{6\pi^2}{2S+1} \frac{N}{V} \\
 &= \frac{3}{5} N E_F .
 \end{aligned}$$

2.

$$\begin{aligned}
 \hbar &= 1.054 \cdot 10^{-34} \text{ Js} \\
 E_F &\stackrel{(3.62)}{=} \frac{\hbar^2}{2m} \left( \frac{6\pi^2 N}{2V} \right)^{2/3} \\
 &= \frac{(1.054 \cdot 10^{-34})^2}{2 \cdot 9.1 \cdot 10^{-31}} \cdot (3\pi^2)^{2/3} \cdot \left( \frac{6 \cdot 10^{23}}{25 \cdot 10^{-6}} \right)^{2/3} \text{ J} \\
 &= 6.098 \cdot 10^{-39} \cdot 9.571 \cdot 8.320 \cdot 10^{18} \text{ J} \\
 &= 4.86 \cdot 10^{-19} \text{ J} \\
 \implies E_F &= 3.03 \text{ eV} .
 \end{aligned}$$

3.

$$\begin{aligned}
 E_F &= \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{2/3} \\
 \frac{N}{V} &= \frac{3}{4\pi} (a_B r_s)^{-3} \\
 \frac{\hbar^2}{2m} &= \frac{a_B e^2}{8\pi \epsilon_0} \\
 \implies E_F &= \frac{e^2}{8\pi \epsilon_0 a_B} \left( \frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} \\
 \implies U(T=0) &= N \frac{3}{5} \left( \frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^2} [\text{ryd}] = N \frac{2.21}{r_s^2} [\text{ryd}] .
 \end{aligned}$$

4.

$$d = (2S + 1) \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \stackrel{(3.62)}{=} (2S + 1) \frac{V}{4\pi^2} \frac{6\pi^2}{2S + 1} n \frac{1}{E_F^{3/2}}$$

$$\implies d = \frac{3N}{2E_F^{3/2}} .$$

5.

$$p \stackrel{(3.45)}{=} \frac{2}{5} \frac{N}{V} E_F = \frac{2}{5} \cdot \frac{6 \cdot 10^{23}}{25 \cdot 10^{-6}} \cdot 4.86 \cdot 10^{-19} \frac{\text{J}}{\text{m}^3}$$

$$= 4.6656 \cdot 10^9 \text{ Pa} = 4.6632 \cdot 10^4 \text{ bar} .$$

### Solution 3.2.4

$N$ : Total number of electrons in the valence band and in the conduction band:

$$N = \sum_i^{\text{VB}} f_-(\varepsilon_i) + \sum_j^{\text{CB}} f_-(\varepsilon_j) ,$$

$N$  is temperature-independent. At  $T = 0$  all electrons are in the valence band, which is then fully occupied.

$$N = \sum_i^{\text{VB}} 1 .$$

If one combines the two equations for  $N$ ,

$$\sum_i^{\text{VB}} (1 - f_-(\varepsilon_i)) = \sum_j^{\text{CB}} f_-(\varepsilon_j) ,$$

one recognizes that the number of holes in the valence band is of course equal to the number of electrons in the conduction band:

$$n_h = n_e .$$



Energy zero = upper edge of the valence band. One-particle energies:

$$\begin{aligned} \text{holes:} \quad \varepsilon_i &= -\frac{\hbar^2 k^2}{2m_h}, \\ \text{electrons:} \quad \varepsilon_j &= E_g + \frac{\hbar^2 k^2}{2m_e}. \end{aligned}$$

Densities of states: (3.50)

$$\begin{aligned} \text{holes:} \quad D_h(E) &= 2 \frac{V}{4\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} \sqrt{-E}, \\ \text{electrons:} \quad D_e(E) &= 2 \frac{V}{4\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_g}. \end{aligned}$$

**Particle densities:**

$$\begin{aligned} \text{electrons:} \quad n_e &= \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \int_{E_g}^{\infty} \frac{\sqrt{E - E_g} dE}{e^{\beta(E-\mu)} + 1}, \\ \text{holes:} \quad n_h &= \frac{1}{2\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} \int_{-\infty}^0 \frac{\sqrt{-E} dE}{e^{\beta(-E+\mu)} + 1}. \end{aligned}$$

Because of the given inequalities the number 1 in the denominators of the integrands can be neglected, in both cases, compared to the exponential function:

$$\begin{aligned} n_e &\approx \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \int_{E_g}^{\infty} \sqrt{E - E_g} e^{-\beta(E-\mu)} dE, \\ n_h &\approx \frac{1}{2\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} \int_{-\infty}^0 \sqrt{-E} e^{\beta(E-\mu)} dE. \end{aligned}$$

We substitute for  $n_e$ :

$$\begin{aligned} x &= \beta(E - E_g) \\ \Rightarrow n_e &\approx \frac{1}{2\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \frac{1}{\beta^{3/2}} e^{-\beta(E_g-\mu)} \int_0^{\infty} dx \sqrt{x} e^{-x}, \end{aligned}$$

$$\int_0^{\infty} dx \sqrt{x} e^{-x} = \Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$$

$$\implies n_e \approx 2 \left(\frac{m_e k_B T}{2\pi \hbar^2}\right)^{3/2} e^{-\beta(E_g - \mu)}.$$

We substitute for  $n_h$ :

$$x = -\beta E$$

$$\implies n_h \approx \frac{1}{2\pi^2} \left(\frac{2m_h}{\hbar^2}\right)^{3/2} \frac{1}{\beta^{3/2}} e^{-\beta\mu} \int_0^{\infty} dx \sqrt{x} e^{-x},$$

$$\implies n_h \approx 2 \left(\frac{m_h k_B T}{2\pi \hbar^2}\right)^{3/2} e^{-\beta\mu}.$$

**Chemical potential:**

$$1 \stackrel{!}{=} \frac{n_e}{n_h} = \left(\frac{m_e}{m_h}\right)^{3/2} e^{2\beta\mu} e^{-\beta E_g}$$

$$\implies \mu(T) = \frac{1}{2}E_g + \frac{3}{4}k_B T \ln \frac{m_h}{m_e},$$

$$\mu(T=0) = \frac{1}{2}E_g$$

**Particle densities:**

$$e^{\beta\mu} = e^{(1/2)\beta E_g} \left(\frac{m_h}{m_e}\right)^{3/4}.$$

It therewith follows the assertion:

$$n_e = n_h \approx 2 \left(\frac{\sqrt{m_e m_h} k_B T}{2\pi \hbar^2}\right)^{3/2} e^{-(1/2)\beta E_g},$$

$$n_e = n_h \xrightarrow{T \rightarrow 0} 0.$$

o

### Solution 3.2.5

1. The one-particle energies and densities of states for electrons and holes are exactly the same as in Exercise 3.2.4:

Electrons (conduction band):

$$\varepsilon_e(\mathbf{k}) = E_g + \frac{\hbar^2 k^2}{2m_e}; \quad D_e(E) = 2 \frac{V}{4\pi^2} \left( \frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_g},$$

Holes (valence band):

$$\varepsilon_h(\mathbf{k}) = -\frac{\hbar^2 k^2}{2m_h}; \quad D_h(E) = 2 \frac{V}{4\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} \sqrt{-E}.$$

The given inequalities correspond to those of Exercise 3.2.4. For the densities of electrons and holes ( $n_e, n_h$ ) one finds therefore the same approximated formulas:

$$n_e \approx 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\beta(E_g - \mu)} = 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} A,$$

$$n_h \approx 2 \left( \frac{m_h k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-\beta\mu}.$$

Also the donor levels now contribute electrons for the conduction band. Their number corresponds to the number of *unoccupied* donor levels, which can at most be simply ionized:

$$n_h^D = \frac{1}{V} \sum_{(D)} \left( 1 - \frac{1}{e^{\beta(E_g - \varepsilon_D - \mu)} + 1} \right) = \frac{n_D}{e^{\beta(\mu + \varepsilon_D - E_g)} + 1} = \frac{n_D}{A e^{\beta\varepsilon_D} + 1};$$

$$n_D = \frac{N_D}{V}; \quad \text{density of the donor levels.}$$

Neutrality condition:

$$n_e = n_h + n_h^D.$$

Because of  $\frac{m_h}{m_e} \approx \left( \frac{m_h}{m_e} \right)^{3/2} e^{-\beta(2\mu - E_g)}$  and  $\mu \approx E_g$  one can estimate:

$$n_h \approx e^{-\beta E_g} n_e \ll n_e.$$

$n_h$  can thus be neglected compared to  $n_e$ , and the neutrality condition simplifies:

$$n_e \approx n_h^D ; \quad 2A \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} \approx \frac{n_D}{Ae^{\beta \varepsilon_D} + 1}$$

$$\implies n_D = 2A (Ae^{\beta \varepsilon_D} + 1) \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2}$$

2. It is now presumed:

$$Ae^{\beta \varepsilon_D} \gg 1 .$$

This simplifies the last relation from part 1.:

$$n_D e^{-\beta \varepsilon_D} \approx 2A^2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} .$$

It thus follows for  $A$ :

$$A \approx \sqrt{\frac{n_D}{2}} \left( \frac{2\pi \hbar^2}{m_e k_B T} \right)^{3/4} e^{-\frac{1}{2}\beta \varepsilon_D} .$$

This is inserted into the relation for  $n_e$  from part 1.:

$$n_e \approx 2 \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} A \approx \sqrt{2n_D} \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/4} e^{-\frac{1}{2}\beta \varepsilon_D}$$

The chemical potential results from

$$\mu = E_g + k_B T \ln A$$

$$\implies \mu = E_g - \frac{1}{2}\varepsilon_D + \frac{1}{2}k_B T \ln \frac{4\pi^3 \hbar^3 n_D}{(2\pi m_e k_B T)^{\frac{3}{2}}}$$

Since, according to the precondition,  $A \ll 1$ , the given condition can be fulfilled only for  $\varepsilon_D \gg k_B T \implies$  low-temperature region;  $n_e$  very small, i.e., only very few electrons are excited into the conduction band. For these it holds:  $n_e \sim \sqrt{n_D}$ .

3. Now

$$Ae^{\beta \varepsilon_D} \ll 1$$

is presumed. According to part 1. this means:

$$n_D \approx 2A \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} .$$

That means (part 1.):  $n_D \approx n_e$ . Almost all donor levels are emptied. Because of  $A \ll 1$  the  $n_D$ -relation is satisfiable only for high temperatures.

Chemical potential:

$$\mu = E_g + k_B T \ln A = E_g + k_B T \ln \frac{4\pi^3 \hbar^3 n_D}{(2\pi m_e k_B T)^{3/2}}.$$

4. Material parameters:

$$E_g = 2\text{eV}; \quad \varepsilon_D = 0.02\text{eV}; \quad m_e = 10^{-27}\text{g}; \quad n_D = 10^{16}\text{cm}^{-3}.$$

a)  $T = 3\text{K}$

We calculate at first (see part 2.)

$$A = \sqrt{\frac{n_D}{2}} \left( \frac{2\pi \hbar^2}{m_e k_B T} \right)^{3/4} e^{-\frac{1}{2}\beta\varepsilon_D}.$$

$$\begin{aligned} k_B &= 0.862 \cdot 10^{-4} \frac{\text{eV}}{\text{K}} &\implies& k_B T = 2.586 \cdot 10^{-4} \text{eV} \\ \implies \beta\varepsilon_D &= 77.34 &\implies& e^{\beta\varepsilon_D} = 3.87 \cdot 10^{33}, \\ & && e^{-\frac{1}{2}\beta\varepsilon_D} = 1.607 \cdot 10^{-17}. \end{aligned}$$

$$\begin{aligned} \hbar &= 1.055 \cdot 10^{-34} \text{Js} = 1.055 \cdot 10^{-27} \text{g} \frac{\text{cm}^2}{\text{s}} &\implies& \frac{\hbar}{m_e} = 1.055 \frac{\text{cm}^2}{\text{s}} \\ \hbar &= 0.6585 \cdot 10^{-15} \text{eV} \cdot \text{s} &\implies& \frac{\hbar}{k_B T} = 0.2546 \cdot 10^{-11} \text{s} \end{aligned}$$

$$\implies \frac{2\pi \hbar^2}{m_e k_B T} = 1.688 \cdot 10^{-11} \text{cm}^2; \quad \frac{1}{\sqrt{2}} \left( \frac{2\pi \hbar^2}{m_e k_B T} \right)^{3/4} = 5.889 \cdot 10^{-9} \text{cm}^{3/2}$$

$$\implies A \approx \sqrt{n_D} \cdot 9.463 \cdot 10^{-26} = 9.463 \cdot 10^{-18}; \quad A e^{\beta\varepsilon_D} = 3.662 \cdot 10^{16}.$$

The conditions

$$A \ll 1; \quad A e^{\beta\varepsilon_D} \gg 1$$

are therefore optimally fulfilled. In addition

$$\mu = E_g + k_B T \ln A = E_g - 0.010\text{eV},$$

so that also the precondition  $\mu \approx E_g$  is confirmed.

b)  $T = 300\text{K}$ :

We have to check (see part 3.)

$$A = \frac{n_D}{2} \left( \frac{2\pi\hbar^2}{m_e k_B T} \right)^{3/2} .$$

$$\frac{2\pi\hbar^2}{m_e k_B T} = 1.688 \cdot 10^{-13} \text{cm}^2 \quad \Longrightarrow \quad \left( \frac{2\pi\hbar^2}{m_e k_B T} \right)^{3/2} = 6.935 \cdot 10^{-20} \text{cm}^3$$

$$\Longrightarrow A \approx 0.000347 \ll 1$$

$$\beta \varepsilon_D = 0.7734 \quad \Longrightarrow \quad e^{\beta \varepsilon_D} = 2.167$$

$$\Longrightarrow A e^{\beta \varepsilon_D} \approx 0.00752 \ll 1 .$$

Also here the two conditions are optimally fulfilled.

Chemical potential:

$$\mu = E_g + k_B T \ln A = E_g - 0.206 \text{eV} .$$

The comparison with the low-temperature case a) demonstrates the distinct temperature-dependence of the chemical potential.  $\mu \approx E_g$  is no longer well fulfilled.

### Solution 3.2.6

For the one-dimensional density of states it holds according to Exercise 3.1.5:

$$D_1(E) = \begin{cases} d_1 \frac{1}{\sqrt{E}} & \text{for } E > 0 , \\ 0 & \text{otherwise} . \end{cases}$$

The constant  $d_1$ ,

$$d_1 = \frac{2S+1}{\pi} L \sqrt{\frac{m}{2\hbar^2}} ,$$

can be expressed also by  $N$  and  $E_F$ :

$$N = \int_0^{E_F} dE D_1(E) = 2d_1 \sqrt{E_F}$$

$$\Longrightarrow d_1 = \frac{1}{2} \frac{N}{\sqrt{E_F}} .$$

We calculate (3.53) by exploitation of (3.73):

$$\begin{aligned}
 N &= \int_{-\infty}^{\infty} dE D_1(E) f_-(E) \approx \int_{-\infty}^{\mu} dE D_1(E) + \frac{\pi^2}{6} (k_B T)^2 D_1'(\mu) \\
 &= 2d_1 \sqrt{\mu} + \frac{\pi^2}{6} (k_B T)^2 \left( -\frac{1}{2} d_1 \frac{1}{\mu^{3/2}} \right) = N \sqrt{\frac{\mu}{E_F}} - \frac{\pi^2}{24} \left( \frac{k_B T}{\mu} \right)^2 N \sqrt{\frac{\mu}{E_F}} \\
 \Rightarrow 1 &\approx \sqrt{\frac{\mu}{E_F}} \left[ 1 - \frac{\pi^2}{24} \left( \frac{k_B T}{\mu} \right)^2 \right] \\
 \Rightarrow \mu(T) &\approx E_F \left[ 1 + \frac{\pi^2}{12} \left( \frac{k_B T}{\mu} \right)^2 \right].
 \end{aligned}$$

In contrast to the three-dimensional case,  $\mu(T)$  increases in the one-dimensional system with increasing temperature!

### Solution 3.2.7

We use the thermodynamic relation (1.154) and the Gibbs-Duhem relation:

$$F = -pV + G = -pV + \mu N.$$

It follows then with (3.75) and (3.81):

$$\begin{aligned}
 F &\approx NE_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right] - \frac{2}{5} NE_F \left[ 1 + \frac{5\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right] \\
 &= \frac{3}{5} NE_F \left[ 1 - \frac{5\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right].
 \end{aligned}$$

### Solution 3.2.8

1. The same energy zero inside as well as outside the metal.

One-particle energies:

$$\begin{aligned}
 \text{inside: } \varepsilon_{in}(\mathbf{k}) &= \frac{\hbar^2 k^2}{2m}, \\
 \text{outside: } \varepsilon_{ex}(\mathbf{k}) &= V_0 + \frac{\hbar^2 k^2}{2m}.
 \end{aligned}$$

Density of states:

$$\begin{aligned} \text{inside: } D_{in}(E) &= \begin{cases} d\sqrt{E}, & \text{if } E \geq 0, \\ 0 & \text{otherwise,} \end{cases} \\ \text{outside: } D_{ex}(E) &= \begin{cases} d\sqrt{E-E_0}, & \text{if } E \geq V_0, \\ 0 & \text{otherwise.} \end{cases} \\ d &\stackrel{(3.51)}{=} \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2}. \end{aligned}$$

Average occupation numbers:

$$\begin{aligned} \text{inside: } \langle \hat{n}_{\mathbf{k}\sigma}^{(in)} \rangle &= \left\{ \exp \left[ \beta \left( \frac{\hbar^2 k^2}{2m} - \mu \right) \right] + 1 \right\}^{-1}, \\ \text{outside: } \langle \hat{n}_{\mathbf{k}\sigma}^{(ex)} \rangle &= \left\{ \exp \left[ \beta \left( \frac{\hbar^2 k^2}{2m} + V_0 - \mu \right) \right] + 1 \right\}^{-1}, \end{aligned}$$

2.

$$n_{ex} = \frac{1}{V} \int_{V_0}^{\infty} dE \frac{D_{ex}(E)}{e^{\beta(E-\mu)} + 1}.$$

The work function is of the order eV. Therefore for realistic temperatures  $\beta(V_0 - \mu) \gg 1$ . (Otherwise the metal would not be stable!) We thus can confidently neglect the 1 in the denominator compared to the exponential function.

$$\begin{aligned} n_{ex} &\approx \frac{1}{V} \int_{V_0}^{\infty} dE D_{ex}(E) e^{-\beta(E-\mu)} = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_{V_0}^{\infty} dE \sqrt{E-V_0} e^{-\beta(E-\mu)} \\ &= \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} dx \sqrt{x} e^{-\beta(x+V_0-\mu)} \\ &= \frac{1}{2\pi^2} \left( \frac{2m}{\beta\hbar^2} \right)^{3/2} e^{-\beta(V_0-\mu)} \underbrace{\int_0^{\infty} dy \sqrt{y} e^{-y}}_{\Gamma(\frac{3}{2}) = \frac{1}{2}\sqrt{\pi}}. \\ n_{ex} &\approx \frac{1}{4} \left( \frac{2mk_B T}{\pi\hbar^2} \right)^{3/2} e^{-\beta(V_0-\mu)}. \end{aligned}$$

$V_0 - \mu$  is practically equal to the work function.



3. Because of  $e^{\beta(V_0-\mu)} \gg 1$

$$\langle \hat{n}_{\mathbf{k}\sigma}^{(ex)} \rangle \approx \exp \left[ -\beta \left( \frac{\hbar^2 k^2}{2m} + V_0 - \mu \right) \right].$$

We calculate therewith the emission current:

$$j_z \approx \frac{-e}{V} \exp[-\beta(V_0 - \mu)] 2 \frac{V}{(2\pi)^3} \int_0^\infty dk_z \frac{\hbar k_z}{m} \iint_{-\infty}^{+\infty} dk_x dk_y \cdot \exp \left[ -\beta \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \right].$$

The factor 2 stems from the spin summation!

$$\begin{aligned} j_z &\approx -2e \exp[-\beta(V_0 - \mu)] \frac{1}{h^3} \int_0^\infty dp_z \frac{p_z}{m} \exp \left( -\beta \frac{p_z^2}{2m} \right) \cdot \left[ \int_{-\infty}^{+\infty} dp_x \exp \left( -\beta \frac{p_x^2}{2m} \right) \right]^2 \\ &\stackrel{(1.137)}{=} -e \frac{4\pi m k_B T}{h^3} \exp[-\beta(V_0 - \mu)] \left( -\frac{1}{\beta} \right) \int_0^\infty dp_z \frac{d}{dp_z} \exp \left( -\beta \frac{p_z^2}{2m} \right) \\ &\implies j_z \approx \frac{-4\pi m e}{h^3} (k_B T)^2 \exp[-\beta(V_0 - \mu)] \end{aligned}$$

*Richardson formula* ((1.47), Vol. 6).

### Solution 3.2.9

1. We use for the one-particle Hamilton operator of noninteracting electrons,

$$H_1^{(0)} = -\frac{\hbar^2}{2m} \Delta,$$

spherical coordinates

$$\begin{aligned} \Delta &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \Delta_{\vartheta, \varphi} \\ \Delta_{\vartheta, \varphi} &= \frac{1}{r^2 \sin^2 \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{\partial^2}{\partial \varphi^2} \right) \\ &= -\frac{\mathbf{L}^2}{r^2 \hbar^2}. \end{aligned}$$

$\mathbf{L}^2$  is the operator of the square of the angular momentum. The fermions are thought to be bound to the surface of a sphere  $r = R$ . Hence in particular, the derivatives with respect to the variable  $r$  will vanish, so that it is left for the one-particle Hamilton operator:

$$H_1^{(0)} = + \frac{\mathbf{L}^2}{2mR^2}$$

The eigen-states of  $H_1^{(0)}$  are eigen-states of the angular momenta  $|lm_l m_s\rangle$ . This yields the energy-eigen values

$$E_l = \frac{\hbar^2}{2mR^2} l(l+1) \quad l = 0, 1, 2, \dots$$

Degree of degeneracy:

$$g_l = (2S+1)(2l+1) = 2(2l+1)$$

2. Including the Pauli principle it holds for the ground-state energy  $E^{(0)}$  of the fermions:

$$E^{(0)} = \sum_l g_l E_l = \frac{27\hbar^2}{mR^2} = \frac{\hbar^2}{2mR^2} (2 \cdot 0 + 6 \cdot 2 + x \cdot 6)$$

$x$  is the number of fermions with the energy  $E_2$  for realizing the total energy  $E^{(0)}$ . It results  $x = 7$  and therewith the particle number:

$$N = 2 + 6 + x = 15$$

Fermi energy as the highest occupied level at  $T = 0$ :

$$E_F = \mu(T = 0) = \frac{3\hbar^2}{mR^2}$$

### **Solution 3.2.10**

1. The derivation of the density of states follows the same line as that for (3.50):

$$D(E) = (2S+1) \frac{V}{(2\pi)^3} \frac{d}{dE} \varphi(E) .$$

The phase volume, though, now looks different:

$$\begin{aligned} \varphi(E) &= \frac{4\pi}{3} k^3 \Big|_{c\hbar k=E} = \frac{4\pi}{3c^3\hbar^3} E^3 \\ \implies D(E) &= \begin{cases} (2S+1) \frac{V}{2\pi^2 c^3 \hbar^3} E^2 & \text{for } E \geq 0, \\ 0 & \text{otherwise.} \end{cases} \end{aligned}$$

2. Let

$$Q(E) = \int D(E) dE = \frac{1}{3} E D(E)$$

be the antiderivative of the density of states. According to (3.22):

$$\begin{aligned} \beta pV &= \sum_r \ln \left[ 1 + e^{-\beta(\varepsilon_r - \mu)} \right] \\ &\rightarrow \int_0^\infty dE D(E) \ln \left[ 1 + e^{-\beta(E - \mu)} \right] \\ &= Q(E) \ln \left[ 1 + e^{-\beta(E - \mu)} \right] \Big|_0^\infty - \int_0^\infty dE Q(E) \frac{-\beta e^{-\beta(E - \mu)}}{1 + e^{-\beta(E - \mu)}}. \end{aligned}$$

The integrated part vanishes (why?):

$$pV = \int_0^\infty Q(E) \frac{dE}{e^{\beta(E - \mu)} + 1} = \frac{1}{3} \int_0^\infty ED(E) f_-(E) dE = \frac{1}{3} U$$

3.

$$\begin{aligned} p(T=0) &\stackrel{?}{=} \frac{1}{3V} U(T=0) \\ U(T=0) &= \int_0^{E_F} ED(E) dE = \frac{V(2S+1)}{2\pi^2 c^3 \hbar^3} \frac{1}{4} E_F^4. \\ E_F &= \hbar c k_F \stackrel{(3.61)}{=} c\hbar \left( \frac{6\pi^2}{2S+1} \frac{N}{V} \right)^{1/3}. \end{aligned}$$

Zero-point pressure:

$$p(T = 0) = \frac{1}{4} \left( \frac{6\pi^2}{2S + 1} \right)^{1/3} c\hbar \left( \frac{N}{V} \right)^{4/3} .$$

### Solution 3.2.11

According to Exercise 3.2.10 the density of states of extremely relativistic fermions is given by

$$D(E) = (2S + 1) \frac{V}{2\pi^2 c^3 \hbar^3} E^2 \equiv \hat{d} E^2 \quad \text{for } E \geq 0 .$$

( $D(E) = 0$  for  $E < 0$ .)

1. *Chemical potential:*

$D(E)$  fulfills the preconditions of the Sommerfeld expansion. The particle number  $N$  is  $T$ -independent. Therefore it holds

$$N = \int_{-\infty}^{E_F} dE D(E) \quad (T = 0)$$

as well as

$$N = \int_{-\infty}^{\mu} dE D(E) + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) .$$

Equating yields:

$$\begin{aligned} \frac{1}{3} E_F^3 &\approx \frac{1}{3} \mu^3 + \frac{\pi^2}{6} (k_B T)^2 2\mu \\ \implies \mu &\approx E_F \left[ 1 - \left( \frac{\pi k_B T}{E_F} \right)^2 \frac{\mu}{E_F} \right]^{1/3} , \end{aligned}$$

*degenerate Fermi gas*  $\implies$  the second term is very small,  $\mu \approx E_F$

$$\implies \mu(T) \approx E_F \left[ 1 - \frac{\pi^2}{3} \left( \frac{k_B T}{E_F} \right)^2 \right] .$$

This result has the same structure as in (3.75), only the numerical factor in front of the correction term has changed.

$$E_F = c\hbar \left( \frac{6\pi^2 N}{2S+1 V} \right)^{1/3} \quad (\text{see Exercise 3.2.10}).$$

2. *Internal energy:*

$$\begin{aligned} U(T=0) &= \frac{V(2S+1) E_F^4}{2\pi^2 c^3 \hbar^3} \frac{1}{4} = \frac{1}{4} \hat{d} E_F^4, \\ U(T) &\approx \int_0^\mu dE E D(E) + \frac{\pi^2}{6} (k_B T)^2 (\mu D'(\mu) + D(\mu)) \\ &= \frac{1}{4} \hat{d} \mu^4 + \frac{\pi^2}{6} (k_B T)^2 3 \hat{d} \mu^2 \\ &= U(0) \left[ \left( \frac{\mu}{E_F} \right)^4 + 2\pi^2 \left( \frac{k_B T}{E_F} \right)^2 \left( \frac{\mu}{E_F} \right)^2 \right]. \end{aligned}$$

According to 1.:

$$\begin{aligned} \left( \frac{\mu}{E_F} \right)^n &\approx 1 - n \frac{\pi^2}{3} \left( \frac{k_B T}{E_F} \right)^2 \\ \Rightarrow U(T) &= U(0) \left[ 1 + \frac{2\pi^2}{3} \left( \frac{k_B T}{E_F} \right)^2 \right], \quad U(0) = \frac{3}{4} N E_F. \end{aligned}$$

3. *Heat capacity:*

$$C_V = \hat{\gamma} T, \quad \hat{\gamma} = N \frac{\pi^2 k_B^2}{E_F}.$$

$C_V$  has the same low-temperature dependence as in the non-relativistic case. Even the coefficient  $\hat{\gamma}$ , except for the factor  $\frac{1}{2}$ , has the same structure as  $\gamma$ . The Fermi energies, though, are different:

$$\frac{\hat{\gamma}}{\gamma} = \frac{\hbar}{mc} \left( \frac{6\pi^2 N}{2S+1 V} \right)^{1/3} \gg 1.$$

**Solution 3.2.12**

One-particle energies:

$$\eta_{m_S}(\mathbf{k}) = \varepsilon(\mathbf{k}) + 2m_S\mu_B B$$

$$m_S = -S, -S + 1, \dots, +S.$$

$m_S$ -part of the density of states:

$$D_{m_S}(E)dE = \frac{1}{\Delta k} \int_{E \leq \eta_{m_S}(\mathbf{k}) \leq E+dE} d^3k = \frac{V}{(2\pi)^3} \frac{d}{dE} \varphi_{m_S}(E) dE.$$

Phase volume:

$$\varphi_{m_S}(E) = \int_{\eta_{m_S}(\mathbf{k}) \leq E} d^3k = \int_{\varepsilon(\mathbf{k}) \leq E - 2m_S\mu_B B} d^3k.$$

$$\varepsilon(\mathbf{k}) \geq 0 \implies \text{necessary: } E \geq 2m_S\mu_B B$$

$$\varphi_{m_S}(E) = 0, \quad \text{if } E < 2m_S\mu_B B,$$

otherwise

$$\varphi_{m_S}(E) = \frac{4\pi}{3} k^3 \Big|_{\varepsilon(\mathbf{k})=E-2m_S\mu_B B} = \frac{4\pi}{3} \left[ \frac{2m}{\hbar^2} (E - 2m_S\mu_B B) \right]^{3/2}$$

$$\implies D_{m_S}(E) = \begin{cases} d_{m_S} \sqrt{E - 2m_S\mu_B B}, & \text{if } E \geq 2m_S\mu_B B, \\ 0 & \text{otherwise,} \end{cases}$$

$$d_{m_S} = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \stackrel{(3.51)}{=} \frac{1}{2S+1} d.$$

Hence it is:

$$D_{m_S}(E) = \frac{1}{2S+1} D(E - 2m_S\mu_B B).$$

Total density of states:

$$D_{\text{tot}}(E; B) = \frac{1}{2S+1} \sum_{m_S=-S}^{+S} D(E - 2m_S\mu_B B)$$

with  $D$  as in (3.50).

**Solution 3.2.13**

Spin-dependent particle numbers (Sect. 3.2.6):

$$N_\sigma = \frac{1}{2} \int_{-\infty}^{+\infty} dE f_{-}(E) D(E - z_\sigma \mu_B B) .$$

Sommerfeld expansion (3.73):

$$\begin{aligned} N_\sigma &= \frac{1}{2} \left[ \int_{-\infty}^{\mu} dE D(E - z_\sigma \mu_B B) + \frac{\pi^2}{6} (k_B T)^2 D'(\mu - z_\sigma \mu_B B) \right] \\ &= \frac{d}{2} \left[ \frac{2}{3} (\mu - z_\sigma \mu_B B)^{3/2} + \frac{\pi^2}{12} (k_B T)^2 (\mu - z_\sigma \mu_B B)^{-1/2} \right] \\ &= \frac{1}{2} N \left( \frac{\mu}{E_F} \right)^{3/2} \left[ \left( 1 - \frac{z_\sigma \mu_B B}{\mu} \right)^{3/2} + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 \left( 1 - \frac{z_\sigma \mu_B B}{\mu} \right)^{-1/2} \right] . \end{aligned}$$

Series expansion:

$$\begin{aligned} (1+x)^{n/m} &= 1 + \frac{n}{m}x - \frac{n(m-n)}{2!m^2}x^2 + \dots \quad (-1 < x < +1) \\ \Rightarrow N_\sigma &= \frac{1}{2} N \left( \frac{\mu}{E_F} \right)^{3/2} \left[ 1 - z_\sigma \frac{3}{2} \frac{\mu_B B}{\mu} + \frac{3}{8} \left( \frac{\mu_B B}{\mu} \right)^2 + \right. \\ &\quad \left. + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 \left( 1 + \frac{1}{2} z_\sigma \frac{\mu_B B}{\mu} + \frac{3}{8} \left( \frac{\mu_B B}{\mu} \right)^2 + \dots \right) \right] . \end{aligned}$$

Summation over both spin-directions and dividing by  $N = N_\uparrow + N_\downarrow$ :

$$1 = \left( \frac{\mu}{E_F} \right)^{3/2} \left[ 1 + \frac{3}{8} \left( \frac{\mu_B B}{\mu} \right)^2 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 + \dots \right] .$$

It follows therewith, if we exploit once more the above series expansion and replace eventually in the quadratic correction terms  $\mu$  by  $E_F$ :

$$\mu(T, B) \approx E_F \left[ 1 - \frac{1}{4} \left( \frac{\mu_B B}{E_F} \right)^2 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right] .$$

For  $B = 0$  we regain the 'old' result (3.75).

**Solution 3.2.14**

One can write for  $f(x)$ :

$$f(x) = \delta\left(x - \frac{1}{2}\right) + \delta\left(x + \frac{1}{2}\right) \quad \text{for } -1 \leq x \leq +1$$

with  $f(x) = f(x + 2)$ .

$f(x)$  is thus periodic with the period 2, and furthermore symmetric:

$$f(-x) = f(x).$$

Ansatz as Fourier-series ((4.174), Vol. 3):

$$f(x) = f_0 + \sum_{m=1}^{\infty} [a_m \cos(m\pi x) + b_m \sin(m\pi x)],$$

$$f_0 = \frac{1}{2} \int_{-1}^{+1} f(x) dx = 1,$$

$$a_m = \int_{-1}^{+1} f(x) \cos(m\pi x) dx = \begin{cases} 0 & \text{for } m = 2p + 1, \\ 2(-1)^p & \text{for } m = 2p, \end{cases}$$

$b_m \equiv 0$ , because  $f(x)$  symmetric

$$\Rightarrow f(x) = 1 + \sum_{p=1}^{\infty} 2(-1)^p \cos(2p\pi x) = 1 + \sum_{p=1}^{\infty} (-1)^p (e^{i2p\pi x} + e^{-i2p\pi x})$$

$$= \sum_{p=-\infty}^{+\infty} (-1)^p e^{i2p\pi x}.$$

**Solution 3.2.15**

Special representation of the derivative of the Fermi function:

$$\hat{f}'_-(\varepsilon) = -\frac{b}{4 \cosh^2 \left[ \frac{1}{2} b (\varepsilon - \mu_0) \right]}.$$



With  $\rho = b(\varepsilon - \mu_0)$  it then remains to be calculated:

$$I_p = -\operatorname{Re} \left[ \exp \left( i 2\pi p \mu_0 - \frac{\pi}{4} \right) K_p \right],$$

$$K_p = \int_{-\infty}^{+\infty} d\rho \frac{\exp \left( i \frac{2\pi p \rho}{b} \right)}{4 \cosh^2 \left( \frac{1}{2} \rho \right)}.$$

The integral is solved by the use of the residue theorem, where, because of  $p > 0$ , the integration path is closed in the upper complex half plane. Because of  $\cosh x = \cos(ix)$  the integrand has poles at the positions  $\rho = \rho_n$ ,

$$\rho_n = i(2n + 1)\pi,$$

where only those with  $n \geq 0$  lie inside the region of integration. We get with

$$\cosh \left( \frac{1}{2} \rho_n \right) = 0; \quad \sinh \left( \frac{1}{2} \rho_n \right) = i(-1)^n$$

the Taylor expansion:

$$\begin{aligned} \cosh \left( \frac{1}{2} \rho \right) &= \frac{1}{2} i (-1)^n (\rho - \rho_n) + \frac{1}{48} i (-1)^n (\rho - \rho_n)^3 + \dots \\ &= \frac{1}{2} i (-1)^n (\rho - \rho_n) \left[ 1 + \frac{1}{24} (\rho - \rho_n)^2 + \dots \right]. \end{aligned}$$

Therewith it also holds:

$$\frac{1}{\cosh^2 \left( \frac{1}{2} \rho \right)} = \frac{-4}{(\rho - \rho_n)^2} \left[ 1 - \frac{1}{12} (\rho - \rho_n)^2 + \dots \right].$$

The integrand of  $K_p$  thus has at  $\rho_n$  a pole of second order. We calculate the residue:

$$\begin{aligned} \operatorname{Res}_{\rho_n} \frac{\exp \left( i \frac{2\pi p \rho}{b} \right)}{4 \cosh^2 \left( \frac{1}{2} \rho \right)} &= \lim_{\rho \rightarrow \rho_n} \frac{d}{d\rho} \left[ (\rho - \rho_n)^2 \frac{\exp \left( i \frac{2\pi p \rho}{b} \right)}{4 \cosh^2 \left( \frac{1}{2} \rho \right)} \right] \\ &= - \lim_{\rho \rightarrow \rho_n} \frac{d}{d\rho} \left[ \exp \left( i \frac{2\pi p \rho}{b} \right) \left( 1 - \frac{1}{12} (\rho - \rho_n)^2 + \dots \right) \right] \\ &= -i \frac{2\pi p}{b} \exp \left[ -\frac{2\pi^2}{b} (2n + 1)p \right]. \end{aligned}$$

With the residue theorem it then follows:

$$\begin{aligned} K_p &= 4\pi^2 \frac{p}{b} \sum_{n=0}^{\infty} \exp\left[-\frac{2\pi^2}{b}(2n+1)p\right] = 4\pi^2 \frac{p}{b} \exp\left(-\frac{2\pi^2}{b}p\right) \sum_{n=0}^{\infty} \exp\left(-\frac{4\pi^2}{b}np\right) \\ &= 4\pi^2 \frac{p}{b} \frac{\exp\left(-\frac{2\pi^2}{b}p\right)}{1 - \exp\left(-\frac{4\pi^2}{b}p\right)} = \frac{2\pi^2 p}{b \sinh\left(2\pi^2 \frac{p}{b}\right)}. \end{aligned}$$

Because  $K_p$  is real, it follows therewith immediately for  $I_p$  the formula, which we have applied in (3.119):

$$I_p = -2\pi^2 \frac{p}{b} \frac{\cos\left(\frac{\pi}{4} - 2p\pi\mu_0\right)}{\sinh\left(2\pi^2 \frac{p}{b}\right)}.$$

### Solution 3.2.16

1. Energy levels (3.100):

$$E_n(k_z) = 2\mu_B B_0 \left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m}.$$

Degree of degeneracy (3.102):

$$g_y(B_0) = \frac{eL_x L_y}{2\pi\hbar} B_0.$$

Partition function:

$$\begin{aligned} Z_1 &= \frac{1}{2\pi/L_z} \int_{-\infty}^{+\infty} dk_z \sum_{n=0}^{\infty} g_y(B_0) \exp[-\beta E_n(k_z)] \\ &= \frac{eVB_0}{(2\pi\hbar)^2} \left[ \int_{-\infty}^{+\infty} dp_z \exp\left(-\beta \frac{p_z^2}{2m}\right) \right] e^{-\beta\mu_B B_0} \sum_{n=0}^{\infty} e^{-\beta 2\mu_B B_0 n} \\ &\stackrel{(1.137)}{=} \frac{eVB_0}{(2\pi\hbar)^2} \sqrt{\frac{2\pi m}{\beta}} \frac{e^{-\beta\mu_B B_0}}{1 - e^{-2\beta\mu_B B_0}} \\ \implies Z_1 &= V \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \frac{\beta\mu_B B_0}{\sinh(\beta\mu_B B_0)} \quad \left(\mu_B = \frac{e\hbar}{2m}\right). \end{aligned}$$

2. Free energy:

$$dF = -SdT - m dB_0$$

(as to the *magnetization work* see Sect. 3.2.8).

$$\begin{aligned} \implies m &= -\frac{\partial F}{\partial B_0} = k_B T \frac{\partial}{\partial B_0} \ln Z_N = N k_B T \frac{\partial}{\partial B_0} \ln Z_1 \\ &= N k_B T \frac{\partial}{\partial B_0} \ln \frac{\beta \mu_B B_0}{\sinh(\beta \mu_B B_0)} = -N \mu_B \left( \frac{d}{dx} \ln \frac{\sinh x}{x} \right)_{x=\beta \mu_B B_0} . \end{aligned}$$

In the bracket we find the *classical Langevin function* (see the solution of Exercise 1.4.6):

$$\begin{aligned} L(x) &= \coth x - \frac{1}{x} \\ \implies m &= -N \mu_B L \left( \frac{\mu_B B_0}{k_B T} \right) . \end{aligned}$$

sign  $\rightarrow$  induced magnetic moment is oriented antiparallel  
to the field  
 $\rightarrow$  diamagnetism.

### Solution 3.2.17

Eigen-energies (3.101):

$$\begin{aligned} E_{n\sigma}(k_z) &= 2\mu_B^* B_0 \left( n + \frac{1}{2} \right) + \frac{\hbar^2 k_z^2}{2m^*} + z_\sigma \mu_B B_0 , \\ \mu_B &= \frac{e\hbar}{2m} ; \quad \mu_B^* = \frac{e\hbar}{2m^*} . \end{aligned}$$

Degree of degeneracy (3.102):

$$g_y(B_0) = \frac{eL_x L_y}{2\pi\hbar} B_0 .$$

The partition function is calculated as in the preceding exercise:

$$\begin{aligned} Z_1 &= \frac{1}{2\pi/L_z} \int_{-\infty}^{+\infty} dk_z \sum_{n=0}^{\infty} g_y(B_0) \sum_{\bar{v}} \exp[-\beta E_{n\sigma}(k_z)] \\ &= V \left( \frac{m^*}{2\pi\hbar^2\beta} \right)^{3/2} \frac{\beta\mu_B^* B_0}{\sinh(\beta\mu_B^* B_0)} 2 \cosh(\beta\mu_B B_0) \end{aligned}$$

⇒ average magnetic moment:

$$\begin{aligned} m &= -N\mu_B^* L(\beta\mu_B^* B_0) + N\mu_B \tanh(\beta\mu_B B_0), \\ L(x) &= \coth x - \frac{1}{x} \xrightarrow{x \rightarrow 0} \frac{1}{x} + \frac{x}{3} + \dots - \frac{1}{x} \approx \frac{x}{3}. \end{aligned}$$

Weak field:

$$m \approx -\frac{1}{3}N\mu_B^{*2}\beta B_0 + N\mu_B^2\beta B_0.$$

Zero-field susceptibility:

$$\chi(T) = \mu_0 \frac{N}{V} \frac{\mu_B^2 - \frac{1}{3}\mu_B^{*2}}{k_B T} \quad (\text{cf. Sect. 3.2.9})$$

### Solution 3.2.18

Starting point is the intermediate result (3.134) to (3.140) for the *oscillatory part* of the magnetization of a free electron gas in the homogeneous magnetic field:

$$\begin{aligned} \chi_{\text{osc}} &= \mu_0 \left( \frac{\partial M_{\text{osc}}}{\partial B_0} \right)_T = \chi_1 + \chi_2 + \chi_3. \\ \chi_1 &= \mu_0 \left[ -\frac{3}{4} \frac{a}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{3/2}} \cos(z_\sigma p\pi) \frac{\cos(\pi/4 - pc)}{\sinh(pb)} \right. \\ &\quad + \frac{3}{2} \frac{ac}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p\pi) \frac{\sin(\pi/4 - pc)}{\sinh(pb)} \\ &\quad \left. - \frac{3}{2} \frac{ab}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p\pi) \frac{\cos(\pi/4 - pc)}{\sinh(pb)} \coth(pb) \right], \end{aligned}$$

$$\chi_2 = \mu_0 \left[ -\frac{1}{2} \frac{ac}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p \pi) \frac{\sin(\pi/4 - pc)}{\sinh(pb)} \right. \\ \left. + \frac{ac^2}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} (-1)^p p^{1/2} \cos(z_\sigma p \pi) \frac{\cos(\pi/4 - pc)}{\sinh(pb)} \right. \\ \left. + \frac{abc}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} (-1)^p p^{1/2} \cos(z_\sigma p \pi) \frac{\sin(\pi/4 - pc)}{\sinh(pb)} \coth(pb) \right],$$

$$\chi_3 = \mu_0 \left[ \frac{1}{2} \frac{ab}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} \frac{(-1)^p}{p^{1/2}} \cos(z_\sigma p \pi) \frac{\cos(\pi/4 - pc)}{\sinh(pb)} \coth(pb) \right. \\ \left. + \frac{abc}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} (-1)^p p^{1/2} \cos(z_\sigma p \pi) \frac{\sin(\pi/4 - pc)}{\sinh(pb)} \coth(pb) \right. \\ \left. - \frac{ab^2}{B_0} \mu_B \frac{N}{V} \sum_{p=1}^{\infty} (-1)^p p^{1/2} \cos(z_\sigma p \pi) \frac{\cos(\pi/4 - pc)}{\sinh^3(pb)} (1 + \cosh^2(pb)) \right].$$

## Section 3.3.8

### Solution 3.3.1

Equations (3.152), (3.153):

$$(n - n_0) \lambda^3(T) = (2S + 1) g_{3/2}(z),$$

$(n - n_0)$  bounded,  $\lambda(T) \xrightarrow{T \rightarrow \infty} 0$ . It must therefore hold

$$g_{3/2}(z) \xrightarrow{T \rightarrow \infty} 0.$$

$g_{3/2}(z) \rightarrow 0$  obviously means  $z \rightarrow 0$ , and therefore

$$\beta\mu \rightarrow -\infty.$$

Because  $\beta$  tends to zero for  $T \rightarrow \infty$ , it must necessarily be

$$\mu \xrightarrow{T \rightarrow \infty} -\infty.$$

**Solution 3.3.2**

Grand-canonical potential of bosons:

$$\begin{aligned} \Omega(T, V, \mu) &= k_{\text{B}} T \sum_r \ln(1 - e^{-\beta(\varepsilon_r - \mu)}) \\ \implies S(T, V, \mu) &= - \left( \frac{\partial \Omega}{\partial T} \right)_{V, \mu} \\ &= -k_{\text{B}} \sum_r \ln(1 - e^{-\beta(\varepsilon_r - \mu)}) \\ &\quad - k_{\text{B}} T \sum_r \frac{(\varepsilon_r - \mu) e^{-\beta(\varepsilon_r - \mu)}}{1 - e^{-\beta(\varepsilon_r - \mu)}} \left( -\frac{1}{k_{\text{B}} T^2} \right). \\ \langle \hat{n}_r \rangle &= \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1} \\ \implies \beta(\varepsilon_r - \mu) &= \ln\left(\frac{1}{\langle \hat{n}_r \rangle} + 1\right) = \ln(1 + \langle \hat{n}_r \rangle) - \ln \langle \hat{n}_r \rangle; \\ \ln(1 - e^{-\beta(\varepsilon_r - \mu)}) &= -\ln(1 + \langle \hat{n}_r \rangle) \\ \implies S(T, V, \mu) &= k_{\text{B}} \sum_r \left[ \ln(1 + \langle \hat{n}_r \rangle) + \langle \hat{n}_r \rangle (\ln(1 + \langle \hat{n}_r \rangle) - \ln \langle \hat{n}_r \rangle) \right] \\ &= k_{\text{B}} \sum_r \left[ (1 + \langle \hat{n}_r \rangle) \ln(1 + \langle \hat{n}_r \rangle) - \langle \hat{n}_r \rangle \ln \langle \hat{n}_r \rangle \right]; \\ \langle \hat{n}_r \rangle &= \langle a_r^+ a_r \rangle: \quad \text{'particles'}, \\ 1 + \langle \hat{n}_r \rangle &= \langle a_r a_r^+ \rangle: \quad \text{'holes'}. \end{aligned}$$

Behavior for  $T \rightarrow 0$ :

$$\begin{aligned} \text{a)} \quad N \text{ fixed:} \quad \varepsilon_0: \text{ lowest particle energy} \\ \langle \hat{n}_0 \rangle \xrightarrow{T \rightarrow 0} N &\implies 1 + \langle \hat{n}_0 \rangle \approx \langle \hat{n}_0 \rangle \\ &\quad \text{(thermodynamic limit)} \\ &\implies S(T, V, \mu) \xrightarrow{T \rightarrow 0} 0, \\ \text{b)} \quad N(T) \xrightarrow{T \rightarrow 0} 0 &\implies \langle \hat{n}_r \rangle \xrightarrow{T \rightarrow 0} 0 \\ &\implies S(T, V, \mu) \xrightarrow{T \rightarrow 0} 0. \end{aligned}$$

**Solution 3.3.3**

$$I_\alpha(z) \equiv \int_0^\infty \frac{x^{\alpha-1}}{z^{-1}e^x - 1} dx = \int_0^\infty z e^{-x} x^{\alpha-1} \sum_{n=0}^\infty (z e^{-x})^n dx = \sum_{n=1}^\infty z^n \int_0^\infty x^{\alpha-1} e^{-xn} dx .$$

Substitution  $t = xn$ :

$$I_\alpha(z) = \sum_{n=1}^\infty z^n n^{-\alpha} \int_0^\infty t^{\alpha-1} e^{-t} dt = \Gamma(\alpha) \sum_{n=1}^\infty \frac{z^n}{n^\alpha}$$

$$\implies g_\alpha(z) = \frac{1}{\Gamma(\alpha)} I_\alpha(z) \quad \text{q. e. d}$$

**Solution 3.3.4**

In general (see (3.21), (3.22), (3.26)):

$$(pV)^{(\pm)} = \mp k_B T \sum_r \ln(1 \mp e^{-\beta(\varepsilon_r - \mu)})$$

Upper (lower) sign: bosons (fermions)

Density of states from Exercise 3.1.5:

$$D_d(E) = d_d \cdot E^{d/2-1} \cdot \Theta(E)$$

$d_d$ : known constants (see Exercise 3.1.5). Therewith

$$(pV)^{(\pm)} = \mp k_B T \int_{-\infty}^\infty dE D_d(E) \ln(1 \mp e^{-\beta(E-\mu)})$$

Attention: Since there is no condensate, i.e.,  $z < 1$ , the  $(\varepsilon_r = 0)$ -term for bosons need not be treated separately. Even the states with  $\varepsilon_r = 0$  are ‘asymptotically thinly’ occupied. Reformulation of

$$(pV)^{(\pm)} = \mp k_B T d_d \int_0^\infty dE E^{d/2-1} \ln(1 \mp e^{-\beta(E-\mu)})$$

by integration by parts. For the two functions  $f(E)$  and  $g(E)$  it generally holds

$$\int_0^{\infty} dE f'(E) g(E) = f(E) g(E) \Big|_0^{\infty} - \int_0^{\infty} dE f(E) g'(E).$$

We choose here

$$f'(E) = E^{d/2-1} \implies f(E) = \frac{E^{d/2}}{d/2}$$

and

$$\begin{aligned} g(E) &= \ln(1 \mp e^{-\beta(E-\mu)}) \\ \implies g'(E) &= \frac{\pm \beta e^{-\beta(E-\mu)}}{1 \mp e^{-\beta(E-\mu)}} \\ &= \pm \beta \frac{1}{e^{\beta(E-\mu)} \mp 1} \\ &= \pm \beta \langle \hat{n}(E) \rangle^{(\pm)}, \end{aligned}$$

where  $\hat{n}$  is the occupation number operator. After integration by parts the integrated term vanishes:

$$E \longrightarrow 0:$$

$$\frac{2}{d} E^{\frac{d}{2}} \ln(1 \mp e^{-\beta(E-\mu)}) \longrightarrow \frac{2}{d} E^{\frac{d}{2}} \ln(1 \mp z) \longrightarrow 0$$

$$E \longrightarrow \infty:$$

$$\begin{aligned} \frac{2}{d} E^{\frac{d}{2}} \ln(1 \mp e^{-\beta(E-\mu)}) &= -\frac{2}{d} E^{\frac{d}{2}} \sum_{n=1}^{\infty} (\pm 1)^n \frac{e^{-n\beta(E-\mu)}}{n} \\ &\longrightarrow -\frac{2}{d} E^{\frac{d}{2}} (\pm 1) e^{-\beta(E-\mu)} \\ &\longrightarrow 0 \end{aligned}$$

It follows:

$$\begin{aligned} (pV)^{(\pm)} &= \pm k_B T d_d \int_0^{\infty} dE \frac{E^{d/2}}{d/2} (\pm \beta) \langle \hat{n}(E) \rangle^{(\pm)} \\ &= \frac{2}{d} d_d \int_0^{\infty} dE E \cdot E^{\frac{d}{2}-1} \langle \hat{n}(E) \rangle^{(\pm)} \end{aligned}$$



$$\begin{aligned}
 &= \frac{2}{d} \int_{-\infty}^{\infty} dE E \cdot D_d(E) \langle \hat{n}(E) \rangle^{(\pm)} \\
 &= \frac{2}{d} U^{(\pm)}
 \end{aligned}$$

In the last step (3.54) was exploited for fermions, and the analogous equation for bosons.

### Solution 3.3.5

1. According to (3.146) it is to be calculated:

$$\begin{aligned}
 \beta\Omega &= (2S+1) \frac{V}{(2\pi)^3} 4\pi \int_0^{\infty} dk k^2 \ln(1 - ze^{-\alpha k}) + (2S+1) \ln(1-z), \\
 \alpha &\equiv \beta\hbar c > 0.
 \end{aligned}$$

Integration by parts (the integrated part vanishes; why?):

$$\begin{aligned}
 \int_0^{\infty} dk k^2 \ln(1 - ze^{-\alpha k}) &= \left. \frac{1}{3} k^3 \ln(1 - ze^{-\alpha k}) \right|_0^{\infty} - \frac{1}{3} \int_0^{\infty} dk k^3 \frac{+\alpha z e^{-\alpha k}}{1 - ze^{-\alpha k}} \\
 &= -\frac{\alpha}{3} \int_0^{\infty} dk k^3 \frac{1}{z^{-1} e^{\alpha k} - 1} \\
 &\stackrel{(x=\alpha k)}{=} -\frac{1}{3\alpha^3} \int_0^{\infty} dx \frac{x^3}{z^{-1} e^x - 1} = -\frac{1}{3\alpha^3} \Gamma(4) g_4(z).
 \end{aligned}$$

In the last step we have used the integral formula from Exercise 3.3.3. With  $\Gamma(4) = 3!$  it finally remains:

$$\beta\Omega = (2S+1) \ln(1-z) - \frac{(2S+1)V}{\pi^2(\beta\hbar c)^3} g_4(z).$$

2.

$$\begin{aligned}
 pV &= -\Omega \\
 \implies \beta p &= (2S+1) \left[ \frac{g_4(z)}{\pi^2(\beta\hbar c)^3} - \frac{1}{V} \ln(1-z) \right].
 \end{aligned}$$

Particle density according to (2.80):

$$n = \frac{\langle \widehat{N} \rangle}{V} = z \left( \frac{\partial}{\partial z} \beta p \right)_{T,V}$$

$$\implies n = (2S + 1) \left[ \frac{g_3(z)}{\pi^2 (\beta \hbar c)^3} + \frac{1}{V} \frac{z}{1-z} \right].$$

Internal energy according to (2.85):

$$U = - \left( \frac{\partial}{\partial \beta} \ln \Xi_z \right)_{z,V} = \left[ \frac{\partial}{\partial \beta} (\beta \Omega) \right]_{z,V}$$

$$\implies U = \frac{3}{\beta^4} \frac{(2S + 1)V}{\pi^2 (\hbar c)^3} g_4(z).$$

3. We have according to 2.:

$$U = 3pV + 3k_B T (2S + 1) \ln(1 - z).$$

So it is to show:

$$\lim_{V \rightarrow \infty} \frac{1}{V} \ln(1 - z) = 0.$$

That is trivial for  $z < 1$ . For  $z \rightarrow 1$  it follows from the relation for the particle density  $n$ :

$$\frac{1}{V} \frac{z}{1-z} \longrightarrow \frac{n}{2S + 1} - \frac{g_3(1)}{\pi (\beta \hbar c)^3} \equiv x(T).$$

$g_3(z)$  is monotonically increasing in the interval  $0 \leq z \leq 1$  with a finite value for  $z = 1$ :

$$g_3(1) = \xi(3) = 1.202.$$

$x(T)$  is thus finite. This means that  $(1 - z)$  must behave in the limit  $z \rightarrow 1$ ,  $V \rightarrow \infty$  like  $1/V$ . Then, however,  $(1/V) \ln(1 - z)$  indeed tends to zero, and the second term in the above equation for  $U$  can be neglected:

$$U = 3pV,$$

$$p = \frac{2S + 1}{\beta^4} \frac{1}{\pi^2 (\hbar c)^3} g_4(z).$$

4. The relation for  $n$  from part 2. can be written as follows:

$$n_0 = n - \frac{2S+1}{\pi^2(\beta\hbar c)^3} g_3(z),$$

$n_0$ : particle density in the ground state ( $N_0/V$ ). If

$$n > \frac{2S+1}{\pi^2(\beta\hbar c)^3} g_3(1),$$

then  $n_0$  takes macroscopic values  $\implies$  Bose-Einstein condensation. Critical data from

$$n \stackrel{!}{=} \frac{2S+1}{\pi^2(\beta\hbar c)^3} g_3(1).$$

$n$  fixed:

$$k_B T_c(n) = \hbar c \left[ \frac{\pi^2 n}{(2S+1)g_3(1)} \right]^{1/3}.$$

$T$  fixed:

$$n_c(T) = \frac{2S+1}{\pi^2(\beta\hbar c)^3} g_3(1).$$

5.

$$\begin{aligned} \frac{n_0}{n} &= 1 - \frac{2S+1}{\pi^2(\beta\hbar c)^3} \frac{g_3(1)}{n} = 1 - \left( \frac{\beta c}{\beta} \right)^3 = \frac{N_0}{N} \\ \implies N_0 &= \left[ 1 - \left( \frac{T}{T_c} \right)^3 \right] N. \end{aligned}$$

6. From the equations

$$\begin{aligned} p_c(T) &= (k_B T)^4 \frac{2S+1}{\pi^2(\hbar c)^3} g_4(1), \\ n_c(T) &= (k_B T)^3 \frac{2S+1}{\pi^2(\hbar c)^3} g_3(1) \end{aligned}$$

the temperature must be eliminated:

$$\begin{aligned} p_c &= c n^{4/3}, \\ c &= \frac{\hbar c \pi^{2/3}}{(2S+1)^{1/3}} \frac{g_4(1)}{(g_3(1))^{4/3}}. \end{aligned}$$

**Solution 3.3.6**

1.

$$\sum_r \dots \implies (2S+1) \frac{V}{4\pi^2} \int d^2k \dots, \quad d^2k = kdkd\varphi.$$

With (3.21) it follows at first:

$$\beta\Omega(T, V, z) = (2S+1) \frac{V}{4\pi^2} 2\pi \int_0^\infty dk k \ln(1 - ze^{-\beta\epsilon(k)}) + (2S+1) \ln(1-z).$$

The second summand explains itself as demonstrated for (3.146). Substitution:

$$y = \frac{\hbar^2 k^2}{2m} \beta = \frac{\lambda^2 k^2}{4\pi} \implies dy = \frac{\lambda^2}{2\pi} kdk.$$

The above integral can be reformulated:

$$\begin{aligned} & \frac{\lambda^2}{2\pi} \int_0^\infty dk k \ln \left[ 1 - z \exp \left( -\beta \frac{\hbar^2 k^2}{2m} \right) \right] \\ &= \int_0^\infty dy \ln(1 - ze^{-y}) \\ &= y \ln(1 - ze^{-y}) \Big|_0^\infty - \int_0^\infty dy y \frac{ze^{-y}}{1 - ze^{-y}} \\ &= - \int_0^\infty dy \frac{y}{z^{-1}e^y - 1} = -\Gamma(2)g_2(z) = -g_2(z). \end{aligned}$$

At the end we have used the integral formula from Exercise 3.3.3.

$$\beta\Omega(T, V, z) = -\frac{(2S+1)V}{\lambda^2} g_2(z) + (2S+1) \ln(1-z).$$

2. With (2.80) and (3.158) one finds for the particle density:

$$n = z \left( \frac{\partial}{\partial z} \beta p \right)_{T,V} = -z \left( \frac{\partial}{\partial z} \frac{\beta\Omega}{V} \right)_{T,V} = \frac{2S+1}{\lambda^2} g_1(z) + \frac{2S+1}{V} \frac{z}{1-z}.$$

3.

$$g_1(z) = \sum_{n=1}^{\infty} \frac{z^n}{n} \quad \text{diverges for } z \rightarrow 1 .$$

The condition for the transition into the *region of condensation* would be in analogy to (3.161):  
 $n$  fixed and finite:

$$n\lambda_c^2 \stackrel{!}{=} (2S+1)g_1(1) = \infty \quad \implies \quad T_C = 0 .$$

There is thus no Bose-Einstein condensation in the two-dimensional ideal Bose gas, if the one-particle energies are of the given type (cf. Exercise 3.3.10).

### Solution 3.3.7

We start at (3.23) and evaluate the equation in the thermodynamic limit (3.37):

$$\begin{aligned} n &= \frac{1}{V} \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1} = z \frac{1}{V} \sum_r \frac{1}{e^{\beta\varepsilon_r} - z} \\ &= z(2S+1) \underbrace{\frac{1}{(2\pi)^d} \int d^d k \frac{1}{e^{\beta\varepsilon(k)} - z}}_{I_d(z)} \\ &= (2S+1) z I_d(0) \frac{I_d(z)}{I_d(0)} \\ I_d(0) &= \frac{1}{(2\pi)^d} \int d^d k \exp\left(-\beta \frac{\hbar^2}{2m} k^2\right) \\ &= \prod_{i=1}^d \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk_i \exp\left(-\beta \frac{\hbar^2}{2m} k_i^2\right) \\ &= \prod_{i=1}^d \frac{1}{2\pi} \sqrt{\frac{2\pi m}{\beta \hbar^2}} \\ &= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{\frac{d}{2}} . \end{aligned}$$

Because of the **isotropic** energy dispersion it can be written by means of a suitable substitution:

$$\frac{I_d(z)}{I_d(0)} = \frac{A_d(z)}{A_d(0)} \quad \text{with} \quad A_d(z) = \int_0^\infty dx x^{d-1} \frac{1}{e^{x^2} - z} .$$

Then:

$$A_d(0) = \int_0^\infty dx x^{d-1} e^{-x^2} = \frac{1}{2} \int_0^\infty dy y^{\frac{d}{2}-1} e^{-y} = \frac{1}{2} \Gamma\left(\frac{d}{2}\right) .$$

In the second step  $y = x^2$  was substituted; on the right-hand side the Gamma-function appears. It therewith remains for the particle density:

$$n = (2S + 1) z \left( \frac{m}{2\pi\beta\hbar^2} \right)^{\frac{d}{2}} \underbrace{\frac{2}{\Gamma\left(\frac{d}{2}\right)} \int_0^\infty dx x^{d-1} \frac{1}{e^{x^2} - z}}_{B_d(z)} .$$

$B_d(z)$  can be calculated analytically for  $d = 2$ .

$$B_2(z) = \int_0^\infty dx x \frac{1}{e^{x^2} - z} = \frac{1}{2} \int_0^\infty dy \frac{1}{e^y - z} = \frac{1}{2} \int_0^\infty dy \frac{e^{-y}}{1 - z e^{-y}} .$$

We choose:

$$v = 1 - z e^{-y} \quad \curvearrowright \quad \frac{dv}{dy} = z e^{-y} \quad \curvearrowright \quad e^{-y} dy = \frac{1}{z} dv .$$

One finds therewith:

$$B_2(z) = \frac{1}{2z} \int_{1-z}^1 dv \frac{1}{v} = -\frac{1}{2z} \ln(1 - z) .$$

One therefore gets for the particle density of the two-dimensional ideal Bose gas ( $\Gamma(1) = 1$ ):

$$n = -(2S + 1) \frac{m}{2\pi\beta\hbar^2} \ln(1 - z) .$$

With the abbreviation

$$\alpha = \frac{2\pi\hbar^2}{(2S+1)m}$$

it follows:

$$\ln(1-z) = -n \frac{\alpha}{k_B T} \curvearrowright 1-z = e^{-n \frac{\alpha}{k_B T}} \curvearrowright z = 1 - e^{-n \frac{\alpha}{k_B T}} \stackrel{!}{=} e^{\beta\mu} .$$

This eventually leads to :

$$\mu_{d=2} = k_B T \ln \left( 1 - \exp \left( - \frac{2\pi\hbar^2}{(2S+1)m} \cdot \frac{n}{k_B T} \right) \right) .$$

### **Solution 3.3.8**

In the *gaseous* phase of the ideal Bose gas it holds according to (3.152):

$$n = \frac{2S+1}{\lambda^3} g_{3/2}(z) ,$$

$$g_{3/2}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}} .$$

In lowest order (Sect. 3.3.2):

$$z \approx z^{(0)} = \frac{n\lambda^3}{2S+1} .$$

Ansatz:

$$z = \alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \alpha_3 (z^{(0)})^3 + \dots$$

Insertion into the relation for  $n$ :

$$\begin{aligned} z^{(0)} &= \alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \alpha_3 (z^{(0)})^3 + \dots \\ &+ \frac{1}{2^{3/2}} \left( \alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \dots \right)^2 \\ &+ \frac{1}{3^{3/2}} \left( \alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \dots \right)^3 + \dots . \end{aligned}$$

Grouping according to the powers of  $z^{(0)}$ :

$$\begin{aligned} 0 &= (\alpha_1 - 1)z^{(0)} && \implies \alpha_1 = 1, \\ 0 &= \left(\alpha_2 + \frac{\alpha_1}{2^{5/2}}\right)(z^{(0)})^2 && \implies \alpha_2 = -\frac{1}{2^{5/2}}, \\ 0 &= \left(\alpha_3 + \frac{2}{2^{5/2}}\alpha_1\alpha_2 + \frac{\alpha_1^3}{3^{5/2}}\right)(z^{(0)})^3 && \implies \alpha_3 = \frac{1}{4} - \frac{1}{3^{5/2}}. \end{aligned}$$

The pressure results from (3.151):

$$\begin{aligned} \beta pV &= \frac{(2S+1)V}{\lambda^3} g_{5/2}(z) = \frac{(2S+1)V}{\lambda^3} \left( z + \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \dots \right) \\ &= \frac{(2S+1)V}{\lambda^3} \left[ \alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \alpha_3 (z^{(0)})^3 + \dots \right. \\ &\quad \left. + \frac{1}{2^{5/2}} (\alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \dots)^2 \right. \\ &\quad \left. + \frac{1}{3^{5/2}} (\alpha_1 z^{(0)} + \alpha_2 (z^{(0)})^2 + \dots)^3 + \dots \right] \\ &= nV \left[ 1 + z^{(0)} \left( \alpha_2 + \frac{1}{2^{5/2}} \right) \right. \\ &\quad \left. + (z^{(0)})^2 \left( \alpha_3 + \frac{2\alpha_1\alpha_2}{2^{5/2}} + \frac{1}{3^{5/2}} \right) + \dots \right]. \end{aligned}$$

Inserting the numerical values for  $\alpha_1, \alpha_2, \alpha_3$ :

$$pV = Nk_B T \left( 1 - \frac{1}{2^{5/2}} z^{(0)} + \left( \frac{1}{8} - \frac{2}{3^{5/2}} \right) (z^{(0)})^2 + \dots \right).$$

The first two terms of the expansion were already found in (3.156).

### Solution 3.3.9

$$\begin{aligned} n &= \frac{2S+1}{\pi^2(\beta\hbar c)^3} g_3(z), \\ p &= \frac{2S+1}{\beta^4} \frac{1}{\pi^2(\hbar c)^3} g_4(z) = \frac{k_B T n}{z^{(0)}} g_4(z). \end{aligned}$$



In lowest order ( $z \ll 1$ ):

$$z^{(0)} = g_3(z) \approx z .$$

Ansatz:

$$z = \sum_{n=1}^{\infty} \alpha_n (z^{(0)})^n .$$

Inserting into

$$z^{(0)} = \sum_{n=1}^{\infty} \frac{z^n}{n^3}$$

and grouping according to powers of  $z^{(0)}$ :

$$0 = (\alpha_1 - 1)z^{(0)} \quad \implies \alpha_1 = 1 ,$$

$$0 = \left( \alpha_2 + \frac{\alpha_1}{2^3} \right) (z^{(0)})^2 \quad \implies \alpha_2 = -\frac{1}{2^3} ,$$

$$0 = \left( \alpha_3 + \frac{2}{2^3} \alpha_1 \alpha_2 + \frac{\alpha_1^3}{3^3} \right) (z^{(0)})^3 \quad \implies \alpha_3 = \frac{1}{2^5} - \frac{1}{3^3} .$$

Thermal equation of state:

$$\begin{aligned} pV &= Nk_B T \frac{1}{z^{(0)}} \left( z + \frac{z^2}{2^4} + \frac{z^3}{3^4} + \dots \right) \\ &= Nk_B T \left[ \alpha_1 + \alpha_2 z^{(0)} + \alpha_3 (z^{(0)})^2 \right. \\ &\quad \left. + \frac{1}{2^4 z^{(0)}} (\alpha_1 z^{(0)} + \alpha_2 z^{(0)} + \dots)^2 \right. \\ &\quad \left. + \frac{1}{3^4 z^{(0)}} (\alpha_1 z^{(0)} + \alpha_2 z^{(0)} + \dots)^3 + \dots \right] \\ \implies pV &= Nk_B T \left[ 1 + \gamma_1 z^{(0)} + \gamma_2 (z^{(0)})^2 + \dots \right] , \\ \gamma_1 &= \alpha_2 + \frac{1}{2^4} \alpha_1 = -\frac{1}{2^4} , \\ \gamma_2 &= \alpha_3 + \frac{2}{2^4} \alpha_1 \alpha_2 + \frac{1}{3^4} \alpha_1 \\ &= \frac{1}{2^5} - \frac{1}{3^3} - \frac{1}{2^6} + \frac{1}{3^4} = \frac{1}{2^6} - \frac{2}{3^4} . \end{aligned}$$

**Solution 3.3.10**

1. According to (3.146) it is to be calculated:

$$\begin{aligned}\beta\Omega(T, V, z) &= (2S+1)\frac{V}{4\pi^2}2\pi \int_0^\infty dk k \ln(1 - ze^{-\beta\hbar ck}) + (2S+1)\ln(1-z) \\ &= (2S+1)\frac{V}{2\pi(\beta\hbar c)^2} \int_0^\infty dy y \ln(1 - ze^{-y}) + (2S+1)\ln(1-z), \\ \int_0^\infty dy y \ln(1 - ze^{-y}) &= \frac{1}{2}y^2 \ln(1 - ze^{-y}) \Big|_0^\infty - \frac{1}{2} \int_0^\infty dy y^2 \frac{ze^{-y}}{1 - ze^{-y}} \\ &= -\frac{1}{2} \int_0^\infty dy \frac{y^2}{z^{-1}e^y - 1} = -\frac{1}{2}\Gamma(3)g_3(z).\end{aligned}$$

In the last step we have used the integral formula from Exercise 3.3.3:

$$\beta\Omega(T, V, z) = -\frac{(2S+1)V}{(2\pi\beta\hbar c)^2}g_3(z) + (2S+1)\ln(1-z).$$

2. It follows with (2.80) and (3.158):

$$n = -z \left( \frac{\partial \beta\Omega}{\partial z} \frac{1}{V} \right)_{T,V} = \frac{2S+1}{2\pi(\beta\hbar c)^2}g_2(z) + \frac{2S+1}{V} \frac{z}{1-z}.$$

3.  $g_2(1)$  finite  $\implies$  a Bose-Einstein condensation does exist!

For fixed  $n$ :

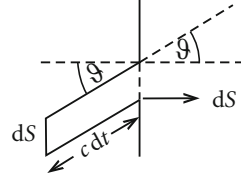
$$k_B T_C(n) = \hbar c \sqrt{\frac{n}{(2S+1)g_2(1)}}; \quad g_2(1) = \zeta(2) = \frac{\pi}{6}.$$

**Solution 3.3.11**

Planck's radiation formula (3.206) has at first to be rewritten for wave lengths:

$$\begin{aligned}\omega &= \frac{2\pi c}{\lambda} \rightarrow \left| \frac{d\omega}{d\lambda} \right| = \frac{2\pi c}{\lambda^2}, \\ \hat{\varepsilon}(\lambda, T)d\lambda &= \hat{\varepsilon} \left( \omega = \frac{2\pi c}{\lambda} \right) \left| \frac{d\omega}{d\lambda} \right| d\lambda \\ \implies \hat{\varepsilon}(\lambda, T) &= \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(\beta\frac{\hbar c}{\lambda}) - 1}.\end{aligned}$$

Fig. A.12



Photons move with the velocity of light. All the photons, which are in the sketched cylinder (Fig. A.12) with a *suitable* direction of motion, arrive in the time  $dt$  at the hole  $dS$ . The directions of the velocity vectors are isotropically distributed. The fractional amount  $d\Omega/4\pi$  will have the *right* direction. The cylinder has the volume:

$$(cdt)(dS \cos \vartheta) .$$

The per time unit escaping spectral energy is therewith given by:

$$\begin{aligned} I_\lambda(T, \vartheta) d\lambda d\Omega dS &= \hat{\varepsilon}(\lambda, T) d\lambda (cdS \cos \vartheta) \frac{d\Omega}{4\pi} \\ \implies I_\lambda(T, \vartheta) &= 2 \cos \vartheta \frac{hc^2}{\lambda^5} \frac{1}{\exp(\beta \frac{hc}{\lambda}) - 1} . \end{aligned}$$

### Solution 3.3.12

1. It holds according to (3.206):

$$\hat{\varepsilon}(\omega, T) = \frac{\hbar\pi}{(\pi\beta c)^3} \frac{x^3}{e^x - 1} .$$

$T$  fixed  $\rightarrow$  extremal condition:

$$\begin{aligned} 0 &\stackrel{!}{=} \frac{d}{dx} \frac{x^3}{e^x - 1} = \frac{(e^x - 1)3x^2 - x^3 e^x}{(e^x - 1)^2} \\ &\implies 0 = 3(e^x - 1) - x e^x \\ &\implies (3 - x)e^x = 3 \quad \iff \quad x = x_0 . \end{aligned}$$

2. The maximum is given, independently of the temperature  $T$ , always by the same  $x_0$ :

$$x_0 = \frac{\hbar\omega}{k_B T} \implies \frac{\omega_1}{T_1} = \frac{\omega_2}{T_2} .$$

**Solution 3.3.13**

Kinetic energy:

$$\begin{aligned}
\sum_{i,\alpha} \dot{u}_{i\alpha}^2(t) &= \sum_{i,\alpha} \frac{1}{N} \sum_{r,r'} \sum_{\mathbf{q},\mathbf{q}'} \dot{Q}_r(\mathbf{q}t) \dot{Q}_{r'}(\mathbf{q}',t) \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\alpha}(\mathbf{q}') e^{i(\mathbf{q}+\mathbf{q}')\mathbf{R}_i} \\
&= \sum_{r,r'} \sum_{\mathbf{q},\mathbf{q}'} \delta_{\mathbf{q}-\mathbf{q}'} \dot{Q}_r(\mathbf{q},t) \dot{Q}_{r'}(\mathbf{q}',t) \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\alpha}(\mathbf{q}') \\
&\stackrel{(3.222)}{=} \sum_{r,r'} \sum_{\mathbf{q}} \dot{Q}_r(\mathbf{q},t) \dot{Q}_{r'}(-\mathbf{q},t) \sum_{\alpha} \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\alpha}^*(\mathbf{q}) \\
&\stackrel{(3.218)}{=} \sum_{r,\mathbf{q}} \dot{Q}_r(\mathbf{q},t) \dot{Q}_r^*(\mathbf{q},t) \\
\implies T &= \frac{1}{2} M \sum_{i,\alpha} \dot{u}_{i\alpha}^2(t) = \frac{1}{2} M \sum_{r,\mathbf{q}} \dot{Q}_r(\mathbf{q}t) \dot{Q}_r^*(\mathbf{q},t) .
\end{aligned}$$

Potential energy:

$$\begin{aligned}
V &= V_0 + \frac{1}{2} \sum_{ij} \sum_{\alpha,\beta} \varphi_{i\alpha}^{j\beta} u_{i\alpha} u_{j\beta} \\
&= V_0 + \frac{1}{2N} \sum_{ij} \sum_{\alpha,\beta} \varphi_{i\alpha}^{j\beta} \sum_{r,r'} \sum_{\mathbf{q},\mathbf{q}'} Q_r(\mathbf{q},t) Q_{r'}(\mathbf{q}',t) \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\beta}(\mathbf{q}') e^{i(\mathbf{q}\mathbf{R}_i+\mathbf{q}'\mathbf{R}_j)} \\
&= V_0 + \frac{1}{2N} \sum_{j,\alpha,\beta} \sum_{r,r'} \sum_{\mathbf{q},\mathbf{q}'} Q_r(\mathbf{q},t) Q_{r'}(\mathbf{q}',t) \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\beta}(\mathbf{q}') \cdot \\
&\quad \cdot \sum_m \phi_{m\alpha}^{0\beta} e^{i\mathbf{q}\mathbf{R}_m} e^{i(\mathbf{q}+\mathbf{q}')\mathbf{R}_j} \\
&= V_0 + \frac{1}{2} \sum_{\alpha,\beta} \sum_{r,r'} \sum_{\mathbf{q},\mathbf{q}'} Q_r(\mathbf{q},t) Q_{r'}(\mathbf{q}',t) \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\beta}(\mathbf{q}') M K_{\alpha\beta}(\mathbf{q}) \delta_{\mathbf{q}-\mathbf{q}'} \\
&\stackrel{(3.216)}{=} V_0 + \frac{1}{2} M \sum_{\alpha} \sum_{r,r'} \sum_{\mathbf{q}} Q_r(\mathbf{q},t) Q_{r'}(-\mathbf{q},t) \varepsilon_{r\alpha}(\mathbf{q}) \omega_r^2(-\mathbf{q}) \varepsilon_{r'\alpha}(-\mathbf{q}) \\
&\stackrel{(3.218)}{=} V_0 + \frac{1}{2} M \sum_{r,r'} \sum_{\mathbf{q}} Q_r(\mathbf{q}t) Q_{r'}^*(\mathbf{q},t) \omega_r^2(\mathbf{q}) \delta_{rr'} \\
\implies V &= V_0 + \frac{1}{2} M \sum_{\mathbf{q},r} \omega_r^2(\mathbf{q}) Q_r(\mathbf{q}t) Q_r^*(\mathbf{q},t) .
\end{aligned}$$

For this derivation we have exploited

$$\omega_r(\mathbf{q} = \omega_r(-\mathbf{q}) ; \quad K_{\alpha\beta}(\mathbf{q}) = K_{\alpha\beta}(-\mathbf{q})$$

(inversion symmetry, time reversal invariance).

**Solution 3.3.14**

The first two relations follow immediately from (3.220) and (3.227). We prove the third relation:

$$\begin{aligned}
 \left[ \widehat{P}_r(\mathbf{q}, t), \widehat{Q}_{r'}(\mathbf{q}, t) \right]_- &= \frac{M}{N} \sum_{i,\alpha} \sum_{j,\beta} \left[ \hat{u}_{i\alpha}(t), \hat{u}_{j\beta}(t) \right]_- \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\beta}^*(\mathbf{q}') e^{i(\mathbf{q}\mathbf{R}_i - \mathbf{q}'\mathbf{R}_j)} \\
 &\stackrel{(3.227)}{=} \frac{1}{N} \sum_{i,\alpha} \frac{\hbar}{i} \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\beta}^*(\mathbf{q}') e^{i(\mathbf{q} - \mathbf{q}')\mathbf{R}_i} \\
 &= \frac{\hbar}{i} \sum_{\alpha} \varepsilon_{r\alpha}(\mathbf{q}) \varepsilon_{r'\beta}^*(\mathbf{q}') \delta_{\mathbf{q}\mathbf{q}'} \stackrel{(3.218)}{=} \frac{\hbar}{i} \delta_{rr'} \delta_{\mathbf{q}\mathbf{q}'} .
 \end{aligned}$$

**Solution 3.3.15**

According to (3.251) it holds for the internal energy in the Debye model:

$$U(T, V) = \gamma (k_B T)^4 \int_0^{\frac{T_D}{T}} dx \frac{x^3}{e^x - 1} ; \quad \gamma = \frac{9N}{(\hbar\omega_D)^3} .$$

Low temperatures  $\curvearrowright T_D/T \gg 1$ :

$$\int_0^{\frac{T_D}{T}} dx \frac{x^3}{e^x - 1} = \underbrace{\int_0^{\infty} dx \frac{x^3}{e^x - 1}}_{\pi^4/15 \text{ (3.247)}} - \int_{\frac{T_D}{T}}^{\infty} dx \frac{x^3}{e^x - 1} .$$

The first summand leads to the well-known result (3.253) for the internal energy. The second summand can be approximated because of  $T_D/T \gg 1$ :

$$\begin{aligned}
 \int_{\frac{T_D}{T}}^{\infty} dx \frac{x^3}{e^x - 1} &\approx \int_{\frac{T_D}{T}}^{\infty} dx x^3 e^{-x} \\
 &= -e^{-x} x^3 \Big|_{\frac{T_D}{T}}^{\infty} + 3 \int_{\frac{T_D}{T}}^{\infty} dx x^2 e^{-x}
 \end{aligned}$$

$$\begin{aligned}
&= \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^3 - 3x^2 e^{-x} \Big|_{\frac{T_D}{T}}^{\infty} + 6 \int_{\frac{T_D}{T}}^{\infty} dx x e^{-x} \\
&= \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^3 + 3 \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^2 \\
&\quad - 6x e^{-x} \Big|_{\frac{T_D}{T}}^{\infty} + 6 \int_{\frac{T_D}{T}}^{\infty} dx e^{-x} \\
&= \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^3 + 3 \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^2 \\
&\quad + 6 \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right) + 6 \exp\left(-\frac{T_D}{T}\right) \\
&= \exp\left(-\frac{T_D}{T}\right) \left[ \left(\frac{T_D}{T}\right)^3 + 3 \left(\frac{T_D}{T}\right)^2 + 6 \left(\frac{T_D}{T}\right) + 6 \right].
\end{aligned}$$

Internal energy at low temperatures:

$$U(T, V) \approx 9N\hbar\omega_D \left(\frac{T}{T_D}\right)^4 \left[ \frac{\pi^4}{15} - \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^3 \right].$$

Heat capacity:

$$\begin{aligned}
C_V &= \frac{\partial U}{\partial T} = 36Nk_B \left(\frac{T}{T_D}\right)^3 \left[ \frac{\pi^4}{15} - \exp\left(-\frac{T_D}{T}\right) \left(\frac{T_D}{T}\right)^3 \right] \\
&\quad + 9N\hbar\omega_D \left(\frac{T}{T_D}\right)^4 \left[ 3\frac{T_D^3}{T^4} \exp\left(-\frac{T_D}{T}\right) - \frac{T_D^4}{T^5} \exp\left(-\frac{T_D}{T}\right) \right] \\
&= C_V^D - 36Nk_B \exp\left(-\frac{T_D}{T}\right) \left(1 - \frac{3}{4} + \frac{1}{4} \frac{T_D}{T}\right).
\end{aligned}$$

$C_V^D$  is the Debye formula (3.254) for the heat capacity. Because of  $T_D/T \gg 1$  it remains as the leading temperature-correction:

$$C_V - C_V^D \approx -9Nk_B \frac{T_D}{T} \exp\left(-\frac{T_D}{T}\right).$$

**Solution 3.3.16**

With (3.243) it is to be calculated ( $\mu = 0$  see (3.189)):

$$\begin{aligned}
 \langle N_p \rangle &= \int_{-\infty}^{+\infty} dE D(E) \frac{1}{e^{\beta E} - 1} \\
 &= \frac{9N}{(\hbar\omega_D)^3} \int_0^{\hbar\omega_D} dE E^2 \frac{1}{e^{\beta E} - 1} \\
 &= \frac{9N}{x_D^3} \int_0^{x_D} dx \frac{x^2}{e^x - 1}; \quad \beta\hbar\omega_D = \frac{T_D}{T} \equiv x_D.
 \end{aligned}$$

- Low temperatures:  $T \ll T_D$ , i.e.  $x_D \gg 1$ :

$$\begin{aligned}
 \frac{x_D^3}{9N} \langle N_p \rangle &\approx \int_0^{\infty} dx \frac{x^2}{e^x - 1} \\
 &= \int_0^{\infty} dx e^{-x} x^2 \frac{1}{1 - e^{-x}} \\
 &= \int_0^{\infty} dx e^{-x} x^2 \sum_{n=0}^{\infty} e^{-nx} = \int_0^{\infty} dx x^2 \sum_{n=1}^{\infty} e^{-nx} \\
 &= \sum_{n=1}^{\infty} \frac{d^2}{dn^2} \int_0^{\infty} dx e^{-nx} = \sum_{n=1}^{\infty} \frac{d^2}{dn^2} \frac{1}{n} \\
 &= 2 \sum_{n=1}^{\infty} \frac{1}{n^3} = 2 \zeta(3) = 2.402 \quad (\text{see Exercise 3.3.3})
 \end{aligned}$$

Hence it holds for the average phonon number in the low-temperature region:

$$\langle N_p \rangle \approx 21.62 \cdot N \left( \frac{k_B T}{\hbar\omega_D} \right)^3.$$

- High temperatures:  $T \gg T_D$ , i.e.  $x_D \ll 1$ :

$$\begin{aligned} \int_0^{x_D} dx \frac{x^2}{e^x - 1} &= \int_0^{x_D} dx x^2 \frac{1}{x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \dots} \\ &\approx \int_0^{x_D} dx x \left(1 - \frac{1}{2}x\right) = \frac{1}{2}x_D^2 - \frac{1}{6}x_D^3 \\ \langle N_p \rangle &\approx \frac{9N}{x_D^3} \left( \frac{1}{2}x_D^2 - \frac{1}{6}x_D^3 \right). \end{aligned}$$

Hence it holds for the average phonon number in the high-temperature region:

$$\langle N_p \rangle = \frac{9}{2} N \frac{k_B T}{\hbar \omega_D} - \frac{3}{2} N + \mathcal{O} \left( \frac{\hbar \omega_D}{k_B T} \right).$$

## Section 4.1.6

### Solution 4.1.1

In the **classical** Ising model the magnetic moment is given by

$$m = \mu \sum_i S_i$$

and therewith

$$H = -J \sum_{ij} S_i S_j - m B_0.$$

Partition function:

$$Z(T, m) = \sum_{\{S_i\}} \exp \left( -\beta \left( -J \sum_{ij} S_i S_j - m B_0 \right) \right)$$

It is summed over **all** spin configurations. The substitution  $S_i \rightarrow -S_i \forall i$  can therefore not affect the partition function. In the exponent the first term does not change thereby its sign, but the second term does:  $m \rightarrow -m$ . This means

$$Z(T, m) = \overline{Z(T, -m)}$$



and therewith:

$$\begin{aligned} F(T, m) &= -k_B T \ln Z(T, m) \\ &= -k_B T \ln Z(T, -m) \\ &= F(T, -m) \end{aligned}$$

### Solution 4.1.2

With the definition of the canonical partition function

$$Z = \text{Tr} \left( e^{-\beta \hat{H}} \right)$$

it follows for the average magnetic moment:

$$\begin{aligned} \langle \hat{m} \rangle &= \frac{1}{Z} \text{Tr} \left( -\frac{d}{dB_0} \hat{H} e^{-\beta \hat{H}} \right) \\ &= \frac{1}{\beta} \frac{1}{Z} \frac{\partial}{\partial B_0} \text{Tr} \left( e^{-\beta \hat{H}} \right) \\ &= \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial B_0}. \end{aligned}$$

From that one gets for the susceptibility:

$$\begin{aligned} \chi_T &= \frac{\mu_0}{V} \left( \frac{\partial}{\partial B_0} \langle \hat{m} \rangle \right)_T \\ &= \frac{\mu_0}{\beta V} \left( -\frac{1}{Z^2} \left( \frac{\partial Z}{\partial B_0} \right)^2 + \frac{1}{Z} \frac{\partial^2 Z}{\partial B_0^2} \right). \end{aligned}$$

The first term is clear:

$$\frac{1}{Z^2} \left( \frac{\partial Z}{\partial B_0} \right)^2 = \beta^2 \langle \hat{m} \rangle^2.$$

The second term is calculated in a bit more involved manner:

$$\begin{aligned} \frac{1}{Z} \frac{\partial^2 Z}{\partial B_0^2} &= \frac{1}{Z} \frac{\partial}{\partial B_0} \left( -\beta \text{Tr} \left( \frac{\partial \hat{H}}{\partial B_0} e^{-\beta \hat{H}} \right) \right) \\ &= \frac{-\beta}{Z} \text{Tr} \left( \frac{\partial^2 \hat{H}}{\partial B_0^2} e^{-\beta \hat{H}} - \beta \left( \frac{\partial \hat{H}}{\partial B_0} \right)^2 e^{-\beta \hat{H}} \right) \end{aligned}$$

$$\begin{aligned}
 &= \frac{\beta^2}{Z} \operatorname{Tr} \left( \left( \frac{\partial \widehat{H}}{\partial B_0} \right)^2 e^{-\beta \widehat{H}} \right) \\
 &= \beta^2 \langle \widehat{m}^2 \rangle .
 \end{aligned}$$

In the third step we have exploited the precondition that it is a permanent magnetic moment. It is left for the susceptibility:

$$\chi_T = \frac{\mu_0}{V} \beta (\langle \widehat{m}^2 \rangle - \langle \widehat{m} \rangle^2) = \frac{1}{k_B T} \frac{\mu_0}{V} \langle (\widehat{m} - \langle \widehat{m} \rangle)^2 \rangle .$$

### **Solution 4.1.3**

Along the coexistence line the two phases 1 and 2 are at equilibrium. This means for the free enthalpy

$$G_1(T, p) = G_2(T, p)$$

$(dT, dp)$ : State change along the coexistence line, i.e.

$$dG_1 = dG_2 .$$

This means

$$\left( \frac{\partial G_1}{\partial T} \right)_p dT + \left( \frac{\partial G_1}{\partial p} \right)_T dp = \left( \frac{\partial G_2}{\partial T} \right)_p dT + \left( \frac{\partial G_2}{\partial p} \right)_T dp .$$

With the partial derivatives of the free enthalpy,

$$\left( \frac{\partial G_i}{\partial T} \right)_p = -S_i ; \quad \left( \frac{\partial G_i}{\partial p} \right)_T = V_i ,$$

it follows the assertion

$$\frac{dp}{dT} = - \frac{\left( \frac{\partial G_2}{\partial T} \right)_p - \left( \frac{\partial G_1}{\partial T} \right)_p}{\left( \frac{\partial G_2}{\partial p} \right)_T - \left( \frac{\partial G_1}{\partial p} \right)_T} = \frac{S_2 - S_1}{V_2 - V_1} .$$

**Solution 4.1.4**

For a second-order phase transition (*‘in the Ehrenfest sense’*) the thermodynamic potentials and their first derivatives are continuous along the coexistence line. This means for entropies and volumes, which are first derivatives:

$$dS_1 = dS_2 ; dV_1 = dV_2 .$$

From that it follows with the thermodynamic variables  $T$  and  $p$ , the *‘natural variables’* of the free enthalpy  $G(T, p)$ :

$$\begin{aligned} \left(\frac{\partial S_1}{\partial T}\right)_p dT + \left(\frac{\partial S_1}{\partial p}\right)_T dp &= \left(\frac{\partial S_2}{\partial T}\right)_p dT + \left(\frac{\partial S_2}{\partial p}\right)_T dp \\ \left(\frac{\partial V_1}{\partial T}\right)_p dT + \left(\frac{\partial V_1}{\partial p}\right)_T dp &= \left(\frac{\partial V_2}{\partial T}\right)_p dT + \left(\frac{\partial V_2}{\partial p}\right)_T dp . \end{aligned}$$

This can be resolved:

$$\frac{dp}{dT} = -\frac{\left(\frac{\partial S_2}{\partial T}\right)_p - \left(\frac{\partial S_1}{\partial T}\right)_p}{\left(\frac{\partial S_2}{\partial p}\right)_T - \left(\frac{\partial S_1}{\partial p}\right)_T} = -\frac{\left(\frac{\partial V_2}{\partial T}\right)_p - \left(\frac{\partial V_1}{\partial T}\right)_p}{\left(\frac{\partial V_2}{\partial p}\right)_T - \left(\frac{\partial V_1}{\partial p}\right)_T} .$$

There are the known relations:

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_p &= \frac{C_p}{T} \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p = -V\beta \\ \left(\frac{\partial V}{\partial p}\right)_T &= -V\kappa_T . \end{aligned}$$

In the second line a Maxwell relation of the free enthalpy was used. Therewith it follows

$$\frac{dp}{dT} = \frac{1}{TV} \frac{C_p^{(1)} - C_p^{(2)}}{\beta^{(1)} - \beta^{(2)}}$$

and

$$\frac{dp}{dT} = \frac{\beta^{(1)} - \beta^{(2)}}{\kappa_T^{(1)} - \kappa_T^{(2)}} .$$

**Solution 4.1.5****1. Slope of the coexistence curve**

We write

$$T_0 = T_C(p = 0) ; \quad p_0 = p_i(T_0) ; \quad V_0 = V_V(T_0) = V(T_0) .$$

Enhancement of the external pressure by  $dp$  leads to

$$\begin{aligned} T_0 &\rightarrow T_C(dp) = T_0 + dT \\ p_0 &\rightarrow p_i(T_0 + dT) = p_0 + dp_i . \end{aligned}$$

The vapor is an ideal gas  $\implies$  equation of state:

$$Nk_B dT = d(p_i V_V)_0 = V_0 dp_i(T_0) + p_0 dV(T_0) . \quad (\text{A.1})$$

We exploit that at  $T_C$ ,  $V_V = V$ . As vapor pressure,  $p_i$  fulfills the Clausius-Clapeyron equation (4.3):

$$dp_i = A \cdot dT \quad A = \frac{S_V - S_L}{V_V - V_L} .$$

$S_V, S_L$ : entropies for the case that all the material consists only of vapor and liquid, respectively. Accordingly the volumes.

Volume change due to  $dp, dp_i$ :

$$dV = -ad\pi = -a(dp - dp_i) = a(AdT - dp) .$$

That yields in (A.1):

$$Nk_B dT = V_0 AdT + p_0 a(AdT - dp) .$$

It thus remains for the coexistence curve:

$$\frac{dp}{dT} = \frac{A(V_0 + ap_0) - Nk_B}{ap_0} . \quad (\text{A.2})$$

**2. Isobaric expansion coefficient**

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p .$$

At constant external pressure it must be:

$$dV = -ad\pi = adp_i .$$

It thus remains to be calculated:

$$\beta = \frac{a}{V} \left( \frac{\partial p_i}{\partial T} \right)_p .$$

$$\boxed{T > T_0 :}$$

The vessel contains only vapor (ideal gas). We therefore use (A.1)

$$Nk_B dT = V_0 dp_i + p_0 a dp_i \rightarrow \frac{dp_i}{dT} = \frac{Nk_B}{V_0 + ap_0} .$$

This means:

$$\beta^{(+)} = \frac{aNk_B}{V_0(V_0 + ap_0)} .$$

$$\boxed{T < T_0 :}$$

Some liquid is still present so that  $p_i$  can be read off from the Clausius-Clapeyron equation:

$$\frac{dp_i}{dT} = A \rightarrow \beta^{(-)} = \frac{aA}{V_0} .$$

It is typical for a second-order phase transition that  $\beta$  exhibits a finite discontinuity at  $T_C$ :

$$\Delta\beta = \beta^{(+)} - \beta^{(-)} = \frac{a}{V_0} \frac{Nk_B - A(V_0 + ap_0)}{V_0 + ap_0} . \quad (\text{A.3})$$

### 3. Isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T .$$

$$\boxed{T > T_0 :}$$

The vessel contains only vapor (ideal gas) at a fixed temperature ( $dT = 0$ ). Therefore it holds with (A.1):

$$\begin{aligned} p_0 dV + V_0 dp_i &= 0 \\ dp_i &= dp - d\pi = dp + \frac{1}{a} dV \\ \rightarrow \left( p_0 + \frac{V_0}{a} \right) dV &= -V_0 dp . \end{aligned}$$

One reads off

$$\kappa_T^{(+)} = \frac{a}{ap_0 + V_0} .$$

$$\boxed{T < T_0 :}$$

Since liquid is still present,  $p_i$  obeys the Clausius-Clapeyron equation. At constant temperature the vapor pressure  $p_i$  is also constant.

$$dp_i = 0 \rightarrow dp = d\pi = -\frac{1}{a}dV .$$

It follows therewith:

$$\kappa_T^{(-)} = \frac{a}{V_0} .$$

The compressibility, too, exhibits a finite discontinuity at the transition point:

$$\Delta\kappa_T = \kappa_T^{(+)} - \kappa_T^{(-)} = -\frac{a}{V_0} \frac{ap_0}{V_0 + ap_0} . \quad (\text{A.4})$$

#### 4. Second-order phase transition

Equations (A.2), (A.3), and (A.4) lead to:

$$\frac{dp}{dT} = \frac{\Delta\beta}{\Delta\kappa_T} .$$

This is one of the two Ehrenfest equations. The Gorter model thus performs a second-order phase transition ‘*in the Ehrenfest sense*’.

### **Solution 4.1.6**

This Ehrenfest equation contains heat capacities. We therefore have to think about entropies.  $S_V, S_L$  are the entropies for the case that at  $(T_0, p_0)$  the *entire* material consists only of vapor and liquid, respectively. Thereby, as in Exercise 4.1.5:

$$T_0 = T_C(p = 0) ; p_0 = p_i(T_0) .$$

For the latent heat, which is necessary to transform the **entire** material from the liquid into the gaseous state, we have:

$$\Delta Q = T_0(S_V - S_L) .$$

1.  $T = T_0 + dT$  In this case there is only vapor and no liquid. The Clausius-Clapeyron equation is therefore not applicable. For the entropy  $\widehat{S}_V$ , only infinitesimally different compared to  $S_V$ , it then holds:

$$\widehat{S}_V - S_V = \left( \frac{\partial S_V}{\partial T} \right)_p dT + \left( \frac{\partial S_V}{\partial p_i} \right)_T \left( \frac{\partial p_i}{\partial T} \right) dT .$$

We use

$$\left( \frac{\partial S_V}{\partial T} \right)_p = \frac{1}{T} C_p^{(V)}$$

and the Maxwell relation:

$$\left( \frac{\partial S_V}{\partial p_i} \right)_T = - \left( \frac{\partial V_V}{\partial T} \right)_p = - \frac{V_V}{T} .$$

The last equality sign results from the fact the the vapor is considered as ideal gas:

$$\widehat{S}_V - S_V = \frac{1}{T} \left( C_p^{(V)} - V_V \left( \frac{\partial p_i}{\partial T} \right) \right) dT . \quad (\text{A.5})$$

We exploit once more that the vapor represents an ideal gas:

$$Nk_B dT = d(p_i V_V)_0 = p_0 dV_V + V_0 dp_i .$$

This means

$$dp_i = \frac{1}{V_0} (Nk_B dT - p_0 dV_V) .$$

Above  $T_0$  the vessel contains only vapor ( $V_V = V$ ), therefore:

$$dV_V = dV = -ad\pi = adp_i .$$

Here it was used that for the calculation of  $C_p$  a constant external pressure is to be assumed. Therewith:

$$\begin{aligned} dp_i &= \frac{1}{V_0} (Nk_B dT - ap_0 dp_i) \\ \implies dp_i &= \frac{Nk_B}{V_0 + ap_0} dT . \end{aligned}$$

Hence:

$$\frac{dp_i}{dT} = \frac{Nk_B}{V_0 + ap_0}.$$

This is inserted into (A.5):

$$dS = \widehat{S}_V - S_V = \frac{1}{T} \left( C_p^{(V)} - \frac{Nk_B V_0}{V_0 + ap_0} \right) dT.$$

This means eventually:

$$C_p^{(+)} = C_p^{(V)} - \frac{Nk_B V_0}{V_0 + ap_0}. \quad (\text{A.6})$$

2.  $T = T_0 - dT$  This case turns out to be a bit more complicated, because there is now also liquid. Let  $\widehat{S}_V$  be further on the contribution of the vapor to the entropy according to (A.5). The pressure  $p_i$ , however, is now determined by the Clausius-Clapeyron equation:

$$dp_i = AdT; \quad A = \frac{S_V - S_L}{V_V - V_L}$$

(A.5) therewith yields for  $dT \rightarrow -dT$ :

$$\widehat{S}_V - S_V = -\frac{1}{T_0} (C_p^{(V)} - AV_0) dT.$$

Let now  $dq$  be the fractional amount of the total material which is condensed. That yields the total entropy:

$$S = S_V - \frac{1}{T_0} (C_p^{(V)} - AV_0) dT - dq(S_V - S_L). \quad (\text{A.7})$$

$S_V - S_L$  can be expressed by the latent heat ( $1/T_0 \Delta Q$ ). But what is  $dq$ ? The determination succeeds by inspecting the volume change  $dV_V$ , which can be found in two different ways:

( $\alpha$ )

Ideal gas equation, which according to the precondition always holds for  $T$ ,  $V_V$ , and  $p_i$  (see above):

$$dV_V = \frac{1}{p_0} (Nk_B dT - V_0 dp_i) = \frac{dT}{p_0} (Nk_B - V_0 A).$$



**(β)**Detailed itemization of the contributions to  $dV_V$ :

$$dV_V = dV_1 + dV_2$$

 $dV_1$  by condensation:

$$dV_1 = dq(V_L - V_V) < 0 .$$

$V_V$  and  $V_L$  are thereby the volumes of the entire material as gas and liquid, respectively, at  $p = 0, p_i = p_0, T = T_0$ .

$dV_2$  results from the change of the vapor pressure and the elasticity of the walls:

$$dV_2 = -ad\pi = adp_i = aAdT \quad (p = \text{const.})$$

Altogether:

$$\begin{aligned} dV_V &= dq(V_L - V_V) + aAdT \\ V_L - V_V &= \frac{1}{A}(S_L - S_V) = -\frac{\Delta Q}{AT_0} = -\frac{\Delta Q Nk_B}{Ap_0 V_0} . \end{aligned}$$

We have therewith for  $dq$ :

$$dq = -\frac{Ap_0 V_0}{\Delta Q Nk_B}(dV_V - aAdT) .$$

With  $dV_V$  from (α):

$$dq = \frac{AV_0}{\Delta Q Nk_B}(A(ap_0 + V_0) - Nk_B)dT .$$

This we use in (A.7) together with  $dS = S - S_V$ :

$$dS = -\frac{dT}{T_0} \left( C_p^{(V)} - 2AV_0 + \frac{A^2 V_0}{Nk_B}(ap_0 + V_0) \right) .$$

This means for the heat capacity (temperature change:  $-dT$ )

$$C_p^{(-)} = C_p^{(V)} - 2AV_0 + \frac{A^2 V_0}{Nk_B}(ap_0 + V_0) . \quad (\text{A.8})$$

## 3. Phase transition

We now discuss the phase transition. With (A.6) and (A.8) we find the discontinuity at the transition point:

$$\begin{aligned}\Delta C_p &= C_p^{(+)} - C_p^{(-)} = -\frac{Nk_B V_0}{V_0 + ap_0} + 2AV_0 - \frac{A^2 V_0}{Nk_B}(ap_0 + V_0) \\ &= -\frac{V_0}{Nk_B(V_0 + ap_0)} \left( (ap_0 + V_0)^2 A^2 + (Nk_B)^2 - 2ANk_B(ap_0 + V_0) \right) \\ &= -\frac{T_0}{p_0(V_0 + ap_0)} (A(ap_0 + V_0) - Nk_B)^2 .\end{aligned}$$

In Exercise 4.1.5 the discontinuity of the isobaric expansion coefficient was calculated:

$$\Delta\beta = \beta^{(+)} - \beta^{(-)} = \frac{a}{V_0} \frac{Nk_B - A(V_0 + ap_0)}{V_0 + ap_0} .$$

Therewith:

$$\frac{\Delta C_p}{\Delta\beta} = \frac{T_0 V_0}{p_0 a} (A(V_0 + ap_0) - Nk_B) .$$

We compare this with the result for the coexistence curve from Exercise 4.1.5:

$$\frac{dp}{dT} = \frac{A(V_0 + ap_0) - Nk_B}{ap_0} .$$

From that we recognize the validity of the Ehrenfest equation (4.4):

$$\frac{dp}{dT} = \frac{1}{V_0 T_0} \frac{\Delta C_p}{\Delta\beta} .$$

**Solution 4.1.7**

(1):

First law of Thermodynamics with  $U = U(T, m)$ :

$$\begin{aligned}\delta Q &= dU - B_0 dm \\ &= \left( \frac{\partial U}{\partial T} \right)_m dT + \left[ \left( \frac{\partial U}{\partial m} \right)_T - B_0 \right] dm .\end{aligned}$$

One reads off:

$$C_m = \left( \frac{\delta Q}{dT} \right)_m = \left( \frac{\partial U}{\partial T} \right)_m$$

$$C_H = \left( \frac{\delta Q}{dT} \right)_H = \left( \frac{\partial U}{\partial T} \right)_m + \left[ \left( \frac{\partial U}{\partial m} \right)_T - B_0 \right] \left( \frac{\partial m}{\partial T} \right)_H .$$

Therewith the first relation is proven:

$$C_H - C_m = \left[ \left( \frac{\partial U}{\partial m} \right)_T - B_0 \right] \left( \frac{\partial m}{\partial T} \right)_H .$$

(2):

In the first law of Thermodynamics,

$$TdS = dU - B_0 dm ,$$

we consider the entropy  $S$  and the internal energy  $U$  as functions of  $T$  and  $m$ , and use the integrability conditions for the total differentials  $dS$  and  $dU$ . From

$$dS = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_m dT + \left[ \frac{1}{T} \left( \frac{\partial U}{\partial m} \right)_T - \frac{B_0}{T} \right] dm$$

it then follows the condition

$$\begin{aligned} \left( \frac{\partial}{\partial m} \left( \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_m \right) \right)_T &= \left( \frac{\partial}{\partial T} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial m} \right)_T - \frac{B_0}{T} \right] \right)_m \\ &= -\frac{1}{T^2} \left( \frac{\partial U}{\partial m} \right)_T + \frac{1}{T} \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial m} \right)_T \right)_m \\ &\quad + \frac{B_0}{T^2} - \frac{1}{T} \left( \frac{\partial B_0}{\partial T} \right)_m . \end{aligned}$$

The term on the left-hand side and the second summand on the right-hand side are identical because of the integrability condition for  $U$ . Hence it is left

$$\left( \frac{\partial U}{\partial m} \right)_T = B_0 - T \left( \frac{\partial B_0}{\partial T} \right)_m .$$

Also the second assertion is therewith proven:

$$C_H - C_m = -T \left( \frac{\partial B_0}{\partial T} \right)_m \left( \frac{\partial m}{\partial T} \right)_H .$$

(3):

We use the chain rule

$$\left(\frac{\partial B_0}{\partial T}\right)_m \cdot \left(\frac{\partial T}{\partial m}\right)_H \cdot \left(\frac{\partial m}{\partial B_0}\right)_T = -1$$

and the susceptibility:

$$\chi_T = \frac{\mu_0}{V} \left(\frac{\partial m}{\partial B_0}\right)_T.$$

That means

$$\left(\frac{\partial B_0}{\partial T}\right)_m = - \left(\frac{\partial m}{\partial T}\right)_H \frac{\mu_0}{V \chi_T}.$$

This is inserted into (2) and yields the third variant:

$$C_H - C_m = \frac{\mu_0}{V} T \chi_T^{-1} \left[ \left(\frac{\partial m}{\partial T}\right)_H \right]^2.$$

(4): We can resolve the above chain rule alternatively also as follows:

$$\left(\left(\frac{\partial m}{\partial T}\right)_H\right)^2 = \left(\left(\frac{\partial B_0}{\partial T}\right)_m\right)^2 \cdot \left(\left(\frac{\partial m}{\partial B_0}\right)_T\right)^2 = \left(\left(\frac{\partial B_0}{\partial T}\right)_m\right)^2 \frac{V^2}{\mu_0^2} \chi_T^2.$$

This we insert into (3) obtaining the fourth version for the difference of the heat capacities:

$$C_H - C_m = \frac{V}{\mu_0} T \chi_T \left[ \left(\frac{\partial B_0}{\partial T}\right)_m \right]^2.$$

**Solution 4.1.8**

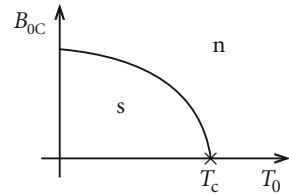
1. It holds the mapping (Fig. A.13):

$$\begin{aligned} p &\iff B_0 = \mu_0 H, \\ V &\iff -m = -VM. \end{aligned}$$

Clausius-Clapeyron equation (4.3):

$$\frac{dp}{dT} = \frac{\Delta Q}{T_0 \Delta V}.$$

Fig. A.13



This means for the superconductor:

$$\Delta Q = T_0 \frac{dB_{0C}}{dT} (-\Delta m) ,$$

$$\Delta m = V(M_n - M_s) \approx -V M_s = V H_C .$$

The last step is an expression of the Meißner-Ochsenfeld effect:

$$\frac{dB_{0C}}{dT} = \mu_0 \frac{dH_C}{dT}$$

$$\implies \Delta Q = -T_0 V \mu_0 \left( H_C \frac{dH_C}{dT} \right)_{T=T_0} .$$

2.

$$G(T, H) = U - T S - \mu_0 V H M ,$$

$$M_n \text{ very small} \implies G_n(T, H) \approx G_n(T, 0) ,$$

$$dG = -S dT - \mu_0 V M dH .$$

Meißner-Ochsenfeld effect:

$$dG_s = -S_s dT + \mu_0 V H dH .$$

We are interested in the isothermal process:

$$(dG_s)_T = \mu_0 V H dH$$

$$\implies G_s(T, H) = G_s(T, 0) + \frac{1}{2} \mu_0 V H^2 .$$

Phase equilibrium:

$$G_n(T, H_C) \stackrel{!}{=} G_s(T, H_C) \approx G_n(T, 0) .$$

Out of this, we obtain the *stabilization energy*:

$$\begin{aligned}\Delta G &= G_s(T, 0) - G_n(T, 0) \approx G_s(T, 0) - G_s(T, H_C) \\ \implies \Delta G &= -\frac{1}{2}\mu_0 V H_C^2(T) .\end{aligned}$$

3.

$$\begin{aligned}S_n &= -\left(\frac{\partial}{\partial T}G_n(T, H)\right)_H \approx -\left(\frac{\partial}{\partial T}G_n(T, H=0)\right)_{H=0} , \\ S_s &= -\left(\frac{\partial}{\partial T}G_s(T, H)\right)_H = -\frac{d}{dT}G_s(T, 0) \\ \implies S_s - S_n &= -\frac{d}{dT}\Delta G = \mu_0 V H_C(T) \frac{dH_C(T)}{dT} .\end{aligned}$$

This is in compliance with part 1.!

Because of  $(dH_C / dT) < 0$ :

$$S_n(T) > S_s(T) .$$

The superconductor thus has the state of higher order. Because of  $H_C(T_C) = 0$  one finds at the critical point:

$$S_n(T_C) = S_s(T_C) .$$

4. Independently of the values of other parameters it holds according to the third law of Thermodynamics:

$$S_s(T) \xrightarrow{T \rightarrow 0} 0 ; \quad S_n(T) \xrightarrow{T \rightarrow 0} 0 .$$

Since on the other hand it shall be

$$H_C(T) \xrightarrow{T \rightarrow 0} H_0 \neq 0 ,$$

it must be fulfilled, according to part 3.

$$\lim_{T \rightarrow 0} \frac{dH_C}{dT} = 0 ,$$

which is indeed guaranteed by our ansatz for  $H_C$ .

5.

$$\begin{aligned}
C_s - C_n &= T \left[ \frac{\partial}{\partial T} (S_s - S_n) \right] \\
&= \mu_0 V T \left[ \left( \frac{dH_C}{dT} \right)^2 + H_C(T) \frac{d^2 H_C(T)}{dT^2} \right], \\
\frac{dH_C}{dT} &= -2 H_0 (1 - \alpha) \frac{T}{T_c^2} - 4 \alpha H_0 \frac{T^3}{T_c^4} \\
&= -2 H_0 \frac{T}{T_c^2} \left( 1 - \alpha + 2 \alpha \frac{T^2}{T_c^2} \right), \\
\left( \frac{dH_C}{dT} \right)^2 &= 4 H_0^2 \frac{T^2}{T_c^4} \left( 1 - \alpha + 2 \alpha \frac{T^2}{T_c^2} \right)^2, \\
\frac{d^2 H_C}{dT^2} &= -2 \frac{H_0}{T_c^2} \left( 1 - \alpha + 6 \alpha \frac{T^2}{T_c^2} \right) \\
\Rightarrow C_s - C_n &= \mu_0 V T 2 \frac{H_0^2}{T_c^2} \left[ \alpha - 1 + 3 \frac{T^2}{T_c^2} (1 - \alpha)^2 + \right. \\
&\quad \left. + 15 \alpha (1 - \alpha) \frac{T^4}{T_c^4} + 14 \alpha^2 \frac{T^6}{T_c^6} \right].
\end{aligned}$$

The critical point  $T = T_C$  is interesting:

$$(C_s - C_n)_{T=T_c} = 4 \mu_0 V \frac{H_0^2}{T_c} (1 + \alpha)^2.$$

6.  $T < T_C$ 

$$S_n(T) \neq S_s(T)$$

$\Rightarrow$  phase transition of first order.

 $T = T_C$ 

$$S_n(T_C) = S_s(T_C),$$

$$C_n(T_C) \neq C_s(T_C) \quad (\text{finite discontinuity})$$

$\Rightarrow$  phase transition of second order.

**Section 4.2.4****Solution 4.2.1**

$$T = T_c(\varepsilon + 1) .$$

$f(T)$  can be written as function of  $\varepsilon$ :

$$f(\varepsilon) = a T_c(\varepsilon + 1) \ln |T_c \varepsilon| + b T_c^2(\varepsilon + 1)^2 .$$

The critical exponent is then determined as follows:

$$\begin{aligned} \varphi &= \lim_{\varepsilon \rightarrow 0} \frac{\ln |f(\varepsilon)|}{\ln |\varepsilon|} = \lim_{\varepsilon \rightarrow 0} \frac{\ln |a T_c(\varepsilon + 1) \ln |T_c \varepsilon||}{\ln |\varepsilon|} \\ &= \lim_{\varepsilon \rightarrow 0} \frac{\ln |a T_c \varepsilon \ln |T_c \varepsilon| + a T_c \ln |T_c \varepsilon||}{\ln |\varepsilon|} = \lim_{\varepsilon \rightarrow 0} \frac{\ln |a T_c \ln |T_c \varepsilon||}{\ln |\varepsilon|} \\ &= \lim_{\varepsilon \rightarrow 0} \frac{\ln |a T_c| + \ln |\ln |T_c \varepsilon||}{\ln |\varepsilon|} = \lim_{\varepsilon \rightarrow 0} \frac{\ln |\ln T_c + \ln |\varepsilon||}{\ln |\varepsilon|} \\ &= \lim_{\varepsilon \rightarrow 0} \frac{\ln |\ln |\varepsilon||}{\ln |\varepsilon|} = \lim_{\varepsilon \rightarrow 0} \frac{\frac{1}{|\ln |\varepsilon||} \frac{1}{|\varepsilon|}}{\frac{1}{|\varepsilon|}} = \lim_{\varepsilon \rightarrow 0} \frac{1}{|\ln |\varepsilon||} = 0 . \end{aligned}$$

**Solution 4.2.2**

Second-order phase transitions according to the Ehrenfest classification are defined by finite discontinuities of the second derivatives of the free enthalpy or free energy:

$$\begin{aligned} (T \rightarrow T_c^{(\pm)}) \quad f(\varepsilon) &\longrightarrow A_{\pm} ; \quad A_+ \neq A_- \\ \implies \quad \varphi &= \lim_{\varepsilon \rightarrow 0} \frac{\ln |f(\varepsilon)|}{\ln |\varepsilon|} = \lim_{\varepsilon \rightarrow 0} \frac{\ln |A_{\pm}|}{\ln |\varepsilon|} = 0 . \end{aligned}$$

**Solution 4.2.3**

1.

$$\begin{aligned} T &= T_c(\varepsilon + 1) \implies f(\varepsilon) = a T_c^{5/2}(\varepsilon + 1)^{5/2} - b \\ \implies \quad \varphi &= \lim_{\varepsilon \rightarrow 0} \frac{\ln |f(\varepsilon)|}{\ln |\varepsilon|} = 0 . \end{aligned}$$



2.

$$f(\varepsilon) = a T_c^2 (\varepsilon + 1)^2 + \frac{C}{T_c} \frac{1}{\varepsilon}$$

$$\implies \varphi = \lim_{\varepsilon \rightarrow 0} \frac{\ln |\frac{C}{T_c \varepsilon}|}{\ln |\varepsilon|} = - \lim_{\varepsilon \rightarrow 0} \frac{\ln |\varepsilon|}{\ln |\varepsilon|} = -1 .$$

3.

$$f(\varepsilon) = a \sqrt{T_c} \sqrt{|\varepsilon|} + d$$

$$\implies \varphi = \lim_{\varepsilon \rightarrow 0} \frac{\ln |d|}{\ln |\varepsilon|} = 0 .$$

**Solution 4.2.4**

We use part 3. of Exercise 4.1.7:

$$\chi_T (C_H - C_m) = \mu_0 V T \beta_H^2; \quad \beta_H = \left( \frac{\partial M}{\partial T} \right)_H$$

$$\implies 1 - R = \mu_0 V T \beta_H^2 \chi_T^{-1} C_H^{-1} .$$

Critical behavior  $T \rightarrow T_c^{(-)}$ :

$$M \sim (-\varepsilon)^\beta; \quad \beta_H^2 \sim (-\varepsilon)^{2\beta-2}; \quad \chi_T^{-1} \sim (-\varepsilon)^{\gamma'}; \quad C_H^{-1} \sim (-\varepsilon)^{\alpha'}$$

$$\implies 1 - R \sim (-\varepsilon)^{2\beta-2+\gamma'+\alpha'} .$$

We read off:

1.  $R \neq 1$  :

The above equation is satisfiable only if:

$$2\beta - 2 + \gamma' + \alpha' = 0 \quad \iff \quad \alpha' + 2\beta + \gamma' = 2 .$$

2.  $R = 1$  :

In the above relation the left-hand side is now zero, and the relation can therefore be fulfilled only by

$$2\beta - 2 + \gamma' + \alpha' > 0 \quad \iff \quad \alpha' + 2\beta + \gamma' > 2 .$$

**Solution 4.2.5**

The scaling hypothesis (4.37) brings about (4.52). There we put

$$\lambda = (\pm\varepsilon)^{-(1/a_\varepsilon)}$$

and obtain with  $H$  instead of  $B_0 = \mu_0 H$ :

$$M(\varepsilon, H) = (\pm\varepsilon)^{(1-a_B)/a_\varepsilon} M(\pm 1, (\pm\varepsilon)^{-(a_B/a_\varepsilon)} H) .$$

We use (4.50), (4.55) and (4.57):

$$\frac{1-a_B}{a_\varepsilon} = \beta ; \quad \frac{a_B}{a_\varepsilon} = \beta\delta .$$

It immediately follows therewith the assertion:

$$\frac{M(\varepsilon, H)}{(\pm\varepsilon)^\beta} = M(\pm 1, (\pm\varepsilon)^{-\beta\delta} H) .$$

One measures the magnetization  $M$  for a multitude of external magnetic fields  $H$  as a function of the temperature (or  $\varepsilon$ ). If one then plots

$$\frac{M(\varepsilon, H)}{|\varepsilon|^\beta} \quad \text{versus} \quad \frac{H}{|\varepsilon|^{\beta\delta}} ,$$

this multitude will be reduced to two curves, one for  $T < T_c$  and one for  $T > T_c$ , provided the scaling hypothesis is valid.

**Solution 4.2.6**

We exploit:

$$(4.57): \quad \beta = \frac{1-a_B}{a_\varepsilon} ,$$

$$(4.55): \quad \delta = \frac{a_B}{1-a_B} ,$$

$$(4.61): \quad \gamma = \gamma' = \frac{2a_B - 1}{a_\varepsilon} ,$$

$$(4.64): \quad \alpha = \alpha' = \frac{2\alpha_\varepsilon - 1}{a_\varepsilon} .$$

1.  $\gamma(\delta + 1) = (2 - \alpha)(\delta - 1)$  is valid exactly when

$$\frac{2a_B - 1}{a_\varepsilon} \frac{1}{1 - a_B} \stackrel{!}{=} \frac{1}{a_\varepsilon} \frac{2a_B - 1}{1 - a_B}$$

is fulfilled. That is obviously the case!

2.  $\delta = (2 - \alpha + \gamma) / (2 - \alpha - \gamma)$  is correct if

$$\frac{a_B}{1 - a_B} \stackrel{!}{=} \frac{2 - \frac{2a_\varepsilon - 1}{a_\varepsilon} + \frac{2a_B - 1}{a_\varepsilon}}{2 - \frac{2a_\varepsilon - 1}{a_\varepsilon} - \frac{2a_B - 1}{a_\varepsilon}}$$

is fulfilled:

$$\begin{aligned} \frac{a_B}{1 - a_B} &\stackrel{!}{=} \frac{2a_\varepsilon - 2a_\varepsilon + 1 + 2a_B - 1}{2a_\varepsilon - 2a_\varepsilon + 1 - 2a_B + 1} \\ \Leftrightarrow \frac{a_B}{1 - a_B} &\stackrel{!}{=} \frac{2a_B}{2 - 2a_B} \quad \text{q. e. d.} \end{aligned}$$

## Section 4.3.10

### Solution 4.3.1

It was shown as equation (2.59) in Vol. 5 (one should recall the derivation!):

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p.$$

This means for the van der Waals gas:

$$\left(\frac{\partial U}{\partial V}\right)_T = a \frac{n^2}{V^2}.$$

After integration:

$$U(T, V) = f(T) - a \frac{n^2}{V}.$$

The heat capacity

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V = \frac{df}{dt}.$$

is therefore independent of the volume, as in the case of the ideal gas. We determine from it the entropy  $S = S(T, V)$ :

$$\begin{aligned} dS &= \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \\ &= \frac{c_V(T)}{T} dT + \left( \frac{\partial p}{\partial T} \right)_V dV \\ &= \frac{c_V(T)}{T} dT + \frac{Nk_B}{V - nb} dV. \end{aligned}$$

In the second step the Maxwell relation of the free energy  $F$ ,

$$dF = -SdT - pdV \implies \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V,$$

was used, and in the last step the equation of state. One gets then for the entropy:

$$S(T, V) = S(T_0, V_0) + \int_{T_0}^T dT' \frac{C_V(T')}{T'} + Nk_B \ln \frac{V - nb}{V_0 - nb}.$$

We use this for calculating the latent heat:

$$\begin{aligned} \Delta Q &= T(S_G - S_L) \\ &= Nk_B T \ln \frac{V_G - nb}{V_L - nb} \\ &= Nk_B T \int_{V_L}^{V_G} dV \frac{1}{V - nb} \\ &= \int_{V_L}^{V_G} dV \left( p + \frac{an^2}{V^2} \right) \\ &= p(V_G - V_L) - an^2 \left( \frac{1}{V_G} - \frac{1}{V_L} \right) \\ &= (V_G - V_L) \left( p + \frac{an^2}{V_G V_L} \right). \end{aligned}$$

### Solution 4.3.2

1. Determination of  $\widehat{F}^*$

Eigen-states of  $H^*$ :

$$|\sigma_1 \sigma_2 \dots \sigma_N\rangle \equiv |\sigma_1\rangle |\sigma_2\rangle \dots |\sigma_N\rangle \quad \text{with} \quad \sigma_i = \pm \frac{1}{2}.$$

Eigen-values:

$$H^* |\sigma_1 \sigma_2 \dots \sigma_N\rangle = -2\mu_B B^* \left( \sum_i \sigma_i \right) |\sigma_1 \sigma_2 \dots \sigma_N\rangle.$$

With the solution of Exercise 2.3.9 one finds:

$$\begin{aligned} Z_N^* &= (Z_1^*)^N = \left( e^{\beta\mu_B B^*} + e^{-\beta\mu_B B^*} \right)^N \\ F_N^* &= -k_B T N \ln \left( e^{\beta\mu_B B^*} + e^{-\beta\mu_B B^*} \right). \end{aligned}$$

We still need

$$\langle H - H^* \rangle^* \equiv \left\langle - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - 2\mu_B (B - B^*) \sum_i S_i^z \right\rangle^*,$$

i.e., in particular  $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle^*$  and  $\langle S_i^z \rangle^*$ .

It holds:

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2} \left( S_i^+ S_j^- + S_i^- S_j^+ \right) + S_i^z S_j^z$$

and

$$\langle \sigma_1 \sigma_2 \dots \sigma_N | S_i^+ S_j^- | \sigma_1 \sigma_2 \dots \sigma_N \rangle = \langle \sigma_i | S_i^+ | \sigma_i \rangle \langle \sigma_j | S_j^- | \sigma_j \rangle = 0$$

(single-spin states are orthonormalized!). Hence it remains:

$$\langle H - H^* \rangle^* = \left\langle - \sum_{ij} J_{ij} S_i^z S_j^z - 2\mu_B (B - B^*) \sum_i S_i^z \right\rangle^*.$$

We calculate in detail:

$$\begin{aligned}
 \langle S_i^z \rangle^* &= \frac{1}{Z_N^*} \sum_{\sigma_1 \dots \sigma_N} \left\langle \sigma_1 \dots \sigma_N \left| e^{2\beta\mu_B B^* \sum_j S_j^z} S_i^z \right| \sigma_1 \dots \sigma_N \right\rangle \\
 &= \frac{1}{Z_N^*} \left( \sum_{\sigma_1} \langle \sigma_1 | e^{2\beta\mu_B B^* S_1^z} | \sigma_1 \rangle \cdot \dots \right. \\
 &\quad \dots \cdot \sum_{\sigma_i} \langle \sigma_i | e^{2\beta\mu_B B^* S_i^z} S_i^z | \sigma_i \rangle \cdot \dots \\
 &\quad \left. \dots \cdot \sum_{\sigma_N} \langle \sigma_N | e^{2\beta\mu_B B^* S_N^z} | \sigma_N \rangle \right) \\
 &= \frac{(Z_1^*)^{N-1}}{Z_N^*} \sum_{\sigma_i} \langle \sigma_i | e^{2\beta\mu_B B^* S_i^z} S_i^z | \sigma_i \rangle \\
 &= \frac{1}{Z_1^*} \left( \frac{1}{2} e^{\beta\mu_B B^*} - \frac{1}{2} e^{-\beta\mu_B B^*} \right).
 \end{aligned}$$

We have therewith:

$$\langle S_i^z \rangle^* = \frac{1}{2} \tanh(\beta\mu_B B^*).$$

$\langle S_i^z \rangle^*$  is thus independent of the lattice site  $i$  (translational symmetry).

We further calculate

$$\begin{aligned}
 \langle S_i^z S_j^z \rangle^* &= \frac{1}{Z_N^*} \sum_{\sigma_1 \dots \sigma_N} \left\langle \sigma_1 \dots \sigma_N \left| e^{2\beta\mu_B B^* \sum_m S_m^z} S_i^z S_j^z \right| \sigma_1 \dots \sigma_N \right\rangle \\
 &= \frac{(Z_1^*)^{N-2}}{Z_N^*} \sum_{\sigma_i, \sigma_j} \langle \sigma_i | \langle \sigma_j | e^{2\beta\mu_B B^* (S_i^z + S_j^z)} S_i^z S_j^z | \sigma_i \rangle | \sigma_j \rangle \\
 &= \frac{1}{(Z_1^*)^2} \left( \sum_{\sigma_i} \langle \sigma_i | e^{2\beta\mu_B B^* S_i^z} S_i^z | \sigma_i \rangle \right) \\
 &\quad \cdot \left( \sum_{\sigma_j} \langle \sigma_j | e^{2\beta\mu_B B^* S_j^z} S_j^z | \sigma_j \rangle \right) \\
 &= \frac{1}{(Z_1^*)^2} \left( \frac{1}{2} e^{\beta\mu_B B^*} - \frac{1}{2} e^{-\beta\mu_B B^*} \right)^2.
 \end{aligned}$$

We obtain:

$$\langle S_i^z S_j^z \rangle^* = \frac{1}{4} \tanh^2(\beta \mu_B B^*) = \langle S_i^z \rangle^* \langle S_j^z \rangle^* .$$

We find therewith as upper bound of the free energy:

$$\begin{aligned} \widehat{F}^* &= -k_B T N \ln(e^{\beta \mu_B B^*} + e^{-\beta \mu_B B^*}) \\ &\quad - z N J \left( \frac{1}{2} \tanh(\beta \mu_B B^*) \right)^2 \\ &\quad - 2 \mu_B N (B - B^*) \cdot \frac{1}{2} \tanh(\beta \mu_B B^*) . \end{aligned}$$

2. ‘Optimal’ mean field  $B_0^* \Leftrightarrow \widehat{F}^*$  minimal ( $B^*$ : variational parameter)

$$\begin{aligned} 0 &= \frac{\partial}{\partial B^*} \widehat{F}^* \\ &= -k_B T N \beta \mu_B \cdot \frac{e^{\beta \mu_B B^*} - e^{-\beta \mu_B B^*}}{e^{\beta \mu_B B^*} + e^{-\beta \mu_B B^*}} \\ &\quad - 2 z N J \left( \frac{1}{2} \tanh(\beta \mu_B B^*) \right) \frac{\partial}{\partial B^*} \left( \frac{1}{2} \tanh(\beta \mu_B B^*) \right) \\ &\quad - 2 \mu_B N (B - B^*) \frac{\partial}{\partial B^*} \left( \frac{1}{2} \tanh(\beta \mu_B B^*) \right) \\ &\quad + 2 \mu_B N \left( \frac{1}{2} \tanh(\beta \mu_B B^*) \right) . \end{aligned}$$

The first and the last term compensate each other. It remains:

$$0 = \frac{\partial}{\partial B^*} \left( \frac{1}{2} \tanh(\beta \mu_B B^*) \right) \left( - z N J \tanh(\beta \mu_B B^*) - 2 \mu_B N (B - B^*) \right)$$

$\Rightarrow$  self-consistent conditional equation for the ‘optimal’ mean field:

$$\begin{aligned} B_0^* &= \frac{z J}{2 \mu_B} \tanh(\beta \mu_B B_0^*) + B \\ &= \frac{z J}{\mu_B} \langle S^z \rangle_0^* + B . \end{aligned}$$

One sees that the mean value  $(zJ)/(\mu_B) \langle S^z \rangle_0^*$  acts as an *effective field*, in addition to the external field  $B$ !

## 3. Phase transition

$$\begin{aligned}
 & \text{ferromagnetism} \\
 & \Leftrightarrow \\
 & \text{spontaneous magnetization, i.e. } M_s(T) \equiv 2\mu_B \langle S_i^z \rangle_0^* \neq 0 \text{ for } B = 0 \\
 & \Leftrightarrow \\
 & B_0^* \neq 0 \text{ for } B = 0.
 \end{aligned}$$

Evaluation of the  $B_0^*$ -conditional equation from part 2. for  $B = 0$ : Introduce the Curie temperature  $T_C$  by

$$k_B T_C = \frac{zJ}{2},$$

Hence:

$$\begin{aligned}
 \tanh(\beta\mu_B B_0^*) &= \tanh\left(\frac{2\beta\mu_B B_0^*}{zJ} \cdot \frac{zJ}{2}\right) \\
 &= \tanh\left(x \cdot \frac{T_C}{T}\right)
 \end{aligned}$$

with  $x = (2\mu_B)/(zJ)B_0^*$ .

$$\Rightarrow x = \tanh\left(x \cdot \frac{T_C}{T}\right).$$

$x = 0$  is always a solution, but does there also exist a solution  $x \neq 0$ ?  
Assumption:  $B_0^*$  and therewith also  $x$  become small for  $T \rightarrow T_C$ :

$$\begin{aligned}
 x \stackrel{x \ll 1}{\approx} x \frac{T_C}{T} - \frac{1}{3} x^3 \left(\frac{T_C}{T}\right)^3 \\
 \Leftrightarrow x^3 &= 3 \left(\frac{T}{T_C}\right)^3 x \left(\frac{T_C}{T} - 1\right) \\
 &= 3 \left(\frac{T}{T_C}\right)^2 x \left(1 - \frac{T}{T_C}\right) \xrightarrow{T \approx T_C} 3x \left(1 - \frac{T}{T_C}\right).
 \end{aligned}$$

Two cases:

(i)  $T > T_C$ :

$$x^3 = -3x \left| \frac{T_C - T}{T_C} \right|$$

Only  $x = 0$  is solution  $\Rightarrow B_0^* = 0 \Rightarrow M_s(T) = 0$ , paramagnetism.



(ii)  $T < T_C$ : $x = 0$  continues to be a solution, but also  $x = \sqrt{3 \frac{T_C - T}{T_C}}$ 

$$\begin{aligned} \Rightarrow M_s(T) &\equiv 2\mu_B \langle S^z \rangle_0^* = 2\mu_B \frac{\mu_B}{zJ} B_0^* = \mu_B x \\ &= \mu_B \sqrt{3 \frac{T_C - T}{T_C}} \neq 0, \text{ ferromagnetism.} \end{aligned}$$

$M_s$ : 'order parameter' (= 0 in the paramagnetic phase,  $\neq 0$  in the ferromagnetic phase)

Critical exponent  $\beta$ :  $M_s(T) \sim ((T_C - T)/(T_C))^\beta$ , i.e. here:  $\beta = 1/2$ , typical for mean field theories

$T_C = (zJ)/(2k_B)$ : transition temperature

4. Curie-Weiß law, susceptibility:

$$\begin{aligned} \frac{\partial}{\partial B} \langle S^z \rangle_0^* &= \frac{\partial}{\partial B_0^*} \left( \frac{1}{2} \tanh(\beta \mu_B B_0^*) \right) \frac{\partial B_0^*}{\partial B} \\ &= \left( \frac{1}{2} \beta \mu_B \right) \left( 1 - \tanh^2(\beta \mu_B B_0^*) \right) \left( \frac{zJ}{\mu_B} \frac{\partial}{\partial B} \langle S^z \rangle_0^* + 1 \right) \end{aligned}$$

For  $T > T_C$ ,  $B \rightarrow 0$  follows:

$$B_0^* = 0 \Rightarrow \tanh^2(\dots) = 0,$$

i.e.:

$$\frac{\partial}{\partial B} \langle S^z \rangle_0^* \Big|_{B=0} \cdot \left( 1 - \frac{zJ}{2k_B T} \right) = \frac{\mu_B}{2k_B T}$$

Susceptibility:

$$\begin{aligned} \chi(T) &= \frac{\partial}{\partial B} M(T, B) \Big|_{B=0} \\ &= 2\mu_B \frac{\partial}{\partial B} \langle S^z \rangle_0^* \Big|_{B=0} \\ &= \frac{\mu_B^2}{k_B} \cdot \frac{1}{T - T_C} \end{aligned}$$

Critical exponent  $\gamma$ :  $\chi(T) \sim ((T - T_C)/(T_C))^{-\gamma}$ , i.e. here:  $\gamma = 1$ ;  $\chi(T)$  diverges for  $T \rightarrow T_C$ !

**Solution 4.3.3**

1. We can begin with the law of corresponding states ((1.19) Vol. 5):

$$\left(\pi + \frac{3}{v^2}\right) (3v - 1) = 8t,$$

Thereby we use:

$$\pi = \frac{P}{P_c}; \quad v = \frac{V}{V_c}; \quad t = \frac{T}{T_c}$$

Recall the derivation of this law!

$$p_r = \pi - 1; \quad V_r = v - 1; \quad \varepsilon = t - 1$$

$$\implies [(1 + p_r) + 3(1 + V_r)^{-2}] [3(V_r + 1) - 1] = 8(1 + \varepsilon)$$

$$\begin{aligned} \implies [4 + 2V_r + V_r^2 + p_r(1 + 2V_r + V_r^2)] (3V_r + 2) \\ = 8(1 + \varepsilon)(1 + 2V_r + V_r^2). \end{aligned}$$

Rearranging leads to:

$$p_r(2 + 7V_r + 8V_r^2 + 3V_r^3) = -3V_r^3 + 8\varepsilon(1 + 2V_r + V_r^2).$$

2. In the critical region all the three quantities  $p_r$ ,  $V_r$ , and  $\varepsilon$  become very small. To a first approximation we can therefore linearize the equation of state from part 1.:

$$p_r \approx 4\varepsilon.$$

In the next step of approximation we insert this lowest-order result again into the equation of state:

$$4\varepsilon(2 + 7V_r + 8V_r^2 + 3V_r^3) = -3V_r^3 + 8\varepsilon(1 + 2V_r + V_r^2)$$

$$\implies 0 \approx V_r(3V_r^2 + 12\varepsilon + 24V_r\varepsilon + 12\varepsilon V_r^2)$$

$$\implies 0 \approx V_r(V_r^2 + 8V_r\varepsilon + 4\varepsilon).$$

This equation has the solutions:

$$V_r^{(0)} = 0; \quad V_r^{(\pm)} = -4\varepsilon \pm 2\sqrt{-\varepsilon} \sqrt{1 - 4\varepsilon}.$$

$$T \xrightarrow{>} T_C \iff \varepsilon \xrightarrow{>} 0 :$$

Only  $V_r = 0$  can be a solution, because  $V_r^{(\pm)}$  are complex.

$$T \xrightarrow{<} T_C \iff \varepsilon \xrightarrow{<} 0 :$$

We know that the solution  $V_r = 0$  is unstable. For the reduced volume of the van der Waals gas it therefore holds:

$$V_r^{(\pm)} = -4\varepsilon \pm 2\sqrt{-\varepsilon} \sqrt{1-4\varepsilon} \sim \pm 2\sqrt{-\varepsilon} .$$

3.  $\beta$  determines the behavior of the order parameter ((4.52) Vol. 5):

$$\begin{aligned} \frac{\Delta\rho}{2\rho_c} &= \frac{1}{2} \frac{\rho^- - \rho^+}{\rho_c} = \frac{V_c}{2} \frac{V^+ - V^-}{V_- V_+} \\ &= \frac{1}{2} \left( \frac{V_c}{V_-} - \frac{V_c}{V_+} \right) = \frac{1}{2} \left( \frac{1}{V_r^{(-)} + 1} - \frac{1}{V_r^{(+)} + 1} \right) \\ &\approx \frac{1}{2} [1 - V_r^{(-)} - (1 - V_r^{(+)})] = \frac{1}{2} (V_r^{(+)} - V_r^{(-)}) \\ \implies \frac{\Delta\rho}{2\rho_c} &\sim 2\sqrt{-\varepsilon} \\ \implies \beta &= \frac{1}{2} ; \quad \text{critical amplitude } B = 2 . \end{aligned}$$

4.  $T = T_C$  means  $\varepsilon = 0$ . Then the equation of state from part 1. reads:

$$p_r = -3V_r^3 (2 + 7V_r + 8V_r^2 + 3V_r^3)^{-1} .$$

Expansion for small  $V_r$ :

$$p_r = -\frac{3}{2} V_r^3 \left( 1 - \frac{7}{2} V_r + \mathcal{O}(V_r^2) \right) .$$

5. The critical exponent  $\delta$  is defined by (4.28):

$$p_c^{(0)} = n \frac{RT_c}{V_c} = \frac{8}{3} p_c .$$

We have thereby exploited the property  $(p_c V_c)/(nRT_c) = 3/8$  of the van der Waals gas (see (1.17) in Vol. 5). Therefore:

$$\frac{p - p_c}{p_c^{(0)}} = \frac{3}{8} \left( \frac{p}{p_c} - 1 \right) = \frac{3}{8} p_r .$$

It further holds:

$$\begin{aligned} \frac{\rho}{\rho_c} - 1 &= \frac{V_c}{V} - 1 = \frac{1}{V_r + 1} - 1 = \frac{-V_r}{V_r + 1} \\ &= -V_r (1 - V_r + \mathcal{O}(V_r^2)) . \end{aligned}$$

On the critical isotherm we have, if we use part 4. and apply  $V_r \rightarrow 0$  for  $p \rightarrow p_c$ :

$$\frac{p - p_c}{p_c^{(0)}} \sim \frac{9}{16} \left| \frac{\rho}{\rho_c} - 1 \right|^3 .$$

The comparison with (4.28) yields:

$$\delta = 3 ; \quad D = \frac{9}{16} .$$

6. Compressibility:

$$\begin{aligned} \kappa_T &= -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} V_c \left( \frac{\partial V_r}{\partial p} \right)_T , \\ dp_r &= d \left( \frac{p}{p_c} - 1 \right) = \frac{1}{p_c} dp , \\ \kappa_T &= -\frac{1}{V} \frac{V_c}{p_c} \left( \frac{\partial V_r}{\partial p_r} \right)_T . \end{aligned}$$

Normalization factor:

$$\kappa_{T_c}^{(0)} = \frac{1}{p_c^{(0)}} = \frac{V_c}{nR T_c} = \frac{3}{8 p_c} .$$

In the last step we have again exploited  $(p_c V_c)/(nR T_c) = 3/8$ :

$$\frac{\kappa_T}{\kappa_{T_c}^{(0)}} = -\frac{8}{3} \frac{1}{V_r + 1} \left( \frac{\partial V_r}{\partial p_r} \right)_T .$$

One finds according to part 1.:

$$\begin{aligned} \left( \frac{\partial p_r}{\partial V_r} \right)_T &= \frac{-9 V_r^2 + 16 \varepsilon (1 + V_r)}{2 + 7 V_r + 8 V_r^2 + 3 V_r^3} \\ &\quad - \frac{[-3 V_r^3 + 8 \varepsilon (1 + 2 V_r + V_r^2)] (7 + 16 V_r + 9 V_r^2)}{(2 + 7 V_r + 8 V_r^2 + 3 V_r^3)^2} . \end{aligned}$$

$$\text{a) } T \underset{\rightarrow}{\geq} T_c \quad \rho = \rho_C, \text{ i.e. } V_r = 0$$

$$\implies \left( \frac{\partial p_r}{\partial V_r} \right)_{T, V_r=0} = 8\varepsilon - 14\varepsilon = -6\varepsilon \implies \frac{\kappa_T}{\kappa_{T_c}^{(0)}} = \frac{4}{9}\varepsilon^{-1}.$$

That holds even everywhere on the critical isochore ( $V_r = 0$ ), not only for  $T \underset{\rightarrow}{\geq} T_c$ .

$$\implies \gamma = 1; \quad C = \frac{4}{9}.$$

$$\text{b) } T \underset{\rightarrow}{<} T_c$$

In the critical region we have according to part 2.:

$$V_r^2 \approx -4\varepsilon.$$

This means:

$$\begin{aligned} \left( \frac{\partial p_r}{\partial V_r} \right)_{\varepsilon \rightarrow 0} &\approx \frac{1}{2}(36\varepsilon + 16\varepsilon) - \frac{1}{4}56\varepsilon = 12\varepsilon, \\ \frac{1}{V_r + 1} &\underset{\varepsilon \rightarrow 0}{\rightarrow} 1. \end{aligned}$$

Hence it remains:

$$\frac{\kappa_T}{\kappa_{T_c}^{(0)}} \sim -\frac{8}{3} \frac{1}{12\varepsilon} = \frac{2}{9}(-\varepsilon)^{-1}.$$

By comparison with (4.26) follows:

$$\gamma' = 1; \quad C' = \frac{2}{9} = \frac{1}{2}C.$$

### **Solution 4.3.4**

Chain rule:

$$\begin{aligned} \left( \frac{\partial V}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_V \left( \frac{\partial p}{\partial V} \right)_T &= -1 \\ \iff (V\beta) \left( \frac{\partial T}{\partial p} \right)_V \left( -\frac{1}{V\kappa_T} \right) &= -1 \\ \implies \beta &= \kappa_T \left( \frac{\partial p}{\partial T} \right)_V. \end{aligned}$$

For the van der Waals gas it holds especially:

$$\beta = \kappa_T \left( \frac{nR}{V - nb} \right).$$

The expression in the bracket behaves analytically for  $T \rightarrow T_c$ , so that the critical behavior of  $\beta$  corresponds to that of the compressibility  $\kappa_T$ .

### Solution 4.3.5

1. According to ((1.28) Vol. 5) the equation of state of the Weiß ferromagnet reads:

$$M = M_0 L \left( m \frac{B_0 + \lambda \mu_0 M}{k_B T} \right),$$

$$\frac{m \lambda \mu_0 M}{k_B T} = \frac{M}{M_0} \frac{\frac{N}{V} m^2 \lambda \mu_0}{k_B T} = \widehat{M} \frac{3 k_B C \lambda}{k_B T} = \widehat{M} \frac{3 T_c}{T}.$$

It follows immediately:

$$\widehat{M} = L \left( b + \frac{3 \widehat{M}}{\varepsilon + 1} \right).$$

2.  $L(x) = (1/3)x - (1/45)x^3 + \mathcal{O}(x^5)$

$$B_0 = 0 \quad \Longrightarrow \quad b = 0,$$

$$T \leq T_c \quad \Longrightarrow \quad \widehat{M} \text{ very small.}$$

It then holds:

$$\widehat{M} \approx \frac{\widehat{M}}{\varepsilon + 1} - \frac{3}{5} \frac{\widehat{M}^3}{(\varepsilon + 1)^3}$$

$$\Longrightarrow \quad \frac{\varepsilon}{\varepsilon + 1} \approx -\frac{3}{5} \frac{\widehat{M}^2}{(\varepsilon + 1)^3} \quad \Longrightarrow \quad \widehat{M}^2 \approx -\frac{5}{3} \varepsilon (\varepsilon + 1)^2.$$

Since  $(\varepsilon + 1)^2 \rightarrow 1$  for  $T \rightarrow T_c$ , it follows:

$$\widehat{M} \sim \sqrt{\frac{5}{3}} (-\varepsilon)^{1/2}.$$

Hence we have, as for the van der Waals gas:

$$\beta = \frac{1}{2}.$$

3. Critical isotherm:  $T = T_c$ ;  $B_0 \rightarrow 0$

$$\implies \varepsilon = 0; \quad \widehat{M} \quad \text{and} \quad b \quad \text{very small.}$$

This means:

$$\begin{aligned} \widehat{M} &\approx \frac{1}{3}b + \widehat{M} - \frac{1}{45}(b + 3\widehat{M})^3 \\ \implies 15b &\approx (b + 3\widehat{M})^3 \iff b + 3\widehat{M} \approx (15b)^{1/3} \\ \implies 3\widehat{M} &\approx (15b)^{1/3} - b \approx (15b)^{1/3}, \quad \text{since } b \rightarrow 0. \end{aligned}$$

This yields

$$b \sim \frac{3}{5}\widehat{M}^3$$

and leads to the critical exponent

$$\delta = 3.$$

4.

$$\chi_T = \left( \frac{\partial M}{\partial H} \right)_T = \frac{M_0 \mu_0 m}{k_B T} \left( \frac{\partial \widehat{M}}{\partial b} \right)_{T, b=0} = \frac{3}{\lambda(\varepsilon + 1)} \left( \frac{\partial \widehat{M}}{\partial b} \right)_{T, b=0}.$$

In the critical region  $\widehat{M}$  is very small:

$$\begin{aligned} \frac{\partial L}{\partial b} \Big|_{b=0} &= \frac{\partial x}{\partial b} \left( \frac{1}{3} - \frac{1}{15}x^2 \right) \Big|_{b=0} + \dots \\ \frac{\partial \widehat{M}}{\partial b} \Big|_{b=0} &= \left( 1 + \frac{3}{\varepsilon + 1} \frac{\partial \widehat{M}}{\partial b} \Big|_{b=0} \right) \left( \frac{1}{3} - \frac{1}{15} \frac{9\widehat{M}^2}{(\varepsilon + 1)^2} \right) + \dots \\ \implies \frac{\partial \widehat{M}}{\partial b} \Big|_{b=0} &\cdot \left( 1 - \frac{1}{\varepsilon + 1} + \frac{9}{5} \frac{\widehat{M}^2}{(\varepsilon + 1)^3} \right) = \frac{1}{3} \left( 1 - \frac{9}{5} \frac{\widehat{M}^2}{(\varepsilon + 1)^2} \right). \end{aligned}$$

$T \rightarrow T_C$  means  $\widehat{M} \rightarrow 0$ :

$$\left(\frac{\partial \widehat{M}}{\partial b}\right)_{T, b=0} \approx \frac{1}{3} \frac{1}{\frac{\varepsilon}{\varepsilon+1} + \frac{9}{5} \frac{\widehat{M}^2}{(\varepsilon+1)}}.$$

a)  $T \xrightarrow{>} T_C$  :

Above  $T_C$  it is  $\widehat{M} \equiv 0$ , so that with  $(\varepsilon + 1) \rightarrow 1$  for  $T \rightarrow T_C$  follows:

$$\left(\frac{\partial \widehat{M}}{\partial b}\right) \sim \frac{1}{3} \varepsilon^{-1}.$$

This means for the susceptibility:

$$\chi_T \sim \frac{1}{\lambda} \varepsilon^{-1} \implies \gamma = 1.$$

b)  $T \xrightarrow{\leq} T_C$  :

According to part 2. we now have to insert  $\widehat{M}^2 \sim 5/3(-\varepsilon)$ :

$$\chi_T \sim \frac{1}{2\lambda} (-\varepsilon)^{-1} \implies \gamma' = 1.$$

For the critical amplitude one finds, as for the van der Waals gas:

$$C' = \frac{1}{2} C.$$

### Solution 4.3.6

1. One finds the equation of state with the free energy:

$$\begin{aligned} B_0 &= \left(\frac{\partial F}{\partial m}\right)_T = B_0(T, m) \\ \implies B_0(T, m) &= \sum_{n=0}^{\infty} L_{2n}(T) \cdot 2n \cdot m^{2n-1} \\ &= 2L_2(T) \cdot m + 4L_4(T) \cdot m^3 + \dots \end{aligned}$$



## 2. Susceptibility:

$$\chi_T = \frac{\mu_0}{V} \left( \frac{\partial m}{\partial B_0} \right)_T \iff \chi_T^{-1} = \frac{V}{\mu_0} \left( \frac{\partial B_0}{\partial m} \right)_T .$$

Volume  $V$ : parameter, not a thermodynamic variable in the case of the magnetic system.

With part 1. the inverse susceptibility can be expanded:

$$\begin{aligned} \chi_T^{-1}(T, m) &= \frac{V}{\mu_0} \sum_{n=0}^{\infty} L_{2n}(T) \cdot 2n(2n-1) \cdot m^{2n-2} \\ &= \frac{V}{\mu_0} (2L_2(T) + 12L_4(T) \cdot m^2 + \dots) . \end{aligned}$$

$m = 0$  for temperatures above  $T_C$ . It then remains:

$$\begin{aligned} \chi_T^{-1}(T, 0) &= \frac{2V}{\mu_0} L_2(T) \\ &= \frac{2V}{\mu_0} (l_{20} + l_{21}(T - T_C) + l_{22}(T - T_C)^2 + \dots) . \end{aligned}$$

This means in the critical region:

$$\chi_T^{-1}(T \rightarrow T_C, 0) \approx \frac{2V}{\mu_0} (l_{20} + l_{21}(T - T_C)) . \quad (\text{A.9})$$

$\chi_T^{-1}$  should have a zero at  $T_C$ , what can only be the case when  $l_{20} = 0$ .

3. We calculate at first  $\beta$ . For  $B_0 = 0$  and in the neighborhood of  $T_C$ , ( $T < T_C$ ),  $m$  is very small, but unequal zero. We therefore divide the equation of state from part 1. by  $2m$ :

$$\begin{aligned} 0 &= L_2(T) + 2L_4(T) \cdot m^2 + \dots \\ &= (l_{21}(T - T_C) + \mathcal{O}((T - T_C)^2)) \\ &\quad + 2m^2 (l_{40} + l_{41}(T - T_C) + \mathcal{O}((T - T_C)^2)) . \end{aligned}$$

$T < T_C$  :

$$m^2 = \frac{l_{21}}{2l_{40}}(T_C - T) \Rightarrow m = \sqrt{\frac{l_{21}}{2l_{40}}}(T_C - T)^{\frac{1}{2}} . \quad (\text{A.10})$$

Therewith it holds for the critical exponent of the order parameter:

$$\beta = \frac{1}{2} .$$

We now discuss the critical exponents  $\gamma, \gamma'$  of the susceptibility:

$$\chi_T^{-1}(T, m) = \frac{V}{\mu_0} (2L_2(T) + 12L_4(T)m^2 + \dots) . \quad (\text{A.11})$$

$T > T_C$  :

That means  $m = 0$ , if  $B_0 = 0$ . It follows therewith according to part 2.:

$$\chi_T^{-1}(T, 0) \approx \frac{2V}{\mu_0} l_{21}(T - T_C) . \quad (\text{A.12})$$

One reads off:

$$\gamma = 1 .$$

$T < T_C$  :

Now  $m \neq 0$ , but it becomes arbitrarily small for  $T \rightarrow T_C$  (see (A.10)):

$$\begin{aligned} \frac{\mu_0}{V} \chi_T^{-1}(T, m) &= 2l_{21}(T - T_C) + \dots \\ &\quad + 12m^2(l_{40} + l_{41}(T - T_C) + \dots) \\ &\approx 2l_{21}(T - T_C) + \dots + 6l_{21}(T_C - T) + \dots \end{aligned}$$

In the second step we have exploited the result (A.10) for the magnetization. Hence it remains:

$$\chi_T^{-1}(T, m) = \frac{4V}{\mu_0} l_{21}(T_C - T) . \quad (\text{A.13})$$

It follows for the critical exponent:

$$\gamma' = 1 .$$

Note the twice as much pre-factor in (A.13) compared to that in (A.12)!

We discuss at the end the critical isotherm and use for that the equation of state for  $T = T_C$ . From the sum for an  $L_n$ -coefficient only the  $j = 0$ -terms contribute, where in addition  $l_{20} = 0$ :

$$B_0(T_C, m) = 4l_{40} \cdot m^3 + \dots \quad (6) \quad (\text{A.14})$$

That means:

$$\delta = 3 .$$

Equation (A.14) gives evidence that for a ferromagnet or paramagnet  $l_{40} > 0!$

### **Solution 4.3.7**

The case

$$T > T_C$$

is relatively simple because then the magnetization vanishes in case of a switched off field  $B_0 = 0$ , and therewith:

$$C_m = C_H$$

It follows

$$\begin{aligned} C_{m=0} &= -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{m=0} \\ &= -T \frac{d^2 L_0}{dT^2} \\ &= -T (2l_{02} + 6l_{03}(T - T_C) + \mathcal{O}((T - T_C)^2)) . \end{aligned}$$

This means

$$C_H^{(+)} = C_m^{(+)} \rightarrow -2T_C l_{02} . \quad (\text{A.15})$$

It yields the critical exponent:

$$\alpha = 0 .$$

The case

$$T < T_C$$

is somewhat more complicated because now  $m \neq 0$ . It follows from the equation of state (Exercise 4.3.6):

$$\begin{aligned} \left( \frac{\partial B_0}{\partial T} \right)_m &= 2L'_2 \cdot m + 4L'_4 \cdot m^3 + \dots \\ &= 2m \cdot (l_{21} + 2l_{22}(T - T_C) + \dots) + 4m^3 \cdot (l_{41} + 2l_{42}(T - T_C) + \dots) + \dots \end{aligned}$$

For  $T \rightarrow T_C$  and therewith  $m \rightarrow 0$  it thus holds:

$$\left( \frac{\partial B_0}{\partial T} \right)_m \rightarrow 2ml_{21} .$$

In Exercise 4.3.6 we had found for the susceptibility:

$$\chi_T \approx \frac{\mu_0}{4V} l_{21}^{-1} \frac{1}{T_C - T} .$$

We insert the two last equations into the relation for the difference of the two heat capacities, derived in Exercise 4.1.7,

$$C_H - C_m = \frac{V}{\mu_0} T \chi_T \left[ \left( \frac{\partial B_0}{\partial T} \right)_m \right]^2 .$$

It is then left for the critical region:

$$C_H - C_m = T_C \frac{l_{21}^2}{l_{40}} (1 + \mathcal{O}(T_C - T)) .$$

We now still need  $C_m$  with  $m^2$  from Exercise 4.3.6:

$$\begin{aligned} C_m &= -T \frac{\partial^2}{\partial T^2} (L_0 + L_2 \cdot m^2 + \dots) \Big|_m \\ &= -T (L_0'' + L_2'' \cdot m^2 + \dots) \\ &= -T \left( 2l_{02} + 6l_{03} (T - T_C) + \dots + 2l_{22} \frac{l_{21}}{2l_{40}} (T_C - T) + \dots \right) \\ &\rightarrow -2T_C l_{02} + \mathcal{O}(T_C - T) . \end{aligned}$$

In the third step we have inserted the result  $m^2 = \frac{l_{21}}{2l_{40}} (T_C - T)$  from Exercise 4.3.6. Therewith we have:

$$C_H^{(-)} \approx T_C \left( -2l_{02} + \frac{l_{21}^2}{l_{40}} + \mathcal{O}(T_C - T) \right) . \quad (\text{A.16})$$

For  $l_{02} \neq 0$  one therewith gets for the critical exponent of the heat capacity:

$$\alpha' = 0$$

Finally, it follows from (A.15) and (A.16):

$$\Delta C_H = C_H^{(+)} - C_H^{(-)} = -\frac{l_{21}^2}{l_{40}} T_C .$$

If  $l_{21} \neq 0$ , then the heat capacity exhibits a finite discontinuity according to a second-order phase transition *in the Ehrenfest sense*. Note, however:

$$\Delta C_m = C_m^{(+)} - C_m^{(-)} = 0 .$$

### **Solution 4.3.8**

Equation of state:

$$B_0(M, T) = \sum_{n=1}^{\infty} 2n \cdot L_{2n}(T) \cdot m^{2n-1} . \quad (\text{A.17})$$

Susceptibility:

$$\chi_T^{-1}(T, m) = \frac{V}{\mu_0} \sum_{n=1}^{\infty} 2n(2n-1)L_{2n}(T)m^{2n-2} . \quad (\text{A.18})$$

It holds for the coefficients

$$L_{2n}(T) = \sum_{m=0}^{\infty} l_{nm}(T - T_C)^m . \quad (\text{A.19})$$

In addition it shall be assumed:

$$l_{20} = 0, \quad l_{40} = 0, \quad l_{60} \geq 0 . \quad (\text{A.20})$$

Critical exponents:

1. order parameter ( $\beta$ ) :

We investigate:

$$B_0 = 0 ; \quad T \rightarrow T_C^{(-)} . \quad (\text{A.21})$$

We divide the equation of state for  $B_0 = 0$  by  $2m$ :

$$\begin{aligned} 0 &= (l_{21}(T - T_C) + \dots) + 2m^2(l_{41}(T - T_C) + \dots) \\ &\quad + 3m^4(l_{60} + l_{61}(T - T_C) + \dots) + \dots \\ \implies 0 &\approx (T - T_C)(l_{21} + \dots) + 3m^4 l_{60} + \dots \\ \implies m &\approx (T_C - T)^{1/4} \left( \frac{l_{21}}{3l_{60}} \right)^{1/4} . \end{aligned}$$

That yields the critical exponent of the order parameter:

$$\beta = \frac{1}{4}. \quad (\text{A.22})$$

2. Susceptibility  $(\gamma, \gamma')$  :

We investigate:

$$B_0 = 0; T \rightarrow T_C^{(\pm)}. \quad (\text{A.23})$$

Then the above expansion of the susceptibility yields:

$$\begin{aligned} \frac{\mu_0}{V} \chi_T^{-1}(T, m) &= 2(l_{21}(T - T_C) + \dots) + 12 \cdot m^2(l_{41}(T - T_C) + \dots) \\ &\quad + 30 \cdot m^4(l_{60} + l_{61}(T - T_C) + \dots) + \dots \end{aligned}$$

$$T \rightarrow T_C^{(+)}$$

$$m = 0 \implies \chi_T^{-1} = 2 \frac{V}{\mu_0} (l_{21}(T - T_C) + \dots). \quad (\text{A.24})$$

This means

$$\gamma = 1. \quad (\text{A.25})$$

$$T \rightarrow T_C^{(-)}$$

Now  $m \neq 0$ . We use for  $m^2$  the result from Exercise 4.3.6, where, because of  $l_{40} = 0$  it must now hold  $m^4 \approx \frac{l_{21}}{3l_{60}}(T_C - T)$ :

$$\begin{aligned} \frac{\mu_0}{V} \chi_T^{-1}(T, m) &= 2(l_{21}(T - T_C) + \dots) + 12 \left( \frac{l_{21}}{3l_{60}} \right)^{1/2} (-l_{41}(T_C - T)^{3/2} + \dots) \\ &\quad + 10 \frac{l_{21}}{l_{60}} (T_C - T)(l_{60} + l_{61}(T - T_C) + \dots) + \dots \\ &\approx 8l_{21}(T_C - T). \end{aligned}$$

This gives the critical exponent:

$$\gamma' = 1. \quad (\text{A.26})$$

3. Critical isotherm ( $\delta$ )

On the critical isotherm there are, because of  $l_{20} = l_{40} = 0$ , also  $L_2(T_C) = L_4(T_C) = 0$ . It thus holds:

$$B_0(T_C, m) = 6L_6(T_C) \cdot m^5 + \dots = 6l_{60} \cdot m^5 + \dots \quad (\text{A.27})$$

One thus finds:

$$\delta = 5. \quad (\text{A.28})$$

4. Heat capacity ( $\alpha, \alpha'$ )

We use the definition

$$C_m = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_m \quad (\text{A.29})$$

and the relation derived in Exercise 4.1.7

$$C_H = C_m + \frac{v}{\mu_0} T \chi_T \left( \left( \frac{\partial B_0}{\partial T} \right)_m \right)^2. \quad (\text{A.30})$$

$T \rightarrow T_C^{(+)}$

$B_0 = 0$  brings about  $m = 0$  and therewith

$$\begin{aligned} C_{H=0} = C_{m=0} &= -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{m=0} = T \frac{d^2 L_0(T)}{dT^2} \\ &= -T(2l_{02} + 6l_{03}(T - T_C) + \dots). \end{aligned}$$

If  $l_{02} \neq 0$ , this means:

$$\alpha = 0. \quad (\text{A.31})$$

$T \rightarrow T_C^{(-)}$

Now it holds because of  $m \neq 0$ :

$$\begin{aligned} C_m &= -T \left( \left( \frac{d^2 L_0}{dT^2} \right)_{T \rightarrow T_C} + \left( m^2 \frac{d^2 L_2}{dT^2} \right)_{T \rightarrow T_C} + \dots \right) \\ &= -T_C (2l_{02} + 6l_{03}(T - T_C) + 2l_{22} \cdot m^2 + \dots). \end{aligned}$$

It remains because of  $m^2 \propto (T - T_C)^{1/2}$

$$C_m \approx -2l_{02}T_C . \quad (\text{A.32})$$

$C_m$  is thus non-critical. We still need:

$$\begin{aligned} \left( \frac{\partial B_0}{\partial T} \right)_m &= 2m \cdot \frac{dL_2}{dT} + 4m^3 \cdot \frac{dL_4}{dT} + \dots \\ &= 2m (l_{21} + 2l_{22}(T - T_C) + \dots + 2m^2 (l_{41} + 2l_{42}(T - T_C) + \dots)) . \end{aligned}$$

It follows with the above results for the susceptibility and the magnetization:

$$\begin{aligned} T_C \cdot \chi_T \cdot \left( \left( \frac{\partial B_0}{\partial T} \right)_m \right)^2 &= \frac{\mu_0}{V} \frac{T_C}{8l_{21}} \frac{1}{T_C - T} 4l_{21}^2 \left( \frac{l_{21}}{3l_{60}} (T_C - T) \right)^{1/2} \\ &= \frac{\mu_0}{V} \frac{T_C l_{21}}{2} \left( \frac{l_{21}}{3l_{60}} \right)^{1/2} (T_C - T)^{-1/2} . \end{aligned}$$

From that one reads off:

$$\alpha' = \frac{1}{2} . \quad (\text{A.33})$$

But now we have the thermodynamically exact inequality:

$$\gamma(\delta + 1) \geq (2 - \alpha)(\delta - 1) . \quad (\text{A.34})$$

That would require here

$$1(5 + 1) = 6 \geq (2 - 0)4 = 8 . \quad (\text{A.35})$$

The choice  $l_{20} = 0$ ,  $l_{40} = 0$ ,  $l_{60} > 0$  thus leads to a contradiction, is therefore not acceptable for thermodynamic reasons. One should note, however, that all the other known thermodynamically exact inequalities are fulfilled, as for instance (4.34) to (4.36).

### Solution 4.3.9

$$\begin{aligned} g(\mathbf{r}) &= \frac{1}{V} \int d^3 q S(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \\ &= -\frac{1}{Vc_2} \int d^3 q \frac{1}{\xi^{-2} + q^2} e^{i\mathbf{q}\cdot\mathbf{r}} \end{aligned}$$



$$\begin{aligned}
&= -\frac{2\pi}{Vc_2} \int_0^\infty dq q^2 \frac{1}{\xi^{-2} + q^2} \int_{-1}^{+1} dx e^{iqrx} \\
&= -\frac{2\pi}{Vc_2} \frac{1}{ir} \int_0^\infty dq \frac{q}{\xi^{-2} + q^2} (e^{iqr} - e^{-iqr}) \\
&= \frac{2\pi i}{Vc_2} \frac{1}{r} \left[ \int_0^\infty dq \frac{q}{\xi^{-2} + q^2} e^{iqr} - \int_0^\infty dq' \frac{q'}{\xi^{-2} + q'^2} e^{iq'r} \right] \\
&= \frac{\pi i}{Vc_2} \frac{1}{r} \int_{-\infty}^{+\infty} dq \left( \frac{1}{q + \frac{i}{\xi}} + \frac{1}{q - \frac{i}{\xi}} \right) e^{iqr} \\
&= \frac{\pi i}{Vc_2} \frac{1}{r} \int dq \left( \frac{1}{q + \frac{i}{\xi}} + \frac{1}{q - \frac{i}{\xi}} \right) e^{iqr} .
\end{aligned}$$

Let the path of integration consist of the real axis and the semi-circle closed at infinity in the upper complex half-plane. On the semi-circle the integrand does not anyway contribute. Only the second summand has a pole in the circumvented region at  $q = i/\xi$  with the residue  $\exp(-r/\xi)$ , so that it eventually follows with the residue theorem:

$$g(\mathbf{r}) = -\frac{2\pi^2}{Vc_2} \frac{\exp(-\frac{r}{\xi})}{r}$$

## Section 4.4.8

### Solution 4.4.1

1.

$$\begin{aligned}
Z_N(T, B_0) &= \text{Tr}(\exp(-\beta H)) \\
&= \text{Tr}(\mathbb{1}) - \beta \text{Tr}(H) + \frac{1}{2} \beta^2 \text{Tr}(H^2) - \frac{1}{3!} \beta^3 \text{Tr}(H^3) + \dots \\
&= \sum_{l=0}^{\infty} \frac{1}{l!} (-\beta)^l \text{Tr}(H^l) \\
&= \text{Tr}(\mathbb{1}) \left[ 1 + \sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} m_l \right] .
\end{aligned}$$

Each spin has two possibilities of orientation  $S_i = \pm 1$ . That yields altogether  $2^N$  spin configurations. Therefore:

$$\text{Tr}(\mathbb{1}) = 2^N .$$

2.

$$\begin{aligned} C_{B_0} &= -T \left( \frac{\partial^2 F_N(T, B_0)}{\partial T^2} \right)_{B_0} \\ &= -T \left( \frac{\partial^2}{\partial T^2} (-k_B T \ln Z_N(T, B_0)) \right)_{B_0} \\ &= k_B \beta^2 \left( \left( \beta \frac{\partial^2}{\partial \beta^2} + 2 \frac{\partial}{\partial \beta} \right) \left( \frac{1}{\beta} \ln Z_N(T, B_0) \right) \right)_{B_0} \\ &= k_B \beta^2 \left( \frac{\partial^2}{\partial \beta^2} \ln Z_N(T, B_0) \right)_{B_0} \\ &= k_B \beta^2 \left( \frac{\partial}{\partial \beta} \frac{\partial}{\partial \beta} \ln Z_N(T, B_0) \right)_{B_0} \\ &= k_B \beta^2 \left( \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \frac{1}{Z_N^2} \left( \frac{\partial Z_N}{\partial \beta} \right)^2 \right) \\ &= k_B \beta^2 \left( \frac{\text{Tr}(\mathbb{1})}{Z_N} \sum_{l=1}^{\infty} \frac{l(l-1)}{l!} (-\beta)^{l-2} m_l - \left( \frac{\text{Tr}(\mathbb{1})}{Z_N} \sum_{l=1}^{\infty} \frac{l}{l!} (-\beta)^{l-1} m_l \right)^2 \right) \\ &= k_B \beta^2 \left( \frac{2}{2!} m_2 - m_1^2 + \mathcal{O}(\beta) \right) \\ &= \frac{1}{k_B T^2} (m_2 - m_1^2) + \dots . \end{aligned}$$

In the last step we have restricted ourselves to the lowest term in  $1/T$  ( $\text{Tr} \mathbb{1} / Z_N = 1 + \mathcal{O}(\beta)$ ). Note that the moments are temperature-independent. This result for the high-temperature behavior of the heat capacity holds, by the way, for all (!) magnetic systems, not only for Ising-spins.

### Solution 4.4.2

According to (4.16) we have:

$$\chi_T = \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 \sum_{ij} \langle (S_i - \langle S_i \rangle) (S_j - \langle S_j \rangle) \rangle$$

or:

$$\chi_T = \frac{1}{k_B T} \frac{\mu_0}{V} \left( \mu^2 \sum_{ij} \langle S_i S_j \rangle - \langle \widehat{m} \rangle^2 \right).$$

1. The spin chain does not show a spontaneous magnetization. Therefore  $\langle \widehat{m} \rangle \equiv 0$  in the case of a switched off external field. According to (4.186) it holds for the spin correlation in the one-dimensional chain:

$$\langle S_i S_j \rangle = v^{|i-j|}.$$

One now easily realizes that there are  $N$  terms in the double sum with  $|i-j| = 0$  and the contribution  $v^0 = 1$ ;  $2(N-1)$  terms with  $|i-j| = 1$  and  $v^1$ ;  $2(N-2)$  terms with  $|i-j| = 2$  and  $v^2, \dots$ , and finally 2 terms with  $|i-j| = N-1$  and the contribution  $v^{N-1}$ . That can be gathered to

$$\chi_T(T, B_0) = \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 \left( N + 2 \sum_{k=1}^{N-1} (N-k)v^k \right).$$

One calculates:

$$\begin{aligned} 2 \sum_{k=1}^{N-1} N v^k &= 2N \frac{1-v^N}{1-v} - 2N \\ -2 \sum_{k=1}^{N-1} k v^k &= -2 \sum_{k=0}^{N-1} k v^k = -2v \frac{d}{dv} \frac{1-v^N}{1-v} \\ &= -2v \frac{(1-v)(-Nv^{N-1}) + (1-v^N)}{(1-v)^2} \\ \curvearrowright 2 \sum_{k=1}^{N-1} (N-k)v^k &= 2N \frac{v}{1-v} - 2v \frac{1-v^N}{(1-v)^2}. \end{aligned}$$

It follows from that:

$$\chi_T(T, B_0 = 0) = \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 \left( N \left( 1 + \frac{2v}{1-v} \right) - 2v \frac{1-v^N}{(1-v)^2} \right).$$

2. For  $N \rightarrow \infty$  the expression for the susceptibility can be simplified:

$$\begin{aligned} \frac{1}{N} \chi_T(T, B_0 = 0) &= \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 \frac{1+v}{1-v} \\ &= \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 \frac{1 + \tanh(\beta J)}{1 - \tanh(\beta J)} \\ &= \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 \frac{e^{\beta J} + e^{-\beta J} + e^{\beta J} - e^{-\beta J}}{e^{\beta J} + e^{-\beta J} - e^{\beta J} + e^{-\beta J}} \\ &= \frac{1}{k_B T} \frac{\mu_0}{V} \mu^2 e^{2\beta J} . \end{aligned}$$

Although *at first glance* distinctly different from the result (4.201) for the Ising ring, nevertheless the same qualitative temperature behavior results. For high temperatures the *Curie law* (4.137) is obviously fulfilled. For  $T \rightarrow 0$   $\chi_T$  diverges.

### Solution 4.4.3

1. The partition function

$$Z_N(T) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} \exp \left( \sum_{i=1}^{N-1} \beta J_i S_i S_{i+1} \right)$$

we have already calculated with (4.183):

$$Z_N(T) = 2^N \prod_{i=1}^{N-1} \cosh \beta J_i .$$

Four-spin correlation function  $i \neq j$ :

$$\begin{aligned} \langle S_i S_{i+1} S_j S_{j+1} \rangle &= \frac{1}{Z_N} \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} S_i S_{i+1} S_j S_{j+1} \exp \left( \sum_{i=1}^{N-1} \beta J_i S_i S_{i+1} \right) \\ &= \frac{1}{\beta^2 Z_N} \frac{\partial^2 Z_N}{\partial J_i \partial J_j} \\ &= \frac{\cosh \beta J_1 \cdots \sinh \beta J_i \cdots \sinh \beta J_j \cdots \cosh \beta J_{N-1}}{\cosh \beta J_1 \cdots \cosh \beta J_{N-1}} \\ &= \tanh \beta J_i \tanh \beta J_j . \end{aligned}$$

For  $i = j$  the four-spin correlation is equal to 1. When we now still take  $J_i = J \forall i$ , it is left:

$$\langle S_i S_{i+1} S_j S_{j+1} \rangle = \begin{cases} 1 & \text{if } i = j \\ \tanh^2 \beta J & \text{if } i \neq j. \end{cases}$$

2. We adopt from the solution of Exercise 4.4.1:

$$\begin{aligned} C_{B_0} &= k_B \beta^2 \left( \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \frac{1}{Z_N^2} \left( \frac{\partial Z_N}{\partial \beta} \right)^2 \right) \\ &= k_B \beta^2 (\langle H^2 \rangle - \langle H \rangle^2). \end{aligned}$$

With

$$\langle H^2 \rangle = J^2 \sum_{ij} \langle S_i S_{i+1} S_j S_{j+1} \rangle$$

follows:

$$\begin{aligned} C_{B_0=0} &= k_B \beta^2 J^2 \sum_{i,j=1}^{N-1} (\langle S_i S_{i+1} S_j S_{j+1} \rangle - \langle S_i S_{i+1} \rangle \langle S_j S_{j+1} \rangle) \\ &= k_B \beta^2 J^2 \sum_{i,j=1}^{N-1} (\delta_{ij} + (1 - \delta_{ij}) \tanh^2 \beta J - \tanh^2 \beta J) \\ &= k_B \beta^2 J^2 \sum_{i,j=1}^{N-1} \delta_{ij} (1 - \tanh^2 \beta J) \\ C_{B_0=0} &= (N-1) k_B \beta^2 J^2 \frac{1}{\cosh^2 \beta J}. \end{aligned}$$

One should compare the result with (4.200).

### **Solution 4.4.4**

1. The open linear chain does not possess closed polygons of interaction lines. It therefore holds

$$g_0 = 1; \quad g_l = 0 \quad \forall l \neq 0; \quad p = N - 1$$

and therewith

$$Z_N(T) = 2^N \cosh^{N-1}(\beta J) .$$

That corresponds to (4.184).

2. For the ring we have:

$$g_0 = g_N = 1 ; \quad g_l = 0 \quad \forall l \neq 0, N ; \quad p = N .$$

It follows:

$$\begin{aligned} Z_N(T) &= 2^N \cosh^N(\beta J) (1 + v^N) \\ &= 2^N \cosh^N(\beta J) (1 + \tanh^N(\beta J)) \\ &\xrightarrow{N \gg 1} 2^N \cosh^N(\beta J) . \end{aligned}$$

This corresponds to (4.196).

The two results for the partition function of the 1d-Ising model therefore match only in the thermodynamic limit, because then the special boundary conditions do no longer play a role.

### Solution 4.4.5

1. It holds (reason as to (4.204)):

$$\exp(\beta J S_i S_j) = \cosh(\beta J) (1 + v(S_i S_j)) .$$

It follows analogously to (4.205)

$$\begin{aligned} \langle S_m S_n \rangle &= \frac{1}{Z_N} \sum_{\{S_i\}} S_m S_n \prod_{(i,j)} \exp(\beta J S_i S_j) \\ &= \frac{1}{Z_N} \cosh^p(\beta J) \sum_{\{S_i\}} \left[ S_m S_n + v S_m S_n \sum_{v=1}^p (S_{i_v} S_{j_v}) \right. \\ &\quad \left. + v^2 S_m S_n \sum_{v,\mu=1}^p (S_{i_v} S_{j_v})(S_{i_\mu} S_{j_\mu}) + \dots \right] . \end{aligned}$$

$p$  is the number of the pairwise different next-neighbor interactions. The single spin products can be represented as in Sect. 4.4.4 by diagrams. In a typical spin

product

$$S_m S_n \sum_{\{S_i\}} (S_{i_1} S_{j_1}) \cdots (S_{i_p} S_{j_p})$$

the summation  $\sum_{\{S_i\}}$  is performed over all  $2^N$  spin configurations. Because of  $S_i = \pm 1$  only those terms deliver a finite contribution, which contain only even powers of the  $S_i$  (even vertexes), except for the spins at the sites  $m$  and  $n$ , which because of the pre-factor  $S_m S_n$  must exhibit an odd power. If this is the case, then the spin products yield all  $+1$  and therewith after spin summation the factor  $2^N$ .

We define:

$\rho_{mn}(l)$  = number of diagrams of  $l$  ( $l \geq 1$ ) pieces, which somehow contain the points  $n$  and  $m$ . All vertexes are even, except for those at  $n$  and  $m$ , which shall be odd.

Then it obviously holds:

$$\langle S_m S_n \rangle = \frac{2^N}{Z_N} \cosh^p(\beta J) \sum_{l=1}^{\infty} \rho_{mn}(l) v^l .$$

2. For the linear open chain there is only one diagram, which fulfills the conditions, namely that for which  $m$  and  $n$  are directly connected:

$$\rho_{mn}(l) = \begin{cases} 1 & \text{for } l = |m - n| \\ 0 & \text{otherwise.} \end{cases}$$

With  $p = N - 1$  and  $Z_N$  from Exercise 4.4.4 it then remains:

$$\begin{aligned} \langle S_m S_n \rangle &= \frac{2^N}{2^N \cosh^{N-1}(\beta J)} \cosh^{N-1}(\beta J) v^{|m-n|} \\ &= \tanh^{|m-n|}(\beta J) . \end{aligned}$$

This is identical to (4.186).

3. For the ring we have two allowed diagrams, because the points  $m$  and  $n$  can be connected on the circle in two directions. Lengths:  $l = |m-n|$  and  $l = N - |m-n|$ . It follows then with  $p = N$  and  $Z_N$  from Exercise 4.4.4:

$$\begin{aligned} \langle S_m S_n \rangle &= \frac{1}{1 + \tanh^N(\beta J)} \left( \tanh^{|m-n|}(\beta J) + \tanh^{N-|m-n|}(\beta J) \right) \\ &= \tanh^{|m-n|}(\beta J) \frac{1 + \tanh^{N-2|m-n|}(\beta J)}{1 + \tanh^N(\beta J)} . \end{aligned}$$

The second factor becomes equal to 1 in the thermodynamic limit ( $N \rightarrow \infty$ ), because  $\tanh(\beta J) < 1$  for  $T > 0$ . The two expressions for the open chain and for the ring are therewith same in the thermodynamic limit.

### Solution 4.4.6

1. We investigate  $\chi_T$  in the critical region,

$$\chi_T^c = c \left( \frac{T - T_C}{T_C} \right)^{-\gamma}$$

and try to bring it into the form

$$\chi_T^c = \sum_l \alpha_l (\beta J)^l$$

by the following manipulations:

$$\begin{aligned} \chi_T^c &= c \left( \frac{J\beta_c}{J\beta} - 1 \right)^{-\gamma} = c \left( \frac{j_c}{j} - 1 \right)^{-\gamma} \\ &= c \left( \frac{j}{j_c} \right)^\gamma \left( 1 - \frac{j}{j_c} \right)^{-\gamma} \\ &= c \left( \frac{j}{j_c} \right)^\gamma \left( 1 + \gamma \frac{j}{j_c} + \frac{1}{2!} \gamma(\gamma+1) \left( \frac{j}{j_c} \right)^2 + \dots \right. \\ &\quad \left. + \frac{\gamma(\gamma+1)(\gamma+2)\dots(\gamma+k-1)}{k!} \left( \frac{j}{j_c} \right)^k + \dots \right). \end{aligned}$$

This means:

$$\chi_T^c = c \left( \frac{j}{j_c} \right)^\gamma \sum_{l=0}^{\infty} \hat{\alpha}_l j^l \quad \text{with} \quad \hat{\alpha}_l = \frac{\gamma(\gamma+1)\dots(\gamma+l-1)}{j_c^l l!}.$$

The pre-factor behaves uncritically for  $T \rightarrow T_C$  ( $c(j/j_c)^\gamma \rightarrow c$ ). The radius of convergence of  $\chi_T$  is thus identical with that of the sum. It then remains:

$$f(l) \equiv \frac{\hat{\alpha}_l}{\hat{\alpha}_{l-1}} = \frac{\gamma+l-1}{j_c l} = \left( \frac{\gamma-1}{j_c} \right) \frac{1}{l} + \frac{1}{j_c}.$$



$f(l)$  represents as function of  $1/l$  a straight line with the slope  $(\gamma - 1)/j_c$  and the axis intercept  $1/j_c = k_B T_C/J$ . As expected:

$$R = \left( \lim_{l \rightarrow \infty} \frac{\widehat{\alpha}_l}{\widehat{\alpha}_{l-1}} \right)^{-1} = j_c = \beta_c J .$$

If one knows only a finite number of  $\alpha_l$ , then one can hope to get by an *extrapolation* of  $\alpha_l/\alpha_{l-1}$  as function of  $1/l$  an (approximative) determination of  $\gamma$  from the slope of  $f(l)$  and  $T_C$  from the axis intercept. The correction terms in the ansatz for  $\chi_T$  can still lead for small  $l$  to oscillations. With increasing  $l$ , however, the critical behavior will dominate. The method of extrapolation therefore represents a powerful means for the determination of critical quantities of not exactly solvable models (e.g. the 3d-Ising model).

2. The mean-field approximation of the Heisenberg model predicts for the isothermal susceptibility the Curie-Weiß law (4.151):

$$\begin{aligned} \chi_T &= \frac{C}{T - T_C} = \frac{C}{\frac{1}{k_B \beta} - \frac{1}{k_B \beta_c}} \\ &= C k_B \beta \beta_c \frac{1}{\beta_c - \beta} = C k_B \beta \frac{1}{1 - \frac{J\beta}{J\beta_c}} \\ &= C k_B \beta \sum_{l=0}^{\infty} \left( \frac{J\beta}{J\beta_c} \right)^l = \sum_{l=0}^{\infty} \frac{C k_B}{J^{l+1}} \frac{1}{\beta_c^l} (J\beta)^{l+1} \\ &= \sum_{l=1}^{\infty} \underbrace{\left( \frac{C k_B}{J^l} \frac{1}{\beta_c^{l-1}} \right)}_{\alpha_l} (J\beta)^l . \end{aligned}$$

It thus follows:

$$\frac{\alpha_l}{\alpha_{l-1}} = \frac{J^{l-1} \beta_c^{l-2}}{J^l \beta_c^{l-1}} = \frac{1}{J\beta_c} .$$

That means

$$R = J\beta_c$$

and

$$\frac{\gamma - 1}{J\beta_c} = 0 \quad \curvearrowright \quad \gamma = 1 .$$

This is the well-known result!

3. According to part 2. of Exercise 4.4.3 it holds for  $N \rightarrow \infty$  (the ‘volume’ of the spin-chain is the length of the chain):

$$\begin{aligned}
 \chi_T(T, B_0 = 0) &= \beta \mu_0 \mu^2 \frac{N}{V} \exp(2\beta J) \\
 &= \beta \mu_0 \mu^2 \frac{N}{V} \sum_{l=0}^{\infty} \frac{(2\beta J)^l}{l!} \\
 &= \sum_{l=1}^{\infty} \left( \mu_0 \mu^2 \frac{N}{V} \frac{2^{l-1}}{J(l-1)!} \right) (\beta J)^l \\
 &= \sum_{l=1}^{\infty} \alpha_l (\beta J)^l \quad \text{with} \quad \alpha_l = \mu_0 \mu^2 \frac{N}{V} \frac{2^{l-1}}{J(l-1)!} .
 \end{aligned}$$

Therewith

$$\frac{\alpha_{l+1}}{\alpha_l} = \frac{2^l (l-1)!}{l! 2^{l-1}} = \frac{2}{l} .$$

The radius of convergence is thus infinitely large, what corresponds to  $T_C = 0$ :

$$R = \left( \lim_{l \rightarrow \infty} \frac{\alpha_{l+1}}{\alpha_l} \right)^{-1} = \infty = \frac{J}{k_B T_C} .$$

### Solution 4.4.7

1. The partition function

$$Z_N(j) = \sum_{S_1}^{\pm 1} \sum_{S_2}^{\pm 1} \dots \sum_{S_N}^{\pm 1} \exp \left( j \sum_{i=1}^N S_i S_{i+1} \right)$$

can be reformulated as follows:

$$Z_N(j) = \sum_{S_1}^{\pm 1} \dots \sum_{S_N}^{\pm 1} e^{j(S_1 S_2 + S_2 S_3)} e^{j(S_3 S_4 + S_4 S_5)} \dots e^{j(S_{N-1} S_N + S_N S_1)} .$$

We can assume, without any restriction of generality, that  $N$  is an even number. We now perform the summations over all spins with even (!) indexes:

$$\begin{aligned}
 Z_N(j) &= \sum_{S_1}^{\pm 1} \sum_{S_3}^{\pm 1} \dots \sum_{S_{N-1}}^{\pm 1} (e^{j(S_1 + S_3)} + e^{-j(S_1 + S_3)}) \times \\
 &\quad \times (e^{j(S_3 + S_5)} + e^{-j(S_3 + S_5)}) \times \dots \times (e^{j(S_{N-1} + S_1)} + e^{-j(S_{N-1} + S_1)}) .
 \end{aligned}$$

Because of

$$e^{j(S_i+S_j)} + e^{-j(S_i+S_j)} = \begin{cases} 2 \cosh(2j) & \text{if } S_i = S_j \\ 2 & \text{if } S_i = -S_j . \end{cases}$$

it can be written for arbitrary  $i, j$ :

$$e^{j(S_i+S_j)} + e^{-j(S_i+S_j)} = f(j) e^{j' S_i S_j}$$

with

$$\begin{aligned} f(j) &= 2 \cosh^{\frac{1}{2}}(2j) \\ j' &= \frac{1}{2} \ln(\cosh(2j)) . \end{aligned} \tag{A.36}$$

That means for the partition function:

$$Z_N(j) = (f(j))^{\frac{N}{2}} \sum_{S_1}^{\pm 1} \sum_{S_3}^{\pm 1} \dots \sum_{S_{N-1}}^{\pm 1} e^{j'(S_1 S_3 + S_3 S_5 + \dots)} .$$

On the right-hand side there appears a partition function with half the spin number and with modified coupling:

$$Z_N(j) = 2^{\frac{N}{2}} \cosh^{\frac{N}{4}}(2j) Z_{\frac{N}{2}}(j') .$$

Because of

$$j > 0 \curvearrowright e^{2j} > e^{-2j} \curvearrowright e^{2j} > \frac{1}{2}(e^{2j} + e^{-2j}) \curvearrowright 2j > \ln(\cosh(2j)) = 2j'$$

$j' < j$ , i.e. the modified coupling is weaker than the original one. At fixed  $J$  this means that the *new* partition function belongs to a higher temperature.

2. Extensivity of the free energy:

$$\ln Z_N(j) = N P(j) .$$

Then it holds with the results from part 1.:

$$\begin{aligned} \ln Z_N(j) &= \frac{N}{2} \ln f(j) + \ln Z_{\frac{N}{2}}(j') \\ \Leftrightarrow NP(j) &= \frac{N}{2} \ln f(j) + \frac{N}{2} P(j') \\ \Leftrightarrow P(j) &= \frac{1}{2} \left( \ln 2 + \frac{1}{2} \ln \cosh(2j) + P(j') \right) . \end{aligned}$$

It remains:

$$P(j) = \frac{1}{2} \left( \ln 2 + j' + P(j') \right). \quad (\text{A.37})$$

$j \ll 1$  means at fixed  $J$  very high temperature. But then the interaction between the Ising-spins becomes relatively unimportant, and  $Z_N \approx 2^N$ . If one thus starts with a  $j' \ll 1$ , then one can at first assume  $P(j') \approx \ln 2$ . In the next step it is then fixed a new  $j$  by (A.36) and a new  $P(j)$  by (A.37). By iteration  $\ln Z_N(T)$  can in this way be determined for arbitrary temperatures.

3. According to (4.198) we have:

$$F(j) = -Nk_B T \ln(2 \cosh j) \quad \curvearrowright \quad P(j) = \ln(2 \cosh j).$$

We thus insert into (A.37)

$$P(j') = \ln(2 \cosh j') ; \quad j' = \frac{1}{2} \ln(\cosh(2j)).$$

That leads to:

$$\begin{aligned} \cosh j' &= \frac{1}{2} \left( \exp \left( \ln \cosh^{\frac{1}{2}}(2j) \right) + \exp \left( -\ln \cosh^{\frac{1}{2}}(2j) \right) \right) \\ &= \frac{1}{2} \left( \cosh^{\frac{1}{2}}(2j) + \frac{1}{\cosh^{\frac{1}{2}}(2j)} \right) = \frac{1}{2} \frac{\cosh(2j) + 1}{\cosh^{\frac{1}{2}}(2j)} \\ \curvearrowright P(j') &= \ln \frac{\cosh(2j) + 1}{\cosh^{\frac{1}{2}}(2j)} = \ln(2 \cosh^2(j)) - \frac{1}{2} \ln \cosh(2j) \\ \curvearrowright j' + P(j') &= \ln(2 \cosh^2(j)) \\ \curvearrowright \ln 2 + j' + P(j') &= \ln(2^2 \cosh^2(j)) = 2 \ln(2 \cosh(j)) = 2P(j). \end{aligned}$$

It is shown therewith that the recursion formula (A.37) reproduces the exact solution.

### Solution 4.4.8

It is to be calculated:

$$\det(1 - v m(q)) = \begin{vmatrix} 1 - vQ_1 & -v\lambda Q_1 & 0 & -v\lambda^* Q_1 \\ -v\lambda^* Q_2 & 1 - vQ_2 & -v\lambda Q_2 & 0 \\ 0 & -v\lambda^* Q_1^* & 1 - vQ_1^* & -v\lambda Q_1^* \\ -v\lambda Q_2^* & 0 & -v\lambda^* Q_2^* & 1 - vQ_2^* \end{vmatrix}.$$

Expansion with respect to the first line:

$$\begin{aligned}
 \det(1 - v m(q)) &= (1 - v Q_1) \begin{vmatrix} 1 - v Q_2 & -v \lambda Q_2 & 0 \\ -v \lambda^* Q_1^* & 1 - v Q_1^* & -v \lambda Q_1^* \\ 0 & -v \lambda^* Q_2^* & 1 - v Q_2^* \end{vmatrix} \\
 &+ v \lambda Q_1 \begin{vmatrix} -v \lambda^* Q_2 & -v \lambda Q_2 & 0 \\ 0 & 1 - v Q_1^* & -v \lambda Q_1^* \\ -v \lambda Q_2^* & -v \lambda^* Q_2^* & 1 - v Q_2^* \end{vmatrix} \\
 &+ v \lambda^* Q_1 \begin{vmatrix} -v \lambda^* Q_2 & 1 - v Q_2 & -v \lambda Q_2 \\ 0 & -v \lambda^* Q_1^* & 1 - v Q_1^* \\ -v \lambda Q_2^* & 0 & -v \lambda^* Q_2^* \end{vmatrix} \\
 &= \det A + \det B + \det C .
 \end{aligned}$$

We use in the following

$$\lambda \lambda^* = Q_1 Q_1^* = Q_2 Q_2^* = 1 ; \quad \lambda^4 = \lambda^{*4} = -1 ; \quad Q_{1,2} + Q_{1,2}^* = 2 \cos q_{1,2}$$

and evaluate the various summands separately:

$$\begin{aligned}
 \det A &= (1 - v Q_1) \left( (1 - v Q_2)(1 - v Q_1^*)(1 - v Q_2^*) \right. \\
 &\quad \left. - v^2 Q_1^* Q_2^* (1 - v Q_2) - v^2 (1 - v Q_2^*) Q_1^* Q_2 \right) \\
 &= (1 - v Q_1) \left( (1 - v Q_1^*)(1 - v(Q_2 + Q_2^*) + v^2) \right. \\
 &\quad \left. - v^2 Q_1^* (Q_2 + Q_2^*) + 2v^3 Q_1^* \right) \\
 &= (1 - v Q_1) \left( 1 - 2v \cos q_2 + v^2 - v Q_1^* + v^3 Q_1^* \right) \\
 &= 1 - 2v(\cos q_1 + \cos q_2) + 2v^2(1 + Q_1 \cos q_2) + v^3(Q_1^* - Q_1) - v^4
 \end{aligned}$$

$$\begin{aligned}
 \det B &= v \lambda Q_1 \left( -v \lambda^* Q_2 (1 - v Q_1^*)(1 - v Q_2^*) - v^3 \lambda^3 Q_1^* + v^3 \lambda^* Q_1^* \right) \\
 &= -v^2 Q_1 Q_2 \left( 1 - v(Q_1^* + Q_2^*) + v^2 Q_1^* Q_2^* \right) + 2v^4 \\
 &= -v^2 Q_1 Q_2 + v^3(Q_2 + Q_1) + v^4
 \end{aligned}$$

$$\begin{aligned}
 \det C &= v \lambda^* Q_1 \left( -v^3 \lambda^{*3} Q_1^* - v \lambda Q_2^* (1 - v Q_2)(1 - v Q_1^*) + v^3 \lambda Q_1^* \right) \\
 &= v^4 - v^2 Q_1 Q_2^* \left( 1 - v(Q_2 + Q_1^*) + v^2 Q_2 Q_1^* \right) + v^4 \\
 &= 2v^4 - v^2 Q_1 Q_2^* + v^3(Q_1 + Q_2^*) - v^4 \\
 &= -v^2 Q_1 Q_2^* + v^3(Q_1 + Q_2^*) + v^4 .
 \end{aligned}$$

Summary:

$$\begin{aligned}
 \det(1 - v m(q)) &= 1 - 2v(\cos q_1 + \cos q_2) \\
 &\quad + v^2(2 + 2Q_1 \cos q_2 - Q_1(Q_2 + Q_2^*)) \\
 &\quad + v^3(Q_1^* - Q_1 + Q_1 + Q_2 + Q_1 + Q_2^*) + v^4 \\
 &= 1 - 2v(\cos q_1 + \cos q_2) + 2v^2 + 2v^3(\cos q_1 + \cos q_2) + v^4 \\
 &= (1 + v^2)^2 - 2v(1 - v^2)(\cos q_1 + \cos q_2) .
 \end{aligned}$$

This inserted into (4.215) yields (4.216).

## Section 4.6.4

### Solution 4.6.1

1. In Sect. 4.4.7 the equivalence of the Ising model and the lattice-gas model is shown. This presumes that the field term  $2b$  in the canonical partition function of the Ising-spin system is to be identified with the chemical potential  $\mu$  of the grand-canonical partition function of the lattice gas (see text after (4.249) in Sect. 4.4.7). According to the Yang-Lee theory of the phase transition we have to look for the zeros of the partition function as a function of the fugacity  $z = e^{\beta\mu}$ . We therefore try to represent the Ising-partition function as a function of  $z = \exp(2\beta b)$ .

According to (4.193) the partition function can at first be written as follows:

$$\begin{aligned}
 Z_N(T, B_0) &= E_+^N + E_-^N \\
 E_{\pm} &= e^{\beta J} \left\{ \cosh(\beta b) \pm \sqrt{\cosh^2(\beta b) - 2 e^{-2\beta J} \sinh(2\beta J)} \right\} .
 \end{aligned}$$

With the fugacity  $z = e^{2\beta b}$  one finds:

$$\cosh(\beta b) = \frac{1}{2} \left( \sqrt{z} + \frac{1}{\sqrt{z}} \right) ; \quad \cosh^2(\beta b) = \frac{1}{4} \left( z + \frac{1}{z} + 2 \right) .$$

In addition we still introduce the quantity  $x$ , which is independent of  $z$ :

$$x = e^{-2\beta J} \quad \curvearrowright \quad \sinh(2\beta J) = \frac{1}{2} \left( \frac{1}{x} - x \right) .$$

Therewith:

$$E_{\pm} = \frac{1}{\sqrt{x}} \left\{ \frac{1}{2} \left( \sqrt{z} + \frac{1}{\sqrt{z}} \right) \pm \sqrt{\frac{1}{4} \left( z + \frac{1}{z} \right) - \frac{1}{2} + x^2} \right\}.$$

The  $z$ -dependence of the partition function  $Z_N$  is therewith determined.

2. For the  $Z_N$ -zeros  $z_n$  it must hold:

$$E_+^N \stackrel{!}{=} -E_-^N.$$

This is equivalent to:

$$\begin{aligned} & \frac{1}{2} \left( \sqrt{z_n} + \frac{1}{\sqrt{z_n}} \right) + \sqrt{\frac{1}{4} \left( z_n + \frac{1}{z_n} \right) - \frac{1}{2} + x^2} \stackrel{!}{=} \\ & \stackrel{!}{=} (-1)^{1/N} \left\{ \frac{1}{2} \left( \sqrt{z_n} + \frac{1}{\sqrt{z_n}} \right) - \sqrt{\frac{1}{4} \left( z_n + \frac{1}{z_n} \right) - \frac{1}{2} + x^2} \right\}. \end{aligned}$$

We try the ansatz

$$z_n = \exp(i\varphi_n)$$

and can then use:

$$\begin{aligned} \frac{1}{2} \left( \sqrt{z_n} + \frac{1}{\sqrt{z_n}} \right) &= \cos \left( \frac{\varphi_n}{2} \right) = \sqrt{\frac{1}{2} (1 + \cos \varphi_n)} \\ \frac{1}{4} \left( z_n + \frac{1}{z_n} \right) &= \frac{1}{2} \cos \varphi_n. \end{aligned}$$

Furthermore:

$$y_n = (-1)^{1/N} = \exp \left( i\pi \frac{2n-1}{N} \right) ; \quad n = 1, 2, \dots, N.$$

Therewith it is to be solved:

$$\begin{aligned} & \cos \left( \frac{\varphi_n}{2} \right) (1 - y_n) \stackrel{!}{=} -(1 + y_n) \sqrt{\frac{1}{2} (\cos \varphi_n - 1) + x^2} \\ & \curvearrowright \frac{1}{2} (1 + \cos \varphi_n) (1 - y_n)^2 = (1 + y_n)^2 \left( \frac{1}{2} (\cos \varphi_n - 1) + x^2 \right) \\ & \curvearrowright \cos \varphi_n \left\{ 1 - \frac{(1 + y_n)^2}{(1 - y_n)^2} \right\} = \frac{(1 + y_n)^2}{(1 - y_n)^2} (-1 + 2x^2) - 1 \end{aligned}$$

$$\begin{aligned} \curvearrowright \cos \varphi_n \{-4y_n\} &= (1 + y_n)^2(-1 + 2x^2) - (1 - y_n)^2 \\ &= -2(1 + y_n^2) + 2x^2(1 + y_n^2) + 4y_nx^2 \\ &= -2(1 - x^2)(1 + y_n^2) + 4y_nx^2 \\ \curvearrowright \cos \varphi_n &= \frac{1}{2} \left( \frac{1}{y_n} + y_n \right) (1 - x^2) - x^2 . \end{aligned}$$

The zeros of the canonical partition function

$$z_n = \exp(i\varphi_n) ; \quad \cos \varphi_n = (1 - x^2) \cos \left( \pi \frac{2n - 1}{N} \right) - x^2 .$$

are thus located on the unit circle in the complex  $z$ -plane (Fig. A.14). Note that the necessary condition  $|\cos \varphi_n| \leq 1$  can only be fulfilled for  $0 \leq x = \exp(-2\beta J) \leq 1$ . For  $x > 1$ ,  $\cos \varphi_n$  is always smaller than  $-1$ . For this reason a ferromagnetic coupling  $J > 0$  must be assumed.

In the finite system all zeros lie on the unit circle to the left of the vertical parallel line to the imaginary axis, which intersects the real axis at  $1 - 2x^2$ . There is thus **no** zero in the *physical region*, i.e. on the real axis  $z > 0$  (Sect. 4.6.1).

3. In the thermodynamic limit, which is given for the spin lattice with constant lattice distances by  $N \rightarrow \infty$ , the zeros move closer and closer together, eventually building a homogeneous covering of the unit circle to the left of the vertical line through  $\text{Re}z = 1 - 2x^2$  (see Fig. A.15).

For the endpoints it holds:

$$\begin{aligned} \cos \varphi_{\pm} &= 1 - 2x^2 \\ \sin \varphi_{\pm} &= \pm \sqrt{1 - (1 - 2x^2)^2} = \pm 2x\sqrt{1 - x^2} \\ \curvearrowright z_{\pm} &= (1 - 2x^2) \pm i2x\sqrt{1 - x^2} . \end{aligned}$$

Fig. A.14

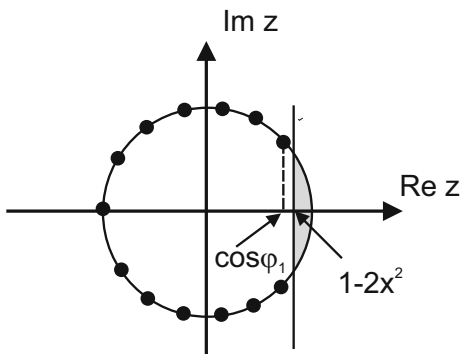
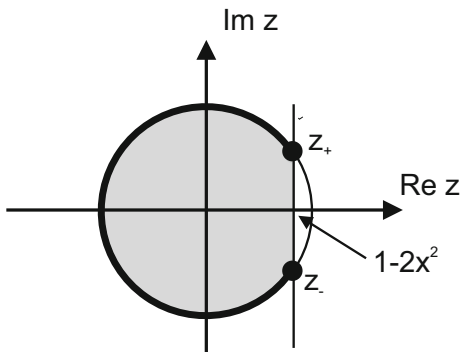




Fig. A.15



$x \neq 0$  for all  $T > 0$ . The endpoints of the distribution  $z_{\pm}$  have thus for finite temperatures a non-vanishing imaginary part. The zero-distribution therefore even in the thermodynamic limit does **not** reach the positive-real axis. The Yang-Lee theory confirms therewith the already otherwise found result that the one-dimensional Ising model does not let allow a phase transition at finite temperatures.

At  $T = 0$  we have  $x = 0$  and therewith  $z_{\pm} = +1$ . Formally, a phase transition thus appears to be possible at  $T = 0$  (4.188). For  $T \rightarrow \infty$  we find  $x = 1$ . Even then the imaginary parts of  $z_{\pm}$  vanish; the zeros ( $z_{\pm} = -1$ ), however, do not lie within the *physical region*.

**Solution 4.6.2**

1. Partition function of the lattice gas II in the  $z$ -representation

$$\begin{aligned} \Xi_z^{(II)}(T, K) &= \sum_{X \subset K} \exp(\beta(\mu N(X) - U_{II}(X))) \\ &= \sum_{X \subset K} z^{N(X)} \prod_{\substack{i \in X \\ j \notin X}} \exp(-\beta \varphi_{II}(i, j)) . \end{aligned}$$

We use here the same notation as in Sect. 4.4.6.  $z = e^{\beta\mu}$ : fugacity;  $K$ : set of all parcels of the lattice gas;  $X$ : set of all occupied parcels;  $N(X)$ : number of the occupied parcels in the set  $X$ .

It is summed over all conceivable partial sets  $X \subset K$ .  $\Xi_z^{(II)}(T, K)$  is obviously a polynomial of  $z$  of the degree  $N(K)$

$$\Xi_z^{(II)}(T, K) = 1 + g_1 z + g_2 z^2 + \dots + g_N z^{N(K)}$$

with real non-negative coefficient  $g_n$ . None of the  $N(K)$  zeros lies on the positive-real (*physical*) axis, at most on the negative-real axis. Apart from that, the zeros are complex (Sect. 4.6.1). If the equation for the zeros

$$0 \stackrel{!}{=} 1 + g_1 z_n + g_2 z_n^2 + \dots + g_N z_n^{N(K)}$$

is fulfilled by  $z_n$ , then obviously also fulfilled by  $z_n^*$ , because the  $g_n$  are all real.

2. According to (4.235) in Sect. 4.4.6 it holds for the lattice gas II the symmetry:

$$\Xi_{\mu}^{(II)}(T, K) = \exp(\beta\mu N(K)) \Xi_{-\mu}^{(II)}(T, K) .$$

That means in the  $z$ -representation:

$$\Xi_z^{(II)}(T, K) = z^{N(K)} \Xi_{1/z}^{(II)}(T, K) .$$

Because of  $z^{N(K)} \neq 0$  it follows from

$$\Xi_{z_n}^{(II)}(T, K) = 0$$

also

$$\Xi_{1/z_n}^{(II)}(T, K) = 0 .$$

Together with  $z_n$  it is thus also  $1/z_n$  a zero!

3. The  $\{z_n\}$  build a complete set of  $N(K)$  zeros, the  $\{1/z_n\}$  likewise. There must exist a connection.

Proposal 1:

$$z_n = z_n^{-1} \quad \forall n \quad \curvearrowright \quad z_n^2 = 1 .$$

This could only be fulfilled by the real zeros ( $z_n = \pm 1$ ), but not by the  $(N(K) - 2)$  other, complex zeros!

Proposal 2:

$$z_n = 1/z_n^* \quad \forall n \quad \curvearrowright \quad |z_n|^2 = 1 .$$

That would be conceivable (see special case in Exercise 4.6.1)!

*The whole lot of the zeros lie on the unit circle in the complex  $z$ -plane.*

That the *plausible* proposal 2 is indeed correct, is the statement of the so-called *circle theorem* (T.D. Lee, C.N. Yang, Phys. Rev. **87**, 410 (1952)), the explicit proof of which, though, proves to be rather involved.

4. In the thermodynamic limit ( $N \rightarrow \infty$ ) the zeros will densely cover the unit circle, totally or partially. Then a phase transition might become possible at  $z = +1$ . That can be so, but need not necessarily be so. It is sure that at  $z \neq +1$  a phase

transition can take place in no way.  $z \neq +1$  means  $\mu \neq 0$ . For non-vanishing chemical potential a phase transition in the lattice-gas model is thus excluded.

5. In Sect. 4.4.7 the thermodynamic equivalence of lattice-gas model and Ising model is shown, where the assignment holds

$$\mu \leftrightarrow 2b = 2g\mu_B B_0 .$$

$\mu \neq 0$  therefore means  $B_0 \neq 0$ . In a finite magnetic field a phase transition is hence impossible, and that too independent of the lattice dimension of the Ising model!

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