Appendix

A. Nernst's Theorem (Third Law)

A.1 Preliminary Remarks on the Historical Development of Nernst's Theorem

Based on experimental results[1], Nernst (1905) originally postulated that changes in the entropy ΔS in isothermal processes (chemical reactions, phase transitions, pressure changes or changes in external fields for $T = \text{const.}$) have the property

$$\Delta S \to 0$$

in the limit $T \to 0$. This postulate was formulated in a more stringent way by Planck, who made the statement $S \to 0$, or, more precisely,

$$\lim_{T \to 0} \frac{S(T)}{N} = 0 \ , \tag{A.1}$$

where, depending on the physical situation, N is the number of particles or of lattice sites. One refers to (A.1) as Nernst's theorem or the Third Law of thermodynamics[2].

According to statistical mechanics, the value of the entropy at absolute zero, $T = 0$, depends on the degeneracy of the ground state. We assume that the ground state energy E_0 is g_0-fold degenerate. Let P_0 be the projection

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[1] The determination of the entropy as a function of the temperature T is carried out by measuring the specific heat $C_X(T)$ in the interval $[T_0, T]$ and integrating according to the equation $S(T) = S_0 + \int_{T_0}^{T} dT \, \frac{C_X(T)}{T}$, where the value S_0 at the initial temperature T_0 is required. Nernst's Theorem in the form (A.1) states that this constant for all systems at $T = 0$ has the value zero.

[2] Nernst's theorem is understandable only in the framework of quantum mechanics. The entropy of classical gases and solids does not obey it. Classically, the energy levels would be continuous, e.g. for a harmonic oscillator, $E = \frac{1}{2} \left(\frac{p^2}{m} + m\omega^2 q^2 \right)$ instead of $E = \hbar\omega \left(n + \frac{1}{2} \right)$. The entropy of a classical crystal, effectively a system of harmonic oscillators, would diverge at $T = 0$, since per vibrational degree of freedom, $S = k + k \log T$. In this sense, Nernst's theorem can certainly be regarded as visionary.

operator onto states with $E = E_0$. Then the density matrix of the canonical ensemble can be cast in the form

$$\rho = \frac{e^{-\beta H}}{\text{Tr}\, e^{-\beta H}} = \frac{\sum_n e^{-\beta E_n} |n\rangle\langle n|}{\sum_n e^{-\beta E_n}} = \frac{P_0 + \sum_{E_n > E_0} e^{-\beta(E_n - E_0)} |n\rangle\langle n|}{g_0 + \sum_{E_n > E_0} e^{-\beta(E_n - E_0)}} \, . \tag{A.2}$$

For $T = 0$, this leads to $\rho(T = 0) = \frac{P_0}{g_0}$, and thus for the entropy to

$$S(T = 0) = -k\langle \log \rho \rangle = k \log g_0 \, . \tag{A.3}$$

The general opinion in mathematical physics is that the ground state of interacting systems should not be degenerate, or that the degree of degeneracy in any case should be considerably less than the number of particles. If $g_0 = \mathcal{O}(1)$ or even if $g_0 = \mathcal{O}(N)$, we find

$$\lim_{N \to \infty} \frac{S(T = 0)}{kN} = 0 \, , \tag{A.4}$$

i.e. for such degrees of degeneracy, Nernst's theorem follows from quantum statistics.

In Sect. A.2, the Third Law is formulated generally taking into account the possibility of a residual entropy. This is in practice necessary for the following reasons: (i) there are model systems with greater ground-state degeneracies (ice, non-interacting magnetic moments); (ii) a very weak lifting of the degeneracy might make itself felt only at extremely low temperatures; (iii) a disordered metastable state can be 'frozen in' by rapid cooling and retains a finite residual entropy. We will discuss these situations in the third section.

A.2 Nernst's Theorem and its Thermodynamic Consequences

The General Formulation of Nernst's Theorem:

$S(T = 0)/N$ is a finite constant which is independent of parameters X such as V and P (i.e. the degeneracy does not change with X) and $S(T)$ is finite for finite T.

Results of Nernst's theorem for the specific heat and other thermodynamic derivatives:

Let A be the thermodynamic state which is attained on increasing the temperature starting from $T = 0$ at constant X. From $C_X = T \left(\frac{\partial S}{\partial T} \right)_X$, it follows that

$$S(T) - S(T = 0) = \int_0^A dT \, \frac{C_X(T)}{T} \, . \tag{A.5}$$

From this, we find furthermore

$$C_X(T) \longrightarrow 0 \quad \text{for} \quad T \longrightarrow 0 \,,$$

since otherwise $S(T) = S(T = 0) + \infty = \infty$. This means that the heat capacity of every substance at absolute zero tends to zero; in particular, we have $C_P \to 0$, $C_V \to 0$, as already found explicitly in Chap. 4 for ideal quantum gases. Thus the specific heat at constant pressure takes on the form

$$C_P = T^x(a + bT + \ldots) \,, \tag{A.6}$$

where x is a positive exponent. For the entropy, (A.5), one obtains from this expression

$$S(T) = S(T = 0) + T^x \left(\frac{a}{x} + \frac{bT}{x+1} + \ldots \right) . \tag{A.7}$$

Other thermodynamic derivatives also vanish in the limit $T \to 0$, as one can see by combining (A.7) with various thermodynamic relations.

The thermal expansion coefficient α and its ratio to the isothermal compressibility fulfill the relations

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T \to 0 \quad \text{for} \quad T \to 0 \tag{A.8}$$

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \to 0 \quad \text{for} \quad T \to 0 \,. \tag{A.9}$$

The first relation can be seen by taking the derivative of (A.7) with respect to pressure

$$V\alpha = \left(\frac{\partial V}{\partial T} \right)_P = -\left(\frac{\partial S}{\partial P} \right)_T = -T^x \left(\frac{a'}{x} + \frac{b'T}{x+1} + \ldots \right) ; \tag{A.10}$$

the second relation is found by taking the derivative of (A.7) with respect to V.

From the ratio of (A.10) and (A.6) we obtain

$$\frac{V\alpha}{C_P} = -\frac{a'}{ax} + \ldots \propto T^0 \,.$$

In an adiabatic pressure change, the temperature changes as[3] $dT = \left(\frac{V\alpha}{C_P} \right) T dP$. A finite temperature change requires that dP increase as $\frac{1}{T}$. *Absolute zero therefore cannot be reached by an adiabatic expansion* .

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[3] $\left(\frac{\partial P}{\partial T} \right)_S = -\frac{\left(\frac{\partial S}{\partial T} \right)_P}{\left(\frac{\partial S}{\partial P} \right)_T} = \frac{T^{-1}C_P}{\left(\frac{\partial V}{\partial T} \right)_P} = \frac{C_P}{TV\alpha}$

To clarify the question of whether absolute zero can be reached at all, we consider the fact that cooling processes always take place between two curves with $X = $ const., e.g. $P = P_1$, $P = P_2$ $(P_1 > P_2)$ (see Fig. A.1). Absolute zero could be reached only after infinitely many steps. An adiabatic change in X leads to cooling. Thereafter, the entropy must be decreased by removing heat; since no still colder heat bath is available, this can be done at best for $T = $ const. If a substance with a $T - S$ diagram like that shown in Fig. A.2 were to exist, i.e. if in contradiction to the Third Law, $S(T = 0)$ were to depend upon X, then one could reach absolute zero.
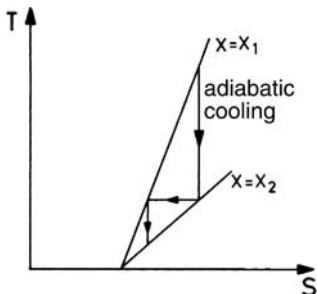
Fig. A.1. The approach to absolute zero by repeated adiabatic changes (e.g. adiabatic expansions)
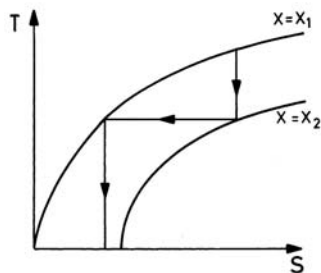
Fig. A.2. Hypothetical adiabats which would violate the Third Law

A.3 Residual Entropy, Metastability, etc.

In this section, we shall consider systems which exhibit a residual entropy even at very low temperatures, or metastable frozen-in states and other particular qualities which can occur in this connection.

(i) Systems which contain non-coupled spins and are not subject to an external magnetic field have the partition function $Z = (2S + 1)^N Z'$ and the free energy $F = -kTN \log(2S+1) + F'$. The spins then have a finite residual entropy even at $T = 0$:

$$S(T = 0) = Nk \log(2S + 1) .$$

For example: paraffin, $C_{20}H_{42}$; owing to the proton spins of H, the partition function is proportional to $Z \sim 2^{42N}$, from which we find for the residual entropy $S = 42kN \log 2$.

(ii) Metastable states in molecular crystals: the ground state of crystalline carbon monoxide, CO, has a uniformly oriented ordered structure of the linear CO molecules. At higher temperatures, the CO molecules are not ordered. If
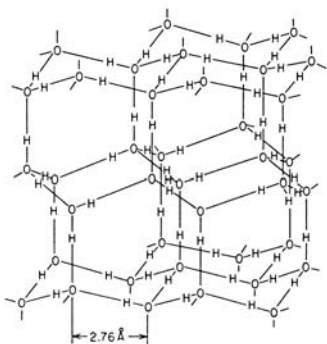
Fig. A.3. The structure of ice[4]
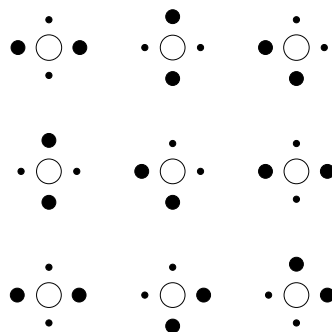
Fig. A.4. Two-dimensional ice: ○ oxygen, ● hydrogen, · other possible positions of H

a sample is cooled to below $T = \frac{\Delta\epsilon}{k}$, where $\Delta\epsilon$ is the very small energy difference between the orientations CO–OC and CO–CO of neighboring molecules, then the molecules undergo a transition into the ordered equilibrium state. Their reorientation time is however very long. The system is in a metastable state in which the residual entropy has the value

$$S(T = 0) = k \log 2^N = Nk \log 2 \,,$$

i.e. $S = 5.76$ J mol^{-1} K^{-1}. The experimental value is somewhat smaller, indicating partial orientation.

(iii) Binary alloys such as β-brass, (CuZn), can undergo a transition from a completely disordered state to an ordered state when they are cooled slowly. This phase transition can also be described by the Ising model, by the way. On the other hand, if the cooling is rapid, i.e. if the alloy is quenched, then the Cu and Zn atoms stay in their disordered positions. At low temperatures, the rate of reordering is so negligibly small that this frozen-in metastable state remains permanent. Such a system has a residual entropy.

(iv) Ice, solid H_2O: ice crystallizes in the Wurtzite structure. Each hydrogen atom has four oxygen atoms as neighbors (Fig. A.3). Neighboring oxygen atoms are connected by hydrogen bonds. The hydrogen atom which forms these bonds can assume two different positions between the two oxygen atoms (Fig. A.4). Because of the Coulomb repulsion, it is unfavorable for an oxygen atom to have more or fewer than two hydrogen atoms as neighbors. Thus one restricts the possible configurations of the hydrogen atoms by the ice rule: the protons are distributed in such a manner that two are close and two are more distant from each oxygen atom[5]. For N lattice sites (N oxygen

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[4] The structure of common (hexagonal) H_2O-ice crystals: S.N. Vinogrado, R.H. Linnell, *Hydrogen Bonding*, p. 201, Van Nostrand Reinhold, New York, 1971.

[5] L. Pauling: J. Am. Chem. Soc., **57**, 2680 (1935)

atoms), there are $2N$ hydrogen bonds. The approximate calculation of the partition function[5] at $T = 0$ yields

$$Z_0 = 2^{2N} \left(\frac{6}{16} \right)^N = \left(\frac{3}{2} \right)^N .$$

(The number of unhindered positions of the protons in the hydrogen bonds) times (reduction factor per lattice site, since of 16 vertices, only 6 are allowed). Using $W = \lim_{N \to \infty} Z_0^{1/N} = 1.5$, we find for the entropy per H_2O:

$$\frac{S(T = 0)}{kN} = \log W = \log 1.5 .$$

An exactly soluble two-dimensional model to describe the structure of ice has been given[6] (Fig. A.4). A square lattice of oxygen atoms is bound together by hydrogen bonds. The near-neighbor structure is the same as in three-dimensional ice. The statistical problem of calculating Z_0 can be mapped onto a vertex model (Fig. A.5). The arrows denote the position of the hydrogen bonds. Here, H assumes the position which is closer to the oxygen towards which the arrow points. Since each of the four arrows of a vertex can have two orientations, there are all together 16 vertices. Because of the ice rule, of these 16 vertices only the six shown in Fig. A.5 are allowed.

Fig. A.5. The vertices of the two-dimensional ice model which obey the ice rule (two hydrogen atoms near and two more distant)

The statistical problem now consists in determining the number of possibilities of ordering the 6 vertices in Fig. A.5 on the square lattice. The exact solution[6] of the two-dimensional problem is obtained using the transfer matrix method (Appendix F.).

$$W = \lim_{N \to \infty} Z_0^{1/N} = \left(\frac{4}{3} \right)^{3/2} = 1.5396007 \ldots .$$

The numerical result for three-dimensional ice is[7]:

$$W = 1.50685 \pm 0.00015, \quad S(T = 0) = 0.8154 \pm 0.0002 \text{ cal/K mole}$$

$$\text{Experiment at 10 K:} \quad S(T = 0) = 0.82 \pm 0.05 \text{ cal/K mole} .$$

[6] E. H. Lieb, Phys. Rev. Lett. **18**, 692 (1967); Phys. Rev. **162**, 162 (1967)

[7] Review: E. H. Lieb and F. Y. Wu in: Domb and Green, *Phase Transitions and Critical Phenomena I*, p. 331, Academic Press, New York, 1972.

The approximate formula of Pauling gives a lower limit for the residual entropy.

If the orientations of the hydrogen bonds were allowed to be completely unhindered, the residual entropy per lattice site would be $\log 2^2 = \log 4$. Due to the ice rule (as a result of the Coulomb repulsion), the residual entropy is reduced to $\log 1.5$. If other interactions of the protons were taken into account, there would be still finer energy splittings among the various configurations of the vertex arrangements. Then, on lowering the temperature, only a smaller number would be allowed and presumably at $T \to 0$ no residual entropy would be present. The fact that ice has a residual entropy even at low temperatures indicates that the reorientation becomes very slow under these conditions.

(v) The entropy of a system with low-lying energy levels typically shows the dependence shown in Fig. A.6. Here, the value of the entropy between T_1 and T_2 is not the entropy S_0. In case energy levels of the order of kT_1 are present, these are practically degenerate with the ground state for $T \gg T_1$, and only for $T < T_1$ is the residual entropy (possibly $S_0 = 0$) attained. An example of this is a weakly coupled spin system. The plateau in the temperature interval
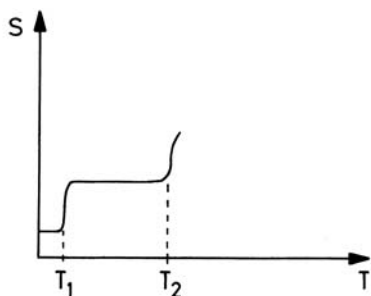
Fig. A.6. The entropy of a system with energy levels of the order of kT_1 and kT_2

$[T_1, T_2]$ could appear as a residual entropy on cooling. In this interval, the specific heat is zero. In the region of T_1, the specific heat again increases with decreasing temperature, then drops below T_1 towards the value zero after the degrees of freedom at the energy kT_1 are frozen out; this could possibly indicate a final decrease of the entropy to its value at $T = 0$.

For degrees of freedom with a discrete excitation spectrum (spins in a field, harmonic oscillators), the excitation energy determines the temperature below which the entropy of these degrees of freedom is practically zero. This is different for translational degrees of freedom, where the energy levels become continuous in the limit $N \to \infty$ and for example the spacing of the first excited state from the ground state is of the order of $\frac{\hbar^2}{mV^{2/3}}$. The corresponding excitation temperature of about 5×10^{-15} K is however unimportant for the region of application of the Third Law, which already applies at considerably higher temperatures. The spacing of the energy levels tends towards zero in the thermodynamic limit, and they are characterized by a density of states.

The temperature dependence of the entropy and the specific heat does not depend on the value of individual energy levels, but instead on the form of the density of states. For crystals, the density of states of the phonons is proportional to the square of the energy and therefore it gives $S \propto T^3$ at low temperatures. The density of states of the electrons at the Fermi energy is constant, and thus one obtains $S \propto T$.

(vi) It is also interesting to discuss chemical substances which exhibit allotropy in connection with the Third Law. Two famous examples are carbon, with its crystalline forms diamond and graphite, and tin, which crystallizes as metallic white tin and as semiconducting grey tin. White tin is the high-temperature form and grey tin the low-temperature form. At $T_0 = 292\,\mathrm{K}$, grey tin transforms to white tin with a latent heat Q_L. Upon cooling, the transformation takes place in the reverse direction, so long as the process occurs slowly and crystallization seeds of grey tin are present. On rapid cooling, white tin remains as a metastable structure. For the entropies of white and grey tin, the following relations hold:

$$S_W(T) = S_W(0) + \int_0^T \frac{dT}{T} C_W(T)$$

$$S_G(T) = S_G(0) + \int_0^T \frac{dT}{T} C_G(T) \, .$$

From the general formulation of Nernst's theorem, it follows that

$$S_W(0) = S_G(0) \, ,$$

since the two forms are present under identical conditions. (Statistical mechanics predicts in addition for these two perfect crystal configurations $S_W(0) = S_G(0) = 0$.) It thus follows that

$$S_W(T) - S_G(T) = \int_0^T \frac{dT}{T} \big(C_W(T) - C_G(T) \big) \, .$$

From this we find in particular that the latent heat at the transition temperature T_0 is given by

$$Q_L(T_0) \equiv T_0 \big(S_W(T_0) - S_G(T_0) \big) = T_0 \int_0^{T_0} \frac{dT}{T} \big(C_W(T) - C_G(T) \big) \, . \quad \text{(A.11)}$$

The temperature dependence of the specific heat at very low temperatures thus has an influence on the values of the entropy at high temperatures.

(vii) Systems with continuous internal symmetry, such as the Heisenberg model: for both the Heisenberg ferromagnet and the Heisenberg antiferromagnet, owing to the continuous rotational symmetry, the ground state is continuously degenerate. Classically, the degree of degeneracy would not, to be sure, depend on the number of lattice sites, but it would be infinitely

large. For N spin-1/2 sites, in quantum mechanics the z-component of the total spin has $N + 1$ possible orientations. The ground state is thus only $(N + 1)$-fold degenerate (see Eq. (A.4)). This degeneracy thus does not lead to a residual entropy at absolute zero.

Reference: J. Wilks, *The Third Law of Thermodynamics*, Oxford University Press, 1961.

B. The Classical Limit and Quantum Corrections

B.1 The Classical Limit

We will now discuss the transition from the quantum-mechanical density matrix to the classical distribution function, beginning with the one-dimensional case. At high temperatures and low densities, the results of quantum statistics merge into those of classical physics (see e.g. Sect. 4.2). The general derivation can be carried out by the following method[8]:

If we enclose the system in a box of linear dimension L, then the position eigenstates $|q\rangle$ and the momentum eigenstates $|p\rangle$ are characterized[9] by[10]

$$\hat{q}\,|q\rangle = q\,|q\rangle \ , \ \langle q|q'\rangle = \delta(q - q') \ , \ \int dq\,|q\rangle\,\langle q| = \mathbb{1} \ , \tag{B.1a}$$

$$\hat{p}\,|p\rangle = p\,|p\rangle \ , \ \langle p|p'\rangle = \delta_{pp'} \ , \quad \sum_p |p\rangle\,\langle p| = \mathbb{1} \ ,$$

$$\langle q|p\rangle = \frac{\mathrm{e}^{ipq/\hbar}}{\sqrt{L}} \ , \quad \text{with } p = \frac{2\pi\hbar}{L}\,n \ . \tag{B.1b}$$

We associate with each operator $\hat{A}$ a function[9] $A(p, q)$,

$$A(p, q) \equiv \langle p|\,\hat{A}\,|q\rangle\,\langle q|p\rangle\ L \ . \tag{B.2a}$$

These matrix elements are related to the classical quantities which correspond to the operators. For example, an operator of the form $\hat{A} = f(\hat{p})g(\hat{q})$ is associated with the function

$$A(p, q) = \langle p|\,f(\hat{p})\,g(\hat{q})\,|q\rangle\,\langle q|p\rangle\ L = f(p)g(p) \ . \tag{B.2b}$$

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[8] E. Wigner, Phys. Rev. **40**, 749 (1932); G. E. Uhlenbeck, L. Gropper, Phys. Rev. **41**, 79 (1932); J. G. Kirkwood, Phys. Rev. **44**, 31 (1933) and **45**, 116 (1934).

[9] For clarity, in this section operators are denoted exceptionally by a 'hat'.

[10] QM I, Chap. 8

The Hamiltonian

$$\hat{H} \equiv H(\hat{p}, \hat{q}) = \frac{\hat{p}^2}{2m} + V(\hat{q}) \tag{B.3a}$$

is thus associated with the classical Hamilton function

$$H(p, q) = \frac{p^2}{2m} + V(q) \ . \tag{B.3b}$$

The commutator of two operators is associated with the function

$$\langle p| \, [\hat{A}, \hat{B}] \, |q\rangle \, \langle q|p\rangle \ L$$

$$= L \int dq' \sum_{p'} \left\{ \langle p| \, \hat{A} \, |q'\rangle \, \langle q'|p'\rangle \, \langle p'| \, \hat{B} \, |q\rangle - \langle p| \, \hat{B} \, |q'\rangle \, \langle q'|p'\rangle \, \langle p'| \, \hat{A} \, |q\rangle \right\}$$

$$\times \langle q|p\rangle$$

$$= L \int dq' \sum_{p'} \Big(A(p, q')B(p', q) - B(p, q')A(p', q) \Big)$$

$$\times \langle p|q'\rangle \, \langle p'|q\rangle \, \langle q'|p'\rangle \, \langle q|p\rangle \tag{B.3c}$$

according to (B.2b), where $\langle p|q'\rangle \, \langle q'|p\rangle = \frac{1}{L}$ was used. We note at this point that for the limiting case of large L relevant to thermodynamics, the summation

$$\sum_{p} \leftrightarrow \frac{L}{2\pi\hbar} \int dp \tag{B.3d}$$

can be replaced by an integral and *vice versa*. The expression in round brackets in (B.3c) can be expanded in $(q' - q)$ and $(p' - p)$:

$$A(p, q')B(p', q) - B(p, q)A(p', q) =$$

$$\left(A(p, q) + (q' - q)\frac{\partial A}{\partial q} + \frac{1}{2}(q' - q)^2\frac{\partial^2 A}{\partial q^2} + \dots \right)$$

$$\times \left(B(p, q) + (p' - p)\frac{\partial B}{\partial p} + \frac{1}{2}(p' - p)^2\frac{\partial^2 B}{\partial p^2} + \dots \right)$$

$$- \left(B(p, q) + (q' - q)\frac{\partial B}{\partial q} + \frac{1}{2}(q' - q)^2\frac{\partial^2 B}{\partial q^2} + \dots \right)$$

$$\times \left(A(p, q) + (p' - p)\frac{\partial A}{\partial p} + \frac{1}{2}(p' - p)^2\frac{\partial^2 A}{\partial p^2} + \dots \right) \ . \tag{B.3e}$$

The zero-order terms cancel, and pure powers of $(q' - q)$ or $(p' - p)$ yield zero on insertion into (B.3c), since the p'-summation and the q'-integration lead to a δ-function. The remaining terms up to second order are

$$\langle p| [\hat{A}, \hat{B}] |q\rangle \langle q|p\rangle L =$$

$$= L \int dq' \sum_{p'} (q' - q)(p' - p) \frac{\partial(A, B)}{\partial(q, p)} \langle p|q'\rangle \langle p'|q\rangle \langle q'|p'\rangle \langle q|p\rangle$$

$$= L \langle p| (\hat{q} - q)(\hat{p} - p) |q\rangle \frac{\partial(A, B)}{\partial(q, p)} \langle q|p\rangle \tag{B.3f}$$

$$= L i\hbar \frac{\partial(A, B)}{\partial(q, p)} | \langle q|p\rangle |^2 = \frac{\hbar}{i} \frac{\partial(A, B)}{\partial(q, p)} \ ,$$

where the scalar product (B.1b) and Eq. (B.1a) have been inserted. For higher powers of $(\hat{q} - q)$ and $(\hat{p} - p)$, double and multiple commutators of $\hat{q}$ and $\hat{p}$ occur, so that, expressed in terms of Poisson brackets (Footnote 4, Sect. 1.3), we finally obtain

$$\langle p| [\hat{A}, \hat{B}] |q\rangle \langle q|p\rangle L = \frac{\hbar}{i}\{A, B\} + \mathcal{O}(\hbar^2) \ . \tag{B.4}$$

Application of the definition (B.2a) and Eq. (B.2b) to the partition function leads to

$$Z = \operatorname{Tr} e^{-\beta \hat{H}} = \sum_p \langle p| e^{-\beta H(\hat{p}, \hat{q})} |p\rangle = \sum_p \int dq \ \langle p| e^{-\beta H(\hat{p}, \hat{q})} |q\rangle \langle q|p\rangle$$

$$= \sum_p \int dq \ \langle p| \left(e^{-\beta K(\hat{p})} e^{-\beta V(\hat{q})} + \mathcal{O}(\hbar) \right) |q\rangle \langle q|p\rangle \tag{B.5}$$

$$= \frac{1}{L} \sum_p \int dq \, e^{-\beta H(p,q)} + \mathcal{O}(\hbar) = \int \frac{dp \, dq}{2\pi\hbar} \, e^{-\beta H(p,q)} + \mathcal{O}(\hbar) \ .$$

Z is thus – apart from terms of the order of $\hbar$, which result from commutators between $K(\hat{p})$ und $V(\hat{q})$ – equal to the classical partition integral. In (B.5), $\hat{K} \equiv K(\hat{p})$ is the operator for the kinetic energy.

Starting from the density matrix $\hat{\rho}$, we define the *Wigner function*:

$$\rho(p, q) = \frac{L}{2\pi\hbar} \langle p|q\rangle \langle q| \hat{\rho} |p\rangle \ . \tag{B.6}$$

Given the normalization of the momentum eigenfunctions, the factor $\frac{L}{2\pi\hbar}$ is introduced in order to guarantee that the Wigner function is independent of L for large L.

The meaning of the Wigner function can be seen from its two important properties:

$$(1) \quad \text{normalization}: \int dq \int dp \ \rho(p, q) = \int dq \sum_p \langle p|q\rangle \langle q| \hat{\rho} |p\rangle \tag{B.7}$$

$$= \operatorname{Tr} \hat{\rho} = 1 \ .$$

Here, the completeness relation for the position eigenstates, (B.1a), was used.

(2)   mean values : $\int dq \int dp\, \rho(p,q)\, A(p,q)$

$$= \int dq \sum_p \frac{L}{2\pi\hbar} \langle p|q\rangle \langle q|\, \hat\rho\, |p\rangle \langle p|\, \hat A\, |q\rangle \langle q|p\rangle \tag{B.8}$$

$$= \int dq \sum_p \langle q|\, \hat\rho\, |p\rangle \langle p|\, \hat A\, |q\rangle = \mathrm{Tr}\,(\hat\rho\hat A)\ .$$

Following the second equals sign, $\langle p|q\rangle \langle q|p\rangle = \frac{1}{L}$ and Eq. (B.3d) were used.

For the canonical ensemble, we find using (B.5)

$$\begin{aligned}
\rho(p,q) &= \frac{L}{2\pi\hbar} \langle p|q\rangle \langle q|\, \frac{\mathrm{e}^{-\beta\hat H}}{Z}\, |p\rangle \\
&= \frac{L}{2\pi\hbar} \langle p|q\rangle \langle q|\, \left(\mathrm{e}^{-\beta\hat K}\mathrm{e}^{-\beta V} + \mathcal{O}(\hbar)\right) |p\rangle\, \frac{1}{Z} \\
&= \frac{L}{2\pi\hbar}\, |\langle p|q\rangle\,|^2\, \frac{\mathrm{e}^{-\beta H(p,q)}}{Z} + \mathcal{O}(\hbar) = \frac{\mathrm{e}^{-\beta H(p,q)}}{2\pi\hbar Z} + \mathcal{O}(\hbar)
\end{aligned} \tag{B.9}$$

and

$$\begin{aligned}
\langle\hat A\rangle &= \frac{\frac{1}{L}\sum_p \int dq\, \mathrm{e}^{-\beta H(p,q)}\, A(p,q)}{\frac{1}{L}\sum_p \int dq\, \mathrm{e}^{-\beta H(p,q)}} + \mathcal{O}(\hbar) \\
&= \frac{\int \frac{dp\,dq}{2\pi\hbar}\, \mathrm{e}^{-\beta H(p,q)}\, A(p,q)}{\int \frac{dp\,dq}{2\pi\hbar}\, \mathrm{e}^{-\beta H(p,q)}} + \mathcal{O}(\hbar)\ .
\end{aligned} \tag{B.10}$$

The generalization to N particles in three dimensions gives:

$$\hat H = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m} + V(\hat{\mathbf{q}}_1,\ldots,\hat{\mathbf{q}}_N)\ . \tag{B.11}$$

We introduce the following abbreviations for many-body states:

$$|q\rangle \equiv |\mathbf{q}_1\rangle\ldots|\mathbf{q}_N\rangle\ ,\quad |p\rangle \equiv |\mathbf{p}_1\rangle\ldots|\mathbf{p}_N\rangle\ , \tag{B.12a}$$

$$\langle p|p'\rangle = \delta_{pp'}\ ,\quad \langle q|p\rangle = \frac{\mathrm{e}^{\mathrm{i}pq/\hbar}}{L^{3N/2}}\ ,\quad \sum_p |p\rangle\langle p| = \mathbb{1}\ . \tag{B.12b}$$

Applying periodic boundary conditions, the $\mathbf{p}_i$ take on the values

$$\mathbf{p}_i = \frac{L}{2\pi\hbar}(n_1,n_2,n_3)$$

with integer numbers n_i.

The many-body states which occur in Nature are either symmetric (bosons) or antisymmetric (fermions):

$$|p\rangle_s = \frac{1}{\sqrt{N!}} \sum_P (\pm 1)^P P \, |p\rangle \ . \tag{B.13}$$

The index s here stands in general for "symmetrization", and includes symmetrical states (upper sign) and antisymmetrical states (lower sign). This sum includes $N!$ terms. It runs over all the permutations P of N objects. For fermions, $(-1)^P = 1$ for even permutations and $(-1)^P = -1$ for odd permutations, while for bosons, $(+1)^P = 1$ always holds. In the case of fermions, all of the $\mathbf{p}_i$ in (B.13) must therefore be different from one another in agreement with the Pauli principle. In the case of bosons, the same $\mathbf{p}_i$ can occur; therefore, these states are in general not normalized: a normalized state is given by

$$|p\rangle_{sn} = \frac{1}{\sqrt{n_1! \, n_2! \ldots}} \, |p\rangle_s \ , \tag{B.14}$$

where n_i is the number of particles with momentum $\mathbf{p}_i$. We have

$$\mathrm{Tr}\, \hat{A} = \sum_{\mathbf{p}_1, \ldots, \mathbf{p}_N}{}' {}_{sn}\langle p| \hat{A} |p\rangle_{sn} = \sum_{\mathbf{p}_1, \ldots, \mathbf{p}_N} \frac{n_1! \, n_2! \ldots}{N!} {}_{sn}\langle p| \hat{A} |p\rangle_{sn}$$
$$= \sum_{\mathbf{p}_1, \ldots, \mathbf{p}_N} \frac{1}{N!} {}_s\langle p| \hat{A} |p\rangle_s \ . \tag{B.15}$$

The prime on the sum indicates that it is limited to different states. For example, $\mathbf{p}_1 \mathbf{p}_2 \ldots$ and $\mathbf{p}_2 \mathbf{p}_1 \ldots$ would give the same state. Rewriting the partition function in terms of the correspondence (B.2b) yields

$$Z = \mathrm{Tr}\, \mathrm{e}^{-\beta H} = \frac{1}{N!} \sum_{\{\mathbf{p}_i\}} {}_s\langle p| \mathrm{e}^{-\beta \hat{H}} |p\rangle_s$$
$$= \frac{1}{N!} \int d^{3N}q \sum_{\{\mathbf{p}_i\}} {}_s\langle p| \mathrm{e}^{-\beta \hat{H}} |q\rangle \langle q|p\rangle_s \tag{B.16}$$
$$= \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3}\right)^N \int d^{3N}p \int d^{3N}q \, \mathrm{e}^{-\beta H(p,q)} |\langle q|p\rangle_s|^2 + \mathcal{O}(\hbar) \ .$$

The last factor in the integrand has the form $|\langle q|p\rangle_s| = V^{-N}(1 + f(p,q))$, where the first term leads to the partition integral

$$Z = \int \frac{d^{3N}p \, d^{3N}q}{N! \, (2\pi\hbar)^{3N}} \, \mathrm{e}^{-\beta H(p,q)} + \mathcal{O}(\hbar) \ . \tag{B.16$'$}$$

Remarks:

(i) In (B.16), the rearrangement ${}_s\langle p| \mathrm{e}^{-\beta \hat{H}} |p\rangle_s = \int d^{3N}q \, {}_s\langle p| \mathrm{e}^{-\beta \hat{K}} \mathrm{e}^{-\beta V} |q\rangle \times \langle q|p\rangle_s + \mathcal{O}(\hbar) = \int d^{3N}q \, \mathrm{e}^{-\beta H(p,q)} |\langle q|p\rangle_s|^2 + \mathcal{O}(\hbar)$ was employed, where the symmetry of $\hat{H}$ under particle exchange enters.

(ii) The quantity $|\langle q|p\rangle_s|^2 = V^{-N}(1 + f(p,q))$ contains, in addition to the leading term V^{-N} in the classical limit, also p- and q-dependent terms. The corrections due to symmetrization yield contributions of the order of $\hbar^3$. Cf. the ideal gas and Sect. B.2.

(iii) Analogously (to B.16), one can show that the distribution function is

$$\rho(p,q) = \frac{\mathrm{e}^{-\beta H(p,q)}}{Z(2\pi\hbar)^{3N} N!} \cdot \tag{B.17}$$

We have thus shown that, neglecting terms of the order of $\hbar$, which result from the non-commutativity of the kinetic and the potential energies and the symmetrization of the wave functions, the *classical partition integral* (B.16′) is obtained.

The classical partition integral (B.16′) shows some features which indicate the underlying quantum nature: the factors $1/N!$ and $(2\pi\hbar)^{-3N}$. The first of these expresses the fact that states of identical particles which are converted into one another by particle exchange must be counted only once. This factor makes the thermodynamic potentials extensive and eliminates the Gibbs paradox which we discuss following Eq. (2.2.3). The factor $(2\pi\hbar)^{-3N}$ renders the partition integral dimensionless and has the intuitively clear interpretation that in phase space, each volume element $(2\pi\hbar)^{3N}$ corresponds to one state, in agreement with the uncertainty relation.

B.2 Calculation of the Quantum-Mechanical Corrections

We now come to the calculation of the quantum-mechanical corrections to the classical thermodynamic quantities. These arise from two sources:

a) The symmetrization of the wave function

b) the noncommutativity of $\hat{K}$ and V.

We will investigate these effects separately; their combination yields corrections of higher order in $\hbar$.

a) We first calculate the quantity $|\langle q|p_s\rangle|^2$, which occurs in the second line of (B.16), inserting Eq. (B.13):

$$
\begin{aligned}
|\langle q|p\rangle_s|^2 &= \frac{1}{N!}\sum_P\sum_{P'}(-1)^P(-1)^{P'}\langle q|\,P'\,|p\rangle\,\langle q|\,P\,|p\rangle^* \\
&= \frac{1}{N!}\sum_P\sum_{P'}(-1)^P(-1)^{P'}\langle P'q|p\rangle\,\langle Pq|p\rangle^* \\
&\,\hat{=}\,\frac{1}{N!}\sum_P\sum_{P'}(-1)^P(-1)^{P'}\langle q|p\rangle\,\langle PP'^{-1}q|p\rangle^* \\
&= \sum_P(-1)^P\langle q|p\rangle\,\langle Pq|p\rangle^* \\
&= \frac{1}{V^N}\sum_P \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\mathbf{p}_1\cdot(\mathbf{q}_1-P\mathbf{q}_1)+\dots+\mathbf{p}_N\cdot(\mathbf{q}_N-P\mathbf{q}_N))} \,.
\end{aligned}
\tag{B.18}
$$

Here, in the second line, we have used the fact that the permutation of the particles in configuration space is equivalent to the permutation of their spatial coordinates. In the third line we have made use of the fact that we can rename the coordinates within the integral $\int d^{3N}q$ which occurs in (B.16), replacing $P'q$ by q. In the next-to-last line, we have used the general property of groups that for any fixed P', the elements PP'^{-1} run through all the elements of the group. Finally, in the last line, the explicit form of the momentum eigenfunctions in their configuration-space representation was inserted.

Inserting the final result of Eq. (B.18) into (B.16), we can express each of the momentum integrals in terms of

$$\int d^3p\,\mathrm{e}^{-\frac{\beta\mathbf{p}^2}{2m}+\mathrm{i}\mathbf{p}\mathbf{x}} = \int d^3p\,\mathrm{e}^{-\frac{\beta\mathbf{p}^2}{2m}}\,f(\mathbf{x})\;, \tag{B.19}$$

with

$$f(\mathbf{x}) = \mathrm{e}^{-\frac{\pi\mathbf{x}^2}{\lambda^2}}\;, \tag{B.20}$$

where $\lambda = \frac{2\pi\hbar}{\sqrt{2\pi\hbar m k T}}$ [Eq. (2.7.20)] is the thermal wavelength. Then we find for the partition function, without quantum corrections which result from non-commutativity,

$$Z = \int \frac{d^{3N}q\,d^{3N}p}{N!(2\pi\hbar)^{3N}}\,\mathrm{e}^{-\beta H(p,q)}\sum_P(-1)^P f(\mathbf{q}_1-P\mathbf{q}_1)\ldots f(\mathbf{q}_N-P\mathbf{q}_N)\;. \tag{B.21}$$

The sum over the $N!$ permutations contains the contribution $f(0)^N = 1$ for the unit element $P = 1$; for transpositions (in which only pairs of particles i and j are exchanged), it contains the contribution $(f(\mathbf{q}_i - \mathbf{q}_j))^2$, etc. Arranging the terms according to increasing number of exchanges, we have

$$\sum_P(-1)^P f(\mathbf{q}_1 - P\mathbf{q}_1)\cdots f(\mathbf{q}_N - P\mathbf{q}_N) =$$
$$= 1 \pm \sum_{i<j}\big(f(\mathbf{q}_i - \mathbf{q}_j)\big)^2 + \sum_{ijk} f(\mathbf{q}_i - \mathbf{q}_j)f(\mathbf{q}_j - \mathbf{q}_k)f(\mathbf{q}_k - \mathbf{q}_i) \pm \ldots\;. \tag{B.22}$$

The upper sign refers to bosons, the lower to fermions. For sufficiently high temperatures, so that the average spacing between the particles obeys the inequality (v is the specific volume)

$$v^{1/3} \gg \lambda\;, \tag{B.23}$$

we find that $f(\mathbf{q}_i - \mathbf{q}_j)$ is vanishingly small for $|\mathbf{q}_i - \mathbf{q}_j| \gg \lambda$, and therefore only the first term in (B.22) is significant; according to the preceding section, it just yields the classical partition integral, (B.16).

The more factors f that are present in (B.22), the stronger the constraints on the spatial integration region in (B.16). The leading quantum correction therefore comes from the second sum in (B.22), which we can rewrite in the following approximate way:

$$1 \pm \sum_{i<j} \big(f(\mathbf{q}_i - \mathbf{q}_j)\big)^2 \approx \prod_{i<j} \big(1 \pm \big(f(\mathbf{q}_i - \mathbf{q}_j)\big)^2\big) = \mathrm{e}^{-\beta \sum_{i<j} \tilde{v}_i(\mathbf{q}_i - \mathbf{q}_j)} \ . \quad \text{(B.24)}$$

Here, the effective potential

$$\tilde{v}_i(\mathbf{q}_i - \mathbf{q}_j) = -kT \log\Big(1 \pm \mathrm{e}^{-2\pi|\mathbf{q}_i - \mathbf{q}_j|/\lambda^2}\Big) \qquad\qquad\qquad \text{(B.25)}$$

is attractive for bosons and repulsive for fermions. This effective potential arises from the symmetry properties of the wave function and not from any microscopic mutual interaction of the particles. It permits us to take the leading quantum correction into account within the classical partition integral. For the ideal gas, these quantum corrections lead to contributions of the order of $\hbar^3$ in the thermodynamic quantities, as we have seen in Sect. 4.2.

b) The exact quantum-mechanical expression for the partition function is given by

$$\begin{aligned}
Z &= \frac{1}{N!} \sum_{\{\mathbf{p}_i\}} {}_s\langle p| \, \mathrm{e}^{-\beta\hat{H}} \, |p\rangle_s \\
&= \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3}\right)^N \int d^{3N}p \int d^{3N}q \ {}_s\langle p| \, \mathrm{e}^{-\beta\hat{H}} \, |q\rangle \, \langle q|p\rangle_s \ .
\end{aligned} \qquad \text{(B.26)}$$

If we neglect exchange effects (symmetrization of the wave function), we obtain

$$\begin{aligned}
Z &= \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3}\right)^N \int d^{3N}p \int d^{3N}q \quad \langle p| \, \mathrm{e}^{-\beta\hat{H}} \, |q\rangle \, \langle q|p\rangle \\
&= \frac{1}{N!} \left(\frac{1}{(2\pi\hbar)^3}\right)^N \int d^{3N}p \int d^{3N}q \, I \ .
\end{aligned} \qquad \text{(B.27)}$$

To compute the integrands which occur in this expression, we introduce the following relation, initially for a single particle,

$$I = \langle p| \, \mathrm{e}^{-\beta\hat{H}} \, |q\rangle \, \langle q|p\rangle \, V = \mathrm{e}^{\mathrm{i}pq/\hbar} \mathrm{e}^{-\beta\hat{H}} \mathrm{e}^{-\mathrm{i}pq/\hbar} \ . \qquad\qquad \text{(B.28)}$$

After the last equals sign and in the following, $\hat{H}$ denotes the Hamiltonian in the coordinate representation. To calculate I, we derive a differential equation for I using the Baker–Hausdorff formula:

$$\frac{\partial I}{\partial \beta} = -\mathrm{e}^{\mathrm{i}pq/\hbar}\hat{H}\mathrm{e}^{-\beta\hat{H}}\mathrm{e}^{-\mathrm{i}pq/\hbar} = -\mathrm{e}^{\mathrm{i}pq/\hbar}\hat{H}\mathrm{e}^{-\mathrm{i}pq/\hbar}I$$

$$= -\left(\hat{H} - \mathrm{i}\left[-\frac{pq}{\hbar}, \hat{H}\right] - \frac{1}{2\hbar^2}[pq, [pq, \hat{H}]] + \dots\right)I \tag{B.29}$$

$$= -\left[\hat{H} - \frac{\hbar^2}{2m}\left(-\frac{2\mathrm{i}}{\hbar}p\frac{\partial}{\partial q} - \frac{p^2}{\hbar^2}\right)I\right] .$$

The higher-order commutators (indicated by dots) vanish, so that

$$\frac{\partial I}{\partial \beta} = \left[-H(p, q) + \frac{\hbar^2}{2m}\left(-\frac{2\mathrm{i}}{\hbar}p\frac{\partial}{\partial q} + \frac{\partial^2}{\partial q^2}\right)\right]I , \tag{B.29'}$$

where $H(p, q)$ is the classical Hamilton function. To solve this differential equation, we use the ansatz:

$$\chi = \mathrm{e}^{\beta H(p, q)}I . \tag{B.30}$$

We find the following differential equation for χ from (B.29'):

$$\frac{\partial \chi}{\partial \beta} = H(p, q)\chi + \mathrm{e}^{\beta H(p, q)}\frac{\partial I}{\partial \beta} = \mathrm{e}^{\beta H(p, q)}\frac{\hbar^2}{2m}\left(\frac{2\mathrm{i}}{\hbar}p\frac{\partial}{\partial q} + \frac{\partial^2}{\partial q^2}\right)I$$

$$= \mathrm{e}^{\beta H(p, q)}\frac{\hbar^2}{2m}\left(\frac{2\mathrm{i}}{\hbar}p\frac{\partial}{\partial q} + \frac{\partial^2}{\partial q^2}\right)\mathrm{e}^{\beta H(p, q)}\chi$$

$$= \frac{\hbar^2 \beta}{2m}\left[\frac{2\mathrm{i}p}{\hbar}\frac{\partial V}{\partial q} - \frac{2\mathrm{i}p}{\hbar\beta}\frac{\partial}{\partial q} - \frac{\partial^2 V}{\partial q^2} + \beta\left(\frac{\partial V}{\partial q}\right)^2\right. \tag{B.31}$$

$$\left. - 2\frac{\partial V}{\partial q}\frac{\partial}{\partial q} + \beta^{-1}\frac{\partial^2}{\partial q^2}\right]\chi .$$

Transferring to a many-body system with the coordinates and momenta q_i and p_i yields

$$\frac{\partial \chi}{\partial \beta} = \sum_i \frac{\hbar^2 \beta}{2m_i}\left[\frac{2\mathrm{i}p_i}{\hbar}\frac{\partial V}{\partial q_i} - \frac{2\mathrm{i}p_i}{\hbar\beta}\frac{\partial}{\partial q_i} - \frac{\partial^2 V}{\partial q_i^2}\right.$$

$$\left. + \beta\left(\frac{\partial V}{\partial q_i}\right)^2 - 2\frac{\partial V}{\partial q_i}\frac{\partial}{\partial q_i} + \beta^{-1}\frac{\partial^2}{\partial q_i^2}\right]\chi . \tag{B.31'}$$

The solution of this equation is obtained with the aid of a power series expansion in $\hbar$:

$$\chi = 1 + \hbar\chi_1 + \hbar^2\chi_2 + \mathcal{O}(\hbar^3) . \tag{B.32}$$

Because of (B.28) and (B.30), χ must obey the boundary condition $\chi = 1$ for $\beta = 0$. Inserting this ansatz into (B.31'), we obtain

$$\frac{\partial \chi_1}{\partial \beta} = \pm \mathrm{i}\beta \sum_i \frac{p_i}{m_i} \frac{\partial V}{\partial q_i} \tag{B.33a}$$

and

$$\frac{\partial \chi_2}{\partial \beta} = \sum_i \frac{1}{2m_i} \left[-2\mathrm{i}\beta p_i \frac{\partial V}{\partial q_i} \chi_1 + 2\mathrm{i}p_i \frac{\partial \chi_1}{\partial q_i} - \beta \frac{\partial^2 V}{\partial q_i{}^2} + \beta^2 \left(\frac{\partial V}{\partial q_i} \right)^2 \right] . \tag{B.33b}$$

From this, it follows that

$$\chi_1 = -\frac{\mathrm{i}\beta^2}{2} \sum_i \frac{p_i}{m_i} \frac{\partial V}{\partial q_i} \tag{B.34a}$$

$$\chi_2 = \pm \frac{\beta^4}{8} \left(\sum_i \frac{p_i}{m_i} \frac{\partial V}{\partial q_i} \right)^2 + \frac{\beta^3}{6} \sum_i \sum_k \frac{p_i}{m_i} \frac{p_k}{m_k} \frac{\partial^2 V}{\partial q_i \partial q_k}$$

$$+ \frac{\beta^3}{6} \sum_i \frac{1}{m_i} \left(\frac{\partial V}{\partial q_i} \right)^2 - \frac{\beta^2}{4} \sum_i \frac{1}{m_i} \frac{\partial^2 V}{\partial q_i{}^2} . \tag{B.34b}$$

Inserting (B.30) and (B.27), we finally obtain the partition function

$$Z = \int \frac{d^{3N}q \, d^{3N}p}{(2\pi\hbar)^{3N} \, N!} \, \mathrm{e}^{-\beta H(p,q)} (1 + \hbar \chi_1 + \hbar^2 \chi_2) . \tag{B.35}$$

The term of order $\mathcal{O}(\hbar)$ vanishes, since χ_1 is an odd function of p_1, so that the remaining expression is

$$Z = \left(1 + \hbar^2 \langle \chi_2 \rangle_{\mathrm{cl}}\right) Z_{\mathrm{cl}} . \tag{B.36}$$

Here, $\langle \ \rangle_{\mathrm{cl}}$ refers to the average value with the classical distribution function, and Z_{cl} is the classical partition function. From it, we thus obtain for the free energy

$$F = -\frac{1}{\beta} \log Z = F_{\mathrm{cl}} - \frac{1}{\beta} \log \left(1 + \hbar^2 \langle \chi_2 \rangle_{\mathrm{cl}}\right) \approx F_{\mathrm{cl}} - \frac{\hbar^2}{\beta} \langle \chi_2 \rangle_{\mathrm{cl}} . \tag{B.37}$$

With

$$\langle p_i p_k \rangle_{\mathrm{cl}} = \frac{m}{\beta} \delta_{ik} \tag{B.38}$$

and

$$\left\langle \frac{\partial^2 V}{\partial q_i{}^2} \right\rangle_{\mathrm{cl}} = \beta \left\langle \left(\frac{\partial V}{\partial q_i} \right)^2 \right\rangle$$

(proof via partial integration), it follows that

$$F = F_{\mathrm{cl}} + \frac{\hbar^2}{24m(kT)^2} \sum_i \left\langle \left(\frac{\partial V}{\partial q_i} \right)^2 \right\rangle_{\mathrm{cl}} . \tag{B.39}$$

The classical approximation is therefore best at high T and large m.

Remark: Using the thermal wavelength $\lambda = 2\pi\hbar/\sqrt{2\pi m k T}$ and the length l which characterizes the spatial variation of the potential (range of the interaction potentials), the correction in Eq. (B.39) becomes $\frac{\lambda^2}{l^2}\frac{V^2}{kT}$. This gives as a condition for the validity of the classical approximation

$$\lambda \ll l \qquad \text{(from the non-commutativity of } \hat{K} \text{ and } \hat{V}) \qquad (B.39a)$$

and, according to Eq. (B.23)

$$\lambda \ll \left(\frac{V}{N}\right)^{1/3} \qquad \text{(from symmetrization of the wave function)}. \qquad (B.39b)$$

Rearranging Eq. (2.7.20), one gets

$$T[\text{K}] = \frac{5 \times 10^{-38}}{\lambda^2[\text{cm}^2]m[\text{g}]} = \frac{5.56 \times 10^5}{\lambda^2[\text{Å}^2]m[m_{\text{e}}]}.$$

For *electrons* in solids, we have $\left(\frac{V}{N}\right)^{1/3} \approx 1\text{Å}$, so that even at a temperature of $T = 5.5 \times 10^5$ K, their behavior remains nonclassical.

For a gas with the mass number A: $m = A \cdot m_{\text{p}}$, $\left(\frac{V}{N}\right)^{1/3} \approx 10^{-7}\text{cm}$, $T \approx \frac{3}{A}$ K

B.3 Quantum Corrections to the Second Virial Coefficient $B(T)$

B.31 Quantum Corrections Due to Exchange Effects

We neglect the interactions; however, the second virial coefficient from Eq. (5.3.7)

$$B(T) = \left(Z_2 - \frac{1}{2}Z_1^2\right)\frac{V}{Z_1^2} \qquad (B.40)$$

is still nonzero due to exchange effects. A two-particle eigenstate has the form

$$|p_1, p_2\rangle = \frac{1}{\sqrt{2!}}\left(|p_1\rangle|p_2\rangle \pm |p_2\rangle|p_1\rangle\right) \qquad \text{for } p_1 \neq p_2$$

$$(B.41)$$

$$|p_1, p_2\rangle = \begin{cases} |p_1\rangle|p_1\rangle & \text{bosons} \\ & \text{for } p_1 = p_2 \\ 0 & \text{fermions}. \end{cases}$$

The partition function for two non-interacting particles is

$$Z_2 = \text{Tr}\, e^{-(\hat{p}_1^2+\hat{p}_2^2)/2mkT} = \frac{1}{2}\sum_{\substack{p_1,p_2 \\ p_1 \neq p_2}} e^{-(p_1^2+p_2^2)/2mkT} + \begin{cases} \sum_p e^{-p^2/mkT} \\ 0 \end{cases}$$

$$= \frac{1}{2}\sum_{p_1}\sum_{p_2} e^{-(p_1^2+p_2^2)/2mkT} \pm \frac{1}{2}\sum_p e^{-p^2/mkT}$$

$$= \frac{1}{2}Z_1^2 \pm \frac{1}{2}\sum_p e^{-p^2/mkT} \qquad \text{for} \qquad \begin{cases} \text{bosons} \\ \text{fermions} \end{cases}. \qquad (B.42)$$

From this[11], we find for the second virial coefficient (5.3.7):

$$B(T) = \mp \frac{\lambda^6}{2V} \sum_p e^{-p^2/mkT} = \mp \frac{\lambda^3}{2^{5/2}}$$

$$= \mp \frac{1}{2} \left(\frac{\pi\hbar^2}{mkT} \right)^{3/2} \quad \text{for} \begin{cases} \text{bosons} \\ \text{fermions} \end{cases} . \quad \text{(B.43)}$$

B.32 Quantum-Mechanical Corrections to $B(T)$ Due to Interactions

In the semiclassical limit (unsymmetrized wave functions), from Eq. (B.35) we obtain for the partition function of two particles

$$Z_2 = \frac{1}{2} \left(\frac{1}{\lambda^3} \right)^2 \int d^3x_1 \, d^3x_2 \, e^{-v_{12}(x_1-x_2)/kT} \left(1 + \underbrace{\hbar\chi_1}_{=0} + \hbar^2\chi_2 \right) . \quad \text{(B.44)}$$

This leads to the following expression for the second virial coefficient ((5.3.7), (B.40)):

$$B = \frac{1}{2} \left(\frac{1}{V} \int d^3x_1 \, d^3x_2 \left(e^{-v_{12}(x_1-x_2)/kT} (1 + \hbar^2\chi_2) - 1 \right) \right) . \quad \text{(B.45)}$$

The quantum correction is therefore given by

$$\begin{aligned} B_{\text{qm}} &= \int d^3y \, e^{-v(\mathbf{y})/kT} \frac{1}{kT} \left(\frac{\partial v}{\partial \mathbf{y}} \right)^2 \frac{\hbar^2}{24m(kT)^2} \\ &= \frac{\hbar^2\pi}{6m(kT)^3} \int_0^\infty dr \, r^2 e^{-v(r)/kT} \left(\frac{\partial v}{\partial r} \right)^2 , \end{aligned} \quad \text{(B.46)}$$

where in the second line we have assumed a central potential. This quantum correction adds to the classical value of B; it is always positive. The exchange corrections (B.43) are of the order $\mathcal{O}(\hbar^3)$. The lowest-order quantum corrections, i.e. (B.46), are of order $\hbar^2$. At low temperatures, these quantum effects (due to non-commuting $\hat{V}$ and $\hat{K}$) become important. The contribution from symmetrization is relatively small.

B.33 The Second Virial Coefficient and the Scattering Phase

One can also represent the second virial coefficient in terms of the phase shift of the interaction potential. The starting point is the formula for the virial

---

[11] $Z_1 \equiv \sum_p e^{-p^2/2mkT} = \frac{V}{\lambda^3}$
   We do not take the spin degeneracy factor $g = 2S + 1$ into account here.

coefficient, Eq. (5.3.7)

$$B = -\left(\frac{Z_2}{Z_1^2} - \frac{1}{2}\right) V \;. \tag{B.47}$$

The interaction does not appear in the partition function for a single particle

$$Z_1 = \sum_{\mathbf{p}} e^{-\frac{\mathbf{p}^2}{2mkT}} = \frac{V}{(2\pi\hbar)^3} \int d^3p \; e^{-\frac{p^2}{2mkT}} = \frac{V}{\lambda^3} \;. \tag{B.48}$$

The Hamiltonian for two particles is given by

$$\hat{H} = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m} + V(\mathbf{x}_1 - \mathbf{x}_2) \tag{B.49}$$

and, introducing coordinates for the center of mass (CM) and the relative position (r):

$$\mathbf{x}_{\mathrm{CM}} = \frac{1}{2}(\mathbf{x}_1 + \mathbf{x}_2) \;, \qquad \mathbf{x}_{\mathrm{r}} = \mathbf{x}_2 - \mathbf{x}_1 \;, \tag{B.50}$$

it can be written as

$$\hat{H} = \frac{\mathbf{p}_{\mathrm{CM}}^2}{4m} + \frac{\mathbf{p}_{\mathrm{r}}^2}{m} + V(\mathbf{x}_{\mathrm{r}}) \;. \tag{B.51}$$

Then the partition function for two particles becomes

$$Z_2 = \mathrm{Tr}_{\mathrm{CM}}\, e^{-\frac{\mathbf{p}_{\mathrm{CM}}^2}{4mkT}} \, \mathrm{Tr}_{\mathrm{r}}\, e^{-\left(\frac{\mathbf{p}_{\mathrm{r}}^2}{m} + V(\mathbf{x}_r)\right)/kT} = 2^{3/2} \frac{V}{\lambda^3} \sum_n e^{-\frac{\varepsilon_n}{kT}} \;. \tag{B.52}$$

In this expression, ε_n denotes the energy levels of the two-particle system in relative coordinates taking into account the different symmetries of bosons and fermions. It leads to

$$B = -\left(2^{3/2}\lambda^3 \sum_n e^{-\varepsilon_n/kT} - \frac{V}{2}\right) \;. \tag{B.53}$$

We now remind the reader that for non-interacting particles, (B.43) gives for the second virial coefficient

$$B^{(0)} = -\left(2^{3/2}\lambda^3 \sum_n e^{-\varepsilon_n^0/kT} - \frac{V}{2}\right) = \mp 2^{-5/2}\lambda^3 \quad \begin{cases} \text{bosons} \\ \text{fermions} \end{cases} . \tag{B.54}$$

The change in the second virial coefficient due to the interactions of the particles is thus given by

$$B(T) - B^0(T) = -2^{3/2}\lambda^3 \sum_n \left(e^{-\beta\varepsilon_n} - e^{-\beta\varepsilon_n^{(0)}}\right) \;. \tag{B.55}$$

The energy levels of the non-interacting system are

$$\varepsilon_n^{(0)} = \frac{\hbar^2 k^2}{m} , \qquad (B.56a)$$

while in the interacting system, along with the continuum states of energy

$$\varepsilon_n = \frac{\hbar^2 k^2}{m} , \qquad (B.56b)$$

bonding states of energy ε_B can also occur. The values of k are found from the boundary conditions and are different for the interacting system and for the free system, so that also different densities of states are obtained. The number of energy levels $g(k)dk$ in the interval $[k, k + dk]$ defines the density of states, $g(k)$. We thus find

$$B(T) - B^{(0)}(T)$$

$$= -2^{3/2}\lambda^3 \left[\sum_B e^{-\varepsilon_B/kT} + \int_0^\infty dk \left(g(k) - g^{(0)}(k) \right) e^{-\varepsilon_k/kT} \right] . \quad (B.57)$$

The change in the density of states which occurs here can be related to the derivative of the scattering phase. We assume that the potential $V(r)$ has rotational symmetry and consider the eigenstates of the relative part of the Hamiltonian. Then we can represent the wave functions for the free and the interacting problem in the form[12]

$$\psi_{klm}^{(0)}(\mathbf{x}) = A_{klm}^{(0)} Y_{lm}(\vartheta, \varphi) R_{kl}^{(0)}(r)$$
$$\psi_{klm}(\mathbf{x}) = A_{klm} Y_{lm}(\vartheta, \varphi) R_{kl}(r) . \qquad (B.58)$$

The free radial functions are given in terms of spherical Bessel functions. The asymptotic forms for $r \to \infty$ are

$$R_{kl}^{(0)}(r) = \frac{1}{kr} \sin\left(kr + \frac{l\pi}{2} \right)$$
$$R_{kl}(r) = \frac{1}{kr} \sin\left(kr + \frac{l\pi}{2} + \delta_l(k) \right) \qquad (B.59)$$

with the phase shifts known from scattering theory, $\delta_l(k)$. The allowed values of k are found from the boundary conditions

$$R_{kl}^{(0)}(R) = R_{kl}(R) = 0 \qquad (B.60)$$

at a large radius R (which finally goes to infinity). From this it follows that

$$kR + \frac{l\pi}{2} = \pi n \qquad \text{and} \qquad kR + \frac{l\pi}{2} + \delta_l(k) = \pi n , \qquad (B.61)$$

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[12] QM I, Chap. 17

where $n = 0, 1, 2, \ldots$. The values of k therefore depend upon l. Neighboring values of k for fixed l differ by

$$\Delta k^{(0)} = \frac{\pi}{R} \qquad \text{and} \qquad \Delta k = \frac{\pi}{R + \frac{\partial \delta_l(k)}{\partial k}} \; . \tag{B.62}$$

We still must take into account the fact that every value of l occurs with a multiplicity of $(2l + 1)$. Since each interval Δk or $\Delta k^{(0)}$ contains a value of k, the densities of states are

$$g_l^{(0)}(k) = \frac{2l + 1}{\pi} R \qquad \text{and} \qquad g_l(k) = \frac{2l + 1}{\pi} \left[R + \frac{\partial \delta_l(k)}{\partial k} \right] \; . \tag{B.63}$$

From this the second virial coefficient follows:

$$B(T) - B^{(0)}(T)$$
$$= -2^{3/2} \lambda^3 \left\{ \sum_B e^{-\varepsilon_B/kT} + \frac{1}{\pi} \int_0^\infty dk \sum_l{}' f_l (2l + 1) \frac{\partial \delta_l(k)}{\partial k} e^{-\frac{\hbar^2 k^2}{mkT}} \right\} \; . \tag{B.64}$$

Now we need to determine the values of l which are allowed by the symmetry properties. For bosons, we have $\psi(-\mathbf{x}) = \psi(\mathbf{x})$, and for spin-1/2 fermions, $\psi(-\mathbf{x}) = \pm\psi(\mathbf{x})$, depending on whether a spin singlet or a triplet state is considered. For spin-0 bosons, we thus have $l = 0, 2, 4, \ldots$ and $f_l = 1$. For spin-1/2 fermions,

$$
\begin{aligned}
l &= 0, 2, 4, \ldots & f_l &= 1 & \text{(singlet)} \\
l &= 1, 3, 5, \ldots & f_l &= 3 & \text{(triplet)} \, .
\end{aligned}
\tag{B.65}
$$

The change in the second virial coefficient is expressed in terms of the binding energies and the phase shifts. An important contribution to the k-integral comes from the resonances. Very sharp resonances have $\frac{\partial \delta_l(k)}{\partial k} = \pi \delta(k - k_0)$, and one obtains a similar contribution to that of the bonding states, however with positive energy. More generally, one can interpret the quantity

$$\frac{1}{\hbar} \frac{\partial \delta_l(k)}{\partial k} = \frac{\partial E}{\partial \hbar k} \frac{\partial \delta_l}{\partial E} = v \frac{\partial \delta_l}{\partial E} \, ,$$

as velocity times the dwell time[13] in the potential. The shorter the dwell time within the potential, the more nearly ideal is the interacting gas.

Literature:
S. K. Ma, *Statistical Mechanics*, Sect. 14.3, World Scientific, Singapore, 1985
E. Beth and G. E. Uhlenbeck, Physics **4**, 915 (1937)
A. Pais and G. E. Uhlenbeck, Phys. Rev. **116**, 250 (1959)

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[13] See e.g. QM I, Eq. (3.126)

Problems for Appendix B.:

B.1 Carry out in detail the rearrangements which occur in Eq. (B.3f).
B.2 Carry out the rearrangement in Eq. (B.28).
B.3 Show that (B.29′) follows from (B.29).
B.4 Determine the behavior of the effective potentials $\tilde{v}(\mathbf{x})$ in Eq. (B.25) for small and large distances. Plot $\tilde{v}(\mathbf{x})$ for bosons and fermions.

C. The Perturbation Expansion

For the calculation of susceptibilities and in other problems in which the Hamiltonian $H = H_0 + V$ is composed of an "unperturbed" part and a perturbation V, we require the relation

$$\mathrm{e}^{H_0+V} = \mathrm{e}^{H_0} + \int_0^1 dt\, \mathrm{e}^{tH_0} V \mathrm{e}^{(1-t)H_0} + \mathcal{O}(V^2)\,. \tag{C.1}$$

To prove this relation, we introduce the definition

$$A(t) = \mathrm{e}^{Ht}\mathrm{e}^{-H_0 t}$$

and take its time derivative

$$\dot{A}(t) = \mathrm{e}^{Ht}(H-H_0)\mathrm{e}^{-H_0 t} = \mathrm{e}^{Ht}V\mathrm{e}^{-H_0 t}\,.$$

By integrating over time between 0 and 1,

$$A(1) - A(0) = \mathrm{e}^{H}\mathrm{e}^{-H_0} - 1 = \int_0^1 dt\, \mathrm{e}^{Ht}V\mathrm{e}^{-H_0 t}\,,$$

we obtain after multiplication by e^{H_0} the exact identity

$$\mathrm{e}^{H} = \mathrm{e}^{H_0} + \int_0^1 dt\, \mathrm{e}^{Ht}V\mathrm{e}^{(1-t)H_0}\,. \tag{C.2}$$

Expanding $\mathrm{e}^{Ht} = \mathrm{e}^{(H_0+V)t}$ in a power series, we obtain the assertion (C.1).

Iteration of the likewise exact identity which follows from (C.2),

$$\mathrm{e}^{Ht} = \mathrm{e}^{H_0 t} + \int_0^t dt'\, \mathrm{e}^{Ht'}V\mathrm{e}^{(t-t')H_0}\,, \tag{C.2′}$$

yields

$$\mathrm{e}^{H} = \mathrm{e}^{H_0} + \int_0^1 dt\, \mathrm{e}^{H_0 t}V\mathrm{e}^{(1-t)H_0} +$$

$$+ \int_0^1 dt \int_0^t dt'\, \mathrm{e}^{H_0 t'}V\mathrm{e}^{(t-t')H_0}V\mathrm{e}^{(1-t)H_0} + \ldots +$$

$$+ \int_0^1 dt_1 \int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n \mathrm{e}^{H_0 t_n}V\mathrm{e}^{(t_{n-1}-t_n)H_0}V\mathrm{e}^{(t_{n-2}-t_{n-1})H_0} \ldots$$

$$\times V\mathrm{e}^{(1-t_1)H_0} + \ldots\,. \tag{C.3}$$

With the substitution

$$1 - t_n = u_n, 1 - t_{n-1} = u_{n-1}, \ldots, 1 - t_1 = u_1$$

we obtain

$$e^H = e^{H_0} + \sum_{n=1}^{\infty} \int_0^1 du_1 \int_{u_1}^1 du_2 \ldots \int_{u_{n-1}}^1 du_n \, e^{(1-u_n)H_0} V e^{(u_n - u_{n-1})H_0} \ldots$$
$$\times V e^{(u_2 - u_1)H_0} V e^{u_1 H_0} .$$

$$(C.3')$$

D. The Riemann ζ-Function and the Bernoulli Numbers

In dealing with fermions, the following integrals occur:

$$\frac{1}{\Gamma(\nu)} \int_0^{\infty} dx \, \frac{x^{\nu-1}}{e^x + 1} = \sum_{k=1}^{\infty} (-1)^{k+1} \frac{1}{k^\nu}$$

$$= \sum_{k=1}^{\infty} \frac{1}{k^\nu} - 2 \sum_{l=1}^{\infty} \frac{1}{(2l)^\nu} = \left(1 - 2^{1-\nu}\right) \zeta(\nu) . \quad (D.1)$$

After the last equals sign, the Riemann ζ-function

$$\zeta(\nu) = \sum_k \frac{1}{k^\nu} \qquad \text{for } \mathrm{Re}\,\nu > 1 \tag{D.2}$$

was introduced. The integrals which occur for bosons can also be related directly to it:

$$\frac{1}{\Gamma(\nu)} \int_0^{\infty} dx \, \frac{x^{\nu-1}}{e^x - 1} = \sum_{k=1}^{\infty} \frac{1}{k^\nu} = \zeta(\nu) . \tag{D.3}$$

According to the theorem of residues, $\zeta(\nu)$ can be written in the following manner:

$$\zeta(\nu) = \frac{1}{4i} \int_C dz \, \frac{\cot \pi z}{z^\nu} = \frac{1}{4i} \int_{C'} dz \, \frac{\cot \pi z}{z^\nu} . \tag{D.4}$$

Definition of the Bernoulli numbers:

$$\frac{1}{2} z \cot \frac{1}{2} z = 1 - \sum_{n=1}^{\infty} B_n \frac{z^{2n}}{(2n)!} , \tag{D.5}$$
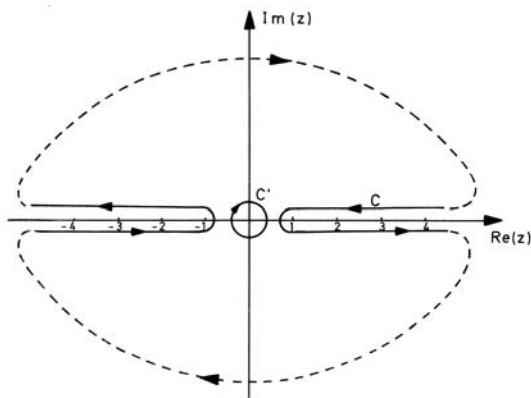
Fig. D.1. The integration path in (D.4)

$$B_1 = \frac{1}{6}, \qquad B_2 = \frac{1}{30}, \qquad B_3 = \frac{1}{42}, \dots$$

$\nu = 2k:$

$$\zeta(2k) = \frac{\pi^{-1}}{4i} \int\limits_{C'} dz \, \frac{1 - \sum_{n=1}^{\infty} B_n \frac{(2z\pi)^{2n}}{(2n)!}}{z^{2k}\pi z} = \frac{(2\pi)^{2k} B_k}{2(2k)!}, \tag{D.6}$$

since only the term $n = k$ makes a nonzero contribution.

$$\frac{1}{\Gamma(2k)} \int dx \, \frac{x^{2k-1}}{e^x + 1} = \frac{\left(2^{2k-1} - 1\right)\pi^{2k} B_k}{(2k)!}$$

$$\int_0^{\infty} dx \, \frac{x^{2k-1}}{e^x + 1} = \frac{\left(2^{2k-1} - 1\right)\pi^{2k} B_k}{2k} \tag{D.7}$$

$$\int_0^{\infty} dx \, \frac{x^{2k-1}}{e^x - 1} = (2k-1)!\frac{(2\pi)^{2k} B_k}{2(2k)!} = \frac{(2\pi)^{2k} B_k}{4k}. \tag{D.8}$$

E. Derivation of the Ginzburg–Landau Functional

For clarity, to carry out the derivation we first consider a system of ferromagnetic Ising spins $(n = 1)$, which are described by the Hamiltonian

$$H = -\frac{1}{2}\sum_{l,l'} J(l - l')S_l S_{l'} - h\sum_l S_l, \tag{E.1}$$

where S_l takes on the values $S_l = \pm 1$. We assume a d-dimensional, simple cubic lattice; its lattice constant is taken to be a_0 and the side length of the crystal to be L. This d-dimensional lattice is then divided into cells of volume
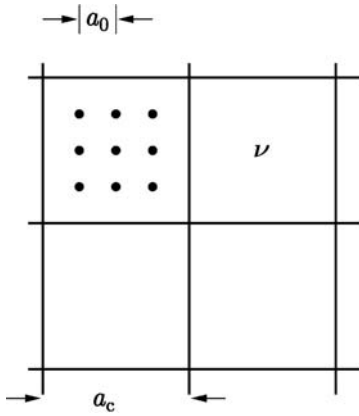
Fig. E.1. Division of the lattice into cells

$v = a_c^d$, whereby the linear dimensions of the cells a_c are assumed to fulfill the inequality $a_0 \ll a_c \ll L$. The number of cells is $N_c = \left(\frac{L}{a_c}\right)^d = \frac{N}{\tilde{N}}$, and the number of lattice points within a cell is $\tilde{N} = \left(\frac{a_c}{a_0}\right)^d$. Finally, we define the cell spin of cell ν:

$$m_\nu = \frac{1}{\tilde{N}} \sum_{l \in \nu} S_l \,, \tag{E.2}$$

whose range of values lies in the interval $-1 \le m_\nu \le 1$. We now define a new, effective Hamiltonian $\mathcal{F}(\{m_\nu\})$ for the cell spins by carrying out the exact rearrangement

$$Z = \mathrm{Tr}\, e^{-\beta H} \equiv \sum_{\{S_l = \pm 1\}} e^{-\beta H} = \sum_{\{m_\nu\}} \mathrm{Tr}\left(e^{-\beta H} \prod_\nu \delta_{\sum_{l \in \nu} S_l, \tilde{N} m_\nu}\right)$$
$$\equiv \sum_{\{m_\nu\}} e^{-\beta \mathcal{F}(\{m_\nu\})} \quad, \tag{E.3}$$

which corresponds to a partial evaluation of the trace, i.e.

$$\mathcal{F}(\{m_\nu\}) = -\frac{1}{\beta} \log \sum_{\{S_l = \pm 1\}} e^{-\beta H} \prod_\nu \delta_{\sum_{l \in \nu} S_l, \tilde{N} m_\nu} \quad. \tag{E.4}$$

For sufficiently many spins per cell, m_ν becomes a continuous variable $\left(\Delta m_\nu = \frac{2}{\tilde{N}}\right)$

$$\sum_{m_\nu} \cdots \longrightarrow \frac{\tilde{N}}{2} \int_{-1}^{1} dm_\nu \cdots \tag{E.5}$$

$$\mathcal{F}(\{m_\nu\}) = \tilde{N} f(\{m_\nu\}) \qquad \text{for sufficiently large } \tilde{N}\,.$$

The field term expressed in the new variables is

$$-h \sum_l S_l = -h \sum_\nu \sum_{l \in \nu} S_l = -h \tilde{N} \sum_\nu m_\nu \quad . \tag{E.6}$$

Thus, the factor $\mathrm{e}^{-h \sum_l S_l} = \mathrm{e}^{-h \tilde{N} \sum_\nu m_\nu}$ is not affected at all by the trace operation after the third equals sign in (E.3), and is transferred unchanged to $\mathcal{F}(\{m_\nu\})$. This has the important effect that all the remaining terms in $\mathcal{F}(\{m_\nu\})$ are independent of h, and due to the invariance of the exchange Hamiltonian (see Chap. 6) under the transformation $\{S_l\} \rightarrow \{-S_l\}$, they are also even functions of the m_ν.

We can decompose $f(\{m_\nu\})$ into terms which depend only on one, two, $\ldots m_\nu$:

$$f(\{m_\nu\}) = \sum_{\nu=1}^{N_z} f_1(m_\nu) + \frac{1}{2} \sum_{\mu \neq \nu} f_2^{\nu\mu}(m_\nu, m_\mu) + \ldots \quad . \tag{E.7}$$

The Taylor expansion of the functions in (E.7) is given by

$$f_1(m_\nu) = f_1(0) + c_2 m_\nu^2 + c_4 m_\nu^4 + \ldots - h m_\nu \tag{E.8a}$$

and

$$f_2(m_\nu, m_\mu) = - \sum_{\mu,\nu} 2 K_{\mu\nu} m_\mu m_\nu + \ldots \quad . \tag{E.8b}$$

It then follows from (E.3) and (E.5) that

$$Z = \prod_\nu \frac{\tilde{N}}{2} \int_{-1}^{1} dm_\nu e^{-\beta \tilde{N} f(\{m_\nu\})} \tag{E.8c}$$

with

$$f(\{m_\nu\}) = N_c f_1(0) + \sum_\nu \left(a m_\nu^2 + \frac{b}{2} m_\nu^4 + \ldots - h m_\nu \right)$$
$$+ \frac{1}{2} \sum_{\mu,\nu} K_{\mu\nu} (m_\mu - m_\nu)^2 + \ldots \quad . \tag{E.8d}$$

The coefficients $f_1(0), a, b$ and $K_{\mu\nu}$ are functions of T and $J_{ll'}$. The cells, like the original lattice, form a simple cubic lattice, which is the cell lattice with lattice constants a_z and lattice vectors $\mathbf{a}_\nu$. Let N_i be the number of lattice points (cells) in the direction i, whose product $N_1 N_2 N_3$ must give N_c; we then define the wavevectors with components

$$k_i = \frac{2\pi r_i}{N_i a_c}, \text{where} - \frac{N_i}{2} < r_i \leq \frac{N_i}{2} \quad . \tag{E.9}$$

The reciprocal lattice vectors for the cell lattice are given by

$$\mathbf{g} = \frac{2\pi}{a_z}(n_1, n_2, n_3) \ . \tag{E.10}$$

The Fourier transform of the cell spins is introduced via

$$m_\nu = \frac{1}{\sqrt{N_c}} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{a}_\nu} m_{\mathbf{k}} \tag{E.11a}$$

$$m_{\mathbf{k}} = \frac{1}{\sqrt{N_c}} \sum_{\nu} e^{-i\mathbf{k}\mathbf{a}_\nu} m_\nu \ . \tag{E.11b}$$

The orthogonality and completeness relations of the Fourier coefficients are

$$\sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{a}_\nu - \mathbf{a}_{\nu'})} = N_c \delta_{\nu\nu'} \tag{E.12a}$$

$$\sum_{\nu} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{a}_\nu} = N_c \Delta(\mathbf{k}-\mathbf{k}') \equiv N_c \begin{cases} 1 & \text{for } \mathbf{k}-\mathbf{k}' = \mathbf{g} \\ 0 & \text{otherwise} \end{cases} \ , \tag{E.12b}$$

where $\mathbf{g}$ is an arbitrary vector of the reciprocal lattice.

The transformation of the individual terms of the free energy is given by

$$a \sum_{\nu} m_\nu^2 = a \sum_{\mathbf{k}} m_{\mathbf{k}} m_{-\mathbf{k}} \ ,$$

$$b \sum_{\nu} m_\nu^4 = \frac{b}{N_c^2} \sum_{\nu} \sum_{\mathbf{k}_1,\ldots,\mathbf{k}_4} e^{i(\mathbf{k}_1+\ldots+\mathbf{k}_4)\mathbf{a}_\nu} m_{\mathbf{k}_1} \ldots m_{\mathbf{k}_4}$$

$$= \frac{b}{N_c} \sum_{\mathbf{k}_1,\ldots\mathbf{k}_4} \Delta(\mathbf{k}_1+\ldots+\mathbf{k}_4) m_{\mathbf{k}_1} m_{\mathbf{k}_2} m_{\mathbf{k}_3} m_{\mathbf{k}_4} \ , \tag{E.13a}$$

$$h\tilde{N} \sum_{\nu} m_\nu = h\tilde{N}\sqrt{N_c} m_{\mathbf{k}=\mathbf{0}} \quad .$$

Due to translational invariance, the interaction $K_{\mu\nu}$ depends only on the separation,

$$\frac{1}{2} \sum_{\nu,\nu'} K(\nu-\nu')(m_\nu - m_{\nu'})^2$$

$$= \frac{1}{2N_c} \sum_{\nu} \sum_{\delta} \sum_{\mathbf{k}\mathbf{k}'} K(\delta) e^{i\mathbf{k}\mathbf{a}_\nu} \left(1 - e^{i\mathbf{k}\mathbf{a}_\delta}\right) m_{\mathbf{k}} e^{-i\mathbf{k}'\mathbf{a}_\nu} \left(1 - e^{-i\mathbf{k}'\mathbf{a}_\delta}\right) m_{-\mathbf{k}'}$$

$$= \sum_{\mathbf{k}} v(\mathbf{k}) m_{\mathbf{k}} m_{-\mathbf{k}} \ .$$

Here, $\delta \equiv \nu - \nu'$ was introduced, and

$$v(\mathbf{k}) = \sum_\delta K(\delta)(1 - \cos \mathbf{ka}_\delta) = \sum_\delta K(\delta)\, 2 \sin^2 \frac{\mathbf{ka}_\delta}{2} \qquad (E.13b)$$

was defined. Due to the short range of the interaction coefficients $K(\delta)$, we can expand $\sin^2 \frac{\mathbf{ka}_\delta}{2}$ for small $\mathbf{k}$ in a Taylor series, and terminate the series after the first term. Taking the cubic symmetry into account, in d dimensions we find

$$v(\mathbf{k}) = \mathbf{k}^2 \frac{1}{2d} \sum_\delta K(\delta)\mathbf{a}_\delta{}^2 + \mathcal{O}(k^4) \quad . \qquad (E.13c)$$

Then the partition function in Fourier space is

$$Z = Z_0 \left(\prod_\mathbf{k} \int dm_\mathbf{k} \right) \exp \left\{ - \beta \tilde{N} \left[\sum_k (a + ck^2) m_\mathbf{k} m_{-\mathbf{k}} \right.\right.$$

$$\left.\left. + \frac{b}{2} \frac{1}{N_c} \sum_{\mathbf{k_1}...\mathbf{k_4}} \Delta(\mathbf{k_1} + ... + \mathbf{k_4})\, m_{\mathbf{k_1}} ... m_{\mathbf{k_4}} - h\sqrt{N_c}\, m_{\mathbf{k=0}} + ... \right] \right\} ,$$

$$(E.14)$$

where Z_0 is the part of the partition function which is independent of $m_\mathbf{k}$, as follows from (E.8c).

Definition of $\int dm_\mathbf{k}$:

Due to $m_\mathbf{k}^* = m_{-\mathbf{k}}$, (E.11a) can be written in the form

$$m_\nu = \frac{1}{\sqrt{N_z}} \sum_{\mathbf{k} \in HS} \left(e^{i\mathbf{ka}_\nu} (\operatorname{Re} m_\mathbf{k} + i \operatorname{Im} m_\mathbf{k}) \right.$$

$$\left. + e^{-i\mathbf{ka}_\nu} (\operatorname{Re} m_\mathbf{k} - i \operatorname{Im} m_\mathbf{k}) \right)$$

$$= \frac{1}{\sqrt{N_z}} \sum_{\mathbf{k} \in HS} \left(\underbrace{\frac{e^{i\mathbf{ka}_\nu} + e^{-i\mathbf{ka}_\nu}}{\sqrt{2}}}_{} \underbrace{(\sqrt{2} \operatorname{Re} m_\mathbf{k})}_{y_\mathbf{k}} \right. \qquad (E.15a)$$

$$\left. + i \underbrace{\frac{e^{i\mathbf{ka}_\nu} - e^{-i\mathbf{ka}_\nu}}{\sqrt{2}}}_{} \underbrace{(\sqrt{2} \operatorname{Im} m_\mathbf{k})}_{y_{-\mathbf{k}}} \right) ,$$

where the sums over $\mathbf{k}$ extend only over half of the $\mathbf{k}$-space (HS). This is an orthogonal transformation

$$\sum_\nu \left(e^{i\mathbf{ka}_\nu} + e^{-i\mathbf{ka}_\nu} \right) \left(e^{i\mathbf{k'a}_\nu} + e^{-i\mathbf{k'a}_\nu} \right) \frac{1}{2N_c} = \delta_{\mathbf{k},\mathbf{k}'} ; \qquad (E.15b)$$

and correspondingly for $\sin \mathbf{k} \mathbf{a}_\nu$. The cross terms give zero. It follows that

$$\int \prod_\nu dm_\nu \ldots = \int \prod_{\mathbf{k} \in HS} \left(\sqrt{2} d\,\mathrm{Re}\,m_\mathbf{k} \right) \left(\sqrt{2} d\,\mathrm{Im}\,m_\mathbf{k} \right) \ldots = \int \prod_\mathbf{k} dy_\mathbf{k} \ldots .$$

(E.15c)

Clearly, from (E.13b),

$$v(\mathbf{k}) = v(-\mathbf{k}) = v(\mathbf{k})^* \tag{E.15d}$$

and

$$\sum_\mathbf{k} v(\mathbf{k}) m_\mathbf{k} m_{-\mathbf{k}} = \sum_{\mathbf{k} \in HS} v(\mathbf{k}) \left(\left(\sqrt{2}\,\mathrm{Re}\,m_\mathbf{k} \right)^2 + \left(\sqrt{2}\,\mathrm{Im}\,m_\mathbf{k} \right)^2 \right)$$

$$= \sum_\mathbf{k} v(\mathbf{k}) y_\mathbf{k}^2 . \quad \text{(E.15e)}$$

In the harmonic approximation, it follows from (E.15d), as will be verified in (7.4.47), that

$$\langle m_\mathbf{k} m_{\mathbf{k}'} \rangle = \int \left(\prod_\mathbf{k} dm_\mathbf{k} \right) \frac{\mathrm{e}^{-\sum_\mathbf{k} v(\mathbf{k}) |m_\mathbf{k}|^2}}{Z} m_\mathbf{k} m_{\mathbf{k}'} = \frac{\delta_{\mathbf{k}', -\mathbf{k}}}{2v(\mathbf{k})} . \tag{E.16}$$

Continuum limit $v = a_c^d \to 0$.

If we consider wavelengths which are large compared to a_z, we take the continuum limit:

$$m(\mathbf{x}_\nu) = \frac{1}{\sqrt{v}} m_\nu \tag{E.17}$$

$$m(\mathbf{x}) = \frac{1}{\sqrt{N_c a_c^d}} \sum_{\mathbf{k} \in B} \mathrm{e}^{i\mathbf{k}\mathbf{x}} m_\mathbf{k} . \tag{E.18}$$

In the strict continuum limit, the Brillouin zone goes to ∞. The terms in the Ginzburg–Landau functional are

$$\sum_\nu m_\nu^2 = \int d^d x\, m(\mathbf{x})^2 , \qquad \sum_\nu m_\nu^4 = v \int d^d x\, m(\mathbf{x})^4 ,$$

$$\sum_\nu h m_\nu = \frac{h}{\sqrt{v}} \int d^d x\, m(\mathbf{x}) , \qquad \sum_\mathbf{k} k^2 |m_\mathbf{k}|^2 = \int d^d x \left(\nabla m(\mathbf{x}) \right)^2 ,$$

(E.19)

$$\int \prod_\nu dm_\nu \ldots \to \int \mathcal{D}[m(\mathbf{x})] \ldots \equiv \int \prod_\nu \left(\sqrt{v} dm(\mathbf{x}_\nu) \right) .$$

The functional integrals are defined by discretization. Then as our result for the *Ginzburg–Landau functional*, we can write

$$\mathcal{F}[m(\mathbf{x})] = \int d^d x \left[am^2(\mathbf{x}) + \frac{b}{2}m^4(\mathbf{x}) + c(\nabla m)^2 - hm(\mathbf{x}) + \dots \right] \quad \text{(E.20)}$$

which yields the partition function in terms of the following functional integral:

$$Z = Z_0(T) \int \mathcal{D}[m(\mathbf{x})]e^{-\beta\mathcal{F}[m(\mathbf{x})]} . \quad \text{(E.21)}$$

(i) Here, we have redefined the coefficients once again; e.g. $\frac{1}{\sqrt{v}}$ was combined with h. The coefficient $Z_0(T)$ is found from the prefactors defined earlier, but it is not important in what follows.

(ii) Owing to the fact that the trace is only partially evaluated, the coefficients a, b, c and $Z_0(T)$ are "uncritical", i.e. they are not singular in $T, J, \dots$ etc.

(iii) In the following, we extend the integration range for $\int_{-1}^1 dm_\nu \dots = \int_{-1/\sqrt{v}}^{1/\sqrt{v}} dm(\mathbf{x}) \to \int_{-\infty}^\infty dm(\mathbf{x})$, since $m(\mathbf{x})$ is in any case limited by e^{-bm^4}. Its *most probable value* is $m(\mathbf{x}) \sim \sqrt{\frac{-a}{b}}$, and thus $m_\nu \sim \sqrt{v}\sqrt{\frac{a}{b}} \ll 1$.

(iv) General statements about the coefficients in the Ginzburg–Landau functional:

$\alpha)\mathcal{F}[m(\mathbf{x})]$ has the same symmetry as the microscopic spin Hamiltonian; i.e. except for the term with h, $\mathcal{F}[m(\mathbf{x})]$ is an even function of $m(\mathbf{x})$.

$\beta)$ From the preceding rearrangement of the h term, it may be seen that a, b, c are independent of h. In particular, the partial evaluation of the trace produces no higher odd terms.

$\gamma)$ Stability requires $b > 0$. Otherwise, one cannot terminate at m^4. At the tricritical point, $b = 0$ and one must take the term of order m^6 into account, also.

$\delta)$ The ferromagnetic interaction favors parallel spins, i.e. nonuniformity of spin direction costs energy. Thus $c\nabla m\nabla m$ with $c > 0$.

$\epsilon)$ Concerning the temperature dependence of the G.-L. coefficient a, we refer to the main part of the text, Eq. (7.4.8).

(v) In the thermodynamic limit, the linear dimension $L \to \infty$,

$$m(\mathbf{x}) = \frac{1}{L^{d/2}} \sum_{\mathbf{k}\in B} e^{i\mathbf{k}\mathbf{x}}m_{\mathbf{k}} = \frac{1}{L^d} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{x}}m(\mathbf{k})$$

and $m(\mathbf{x}) \overset{L\to\infty}{\longrightarrow} \int_B \frac{d^d k}{(2\pi)^d}e^{i\mathbf{k}\mathbf{x}}m(\mathbf{k})$, where the integral is extended over the whole Brillouin zone B: $k_i \in \left[-\frac{\pi}{a_c}, \frac{\pi}{a_c}\right]$, and $m(\mathbf{k}) = L^{d/2}m_{\mathbf{k}}$.

Later, the integral over the cubic Brillouin zone will be approximated by an integral over a sphere:

$$m(\mathbf{x}) = \int_{|\mathbf{k}|<\Lambda} \frac{d^d k}{(2\pi)^d}e^{i\mathbf{k}\mathbf{x}}m(\mathbf{k}) .$$

F. The Transfer Matrix Method

The transfer matrix method is an important tool for the exact solution of statistical-mechanical models. It is particularly useful for two-dimensional and one-dimensional models. We introduce the transfer matrix method by solving the *one-dimensional Ising model*. The one-dimensional *Ising model for N spins with interactions between nearest neighbors* is described by the Hamiltonian

$$\mathcal{H} = -J \sum_{j=1}^{N} \sigma_j \sigma_{j+1} - H \sum_{j=1}^{N} \sigma_j \, , \tag{F.1}$$

where periodic boundary conditions are assumed, $\sigma_{N+1} = \sigma_1$. The partition function ($K \equiv \beta J$, $h \equiv \beta H$) has the form

$$Z_N = \sum_{\{\sigma_i = \pm 1\}} \prod_{j=1}^{N} e^{K\sigma_j \sigma_{j+1} + \frac{h}{2}(\sigma_j + \sigma_{j+1})} = \mathrm{Tr}\left(T^N\right) . \tag{F.2}$$

Following the second equals sign, the *transfer matrix*, defined by

$$T_{\sigma\sigma'} \equiv e^{K\sigma\sigma' + \frac{h}{2}(\sigma+\sigma')} \, , \tag{F.3}$$

was introduced. Its matrix representation is given by

$$\mathcal{T} = \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix} . \tag{F.4}$$

One readily finds the two eigenvalues of this (2×2) matrix:

$$\lambda_{1,2} = e^K \cosh h \pm \left(e^{-2K} + e^{2K} \sinh^2 h\right)^{1/2} . \tag{F.5}$$

The trace in (F.2) is invariant under orthogonal transformations. By transforming to the basis in which $\mathcal{T}$ is diagonal, one can verify that

$$Z_N = \lambda_1^N + \lambda_2^N . \tag{F.6}$$

The *free energy* per spin is given by the logarithm of the partition function

$$f(T, H) = -kT \lim_{N \to \infty} \frac{1}{N} \log Z_N . \tag{F.7}$$

In the thermodynamic limit, $N \to \infty$, the largest eigenvalue dominates:

$$f = -kT \log \lambda_1 \quad (\text{due to } \lambda_1 \geq \lambda_2 \text{ for all } T \geq 0) . \tag{F.8}$$

There is no phase transition in one dimension, since

$$f(T,0) = -kT\big[\log 2 + \log(\cosh\beta J)\big] \tag{F.9}$$

is a smooth function for $T > 0$. Owing to the short range of the interactions, disordered spin configurations (with high entropy S) are more probable than ordered configurations (with low internal energy E) in equilibrium (where $F(T,0) = E - TS$ is a minimum). The isothermal susceptibility $\chi = \left(\frac{\partial m}{\partial H}\right)_T$ for $H = 0$ is found from (F.8) to be $\chi = \beta e^{2\beta J}$ at low T. There is a pseudo-phase transition at $T = 0$: $m_0^2 = 1$, $\chi_0 = \infty$.

Magnetization: $m = -\partial f/\partial B$ $\qquad\qquad$ Specific Heat: $C_H = -T\partial^2 f/\partial T^2$
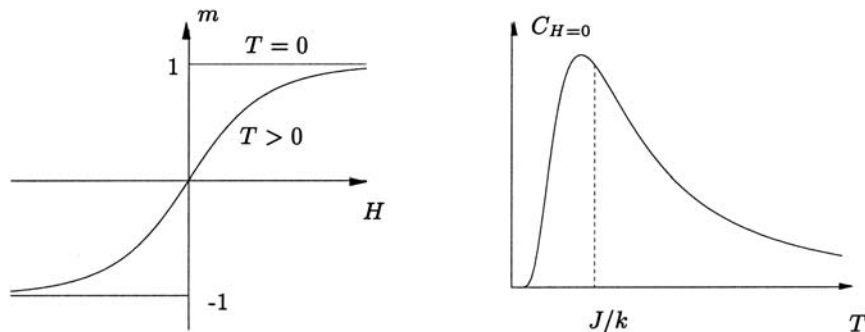
Fig. F.1. The magnetization and specific heat in the one-dimensional Ising model

The *spin correlation function* can also be expressed using the transfer matrix and computed:

$$\langle\sigma_k\sigma_l\rangle_N \equiv \frac{1}{Z_N} \sum_{\{\sigma_i=\pm1\}} e^{-\beta\mathcal{H}}\sigma_k\sigma_l$$

$$= \frac{1}{Z_N} \sum_{\{\sigma_i=\pm1\}} T_{\sigma_1\sigma_2}\dots T_{\sigma_{k-1}\sigma_k}\sigma_k T_{\sigma_k\sigma_{k+1}}\dots T_{\sigma_{l-1}\sigma_l}$$

$$\times\ \sigma_l T_{\sigma_l\sigma_{l+1}}\dots T_{\sigma_{N-1}\sigma_1} \tag{F.10}$$

$$= \frac{1}{Z_N} \sum_{\pm} \langle\chi_\pm|\,T^k\tau_z T^{l-k}\tau_z T^{N-l}\,|\chi_\pm\rangle$$

$$= Z_N^{-1}\,\mathrm{Tr}\left(\tau_z T^{l-k}\tau_z T^{N-l+k}\right),\quad \tau_z \equiv \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\quad l \geq k\,.$$

To distinguish them from $\sigma_i = \pm1$, the Pauli matrices are denoted here by $\tau_{x,y,z}$. The trace in the last line of (F.10) refers to the sum of the two diagonal matrix elements in the Pauli spinor states $\chi_\pm$. Further evaluation is carried out by diagonalizing T:

$$\Gamma\,T\,\Gamma^{-1} = \begin{pmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{pmatrix} \equiv \Lambda\ ,\quad \text{where}\quad \Gamma = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ -1 & 1\end{pmatrix}\ .$$

With

$$\Gamma \, \tau_z \, \Gamma^{-1} = - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \equiv -\tau_x \; ,$$

it follows from (F.10) that

$$\langle \sigma_k \sigma_l \rangle_N = Z_N^{-1} \mathrm{Tr}(\tau_x \Lambda^{l-k} \, \tau_x \Lambda^{N-l+k})$$

and thus for $l - k \ll N$ in the thermodynamic limit $N \to \infty$ we obtain the final result

$$\langle \sigma_k \sigma_l \rangle = \left(\frac{\lambda_2}{\lambda_1} \right)^{l-k} \qquad . \tag{F.11}$$

For $T > 0$, $\lambda_2 < \lambda_1$, i.e. $\langle \sigma_k \sigma_l \rangle$ decreases with increasing distance $l - k$. For $T \to 0$, $\lambda_1 \to \lambda_2$ (asymptotic degeneracy), so that the correlation length $\xi \to \infty$.

By means of the transfer matrix method, the one-dimensional Ising model is mapped onto a zero-dimensional quantum system (one single spin). The two-dimensional Ising model is mapped onto a one-dimensional quantum system. Since it is possible to diagonalize the Hamiltonian of the latter, the two-dimensional Ising model can in this way be solved exactly.

G. Integrals Containing the Maxwell Distribution

$$f^0(\mathbf{v}) = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mv^2}{2kT}} \tag{G.1a}$$

$$\int d^3 v \, f^0(\mathbf{v}) = n \tag{G.1b}$$

$$\int d^3 v \left(\frac{mv^2}{2} \right)^s f^0(\mathbf{v}) = n \left(\frac{m}{2\pi kT} \right)^{3/2} \left(-\frac{\partial}{\partial(1/kT)} \right)^s \underbrace{\int d^3 v \, e^{-\frac{mv^2}{2kT}}}_{\left(\frac{\pi}{m/2kT} \right)^{3/2}} \tag{G.1c}$$

$$= n(kT)^s \frac{3}{2} \frac{5}{2} \cdots \frac{1+2s}{2} \quad s = 1, 2, \dots$$

$$\int d^3 v \, \frac{mv^2}{2} f^0(\mathbf{v}) = \frac{3}{2} nkT \tag{G.1d}$$

$$\int d^3 v \left(\frac{mv^2}{2} \right)^2 f^0(\mathbf{v}) = \frac{15}{4} n(kT)^2 \tag{G.1e}$$

$$\int d^3 v \left(\frac{mv^2}{2} \right)^3 f^0(\mathbf{v}) = \frac{105}{8} n(kT)^3 \tag{G.1f}$$

$$\int d^3v \, v_k v_i v_j v_l f^0(\mathbf{v}) = \lambda \big(\delta_{ki}\delta_{jl} + \delta_{kj}\delta_{il} + \delta_{kl}\delta_{ij} \big) \,, \quad \lambda = \frac{kT}{m} \qquad \text{(G.1g)}$$

Eq. (G.1g) can be demonstrated by first noting that the result necessarily has the form given and then taking the sum $\sum_{k=i}\sum_{j=l}$: comparison with (G.1e) leads using $\int d^3v \, \left(\mathbf{v}^2\right)^2 f^0(\mathbf{v}) = 15\lambda$ to the result $\lambda = \frac{kT}{m}$.

H. Hydrodynamics

In the appendix, we consider the microscopic derivation of the linear hydrodynamic equations. The hydrodynamic equations determine the behavior of a system at low frequencies or over long times. They are therefore the equations of motion of the conserved quantities and of variables which are related to a broken continuous symmetry. Nonconserved quantities relax quickly to their local equilibrium values determined by the conserved quantities. The conserved quantities (energy, density, magnetization...) can exhibit a time variation only by flowing from one spatial region to another. This means that the equations of motion of conserved quantities $E(\mathbf{x})$ typically have the form $\dot{E}(\mathbf{x}) = -\nabla \mathbf{j}_E(\mathbf{x})$. The gradient which occurs here already indicates that the characteristic rate (frequency, decay rate) for the conserved quantities is proportional to the wavenumber q. Since $\mathbf{j}_E$ can be proportional to conserved quantities or to gradients of conserved quantities, hydrodynamic variables exhibit a characteristic rate $\sim q^\kappa$, i.e. a power of the wavenumber q, where in general $\kappa = 1, 2$. In the case of a broken continuous symmetry there are additional hydrodynamic variables. Thus, in an isotropic antiferromagnet, the alternating (staggered) magnetization $\mathbf{N}$ is not conserved. In the ordered phase, its average value is finite and may be oriented in an arbitrary direction in space. Therefore, it costs no energy to rotate the staggered magnetization. This means that microscopic variables which represent fluctuations transverse to the staggered magnetization likewise belong to the set of hydrodynamic variables, Fig. H.1.

(a)

(b)
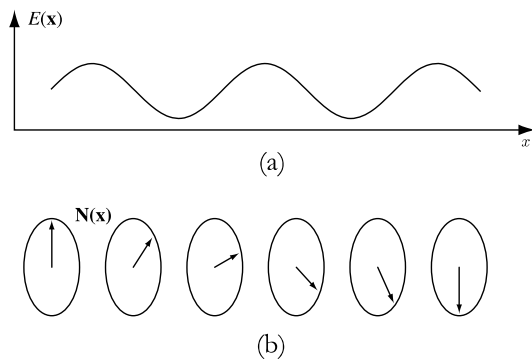
Fig. H.1. Conserved quantities and broken-symmetry variables: (a) the energy density $E(\mathbf{x})$ and (b) the alternating (staggered) magnetization $\mathbf{N}(\mathbf{x})$ in an isotropic or planar antiferromagnet

H.1 Hydrodynamic Equations, Phenomenological Discussion

In order to gain some insight into the structure of the hydrodynamic equations, we first want to consider a simple example: the hydrodynamics of a ferromagnet, for which only the magnetization density is conserved. The magnetization density $M(\mathbf{x})$ obeys the equation of continuity

$$\dot{M}(\mathbf{x}) = -\nabla \mathbf{j}_M(\mathbf{x}) \ . \tag{H.1}$$

Here, $\mathbf{j}_M$ is the magnetization current density. This becomes larger the greater the difference between magnetic fields at different positions in the material. From this fact, we obtain the phenomenological relation

$$\mathbf{j}_M(\mathbf{x}) = -\lambda \nabla H(\mathbf{x}) \ , \tag{H.2}$$

where λ is the magnetization conductivity. The local magnetic field depends on the magnetization density via the relation

$$H(\mathbf{x}) = \frac{1}{\chi} M(\mathbf{x}) \ , \tag{H.3}$$

in which the magnetic susceptibility χ enters. Inserting (H.3) into (H.2) and the latter into (H.1), one finds the diffusion equation

$$\dot{M}(\mathbf{x}, t) = D \nabla^2 M(\mathbf{x}, t) \ , \tag{H.4}$$

where the magnetization diffusion constant is defined by

$$D = \frac{\lambda}{\chi} \ .$$

To solve (H.4), it is expedient to apply a spatial Fourier transform; then the diffusion equation (H.4) takes on the form

$$\dot{M}_{\mathbf{q}} = -D q^2 M_{\mathbf{q}} \ , \tag{H.5}$$

with the obvious result

$$M_{\mathbf{q}}(t) = \mathrm{e}^{-D q^2 t} M_{\mathbf{q}}(0) \ . \tag{H.6}$$

The diffusive relaxation rate $D q^2$ decreases as the wavenumber becomes smaller. For several variables $X_{\mathbf{q}}^c$, whose deviations from equilibrium are denoted by $\delta\langle X_{\mathbf{q}}^c\rangle$, the hydrodynamic equations have the general form

$$\frac{\partial}{\partial t} \delta\langle X_{\mathbf{q}}^c\rangle + M^{cc'}(\mathbf{q})\, \delta\langle X_{\mathbf{q}}^{c'}\rangle = 0 \ . \tag{H.7}$$

Here, $M^{cc'}(\mathbf{q})$ is a matrix which vanishes as $\mathbf{q} \to 0$. For the hydrodynamics of liquids, we recall Eq. (9.4.46a–c).

H.2 The Kubo Relaxation Function

In linear response theory[14], one investigates the effects of an external force $F(t)$ which couples to the operator B. The Hamiltonian then contains the additional term

$$H'(t) = -F(t)B .\tag{H.8}$$

For the change of the expectation value of an operator A with respect to its equilibrium value, one obtains to first order in $F(t)$

$$\delta\langle A(t)\rangle = \int_{-\infty}^{\infty} dt' \chi_{AB}(t-t')F(t')\tag{H.9}$$

with the dynamic susceptibility

$$\chi_{AB}(t-t') = \frac{\mathrm{i}}{\hbar}\Theta(t-t')\langle[A(t), B(t')]\rangle .\tag{H.10}$$

Its Fourier transform reads

$$\chi_{AB}(\omega) = \int_{-\infty}^{\infty} dt\,\mathrm{e}^{\mathrm{i}\omega t}\chi_{AB}(t) .\tag{H.11}$$

We now consider a perturbation which is slowly switched on and then again switched off at the time $t = 0$: $F(t) = \mathrm{e}^{\epsilon t}\Theta(-t)F$. One then finds from (H.9)

$$\begin{aligned}\delta\langle A(t)\rangle &= \int_{-\infty}^{\infty} dt' \chi_{AB}(t-t')F\Theta(-t')\mathrm{e}^{\epsilon t'}\\ &= \int_{t}^{\infty} du\,\chi_{AB}(u)F\mathrm{e}^{\epsilon(t-u)} ,\end{aligned}\tag{H.12}$$

where the substitution $t - t' = u$ has been employed. The decay of the perturbation for $t > 0$ is thus described by

$$\delta\langle A(t)\rangle = \phi_{AB}(t)F\mathrm{e}^{\epsilon t} ,\tag{H.13}$$

where[15] the *Kubo relaxation function* $\phi_{AB}(t)$ is defined by

$$\phi_{AB}(t) \equiv \frac{\mathrm{i}}{\hbar}\int_{t}^{\infty} dt'\langle[A(t'), B(0)]\rangle\mathrm{e}^{-\epsilon t'} .\tag{H.14}$$

Its half-range Fourier transform is given by

$$\phi_{AB}(\omega) \equiv \int_{0}^{\infty} dt\,\mathrm{e}^{\mathrm{i}\omega t}\phi_{AB}(t) .\tag{H.15}$$

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[14] QM II, Sect. 4.3

[15] The factor $\mathrm{e}^{\epsilon t}$ is of no importance in (H.13), since $\phi_{AB}(t)$ relaxes faster.

The Kubo relaxation function has the following properties:

$$\phi_{AB}(t = 0) = \chi_{AB}(\omega = 0) \,, \tag{H.16}$$

$$\dot{\phi}_{AB}(t) = -\chi_{AB}(t) \qquad \text{for } t > 0 \,, \tag{H.17}$$

$$\phi_{AB}(\omega) = \frac{1}{i\omega}\big(\chi_{AB}(\omega) - \chi_{AB}(\omega = 0)\big) \,. \tag{H.18}$$

Eq. (H.16) follows from the comparison with the Fourier transformed dynamical susceptibility, Eq. (H.11). The second relation is obtained immediately by taking the derivative of (H.14). The third relation can be obtained by half-range Fourier transformation of (H.17)

$$-\int_0^\infty dt\, \mathrm{e}^{i\omega t}\chi_{AB}(t) = \int_0^\infty dt\, \mathrm{e}^{i\omega t}\dot{\phi}_{AB}(t)$$

$$= \mathrm{e}^{i\omega t}\phi_{AB}(t)\big|_0^\infty - i\omega \int_0^\infty dt\, \mathrm{e}^{i\omega t}\phi_{AB}(t) = \phi_{AB}(t = 0) - i\omega\phi_{AB}(\omega)$$

and application of $\phi_{AB}(t = \infty) = 0$, (H.16) and

$$\int_0^\infty dt\, \mathrm{e}^{i\omega t}\chi_{AB}(t) = \int_{-\infty}^\infty dt\, \mathrm{e}^{i\omega t}\chi_{AB}(t) = \chi_{AB}(\omega) \,.$$

Further, one can show for $t \geq 0$ that

$$\phi_{\dot{A}B}(t) = \int_t^\infty dt'\, \frac{i}{\hbar}\big\langle[\dot{A}(t'), B(0)]\big\rangle \mathrm{e}^{-\epsilon t'} = -\frac{i}{\hbar}\big\langle[A(t), B(0)]\big\rangle = -\chi_{AB}(t) \,,$$

i.e.

$$\phi_{\dot{A}B}(\omega) = -\chi_{AB}(\omega) \tag{H.19}$$

and, together with (H.18),

$$\omega\phi_{AB}(\omega) = i\phi_{\dot{A}B}(\omega) + i\chi_{AB}(\omega = 0) \,. \tag{H.20}$$

Later, we will also require the identity

$$\chi_{\dot{A}B^\dagger}(\omega = 0) = \frac{i}{\hbar}\int_0^\infty dt'\big\langle[\dot{A}(t'), B(0)^\dagger]\big\rangle = -\frac{i}{\hbar}\big\langle[A(0), B(0)^\dagger]\big\rangle \,, \tag{H.21}$$

which follows from the Fourier transform of (H.10) and the fact that the expectation value $\big\langle[A(\infty), B(0)^\dagger]\big\rangle$ vanishes.

H.3 The Microscopic Derivation of the Hydrodynamic Equations

H.31 Hydrodynamic Equations and Relaxation

We introduce the following notation here:

$$X^i(\mathbf{x}, t) \qquad i = 1, 2, \dots \qquad\qquad \text{densities (Hermitian)}$$

$$X_{\mathbf{q}}^i(t) = \frac{1}{\sqrt{V}} \int d^3x \, \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{x}} X^i(\mathbf{x}, t) \qquad \text{Fourier transforms} \qquad \text{(H.22a)}$$

$$X^i(\mathbf{x}, t) = \frac{1}{\sqrt{V}} \sum_{\mathbf{q}} \mathrm{e}^{\mathrm{i}\mathbf{q}\mathbf{x}} X_{\mathbf{q}}^i(t) \,, \qquad\qquad X_{\mathbf{q}}^{i\dagger} = X_{-\mathbf{q}}^i \qquad \text{(H.22b)}$$

$$\chi^{ij}(\mathbf{q}, t) \equiv \chi_{X_{\mathbf{q}}^i, X_{-\mathbf{q}}^j}(t) \qquad\qquad \text{etc.}$$

Conserved densities are denoted by indices $c, c', \dots$ etc. and nonconserved densities by $n, n', \dots$.

We now consider a perturbation which acts on the conserved densities. At $t = 0$, it is switched off, so that the perturbation Hamiltonian takes on the form

$$H' = -\int d^3x X^c(\mathbf{x}, t) K^c(\mathbf{x}) \Theta(-t) \mathrm{e}^{\epsilon t} = -\sum_{\mathbf{q}} X_{-\mathbf{q}}^c(t) K_{\mathbf{q}}^c \Theta(-t) \mathrm{e}^{\epsilon t}$$

and leads according to Eq. (H.13) to the following changes in the conserved quantities for $t > 0$:

$$\delta\langle X_{\mathbf{q}}^c(t) \rangle = \phi^{cc'}(\mathbf{q}, t) K_{\mathbf{q}}^{c'} \mathrm{e}^{\epsilon t} \,. \tag{H.23}$$

The decay of the perturbation is determined by the relaxation function.

The situation considered here is, on the other hand, also described by the hydrodynamic equations (H.7)

$$\left\{ \delta^{cc'} \frac{\partial}{\partial t} + M^{cc'}(\mathbf{q}) \right\} \delta\langle X_{\mathbf{q}}^{c'}(t) \rangle = 0 \,. \tag{H.24a}$$

If we insert Eq. (H.23) into (H.24a), we obtain

$$\left\{ \delta^{cc'} \frac{\partial}{\partial t} + M^{cc'}(\mathbf{q}) \right\} \phi^{c'c''}(\mathbf{q}, t) K_{\mathbf{q}}^{c''} = 0 \,.$$

Since this equation is valid for arbitrary $K_{\mathbf{q}}^{c''}$, it follows that

$$\left\{ \delta^{cc'} \frac{\partial}{\partial t} + M^{cc'}(\mathbf{q}) \right\} \phi^{c'c''}(\mathbf{q}, t) = 0 \,. \tag{H.24b}$$

From this, we find $\phi^{c'c''}(\mathbf{q}, \omega)$ by taking the half-range Fourier transform

$$\int_0^\infty dt\,\mathrm{e}^{\mathrm{i}\omega t}\Big\{\delta^{cc'}\frac{\partial}{\partial t}+M^{cc'}(\mathbf{q})\Big\}\phi^{c'c''}(\mathbf{q},t)=0$$

and carrying out an integration by parts, i.e.

$$-\phi^{cc''}(\mathbf{q},t=0)+\Big\{-\mathrm{i}\omega\delta^{cc'}+M^{cc'}(\mathbf{q})\Big\}\phi^{c'c''}(\mathbf{q},\omega)=0\;.$$

Using (H.16), we obtain finally

$$\Big\{-\mathrm{i}\omega\delta^{cc'}+M^{cc'}(\mathbf{q})\Big\}\phi^{c'c''}(\mathbf{q},\omega)=\chi^{cc''}(\mathbf{q})\;. \tag{H.24c}$$

Therefore, the relaxation functions $\phi^{cc'}(\mathbf{q},\omega)$ and thus the dynamic response functions are obtained from hydrodynamics for small $\mathbf{q}$ and ω.

If, conversely, we can determine $\phi^{cc'}(\mathbf{q},\omega)$ for small $\mathbf{q}$ and ω from a microscopic theory, we can then read off the hydrodynamic equations by comparing with (H.24a) and (H.24c).

We consider an arbitrary many-body system (liquid, ferromagnet, antiferromagnet, etc.) and divide up the complete set of operators $X_{\mathbf{q}}^i$ into conserved quantities $X_{\mathbf{q}}^c$ and nonconserved quantities $X_{\mathbf{q}}^n$. Our strategy is to find equations of motion for the $X_{\mathbf{q}}^c$, where the forces are decomposed into a part which is proportional to the $X_{\mathbf{q}}^c$ and a part which is proportional to the $X_{\mathbf{q}}^n$. The latter fluctuate rapidly and will lead after its elimination to damping terms in the equations of motion, which then contain only the $X_{\mathbf{q}}^c$.

In order to visualize this decomposition in a clear way, it is expedient to choose the operators in such a manner that they are orthogonal. To do this, we must first define the *scalar product* of two operators A and B:

$$\langle A|B\rangle=\chi_{A,B^\dagger}(\omega=0)\;. \tag{H.25}$$

Remark: one can readily convince oneself that this definition fulfills the properties of a scalar product:

$$\langle A|B\rangle^*=\langle B|A\rangle$$
$$\langle c_1 A_1+c_2 A_2|B\rangle=c_1\,\langle A_1|B\rangle+c_2\,\langle A_2|B\rangle$$
$$\langle A|A\rangle\quad\text{is real and }\langle A|A\rangle\geq 0\text{ (0 only for }A\equiv 0)\;.$$

We now choose our operators to be orthonormalized:

$$\langle X_{\mathbf{q}}^i|X_{\mathbf{q}}^j\rangle=\chi^{ij}(\mathbf{q},\omega=0)=\delta^{ij}\;. \tag{H.26}$$

To construct these operators, one uses the Schmidt orthonormalization procedure.

The Heisenberg equations of motion $\dot{X}_{\mathbf{q}}^c=\frac{\mathrm{i}}{\hbar}[H,X_{\mathbf{q}}^c]$ etc. can now be written in the form

$$\dot{X}_{\mathbf{q}}^c=-\mathrm{i}C^{cc'}(\mathbf{q})X_{\mathbf{q}}^{c'}-\mathrm{i}C^{cn}(\mathbf{q})X_{\mathbf{q}}^n \tag{H.27a}$$
$$\dot{X}_{\mathbf{q}}^n=-\mathrm{i}C^{nc}(\mathbf{q})X_{\mathbf{q}}^c-\mathrm{i}D^{nn'}(\mathbf{q})X_{\mathbf{q}}^{n'}\;. \tag{H.27b}$$

Here, the derivatives $\dot{X}_{\mathbf{q}}^{c}$ and $\dot{X}_{\mathbf{q}}^{n}$ were projected onto $X_{\mathbf{q}}^{c'}$ and $X_{\mathbf{q}}^{n'}$. If we take e.g. the scalar product of $\dot{X}_{\mathbf{q}}^{c}$ with $X_{\mathbf{q}}^{c'}$, we find using Eq. (H.21)

$$\langle \dot{X}_{\mathbf{q}}^{c} | X_{\mathbf{q}}^{c'} \rangle \equiv -\mathrm{i} C^{cc'}(\mathbf{q}) = -\frac{\mathrm{i}}{\hbar} \langle [X_{\mathbf{q}}^{c}, X_{\mathbf{q}}^{c'\dagger}] \rangle \ .$$

That is:

$$C^{cc'}(\mathbf{q}) = \frac{1}{\hbar} \langle [X_{\mathbf{q}}^{c}, X_{\mathbf{q}}^{c'\dagger}] \rangle \ , \tag{H.28a}$$

and analogously

$$C^{cn}(\mathbf{q}) = \frac{1}{\hbar} \langle [X_{\mathbf{q}}^{c}, X_{\mathbf{q}}^{n\dagger}] \rangle \ , \qquad D^{nn'}(\mathbf{q}) = \frac{1}{\hbar} \langle [X_{\mathbf{q}}^{n}, X_{\mathbf{q}}^{n'\dagger}] \rangle \ . \tag{H.28}$$

These coefficients obey the following symmetry relations:

$$C^{cc'*}(\mathbf{q}) = C^{c'c}(\mathbf{q}) \ , \quad C^{nc*}(\mathbf{q}) = C^{cn}(\mathbf{q}) \ , \quad D^{nn'*}(\mathbf{q}) = D^{n'n}(\mathbf{q}) \ . \tag{H.29}$$

It thus follows from (H.20) that

$$\begin{aligned}
\omega \phi^{cc'}(\mathbf{q}, \omega) &= C^{cc''}(\mathbf{q}) \phi^{c''c'}(\mathbf{q}, \omega) + C^{cn}(\mathbf{q}) \phi^{nc'}(\mathbf{q}, \omega) + \mathrm{i} \delta^{cc'} \\
\omega \phi^{nc}(\mathbf{q}, \omega) &= C^{nc'}(\mathbf{q}) \phi^{c'c}(\mathbf{q}, \omega) + D^{nn'}(\mathbf{q}) \phi^{n'c}(\mathbf{q}, \omega) \\
\omega \phi^{nn'}(\mathbf{q}, \omega) &= C^{nc}(\mathbf{q}) \phi^{cn'}(\mathbf{q}, \omega) + D^{nn''}(\mathbf{q}) \phi^{n''n'}(\mathbf{q}, \omega) + \mathrm{i} \delta^{nn'} \\
\omega \phi^{cn}(\mathbf{q}, \omega) &= C^{cc'}(\mathbf{q}) \phi^{c'n}(\mathbf{q}, \omega) + C^{cn'}(\mathbf{q}) \phi^{n'n}(\mathbf{q}, \omega) \ .
\end{aligned} \tag{H.30}$$

From (H.30b) we read off the result

$$\phi^{nc}(\mathbf{q}, \omega) = (\omega \mathbb{1} - D(\mathbf{q}))_{nn'}^{-1} C^{n'c'}(\mathbf{q}) \phi^{c'c}(\mathbf{q}, \omega) \ ; \tag{H.31}$$

then inserting (H.31) into (H.30a) leads to

$$\left[\omega \delta^{cc'} - C^{cc'}(\mathbf{q}) - C^{cn}(\mathbf{q}) \left(\frac{1}{\omega \mathbb{1} - D(\mathbf{q})} \right)_{nn'} C^{n'c'}(\mathbf{q}) \right] \phi^{c'c''}(\mathbf{q}, \omega)$$
$$= \mathrm{i} \delta^{cc''} \ . \tag{H.32}$$

For the conserved quantities, the coefficients $C^{cc'}(\mathbf{q})$ and $C^{cn}(\mathbf{q})$ vanish in the limit $\mathbf{q} \to 0$. Therefore, in the limit of small $\mathbf{q}$, we find

$$\mathrm{i} \left(C^{cc'}(\mathbf{q}) X_{\mathbf{q}}^{c'} + C^{cn}(\mathbf{q}) X_{\mathbf{q}}^{n} \right) = \mathrm{i} q_{\alpha} j_{\alpha}^{c}(\mathbf{q}) \ . \tag{H.33}$$

We define also the nonconserved part of the current density

$$C^{cn}(\mathbf{q}) X_{\mathbf{q}}^{n} = q_{\alpha} \tilde{j}_{\alpha}^{c}(\mathbf{q}) \ . \tag{H.34}$$

In contrast to (H.33) and (H.34), the $D_{nn'}(\mathbf{q})$ remain finite in the limit $\mathbf{q} \to 0$. For the behavior at long wavelengths ($\mathbf{q} \to 0$), we can therefore take $\frac{1}{\omega \mathbb{1} - D}$

in the limit $\omega, \mathbf{q} \to 0$, whereby due to the finiteness of $D(\mathbf{q})$, we can expect that

$$\lim_{\omega \to 0} \lim_{\mathbf{q} \to 0} \frac{1}{\omega \mathbb{1} - D(\mathbf{q})} = \lim_{\mathbf{q} \to 0} \lim_{\omega \to 0} \frac{1}{\omega \mathbb{1} - D(\mathbf{q})} \ . \tag{H.35}$$

In the limit $\mathbf{q} \to 0$, we can find a relation between $\frac{1}{\omega \mathbb{1} - D}$ from Eq. (H.30c) and a correlation function. Owing to $\lim_{\mathbf{q} \to 0} C^{nc}(\mathbf{q}) = 0$, it follows from (H.30c), with the abbreviation $D \equiv \lim_{\mathbf{q} \to 0} D(\mathbf{q})$, that

$$\left(\omega \mathbb{1} - D\right)^{nn''} \lim_{\mathbf{q} \to 0} \phi^{n''n'}(\mathbf{q}, \omega) = \mathrm{i}\delta^{nn'}$$

or

$$\left(\frac{1}{\omega \mathbb{1} - D}\right)_{nn'} = -\mathrm{i} \lim_{\mathbf{q} \to 0} \phi^{nn'}(\mathbf{q}, \omega) \ . \tag{H.36}$$

Inserting this into (H.32) and taking the the double limits, we obtain

$$\left(\omega \delta^{cc'} - C^{cc'}(\mathbf{q}) + \mathrm{i}C^{cn}(\mathbf{q})\left(\lim_{\omega \to 0} \lim_{\mathbf{q} \to 0} \phi^{nn'}(\mathbf{q}, \omega)\right)C^{n'c'}(\mathbf{q})\right)\phi^{c'c''}(\mathbf{q}, \omega)$$
$$= \mathrm{i}\delta^{cc''} \ ,$$

i.e. finally:

$$\left(\omega \delta^{cc'} - C^{cc'}(\mathbf{q}) + \mathrm{i}q_\alpha q_\beta \Gamma^{cc'}_{\alpha\beta}\right)\phi^{c'c''}(\mathbf{q}, \omega) = \mathrm{i}\delta^{cc''} \ , \tag{H.37}$$

with the damping coefficients

$$\Gamma^{cc'}_{\alpha\beta} \equiv \lim_{\omega \to 0} \lim_{q \to 0} \phi_{\tilde{j}^c_\alpha \tilde{j}^{c'}_\beta}(q, \omega) \ . \tag{H.38}$$

Here, the sums over n and n' were combined into the nonconserved current densities defined in Eq. (H.34).

When the system exhibits symmetry under reflection, rotation, etc., the number of nonvanishing coefficients $\Gamma^{cc'}_{\alpha\beta}$ can be reduced. We assume that for the remaining functions $\phi_{\tilde{j}^c_\alpha \tilde{j}^{c'}_\beta}$, the operators j_c and $j_{c'}$ have the same signature[16] under time reversal: $\epsilon_{j_c} = \epsilon_{j_{c'}}$. Applying (H.18) and the dispersion relations[17], one obtains

$$\phi(\omega) = -\frac{\mathrm{i}}{\omega}\left(\chi'(\omega) - \chi(0)\right) + \frac{\chi''(\omega)}{\omega}$$
$$= -\frac{\mathrm{i}}{\pi}\mathrm{P}\int d\omega' \frac{\chi''(\omega')}{(\omega' - \omega)\omega'} + \underbrace{\frac{\chi''(\omega)}{\omega}}_{\frac{1-e^{-\beta\hbar\omega}}{2\hbar\omega}G^>(\omega)} \ , \tag{H.39}$$

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[16] QM II, Sect. 4.8.2.2
[17] QM II, Sect. 4.4

which, owing to the fluctuation-dissipation theorem[18] and the antisymmetry of $\chi''(\omega)$, finally leads to $\lim_{\omega \to 0} \phi(\omega) = \lim_{\omega \to 0} \frac{\beta}{2} G^>(\omega)$ and

$$\Gamma_{\alpha\beta}^{cc'} = \frac{1}{2kT} \lim_{\omega \to 0} \lim_{\mathbf{q} \to 0} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \tilde{j}_{\alpha\mathbf{q}}^c(t) \tilde{j}_{\beta-\mathbf{q}}^{c'}(0) \rangle . \tag{H.40}$$

This is the *Kubo formula* for the transport coefficients, expressed in terms of current-current correlation functions. Without taking up their straightforward proofs, we mention the following symmetry properties:

$$\Gamma_{\alpha\beta}^{cc'*} = \Gamma_{\beta\alpha}^{c'c} , \quad \Gamma_{\alpha\alpha}^{cc} > 0 , \quad \Gamma_{\alpha\beta}^{cc'} = \Gamma_{\beta\alpha}^{c'c} \text{ real.} \tag{H.41}$$

In summary, one can read off the following *linear hydrodynamic equations* by comparison with Eqns. (H.24c) and (H.24a):

$$\left[\frac{\partial}{\partial t} \delta^{cc'} + iC^{cc'}(\mathbf{q}) + q_\alpha q_\beta \Gamma_{\alpha\beta}^{cc'} \right] \delta \langle X_{\mathbf{q}}^{c'}(t) \rangle = 0 , \tag{H.42a}$$

$$C^{cc'}(\mathbf{q}) = \frac{1}{\hbar} \langle [X_{\mathbf{q}}^c, X_{-\mathbf{q}}^{c'}] \rangle , \tag{H.42b}$$

$$\Gamma^{cc'}(\mathbf{q}) = \frac{1}{4kT} \lim_{\omega \to 0} \lim_{\mathbf{q} \to 0} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle \{ j_{\mathbf{q}}^c(t), j_{-\mathbf{q}}^{c'}(0) \} \rangle . \tag{H.42c}$$

The elements of the *frequency matrix* $C^{cc'}(\mathbf{q}) \sim q$ (or q^2) are functions of expectation values of the conserved quantities and the order parameters and susceptibilities of these quantities. They determine the periodic, reversible behavior of the dynamics. For example, for a ferromagnet, the spinwave frequency (H.42b) follows from $\omega(\mathbf{q}) = \frac{M}{\chi_{\mathbf{q}}^T} \propto q^2$, where M is the magnetization and $\chi_{\mathbf{q}}^T \propto q^{-2}$ the transverse susceptibility. The damping terms result from the elimination of the nonconserved degrees of freedom. They can be expressed via Kubo formulas for the current densities. For the derivation it was important that the nonconserved quantities have a much shorter time scale than the conserved quantities, which also permits taking the limit $\lim_{\omega \to 0} \lim_{\mathbf{q} \to 0}$. We note the similarity of this procedure to that used in the case of the linearized Boltzmann equation (Sect. 9.4). The present derivation is more general, since no constraints were placed on the density or the strength of the interactions of the many-body system.

Literature:
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F. Schwabl and K. H. Michel, Phys. Rev. **B2**, 189 (1970)
K. Kawasaki, Ann. Phys. (N.Y.) **61**, 1 (1970)

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[18] QM II, Sect. 4.6

I. Units and Tables

In this Appendix we give the definitions of units and constants which are used in connection with thermodynamics. We also refer to the Table on page 562.

Conversion Factors

$$
\begin{aligned}
1 \text{ eV} &= 1.60219 \times 10^{-19} \text{ J} \\
1 \text{ N} &= 10^5 \text{ dyn} \\
1 \text{ J} &= 1 \times 10^7 \text{ erg} \\
1 \text{ C} &= 2.997925 \times 10^9 \text{ esu} = 2.997925 \times 10^9 \ \sqrt{\text{dyn cm}^2} \\
1 \text{ K} &\triangleq 0.86171 \times 10^{-4} \text{ eV} \\
1 \text{ eV} &\triangleq 2.4180 \times 10^{14} \text{ Hz} \ \triangleq 1.2399 \times 10^{-4} \text{ cm} \\
1 \text{ T} &= 10^4 \text{ Gauss (G)} \\
1 \text{ Å} &= 10^{-8} \text{ cm} \\
1 \text{ sec} &\equiv 1 \text{ s}
\end{aligned}
$$

Pressure

$$1 \text{ bar} = 10^6 \text{dyn/cm}^2 = 10^5 \text{N/m}^2 = 10^5 \text{Pa}$$

$$1 \text{ Torr} = 1 \text{ mm Hg}$$

Physical Atmosphere:

$$1 \text{ atm} = \text{air pressure at 760 mm Hg} \equiv 760 \text{ Torr} = 1.01325 \text{ bar}$$

This relation between Torr and bar follows from the mass density of mercury $\rho_{\text{Hg}} = 13.5951 \text{g cm}^{-3}$ at $1°C$ and the acceleration of gravity $g = 9.80655 \times 10^2 \text{cm s}^{-2}$. Technical Atmosphere:

$$1 \text{ at} = 1 \text{ kp/cm}^2 = 0.980655 \text{ bar}$$

Temperature

The absolute temperature scale was defined in Sect. 3.4 using $T_t = 273.16$ K, the triple point of H_2O.

The zero point of the Celsius scale $0°C$ lies at 273.15 K. Thus in this scale, absolute zero is at $-273.15°C$. With this definition, the equilibrium temperature of ice and water saturated with air under a pressure of 760 mm Hg $\equiv$ 1 atm is equal to $0°C$.

Table I.1. Fixed points of the international temperature scale:

$0°C$	ice point of water
$100°C$	equilibrium temperature of water and water vapor
$-182.970°C$	boiling point of oxygen
$444.600°C$	boiling point of sulfur
$960.8°C$	solidification point of silver
$1063.0°C$	solidification point of gold

For a comparative characterization of materials, their properties are quoted at standard temperatures and pressures. In the physics literature, these are $0°C$ and 1 atm, and in the technical literature, they are $20°C$ and 1 at.
Physical Standard State $\equiv$ standard pressure (1 atm) and standard temperature $(0°C)$.
Technical Standard State $\equiv$ 1 at and $20°C$.
Density of H_2 at T_t and $P = 1$ atm:

$$\rho = 8.989 \times 10^{-2} \text{g/Liter} = 8.989 \times 10^{-5} \text{g cm}^{-3} .$$

Molar volume under these conditions:

$$V_M = \frac{2.016 \, \text{g}}{8.989 \times 10^{-2} \, \text{g Liter}^{-1}} = 22.414 \, \text{Liter} \left(\hat{=} \, 22.414 \frac{\text{Liter}}{\text{mole}} \right) .$$

1 mole $\hat{=}$ atomic weight in g (e.g. one mole of H_2 corresponds to a mass of 2.016 g).

$$k = \frac{PV}{NT} = \frac{1 \, \text{atm} \, V_M}{L \times 273.16 \, \text{K}} = 1.38065 \times 10^{-16} \text{erg/K} .$$

Loschmidt's number $\equiv$ Avogadro's number:

$$L \equiv N_A = \text{number of molecules per mole}$$
$$= \frac{2.016 \, \text{g}}{\text{mass } H_2} = \frac{2.016}{2 \times 1.6734 \times 10^{-24}} = 6.02213 \times 10^{23} .$$

Energy

The unit calorie (cal) is defined by

$$1 \, \text{cal} = 4.1840 \times 10^7 \text{erg} = 4.1840 \, \text{Joule} .$$

A kilocalorie is denoted by Cal (large calorie). With the previous definition, 1 Cal up to the fourth place past the decimal point has the meaning

$$1 \, \text{Cal} \equiv 1 \, \text{kcal} \equiv 1000 \, \text{cal}$$

= the quantity of heat which is required to warm 1 kg H_2O at 1 atm from 14.5 to $15.5°C$[19].

$$1 \, \text{J} = 1 \, \text{Nm} = 10^7 \, \text{dyn cm} = 10^7 \, \text{erg} .$$

Power

$$1 \, \text{W} = 1 \, \text{VA} = 1 \, \text{J s}^{-1} = 10^7 \text{erg s}^{-1}$$
$$1 \, \text{HP} = 75 \, \text{kp m s}^{-1} = 75 \times 9.80665 \times 10^5 \text{dyn m s}^{-1} = 735.498 \, \text{W} .$$

The universal gas constant R is defined via Loschmidt's/Avogadro's number by

$$R = N_A k = 8.3145 \times 10^7 \text{erg mol}^{-1} \text{K}^{-1} .$$

Using the gas constant R, one can write the equation of state of the ideal gas in the form

$$PV = nRT , \tag{I.1}$$

where n is the amount of matter in moles (mole number).

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[19] Note that the nutritional values of foods are quoted either in kJ or in kilocalories.

We close this section with some numerical values of *thermodynamic quantities*. Table I.2, below, gives values of specific heats (C_P).

As can be seen, the specific heat of water is particularly large. This fact plays an important role in the thermal balance of Nature. Water must take up or release a large quantity of heat in order to change its temperature noticeably. Therefore, the water of the oceans remains cool for a relatively long time in Spring and warm for a relatively long time in Autumn. It therefore acts in coastal regions to reduce the annual temperature fluctuations. This is an essential reason for the typical difference between a coastal climate and a continental climate.

Table I.2. The Specific Heat of Some Materials under Standard Conditions

	Specific heat C [cal K^{-1} g^{-1}]	Molecular weight	Molar heat capacity [cal K^{-1} mole^{-1}]
Aluminum	0.214	27.1	5.80
Iron	0.111	55.84	6.29
Nickel	0.106	58.68	6.22
Copper	0.091	63.57	5.78
Silver	0.055	107.88	5.93
Antimony	0.050	120.2	6.00
Platinum	0.032	195.2	6.25
Gold	0.031	197.2	6.12
Lead	0.031	207.2	6.42
Glass	0.19	—	—
Quartz Glass	0.174	—	—
Diamond	0.12	—	—
Water	1.00	—	—
Ethanol	0.58	—	—
Carbon Disulfide	0.24	—	—

Table I.3. Expansion Coefficients of Some Solid and Liquid Materials in K^{-1}

linear				volume	
Lead	0.0000292	Diamond	0.0000013	Ethanol	0.0011
Iron	120	Graphite	080	Ether	163
Copper	165	Glass	081	Mercury	018
Platinum	090	Quartz Crystal ⊥ axis	144	Water	018
Invar (^{64}Fe+^{36}Ni)	016	Quartz Crystal ∥ axis	080		
		Quartz Glass	005		

The *linear expansion coefficient* α_l is related to the volume or cubic expansion coefficient in (3.2.4) via

$$\alpha = 3\alpha_l \ .$$

This follows for a rectangular prism from $V + \Delta V = (a + \Delta a)(b + \Delta b)(c + \Delta c) = abc\left(1 + \frac{\Delta a}{a} + \frac{\Delta b}{b} + \frac{\Delta c}{c}\right) + O(\Delta^2)$, thus $\frac{\Delta V}{V} = 3\frac{\Delta a}{a}$ under the assumption of

isotropic thermal expansion as found in isotropic materials (liquids, amorphous substances) and cubic crystals.

Table I.4. Some Data for Gases: Boiling Point (at 760 Torr), Critical Temperature, Coefficients in the van der Waals Equation, Inversion Temperature

Gas	Boiling point in K	T_c[K]	$a\left[\dfrac{\text{atm cm}^6}{\text{mole}^2}\right]$	$b\left[\dfrac{\text{cm}^3}{\text{mole}}\right]$	$T_{\text{inv}} = \frac{27}{4}T_c$[K]
He	4.22	5.19	0.0335×10^6	23.5	35
H_2	20.4	33.2	0.246×10^6	26.7	224
N_2	77.3	126.0	1.345×10^6	38.6	850
O_2	90.1	154.3	1.36×10^6	31.9	1040
CO_2	194.7	304.1	3.6×10^6	42.7	2050

Table I.5. Pressure Dependence of the Boiling Point of Water

Pressure in Torr	Boiling Point in °C
720	98.49
730	98.89
740	99.26
750	99.63
760	100.00
770	100.37
780	100.73
790	101.09
800	101.44

Table I.6. Heats of Vaporization of Some Materials in cal·g^{-1}

Ethyl Alcohol	202
Ammonia	321
Ether	80
Chlorine, Cl_2	62
Mercury	68
Oxygen, O_2	51
Nitrogen, N_2	48
Carbon Disulfide	85
Water	539.2
Hydrogen, H_2	110

Table I.7. Heats of Melting of Some Materials in cal · g^{-1}

Aluminum	94	Silver	26.0
Lead	5.5	Table Salt	124
Gold	15.9	Water (Ice)	79.5
Copper	49		

Table I.8. Vapor Pressure of Water (Ice) in Torr

$-60°$C	0.007
$-40°$C	0.093
$-20°$C	0.77
$+0°$C	4.6
$+20°$C	17.5
$+40°$C	55.3
$+60°$C	149.4
$+80°$C	355.1
$+100°$C	760.0
$+200°$C	11665,0

Table I.9. Vapor Pressure of Iodine in Torr

$-48.3°$C	0.00005
$-32.3°$C	0.00052
$-20.9°$C	0.0025
$0°$C	0.029
$15°$C	0.131
$30°$C	0.469
$80°$C	15.9
$114.5°$C	90.0 (melting point)
$185.3°$C	760.0 (boiling point)

Table I.10. Freezing Mixtures and Other Eutectics

Constituents with Melting Points		Eutectic Temperature in °C	Concentration
NH_4Cl	Ice (0)	-15.4	
NaCl	Ice (0)	-21	29/71 NaCl
Alcohol	Ice (0)	-30	
$CaCl_2 \cdot 6H_2O$	Ice (0)	-55	
Alcohol	CO_2(-56)	-72	
Ether	CO_2(-56)	-77	
Sn (232)	Pb (327)	183	74/26
Au (1063)	Si (1404)	370	69/31
Au (1063)	Tl (850)	131	27/73

Table I.11. Important Constants

Quantity	Symbol or Formula cgs	Symbol or Formula SI	Dimensions	Numerical Value and Unit in the cgs System	Numerical Value and Unit in the SI System
Atomic Quantities:					
Planck's Constant	h			6.626075×10^{-27} erg s	6.626075×10^{-34} J s $\;\triangleq 4.135669 \times 10^{-15}$ eV s
	$\hbar = h/2\pi$			1.054572×10^{-27} erg s	1.054572×10^{-34} J s $\;\triangleq 6.582122 \times 10^{-16}$ eV s
Elementary Charge	e_0			4.80324×10^{-10} esu	1.602177×10^{-19} C
Speed of Light in Vacuum	c			2.997925×10^{10} cm s^{-1}	2.997925×10^{8} m s^{-1}
Atomic Mass Unit (amu)	$1\,\mathrm{u} = 1\,\mathrm{amu} = \frac{1}{12}m_{C12}$			1.660540×10^{-24} g	1.660540×10^{-27} kg $\;\triangleq 931.5$ MeV
Rest Mass of the Electron	m_e			9.109389×10^{-28} g	9.109389×10^{-31} kg $\;\triangleq 5.485799 \times 10^{-4}$ amu
–Rest Energy	$m_e c^2$				0.510999 MeV
Rest mass of the Proton	m_p			1.672623×10^{-24} g	1.672623×10^{-27} kg $\;\triangleq 1.0072764$ amu
–Rest Energy	$m_p c^2$				938.272 MeV
Rest Mass of the Neutron	m_n			1.674928×10^{-24} g	1.674928×10^{-27} kg $\;\triangleq 1.0086649$ amu
–Rest Energy	$m_n c^2$				939.565 MeV
Mass Ratio Proton : Electron	m_p/m_e				1836.152
Mass Ratio Neutron : Proton	m_n/m_p				1.0013784
Specific Charge of the Electron	e_0/m_e			5.272759×10^{17} esu/g	1.758819×10^{11} C/kg
Classical Electron Radius	$\frac{e_0^2}{m_e c^2}$	$\frac{e_0^2}{4\pi\epsilon_0 m_e c^2}$	r_e	2.817940×10^{-13} cm	2.817940×10^{-15} m
Compton Wavelength of the Electron	$h/m_e c$	$h/m_e c$	λ_c	2.426310×10^{-10} cm	2.426310×10^{-12} m
	$\hbar/m_e c$	$\hbar/m_e c$	$\bar{\lambda}_c$	3.861593×10^{-11} cm	3.861593×10^{-13} m
Sommerfeld's Fine Structure Constant	$\frac{e_0^2}{\hbar c}$	$\frac{e_0^2}{4\pi\epsilon_0 \hbar c}$	α		$\frac{1}{137.035989}$
Bohr Radius of the Hydrogen Atom's Ground State	$\frac{\hbar^2}{m_e e_0^2}$	$\frac{4\pi\epsilon_0 \hbar^2}{m_e e_0^2}$	a	5.291772×10^{-9} cm	5.291772×10^{-11} m
Rydberg Constant (Ground State Energy of Hydrogen)	$\frac{1}{2}m_e c^2 \alpha^2$	$\frac{1}{2}m_e c^2 \alpha^2$	Ry	2.179874×10^{-11} erg	2.179874×10^{-18} J $\;\triangleq 13.6058$ eV
Bohr Magneton	$\frac{e_0 h}{2 m_e c}$	$\frac{e_0 h}{2 m_e}$	μ_B	9.274015×10^{-21} erg G^{-1}	9.274015×10^{-24} J T^{-1}
Nuclear Magneton	$\frac{e_0 h}{2 m_p c}$	$\frac{e_0 h}{2 m_p}$	μ_K	5.050786×10^{-24} erg G^{-1}	5.050786×10^{-27} J T^{-1}
Magnetic Moment of the Electron			μ_e	9.28477×10^{-21} erg G^{-1}	9.28477×10^{-24} J T^{-1} $= 1.00115965\mu_B$
Magnetic Moment of the Proton			μ_p	1.410607×10^{-23} erg G^{-1}	1.410607×10^{-26} J T^{-1} $= 2.792847\mu_K$

Table I.11. (Continuation)

Thermodynamic Quantities:

Boltzmann's Constant	k_B	$1.380658 \times 10^{-16}\,\mathrm{erg\,K^{-1}}$	$1.380658 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Gas Constant	R	$8.314510 \times 10^7\,\mathrm{erg\,mole^{-1}K^{-1}}$	$8.314510 \times 10^3\,\mathrm{J\,kmole^{-1}K^{-1}}$
Avogadro's Number	L	$6.0221367 \times 10^{23}\,\mathrm{mole^{-1}}$	$6.0221367 \times 10^{26}\,\mathrm{kmole^{-1}}$
Molar Volume (Ideal Gas) under Standard Conditions	V_0	$22.41410 \times 10^3\,\mathrm{cm^3\,mole^{-1}}$	$22.41410\,\mathrm{m^3kmole^{-1}}$
Standard Pressure (atmospheric pressure)	P_0	$1.01325 \times 10^6\,\mathrm{dyn\,cm^{-2}}$	$1.01325 \times 10^5\,\mathrm{Pa}$
Standard Temperature	T_0		$273.15\mathrm{K}\,(\hat{=}\,0°\mathrm{C})$
Temperature of the Triple Point of Water	T_t		$273.16\mathrm{K}$
Stefan–Boltzmann Radiation Constant	σ	$5.67051 \times 10^{-5}\,\mathrm{erg\,s^{-1}cm^{-2}K^{-4}}$	$5.67051 \times 10^{-8}\,\mathrm{W\,m^{-2}K^{-4}}$
Wien's Displacement Constant	A	$0.2897756\,\mathrm{cm\,K}$	$2.897756 \times 10^{-3}\,\mathrm{m\,K}$
Number of Gas Molecules per cm^3 under Standard Conditions	$n_0 = L/V_M$	$2.686763 \times 10^{19}\,\mathrm{cm^{-3}}$	$2.686763 \times 10^{25}\,\mathrm{m^{-3}}$

Gravitation and Electrodynamics:

Gravitational Constant	G	$6.67259 \times 10^{-8}\,\mathrm{dyn\,cm^2g^{-2}}$	$6.67259 \times 10^{-11}\,\mathrm{N\,m^2kg^{-2}}$
Standard Acceleration of Gravity	g	$9.80665 \times 10^2\,\mathrm{cm\,s^{-2}}$	$9.80665\,\mathrm{m\,s^{-2}}$
Permeability Constant of Vacuum	μ_0		$4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}} = 1.2566 \times 10^{-6}\,\mathrm{N\,A^{-2}}$
Dielectric Constant of Vacuum	$\left\{\begin{array}{l}\epsilon_0 = 1/(\mu_0 c^2)\\ 1/(4\pi\epsilon_0)\end{array}\right.$		$\begin{array}{l}8.85418 \times 10^{-12}\,\mathrm{C^2m^{-2}N^{-1}}\\ 8.98755 \times 10^9\,\mathrm{N\,m^2C^{-2}}\end{array}$

Table I.12. Ground States of Ions with Partially Filled Shells According to Hund's Rules

d – shell($l = 2$)

n	$l_z = 2$	1	0	-1	-2	S	$L = \left|\sum l_z\right|$	J	$^{2S+1}L_J$
1	↑					1/2	2	3/2	$^2D_{3/2}$
2	↑	↑				1	3	2	$^3F_2$
3	↑	↑	↑			3/2	3	3/2	$^4F_{3/2}$
4	↑	↑	↑	↑		2	2	0	$^5D_0$
5	↑	↑	↑	↑	↑	5/2	0	5/2	$^6S_{5/2}$
6	↑↓	↑	↑	↑	↑	2	2	4	$^5D_4$
7	↑↓	↑↓	↑	↑	↑	3/2	3	9/2	$^4F_{9/2}$
8	↑↓	↑↓	↑↓	↑	↑	1	3	4	$^3F_4$
9	↑↓	↑↓	↑↓	↑↓	↑	1/2	2	5/2	$^2D_{5/2}$
10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	$^1S_0$

f – shell($l = 3$)

n	$l_z = 3$	2	1	0	-1	-2	-3	S	$L = \left|\sum l_z\right|$	J	$^{2S+1}L_J$
1	↑							1/2	3	5/2	$^2F_{5/2}$
2	↑	↑						1	5	4	$^3H_4$
3	↑	↑	↑					3/2	6	9/2	$^4I_{9/2}$
4	↑	↑	↑	↑				2	6	4	$^5I_4$
5	↑	↑	↑	↑	↑			5/2	5	5/2	$^6H_{5/2}$
6	↑	↑	↑	↑	↑	↑		3	3	0	$^7F_0$
7	↑	↑	↑	↑	↑	↑	↑	7/2	0	7/2	$^8S_{7/2}$
8	↑↓	↑	↑	↑	↑	↑	↑	3	3	6	$^7F_6$
9	↑↓	↑↓	↑	↑	↑	↑	↑	5/2	5	15/2	$^6H_{15/2}$
10	↑↓	↑↓	↑↓	↑	↑	↑	↑	2	6	8	$^5I_8$
11	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	3/2	6	15/2	$^4I_{15/2}$
12	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	1	5	6	$^3H_6$
13	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	1/2	3	7/2	$^2F_{7/2}$
14	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	$^1S_0$

↑= spin $\frac{1}{2}$; ↓= spin $-\frac{1}{2}$.

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