Statistical Physics

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- Many other books and texts mentioned throughout the lecture

Lecture Webpage:

http://www.itp.phys.ethz.ch/education/hs13/StatPhys

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Introduction

Thermodynamics is a phenomenological, empirically derived description of the equilibrium properties of macroscopic physical systems. These systems are usually considered large enough such that the boundary effects do not play an important role (we call this the "thermodynamic limit"). The macroscopic states of such systems can be characterized by several macroscopically measurable quantities whose mutual relation can be cast into equations and represent the theory of thermodynamics.

Much of the body of thermodynamics has been developed already in the 19th century before the microscopic nature of matter, in particular, the atomic picture has been accepted. Thus, the principles of thermodynamics do not rely on the input of such specific microscopic details. The three laws of thermodynamics constitute the essence of thermodynamics.

Statistical Physics provides a road towards thermodynamics from a microscopic models of matter. We consider a macroscopic systems consisting of an extremely large number of (often identical) microscopic entities which can be found in different microstates, whose dynamics is often understood through a Hamiltonian. The number of degrees of freedom (variables) is large enough such that following the evolution of each microscopic entity individually becomes inaccessible. Rather a statistical approach taking averages over the microstates is appropriate to derive the essential and desired information on the macroscopic properties of a macroscopic system.

There are two basic viewpoints to this: (1) kinetic theory such as the Boltzmann kinetic gas theory and (2) statistical physics based on the Gibbsian concept of ensembles.

(1) The kinetic theory is based on statistical time evolution of a macroscopic system using the so-called Master equations. This allows us to discuss systems out of equilibrium which gradually approach equilibrium after long time when they are left on their own . The motion towards equilibrium is most impressively displayed in Boltzmann's H-theorem. Equilibrium is reached when macroscopic quantities do not show any time-dependence. Average properties are obtained through time averages over microstates.

(2) The Gibbsian approach considers a large number of identical copies of the system each one being in another microstate of the system, corresponding to the same macroscopic parameters (energy, volume, etc). Here time does not play a role and the averages are taken over ensembles, as we will see below. In many aspects this is the more accessible approach to derive thermodynamics and is for equilibrium physics equivalent to the kinetic theory if the ergodicity of the system is guaranteed. This means any microstate in the ensembles is (approximately) connected to any other microstate through temporal evolution following the dynamics given by the Hamiltonian.

Chapter 1

Classical statistical Physics

Statistical physics deals with the equilibrium properties of matter and provides the microscopic understanding and basis for thermodynamics. This chapter develops a new practical approach to equilibrium state of macroscopic systems. Time is not a variable anymore and measurements may be considered as averages over a large ensemble of identical systems in different possible microscopic states under the same external parameters.

1.1 Gibbsian concept of ensembles

As a practical example, we consider the state of a gas of N classical particles, given by $3N$ canonical coordinates $q_1, \ldots, q_{3N}$ and by the corresponding $3N$ conjugate momenta $p_1, \ldots, p_{3N}$. These define a $6N$-dimensional space Γ, where each point in Γ represents a state of the microscopic system. Considering the whole system of N particles under certain macroscopic conditions, given external parameter such as temperature, pressure, volume, internal energy, ... , we find that an infinite number of states in Γ are compatible with the same external condition, and would not be distinguishable by macroscopic measurements.

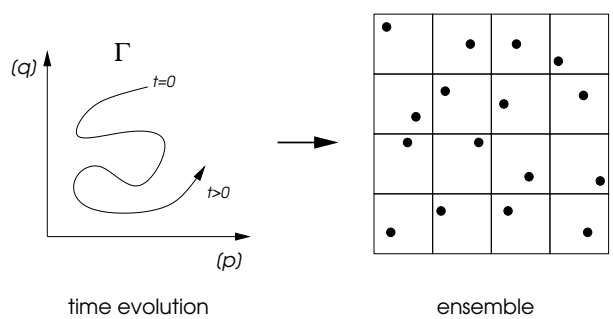

Fig. 1.1: *Time averages are replaced by averages over an ensemble of systems in different microscopic states, but with the same macroscopic conditions.*

If we would like to calculate a certain macroscopic quantity we could perform temporal average of the microscopic variables over a very long evolution time. Based on the states in Γ this is, however, not a practical method as it involves the discussion of the temporal evolution. Gibbs introduced the concept of ensembles to circumvent this problem. Taking a large (infinite) number of systems under identical macroscopic conditions, we can find macroscopic quantities by averaging over an ensemble of states. That this scheme is equivalent to a temporal average is a hypothesis, as it is assumed that the time evolution of the system would lead to all possible states also represented in the ensemble. This is the *ergodicity hypothesis.*[1] The set of states

[1]Ergodicity hypothesis: We consider the subspace defined by $\mathcal{H}(p, q) = E$ in Γ. Due to energy conservation a point in this subspace, evolving in time, does not leave this subspace. The ergodicity hypothesis states, that a point on $\mathcal{H} = E$ can reach in its temporal evolution every point of this subspace (Boltzmann, 1887). This is not

for given macroscopic parameters is then represented by a distribution of points in the space Γ. This distribution is generally continuous for a gas of particles.
For the calculation of averages we introduce the density function $\rho(p,q)$ providing the measure of the density of points in Γ-space ((p,q) stands for the whole state $(p_1,\ldots,p_{3N};q_1,\ldots q_{3N})$). Then

$$\rho(p,q)d^{3N}pd^{3N}q \tag{1.1}$$

gives the number of representative points contained in the small volume $d^{3N}pd^{3N}q$ in Γ, very analogous to the distribution function in Boltzmann theory. This can now be used to calculate averages of any desired quantity which can be expressed in the variable (p,q), $A(p,q)$:

$$\langle A\rangle = \frac{\int dpdqA(p,q)\rho(p,q)}{\int dpdq\rho(p,q)} \ . \tag{1.2}$$

We will use from now on the short notation $dpdq$ for $d^{3N}pd^{3N}q$ where it is not misleading.

1.1.1 Liouville Theorem

The dynamics of the system of N particles shall be described by a Hamiltonian $\mathcal{H}(p,q)$ which yields the equation of motion in the Hamiltonian formulation of classical mechanics,

$$\dot{p}_i = -\frac{\partial\mathcal{H}}{\partial q_i} \quad \text{and} \quad \dot{q}_i = \frac{\partial\mathcal{H}}{\partial p_i} \qquad (i=1,\ldots,3N) \ . \tag{1.3}$$

This equation describes the motion of the points in Γ. If $\mathcal{H}$ does not depend on time derivatives of p_i and/or q_i, then the equations of motion are time reversal invariant. They determine the evolution of any point in Γ uniquely.
Now let us consider the points in the Γ space and note that their number does not change in time, as if they form a fluid. Thus, they satisfy the continuity equation

$$\frac{\partial\rho}{\partial t} + \vec{\nabla}\cdot(\rho\vec{v}) = 0 \tag{1.4}$$

where $\vec{v} = (\dot{p}_1,\ldots,\dot{p}_{3N};\dot{q}_1,\ldots,\dot{q}_{3N})$ and $\vec{\nabla} = (\partial/\partial p_1,\ldots,\partial/\partial p_{3N};\partial/\partial q_1,\ldots,\partial/\partial q_{3N})$. Introducing the generalized substantial derivative we can rewrite this equation as

$$\frac{D\rho}{Dt} + \rho\vec{\nabla}\cdot\vec{v} = 0 \ . \tag{1.5}$$

The divergence of the "velocity" $\vec{v}$ is

$$\vec{\nabla}\cdot\vec{v} = \sum_{i=1}^{3N}\left\{\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right\} = \sum_{i=1}^{3N}\underbrace{\left\{\frac{\partial}{\partial q_i}\frac{\partial\mathcal{H}}{\partial p_i} - \frac{\partial}{\partial p_i}\frac{\partial\mathcal{H}}{\partial q_i}\right\}}_{=0} = 0. \tag{1.6}$$

This means that the points in Γ space evolve like an incompressible fluid. This property is known as *Liouville's theorem*. We may write this also in the form

$$0 = \frac{D\rho}{Dt} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left\{\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right\} = \frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left\{\frac{\partial\mathcal{H}}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \frac{\partial\mathcal{H}}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right\} \ . \tag{1.7}$$

Using Poisson brackets[2] this equation reads

$$\frac{\partial\rho}{\partial t} = \{\mathcal{H},\rho\} \ . \tag{1.9}$$

rigorously valid, however. Ehrenfest's version of this hypothesis (1911) states: The trajectory of a point comes any other point in the same subspace arbitrarily close in the course of time. Of course, it is possible to find (singular) counter examples, for which only a tiny fraction of the subspace is accessed.

[2]The Poisson bracket is defined as

$$\{u,v\} = \sum_i\left\{\frac{\partial u}{\partial q_i}\frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i}\frac{\partial v}{\partial q_i}\right\} = -\{v,u\} \ . \tag{1.8}$$

1.1.2 Equilibrium system

A satisfactory representation of a system in equilibrium requires for an ensemble that the density function does not depend on time t, i.e. $\partial\rho/\partial t = 0$. From Liouville's theorem we get the condition that

$$0 = \sum_{i=1}^{3N} \left\{ \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right\} = \vec{v} \cdot \vec{\nabla} \rho = \{\mathcal{H}, \rho\} \ . \tag{1.10}$$

A general way to satisfy this is to take a density function which depends only on quantities conserved during the motion, such as energy or particle number. Then the system would evolve within a subspace where ρ is constant.

We may use this feature of ρ now to consider averages of certain quantities, based on the above mentioned equivalence between the temporal and ensemble averages. Defining the temporal average of $A(p, q)$ as

$$\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(p(t), q(t)) dt \tag{1.11}$$

for any starting point $(p(t = 0), q(t = 0))$ in the space Γ and $(p(t), q(t))$ obeying the equation of motion (1.3). The hypothesis of ergodicity, even in its restricted sense, implies that this average can be taken as an average of an ensemble of an infinite number of different microscopic states (points in Γ-space). As the evolution of (p, q) conserves the energy, this leads naturally to consider an ensemble of states of a fixed energy (internal energy). We call such ensembles *microcanonical*. Although the microcanonical ensemble is not so frequently used in practice than other ensembles which we will consider later, it is very useful for illustrative purposes. It describes an isolated closed system with no energy exchange with the environment.

We postulate that in equilibrium any state of a macroscopic system satisfying the external conditions appears with equal probability. In our microcanonical description with fixed energy, number of particles N and volume V, we postulate

$$\rho(p, q) = \begin{cases} const. & E \leq \mathcal{H}(p, q) \leq E + \delta E \\ \\ 0 & \text{otherwise} \end{cases} \tag{1.12}$$

where δE is small. The average value of A is then given by (1.2). The validity of this approach is based on the assumption of small mean square fluctuations (standard deviation)

$$\frac{\langle \{A - \langle A \rangle\}^2 \rangle}{\langle A \rangle^2} \ll 1 \ . \tag{1.13}$$

Such fluctuations should be suppressed by the order N^{-1} as we will see below.

1.2 Microcanonical ensemble

We consider a macroscopic system of N particles in a volume V which is isolated and closed. The microcanonical ensemble for a given energy E consists of all systems of this kind, whose energy lies in the range $[E, E + \delta E]$. First we define the phase volume

$$\Phi(E) = \Lambda_N \int_{\mathcal{H}(p,q) \leq E} dp dq \ , \tag{1.14}$$

which contains all point in Γ space with energy lower than or equal to E. Moreover, Λ_N is a renormalization factor

$$\Lambda_N = \frac{1}{N! h^{3N}} \tag{1.15}$$

which compensates for the over-counting of the phase space in the integral by dividing by the number of equivalent states reached by permutations of the particles, $N!$. The factor h^{3N} corrects

for the dimension integral to produce a dimensionless $\Phi(E)$. Thus, h has the units of action ($[pq] = Js$). While this could be Planck constant h, its magnitude is completely unimportant in classical statistical physics. From this we obtain the volume of the microcanonical ensemble as

$$\omega(E) = \Phi(E + \delta E) - \Phi(E) = \frac{d\Phi(E)}{dE}\delta E \ . \tag{1.16}$$

Thus we now can renormalize $\rho(p, q)$ with the condition,

$$1 = \Lambda_N \int dp\ dq\ \rho(p, q) = \frac{\Lambda_N}{\omega(E)} \int_{E \leq \mathcal{H}(p,q) \leq E+\delta E} dp\ dq \tag{1.17}$$

such that

$$\rho(p, q) = \begin{cases} \dfrac{1}{\omega(E)} & E \leq \mathcal{H}(p, q) \leq E + \delta E \\ \\ 0 & \text{otherwise} \end{cases} \ . \tag{1.18}$$

As postulated $\rho(p, q)$ is constant in the energy range $[E, E + \delta E]$.

1.2.1 Entropy

We use $\omega(E)$ to define the entropy

$$S(E, V, N) = k_B \ln \omega(E) \ . \tag{1.19}$$

We can consider $\omega(E)$ or S as a measure of the imprecision of our knowledge of the state of the system. The more states are available in microcanonical ensemble, the less we know in which state the system is at a given time and the larger is the volume ω and the entropy.
We consider a composite system consisting of two subsystems, 1 and 2,

$$\mathcal{H}(p, q) = \mathcal{H}_1(p_1, q_1) + \mathcal{H}_2(p_2, q_2) \ , \tag{1.20}$$

with (N_1, V_1) and (N_2, V_2), resp., for the corresponding particle number and volume. Each of the two systems is characterized by $\omega_1(E_1)$ and $\omega_2(E_2)$, respectively. The volume $\omega(E)$ of the microcanonical ensemble is the product of the subsystems under the conditions

$$E = E_1 + E_2 \ , \quad N = N_1 + N_2 \quad \text{and} \quad V = V_1 + V_2 \ . \tag{1.21}$$

For simplicity we assume that the volumes and particle numbers of the subsystems may be fixed, while they can exchange energy, such that E_1 and E_2 can fluctuate. Therefore the volume of the microcanonical ensemble of the total system for given E reads,

$$\omega(E) = \sum_{0 \leq E' \leq E} \omega_1(E')\ \omega_2(E - E') \ , \tag{1.22}$$

where we assume for the sum a "discrete" mesh of equally spaced E'-values of mesh spacing δE ($\ll E$). We claim that this sum is well approximated by a single value E'_0 giving rise to a sharp maximum among the summands ($E_1 = E'_0$ and $E_2 = E - E'_0$)[3]. The largest term is

[3]Note that $\ln \omega_i \propto N_i$ and $E_i \propto N_i$ ($i = 1, 2$) as both quantities are extensive. We then find quickly the following bounds:

$$\omega_1(E'_0)\omega_2(E - E'_0) \leq \omega(E) \leq \frac{E}{\delta E}\omega_1(E'_0)\omega_2(E - E'_0) \ . \tag{1.23}$$

Note that $E/\delta E$ is the number of summands. Thus, we obtain for the entropy

$$k_B \ln \omega_1(E'_0)\omega_2(E - E'_0) \leq S(E) \leq k_B \ln \omega_1(E'_0)\omega_2(E - E'_0) + k_B \ln \frac{E}{\delta E} \ . \tag{1.24}$$

It is important to see that the last term only scales with system size as $\ln N$ (keeping δE fixed), while the first term scales with N. Therefore in the very large-N limit the last term is irrelevant. Which proves that $S(E)$ is given by the maximal term in the sum (1.22).

obtained by

$$\left.\frac{\partial \omega_1(E')\,\omega_2(E-E')}{\partial E'}\right|_{E'=E'_0} = 0 \tag{1.25}$$

such that

$$\begin{aligned} 0 &= \left\{ \frac{1}{\omega_1(E')}\frac{\partial \omega_1(E')}{\partial E'} + \frac{1}{\omega_2(E-E')}\frac{\partial \omega_2(E-E')}{\partial E'} \right\}_{E'=E'_0} \\ &= \left.\frac{\partial \ln \omega_1(E_1)}{\partial E_1}\right|_{E_1=E'_0} - \left.\frac{\partial \ln \omega_2(E_2)}{\partial E_2}\right|_{E_2=E-E'_0} . \end{aligned} \tag{1.26}$$

From this we obtain with $\bar{E}_1 = E'_0$ and $\bar{E}_2 = E - E'_0$

$$\left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} = \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{E_2=\bar{E}_2} \tag{1.27}$$

which can be considered as the equilibrium condition. Note that this is equivalent to the statement that the equilibrium state corresponds to the macrostate with the largest number of microscopic realizations.
Identifying E as the internal energy U we define the temperature

$$\frac{\partial S}{\partial U} = \frac{1}{T} \qquad \Rightarrow \qquad \frac{1}{T_1} = \frac{1}{T_2} , \tag{1.28}$$

leading to T as an equilibrium state variable. We have ignored the other variables V, N which we will consider later.
Let us assume that there is some impediment which forces the two subsystems to specific variables such that each subsystem independently is at equilibrium, but not the total system. For example, a big vessel of gas may be separated by a wall into two subvessels. Then we find for the corresponding ω of the combined system,

$$\tilde{\omega}(E,V,N) = \omega_1(E_1,V_1,N_1)\omega_2(E_2,V_2,N_2) \qquad \text{with} \quad \begin{cases} E = E_1 + E_2 \\ V = V_1 + V_2 \\ N = N_1 + N_2 \end{cases} \tag{1.29}$$

such that the entropy is given by

$$\tilde{S}(E,V,N) = S_1(E_1,V_1,N_1) + S_2(E_2,V_2,N_2) \leq S(E,V,N) , \tag{1.30}$$

i.e. the entropy is concave. This means also the equilibrium is obtained by the maximal entropy, which is a consequence of the second law of thermodynamics. In terms of the volume of the microcanonical volume ω the equilibrium state assumes among all volumes the maximal one, the most likely one in terms of probability.

1.2.2 Relation to thermodynamics

With (1.19) we have a definition of the entropy which for the variables $E(=U)$, V and N is a thermodynamic potential and allows us to calculate a variety of state variables and relations,

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN . \tag{1.31}$$

This allows also to calculate the thermodynamic equation of state,

$$p = T\left(\frac{\partial S}{\partial V}\right)_{E,N} \tag{1.32}$$

and to determine other thermodynamic potentials. The caloric equation of state is obtained from

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \ , \tag{1.33}$$

by using $U = E$ as the internal energy. The derivative with respect to N yields finally the chemical potential

$$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{E,V} \ , \tag{1.34}$$

the energy in order to add a particle to the system.

1.2.3 Ideal gas - microcanonical treatment

We consider a classical gas of N independent mono-atomic particles in the fixed volume V, which is closed and isolated. The Hamiltonian is simply given by

$$\mathcal{H}(p,q) = \mathcal{H}(p) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \ . \tag{1.35}$$

Hence we obtain the volume

$$\Phi(E) = \Lambda_N \int_{\mathcal{H}(p)\leq E} dpdq = \Lambda_N V^N \int_{\mathcal{H}(p)\leq E} dp \ . \tag{1.36}$$

This p-integral corresponds to the volume of a sphere of radius R in $3N$-dimensional space.[4] The integral is straightforward,

$$\Phi(E) = \Lambda_N V^N C_{3N} \left(2mE\right)^{3N/2} \qquad \text{with} \qquad C_n = \frac{\pi^{n/2}}{\Gamma\left(\frac{n}{2}+1\right)} \tag{1.39}$$

[4]Volume of sphere in ν-dimensional space: $\mathcal{V}(R) = CR^\nu$. The volume enclosed in a thin shell of width δR at the radius R is given by

$$v_{shell} = \mathcal{V}(R) - \mathcal{V}(R-\delta R) = CR^\nu \left[1 - \left(1 - \frac{\delta R}{R}\right)^\nu\right] \tag{1.37}$$

with $\delta R \ll R$, see Fig. 1.2 . In the limit ν very large, $\nu\delta R \gg R$, we find

$$v_{shell} \approx \mathcal{V}(R) \ . \tag{1.38}$$

Thus, the main part of the volume in the sphere is concentrated at the outermost shell.

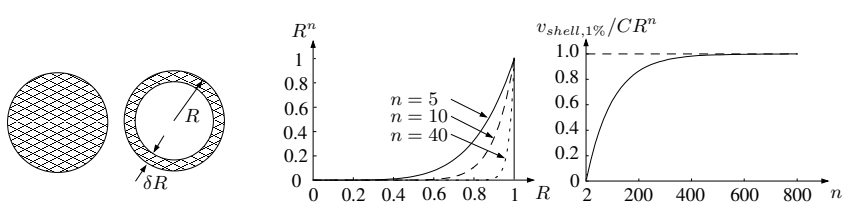

Fig. 1.2: *The volume of the sphere is located close to the surface in high dimensions, see the central diagram. Thus, the fraction of the volume close to the shell and the total volume converges towards one as $n \to \infty$ (diagram on the right hand side).*

where C_{3N} is the proper prefactor for the volume of an $3N$-dimensional sphere.[5] This leads to

$$\omega(E) = \frac{\partial \Phi(E)}{\partial E}\delta E = \Lambda_N C_{3N} V^N \frac{3N}{2} 2m\,(2mE)^{3N/2-1}\,\delta E\ . \tag{1.42}$$

Remarkably, for very large N ($\sim 10^{23}$) we find that the following definitions for the entropy are identical up to terms of order $\ln N$ and constants:

$$S_\omega = k_B \ln \omega(E,V,N) \qquad \text{and} \qquad S_\Phi = k_B \ln \Phi(E,V,N) \tag{1.43}$$

leading to

$$\begin{aligned} S_\omega &= k_B \ln(\Lambda_N V^N C_{3N}) + k_B\left(\frac{3N}{2}-1\right)\ln(2mE) + k_B \ln\left(\frac{3N}{2}2m\delta E\right) \\ &= k_B \ln(\Lambda_N V^N C_{3N}) + k_B \frac{3N}{2}\ln(2mE) + O(\ln N) = S_\Phi + O(\ln N)\ . \end{aligned} \tag{1.44}$$

Since we can drop terms of order $\ln N$ for the extensive entropy, we will continue, for convenience, using S_Φ instead of S_ω,

$$S(E,V,N) = Nk_B \ln\left\{V\left(\frac{2m\pi E}{h^2}\right)^{3/2}\right\} - \frac{3N}{2}k_B \ln\frac{3N}{2} + \frac{3N}{2}k_B - Nk_B \ln N + Nk_B \tag{1.45}$$

where we used Stirling's formula

$$\ln n! \approx n\ln n - n + \frac{1}{2}\ln(2\pi n) \qquad \text{for} \quad n\to\infty\ , \tag{1.46}$$

and neglected all terms of order $\ln N$. We then rewrite

$$S(E,V,N) = Nk_B \ln\left\{\frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right\} + \frac{5}{2}Nk_B\ . \tag{1.47}$$

This equation may now be solved for E so that we obtain the internal energy as a thermodynamic potential

$$U(S,V,N) = E = \frac{3N^{5/3}h}{4\pi m V^{2/3}}\exp\left\{\frac{2S}{3Nk_B} - \frac{5}{3}\right\}\ . \tag{1.48}$$

The thermodynamic quantities are obtained by derivation: the temperature

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} = \frac{2U}{3Nk_B} \qquad \Rightarrow \qquad U = \frac{3}{2}Nk_BT\ , \tag{1.49}$$

the pressure

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = \frac{2}{3}\frac{U}{V} = \frac{Nk_BT}{V} \qquad \Rightarrow \qquad pV = Nk_BT\ , \tag{1.50}$$

and the chemical potential

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \frac{U}{N}\left(\frac{5}{3} - \frac{2}{3}\frac{S}{Nk_B}\right) = -k_BT\ln\left\{\frac{V}{N}\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\right\}\ . \tag{1.51}$$

Through further derivatives it is possible to obtain various response functions. The ideal gas is readily described by means of the microcanonical ensemble.

[5] Prefactor C_n: Use the n-dimensional Gaussian integral in Cartesian coordinates

$$I = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_n e^{-(x_1^2+\cdots+x_n^2)} = \left(\int_{-\infty}^{+\infty} dx e^{-x^2}\right)^n = \pi^{n/2}\ . \tag{1.40}$$

The same integral in spherical coordinates is given by

$$I = nC_n \int_0^\infty dr r^{n-1} e^{-r^2} = \frac{n}{2}C_n \int_0^\infty dt\, t^{\frac{n}{2}-1}e^{-t} = \frac{n}{2}C_n\Gamma\left(\frac{n}{2}\right) = C_n\Gamma\left(\frac{n}{2}+1\right) \tag{1.41}$$

such that we obtain C_n given in (1.39). Note, $\Gamma(n+1) = n!$ for $n \geq 0$ as an integer.

1.3 Canonical ensemble

We change to a macroscopic system for which we control the temperature by connecting it to a very large heat reservoir. The system together with the reservoir forms a closed system of given total energy. Therefore we consider two subsystems, system 1 describing our system and system 2 being the heat reservoir,

$$\mathcal{H}(p,q) = \mathcal{H}_1(p_1,q_1) + \mathcal{H}_2(p_2,q_2) \ . \tag{1.52}$$

The heat reservoir is much larger than system 1, $N_2 \gg N_1$, such that energy transfer between the two subsystems would be too small to change the temperature of the reservoir. Within the microcanonical scheme we determine the phase space of the combined system in the energy range

$$E \leq E_1 + E_2 \leq E + \delta E \ . \tag{1.53}$$

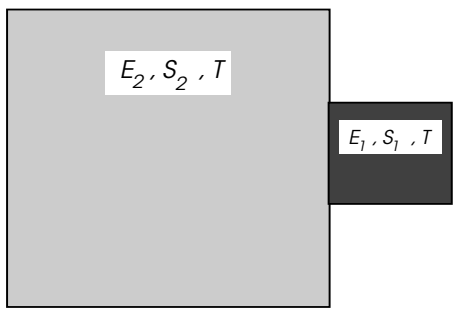

Fig. 1.3: *The two systems 1 and 2 are coupled thermally. System 2 acts as a huge reservoir fixing the temperature of the system 1 which we want to investigate.*

Therefore the volume of the microcanonical ensemble of the total system is

$$\omega(E) = \sum_{0 \leq E_1 \leq E} \omega_1(E_1)\omega_2(E-E_1) \ . \tag{1.54}$$

Analogously to our previous discussion in section 1.2.1, there is one value $\bar{E}_1 = E_0'$ ($\bar{E}_2 = E - E_0'$) which provides the by far dominant contribution. In addition here $\bar{E}_2 \gg \bar{E}_1$ is valid. The corresponding volumes in Γ-space are $\omega_1(\bar{E}_1)$ and $\omega_2(\bar{E}_2)$ and $\omega(E) \approx \omega_1(\bar{E}_1)\omega_2(E-\bar{E}_1)$. Due to this simple product form we can determine the density function $\rho_1(p_1,q_1)$ of the system 1, by considering the mean value of $A(p,q)$ in system 1,

$$\langle A \rangle_1 = \frac{\int_1 dp_1 dq_1 A(p_1,q_1) \int_2 dp_2 dq_2 \rho(p,q)}{\int_1 dp_1 dq_1 \int_2 dp_2 dq_2 \rho(p,q)} = \frac{\int_1 dp_1 dq_1 A(p_1,q_1)\rho_1(p_1,q_1)}{\int_1 dp_1 dq_1 \rho_1(p_1,q_1)} \ . \tag{1.55}$$

Taking into account that $\rho(p,q)$ is constant in the range $E \leq \mathcal{H}_1(p_1,q_1) + \mathcal{H}_2(p_2,q_2) \leq E + \delta E$ we obtain

$$\langle A \rangle_1 = \frac{\int_1 dp_1 dq_1 A(p_1,q_1)\omega_2(E - \mathcal{H}_1(p_1,q_1))}{\int_1 dp_1 dq_1 \omega_2(E - \mathcal{H}_1(p_1,q_1))} \ . \tag{1.56}$$

Using the assumption that $\bar{E}_2 \approx E \gg \bar{E}_1$ we may expand $\omega_2(E - \mathcal{H}_1(p_1,q_1))$ in $\mathcal{H}_1(p_1,q_1))$,

$$\begin{aligned} k_B \ln \omega_2(E - \mathcal{H}_1(p_1,q_1)) &= S_2(E - \mathcal{H}_1(p_1,q_1)) = S_2(E) - \mathcal{H}_1(p_1,q_1) \left.\frac{\partial S_2(\bar{E}_2)}{\partial E_2}\right|_{\bar{E}_2 = E} + \cdots \\ &= S_2(E) - \frac{\mathcal{H}_1(p_1,q_1)}{T} + \cdots \end{aligned} \tag{1.57}$$

from which we derive

$$\omega_2(E - \mathcal{H}_1(p_1, q_1)) = e^{S_2(E)/k_B} e^{-\mathcal{H}_1(p_1,q_1)/k_B T} \ . \tag{1.58}$$

Here T is the temperature of both systems which are in equilibrium.
Within the canoncial ensemble, taking the temperature T as a given parameter, we write generally for the density function, the probability to find the system of N particles in the microstate (p, q),

$$\rho(p, q) = \frac{1}{Z} e^{-\mathcal{H}(p,q)/k_B T} \ , \tag{1.59}$$

where we introduced the *partition function* Z

$$Z = \Lambda_N \int dp\ dq e^{-\beta \mathcal{H}(p,q)} \qquad \text{with} \quad \beta = \frac{1}{k_B T} \ , \tag{1.60}$$

which, up to prefactors, corresponds to the volume of the ensemble of system 1, called *canonical ensemble*, again renormalized by Λ_N.[6]

1.3.1 Thermodynamics

The connection to thermodynamics is given by the relation

$$Z = e^{-\beta F(T,V,N)} \ , \tag{1.61}$$

where $F(T, V, N)$ is the Helmholtz free energy, a thermodynamical potential. Note, F is an extensive quantity, because obviously scaling the system by a factor λ would yield Z^λ. Moreover,

$$F = U - TS \tag{1.62}$$

with

$$U = \langle \mathcal{H} \rangle \qquad \text{and} \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \ . \tag{1.63}$$

This can be proven using the equation,

$$1 = \Lambda_N \int dp\ dq e^{\beta(F - \mathcal{H})} \ , \tag{1.64}$$

which through differentiation with respect to β on both sides gives,

$$\begin{aligned} 0 &= \Lambda_N \int dp\ dq e^{\beta(F-\mathcal{H})} \left\{ F + \beta \left(\frac{\partial F}{\partial \beta}\right)_{V,N} - \mathcal{H} \right\} \\ \Rightarrow \quad & F(T, V, N) - U(T, V, N) - T \left(\frac{\partial F}{\partial T}\right)_{V,N} = 0 \ . \end{aligned} \tag{1.65}$$

Using this formulation for the free energy we obtain for the pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \ , \tag{1.66}$$

which in the case of a gas leads to the thermodynamic equation of state.
The internal energy is easily obtained from the partition function in the following way,

$$U(T, V, N) = \langle \mathcal{H} \rangle = \frac{\Lambda_N}{Z} \int dp\ dq\ \mathcal{H} e^{-\beta \mathcal{H}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z \ . \tag{1.67}$$

This is the caloric equation of state.

[6] Note that there is, rigorously speaking, the constraint $\mathcal{H}_1(p_1, q_1) < E$. However, ignoring this constraint is a good approximation, as the main contribution is from the valid range.

1.3.2 Equipartition law

We now consider a set of special average values which will lead us to the so-called equipartition law, the equal distribution of energy on equivalent degrees of freedom. We examine the mean value,

$$\begin{aligned}\left\langle q_\mu \frac{\partial \mathcal{H}}{\partial q_\nu} \right\rangle &= \frac{\Lambda_N}{Z} \int dp\, dq q_\mu \frac{\partial \mathcal{H}}{\partial q_\nu} e^{-\beta \mathcal{H}} = -\frac{\Lambda_N}{Z\beta} \int dp\, dq q_\mu \frac{\partial}{\partial q_\nu} e^{-\beta \mathcal{H}} \\ &= -\frac{\Lambda_N}{Z\beta} \underbrace{\int' dp\, d'q\, q_\mu e^{-\beta \mathcal{H}}}_{=0} + \frac{\Lambda_N \delta_{\mu\nu}}{Z\beta} \int dp dq e^{-\beta \mathcal{H}} = \delta_{\mu\nu} k_B T \ ,\end{aligned} \tag{1.68}$$

where we used integration by parts leading to the boundary terms in the q_ν-coordinate (expressed by $\int' d'q...$), which we assume to vanish. Analogously we find for the momentum

$$\left\langle p_\mu \frac{\partial \mathcal{H}}{\partial p_\nu} \right\rangle = \delta_{\mu\nu} k_B T \ . \tag{1.69}$$

If the Hamiltonian is separable into a p-dependent kinetic energy and a q-dependent potential energy part and, moreover, if the following scaling behavior is valid

$$\mathcal{H}(p,q) = E_{kin}(p) + V(q) \quad \text{with} \quad E_{kin}(\lambda p) = \lambda^2 E_{kin}(p) \quad \text{and} \quad V(\lambda q) = \lambda^\alpha V(q) \tag{1.70}$$

then we can use the above relations and find for mono-atomic particles

$$\langle E_{kin} \rangle = \frac{3N}{2} k_B T \qquad \text{and} \qquad \langle V \rangle = \frac{3N}{\alpha} k_B T \ . \tag{1.71}$$

The total energy is given by the sum of the two contributions.

1.3.3 Ideal gas - canonical treatment

Consider a gas of N particles without external potential and mutual interactions described by the Hamiltonian

$$\mathcal{H}(p) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \ . \tag{1.72}$$

The partition function is given by

$$\begin{aligned} Z &= \Lambda_N \prod_{i=1}^{N} \int d^3p_i\, d^3q_i\, e^{-\vec{p}_i^{\,2}/2mk_BT} = \Lambda_N \left\{ \int d^3p\, d^3q\, e^{-\vec{p}^2/2mk_BT} \right\}^N \\ &= \Lambda_N V^N \left\{ 2\pi m k_B T \right\}^{3N/2} \ . \end{aligned} \tag{1.73}$$

From this we obtain the free energy and the internal energy using Stirling's formula,

$$\begin{aligned} F(T,V,N) &= -k_BT \ln Z = -Nk_BT \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} - Nk_BT \ , \\ U(T,V,N) &= -\frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} k_B T \quad \text{(caloric equation of state)} \ . \end{aligned} \tag{1.74}$$

The entropy is given by

$$S(T,V,N) = -\left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk_B \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} + \frac{5N}{2} k_B \tag{1.75}$$

and the pressure by

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V} \tag{1.76}$$

which corresponds to the thermodynamic equation of state. Finally the chemical potential is obtained as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \ln\left\{\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right\} . \tag{1.77}$$

An important aspect for the ideal system is the fact that the partition function has a product form because each particle is described independently. In this way it leads to an extensive free energy and internal energy.

1.4 Grand canonical ensemble

We consider now a new situation by allowing beside the heat exchange also the exchange of matter of our system with a very large reservoir, see Fig. 1.4 . Thus we take the system 1 with N_1 particles in a volume V_1 coupled to the reservoir 2 with N_2 particles in the volume V_2 with

$$N_1 \ll N_2 \qquad \text{and} \qquad V_1 \ll V_2 , \tag{1.78}$$

and $N = N_1 + N_2$ and $V = V_1 + V_2$ fixed.

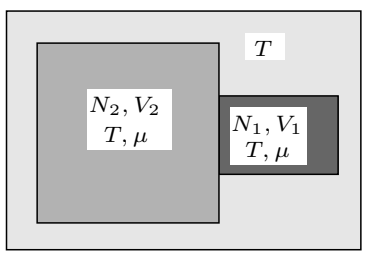

Fig. 1.4: *The two systems 1 and 2 can exchange matter between each other while the surrounding heat reservoir fixes the temperature of system 1 and 2. System 2 acts as a huge particle reservoir fixing the chemical potential μ of the system 1 which we want to investigate.*

The Hamiltonian can be decomposed into two parts

$$\mathcal{H}(p, q, N) = \mathcal{H}(p_1, q_1, N_1) + \mathcal{H}(p_2, q_2, N_2) \tag{1.79}$$

such that the corresponding partition function for given temperature (everything is coupled to an even larger heat reservoir) is given by

$$Z_N(V, T) = \frac{1}{h^{3N} N!} \int dp\, dq\, e^{-\beta \mathcal{H}(p,q,N)} . \tag{1.80}$$

The factor $1/N!$ takes into account that all possible commutation of the particles give the same states (distinguishable classical particles). Now we segregate into the subsystems fixing the volumes and particle numbers ($N_2 = N - N_1$),

$$\begin{aligned} Z_N &= \frac{1}{h^{3N} N!} \sum_{N_1=0}^{N} \frac{N!}{N_1! N_2!} \int dp_1\, dp_2 \int_{V_1} dq_1 \int_{V_2} dq_2 e^{-\beta\{\mathcal{H}(p_1,q_1,N_1)+\mathcal{H}(p_2,q_2,N_2)\}} \\ &= \sum_{N_1=0}^{N} \frac{1}{h^{3N_1} N_1!} \int_{V_1} dp_1\, dq_1\, e^{-\beta \mathcal{H}(p_1,q_1,N_1)} \quad \frac{1}{h^{3N_2} N_2!} \int_{V_2} dp_2\, dq_2\, e^{-\beta \mathcal{H}(p_2,q_2,N_2)} . \end{aligned} \tag{1.81}$$

Note that the distribution of the particles into the two subsystems is not fixed yielding the combinatorial factor of $N!/N_1!N_2!$ (number of configurations with fixed N_1 and N_2 by permuting the particles in each subsystem). From this we define the probability $\rho(p_1, q_1, N_1)$ that we can find N_1 particles in the volume V_1 at the space coordinates (p_1, q_1),

$$\rho(p_1, q_1, N_1) = \frac{e^{-\beta\mathcal{H}(p_1,q_1,N_1)}}{Z_N N_1! h^{3N_2} N_2!} \int_{V_2} dp_2\, dq_2\, e^{-\beta\mathcal{H}(p_2,q_2,N_2)} \tag{1.82}$$

which is renormalized as

$$\sum_{N_1=0}^{N} \frac{1}{h^{3N_1}} \int_{V_1} dp_1 dq_1 \rho(p_1, q_1, N_1) = 1 \; . \tag{1.83}$$

We may write

$$\rho(p_1, q_1, N_1) = \frac{Z_{N_2}}{Z_N} \frac{1}{N_1!} e^{-\beta\mathcal{H}(p_1,q_1,N_1)} \; , \tag{1.84}$$

where we now use the relation

$$\frac{Z_{N_2}(V_2, T)}{Z_N(V, T)} = e^{-\beta\{F(T,V-V_1,N-N_1)-F(T,V,N)\}} \tag{1.85}$$

with

$$F(T, V - V_1, N - N_1) - F(T, V, N) \approx -\left(\frac{\partial F}{\partial V}\right)_{T,N} V_1 - \left(\frac{\partial F}{\partial N}\right)_{T,V} N_1 = -\mu N_1 + pV_1 \; . \tag{1.86}$$

Thus we define

$$z = e^{\beta\mu} \tag{1.87}$$

which we call *fugacity*. Thus within the grand canonical ensemble we write for the density function

$$\rho(p, q, N) = \frac{z^N}{N!} e^{-\beta\{pV+\mathcal{H}(p,q,N)\}} \; . \tag{1.88}$$

μ is the chemical potential as introduced earlier. We now introduce the grand partition function

$$\mathcal{Z}(T, V, z) = \sum_{N=0}^{\infty} z^N Z_N(V, T) \; , \tag{1.89}$$

which incorporates all important information of a system of fixed volume, temperature and chemical potential.

1.4.1 Relation to thermodynamics

We use now (1.88) and integrate both sides

$$1 = e^{-\beta pV} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \frac{dp\, dq}{h^{3N}}\, e^{-\beta\mathcal{H}(p,q,N)} = e^{-\beta pV} \mathcal{Z}(T, V, z) \tag{1.90}$$

which leads to

$$\Omega(T, V, \mu) = -pV = -k_B T \ln \mathcal{Z}(T, V, z) \; , \tag{1.91}$$

the grand potential

$$d\Omega = -SdT - pdV - Nd\mu \; . \tag{1.92}$$

The average value of N is then given by

$$\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} = k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} = z \frac{\partial}{\partial z} \ln \mathcal{Z} = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N z^N Z_N \; . \tag{1.93}$$

It is also convenient to derive again the internal energy

$$U = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} \qquad \Rightarrow \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\mu} \; . \tag{1.94}$$

1.4.2 Ideal gas - grand canonical treatment

For the ideal gas, it is easy to calculate the grand partition function (here for simplicity we set $h = 1$),

$$\mathcal{Z}(T,V,z) = \sum_{N=0}^{\infty} z^N Z_N(T,V) = \sum_{N=0}^{\infty} \frac{z^N}{N!} V^N (2\pi m k_B T)^{3N/2} = \exp\left\{ zV(2\pi m k_B T)^{3/2} \right\} . \quad (1.95)$$

We can also derive the probability P_N of finding the system with N particles. The average value is given by

$$\langle N \rangle = z\frac{\partial}{\partial z} zV(2\pi m k_B T)^{3/2} = zV(2\pi m k_B T)^{3/2} \quad \Rightarrow \quad \mathcal{Z} = e^{\langle N \rangle} . \quad (1.96)$$

From this we conclude that the distribution function for the number of particles is given by

$$P_N = e^{-\langle N \rangle} \frac{\langle N \rangle^N}{N!} \approx \frac{1}{\sqrt{2\pi \langle N \rangle}} e^{-(N-\langle N \rangle)^2/2\langle N \rangle} \quad (1.97)$$

which is strongly peaked at $N = \langle N \rangle \gg 1$.[7] The fluctuations are given by

$$\langle N^2 \rangle - \langle N \rangle^2 = z\frac{\partial \langle N \rangle}{\partial z} = \langle N \rangle \qquad \Rightarrow \quad \kappa_T = \frac{v}{k_B T} = \frac{1}{p} . \quad (1.98)$$

The grand potential is given by

$$\Omega(T,V,\mu) = -k_B T e^{\beta\mu} V (2\pi m k_B T)^{3/2} = -k_B T \langle N \rangle = -pV . \quad (1.99)$$

The chemical potential is obtained by solving Eq.(1.96) for μ

$$\mu = k_B T \ \ln\left(\frac{\langle N \rangle (2\pi m k_B T)^{-3/2}}{V} \right) . \quad (1.100)$$

1.4.3 Chemical potential in an external field

In order to get a better understanding of the role of the chemical potential, we now consider an ideal gas in the gravitational field, i.e. the particles are subject to the potential $\phi(h) = mg\tilde{h}$, where $\tilde{h}$ and g denote the altitude and We introduce a reference chemical potential μ_0 as a constant. Then we write for the chemical potential,

$$\mu = \mu_0 + mg\tilde{h} + k_B T \ \ln\left\{ n(2\pi m k_B T)^{-3/2} \right\} \quad (1.101)$$

where we define $n = \langle N \rangle / V$ as the local number density of particles. In equilibrium the temperature and the chemical potential shall be constant. We may determine μ by the condition that at $\tilde{h} = 0$ the density is $n = n_0$,

$$\mu(T) = \mu_0 + k_B T \ \ln\left\{ n_0 (2\pi m k_B T)^{-3/2} \right\} \quad \Rightarrow \quad mgh = k_B T \ \ln\left(\frac{n_0}{n} \right) . \quad (1.102)$$

We can now solve this equation for $n = n(\tilde{h})$,

$$n(\tilde{h}) = n_0 e^{-\beta mg\tilde{h}} , \quad (1.103)$$

and with the (local) equation of state we find

$$p(\tilde{h}) = n(h) k_B T = p_0 e^{-\beta mg\tilde{h}} . \quad (1.104)$$

This is the famous barometer formula.

[7] Note that for $\mu > 0$ it pays the energy μ to add a particle to the system. Therefore as T goes to 0 the average particle number $\langle N \rangle$ increases (diverges). Oppositely, $\langle N \rangle$ decreases for $T \to 0$, if $\mu < 0$ and energy has to be paid to add a particle.

1.5 Fluctuations

Changing from one type of ensemble to the other we have seen that certain quantities which have been strictly fixed in one ensemble are statistical variables of other ensembles. Obvious examples are the internal energy which is fixed in the microcanonical ensemble but not in the other two, or the particle number which is fixed in the microcanonical and canonical ensembles but not in the grand canonical ensemble. The question arises how well the mean values of these quantities are determined statistically, which is connected with the equivalence of different ensembles. In this context we will also introduce the fluctuation-dissipation theorem which connects the fluctuations (statistical variance) of a quantity with response functions.

1.5.1 Energy

In the canonical ensemble the internal energy is given as the average of the Hamiltonian $U = \langle \mathcal{H} \rangle$. Therefore the following relation holds:

$$\Lambda_N \int dp\, dq\ [U - \mathcal{H}]\, e^{\beta(F-\mathcal{H})} = 0\ . \tag{1.105}$$

Taking the derivative of this equation with respect to β we obtain

$$0 = \frac{\partial U}{\partial \beta} + \Lambda_N \int dp\, dq\, (U - \mathcal{H}) \left[F - T\frac{\partial F}{\partial T} - \mathcal{H} \right] e^{\beta(F-\mathcal{H})} = \frac{\partial U}{\partial \beta} + \langle (U - \mathcal{H})^2 \rangle\ . \tag{1.106}$$

This leads to the relation for the fluctuations of the energy around its average value U,

$$\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \langle (U - \mathcal{H})^2 \rangle = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V\ . \tag{1.107}$$

Because C_V is an extensive quantity and therefore proportional to N, it follows that

$$\frac{\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2}{\langle \mathcal{H} \rangle^2} \propto \frac{1}{N} \tag{1.108}$$

which is a sign of the equivalence of microcanonical and canonical ensembles. In the thermodynamic limit $N \to \infty$, the fluctuations of the energy vanish compared to the energy itself. Therefore the internal energy as $U = \langle \mathcal{H} \rangle = E$ is a well defined quantity in the canonical ensemble as well as it was in the microcanonical ensemble.

We now consider the partition function

$$Z = \Lambda_N \int dp\, dq\, e^{-\beta \mathcal{H}(p,q)} = \int_0^\infty dE\, \omega(E) e^{-\beta E} = \int_0^\infty dE\, e^{-\beta E + \ln \omega(E)} = \int_0^\infty dE\, e^{\beta(TS(E) - E)} \tag{1.109}$$

where the entropy $S(E)$ is defined according to the microcanonical ensemble. The maximum of the integrand at $E = E_0$ is defined by the condition, see Fig. 1.5,

$$T \left.\frac{\partial S}{\partial E}\right|_{E=E_0} = 1 \qquad \text{and} \qquad \left.\frac{\partial^2 S}{\partial E^2}\right|_{E=E_0} < 0\ . \tag{1.110}$$

Note that

$$\left.\frac{\partial^2 S}{\partial E^2}\right|_{E=E_0} = \left.\frac{\partial}{\partial E}\frac{1}{T}\right|_{E=E_0} = -\frac{1}{T^2}\left.\frac{\partial T}{\partial E}\right|_{E=E_0} = -\frac{1}{T^2 C_V} < 0\ . \tag{1.111}$$

If we now expand the exponent in the integrand, we obtain

$$TS(E) - E = TS(E_0) - E_0 - \frac{1}{2TC_V}(E - E_0)^2 + \cdots \tag{1.112}$$

such that with $U = E_0$,

$$Z \approx e^{\beta(TS-U)} \int_0^\infty dE\; e^{-(E-U)^2/2k_BT^2C_V} = e^{\beta(TS-U)}\sqrt{2\pi k_B T^2 C_V}$$
$$\Rightarrow \quad F \approx U - TS - \frac{1}{2}k_BT \ln\left\{2\pi k_B T^2 C_V\right\} = U - TS + O(\ln N)\;. \tag{1.113}$$

Since the free energy is extensive, the term of order $\ln N$ is in the large-N limit irrelevant.

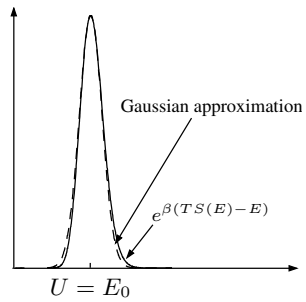

Fig. 1.5: *Saddle point approximation of the partition function, i.e. the approximation of the integrand by a Gaussian.*

1.5.2 Particle number

We consider now the fluctuations of the particle number. The following relation holds

$$\langle N^2\rangle - \langle N\rangle^2 = z\frac{\partial}{\partial z} z\frac{\partial}{\partial z}\ln\mathcal{Z} = z\frac{\partial}{\partial z}\frac{1}{\mathcal{Z}}\sum_N N z^N Z_N = \frac{1}{\mathcal{Z}}\sum_N N^2 z^N Z_N - \left\{\frac{1}{\mathcal{Z}}\sum_N N z^N Z_N\right\}^2 \tag{1.114}$$

from which we derive

$$\langle N^2\rangle - \langle N\rangle^2 = -k_BT\frac{\partial^2}{\partial\mu^2}\Omega(T,V,\mu) = k_BT\frac{\partial\langle N\rangle}{\partial\mu}\;. \tag{1.115}$$

We now relate the right hand side with the isothermal compressibility. Introducing the specific volume $v = V/N$ we consider $\mu = \mu(v,T)$ (note that μ is not extensive). Moreover we use the Gibbs-Duhem relation

$$SdT - Vdp + Nd\mu = 0 \tag{1.116}$$

which derives from considerations on the Gibbs free energy (see thermodynamics course) and obtain

$$d\mu = v\;dp - \frac{S}{N}\;dT \qquad \Rightarrow \qquad \left(\frac{\partial\mu}{\partial v}\right)_T = v\left(\frac{\partial p}{\partial v}\right)_T\;. \tag{1.117}$$

Since $v = V/N$ depends on both V and N, the following derivatives are useful

$$\left(\frac{\partial}{\partial v}\right)_{V,T} = \left(\frac{\partial N}{\partial v}\right)_{V,T}\left(\frac{\partial}{\partial N}\right)_{V,T} = -\frac{N^2}{V}\left(\frac{\partial}{\partial N}\right)_{V,T}\;,$$
$$\left(\frac{\partial}{\partial v}\right)_{N,T} = \left(\frac{\partial V}{\partial v}\right)_{N,T}\left(\frac{\partial}{\partial V}\right)_{N,T} = N\left(\frac{\partial}{\partial V}\right)_{N,T}\;. \tag{1.118}$$

From (1.117) then conclude

$$-\frac{N^2}{V}\left(\frac{\partial\mu}{\partial N}\right)_{V,T} = V\left(\frac{\partial p}{\partial V}\right)_{N,T} \quad \Rightarrow \quad \frac{1}{N}\left(\frac{\partial N}{\partial\mu}\right)_{V,T} = -\frac{1}{vV}\left(\frac{\partial V}{\partial p}\right)_{N,T} = \frac{\kappa_T}{v}\;. \tag{1.119}$$

Consequently the fluctuations of the particle number is connected with the response function, κ_T, the isothermal compressibility,

$$\kappa_T = \frac{v}{\langle N\rangle k_BT}\left\{\langle N^2\rangle - \langle N\rangle^2\right\}\;. \tag{1.120}$$

1.5.3 Magnetization

Considering a system of N classical magnetic moments $\vec{m}_i$ which have fixed magnitude m and can be fully rotated, we define the magnetization

$$\vec{M} = \sum_{i=1}^{N} \vec{m}_i \,. \tag{1.121}$$

The average value of the magnetization is

$$\langle M_z \rangle = N \langle m_{1,z} \rangle = \int \prod_{i=1}^{N} d\Omega_i M_z e^{\beta[F - \mathcal{H}(\vec{m}_1, \ldots, \vec{m}_N; \vec{H})]} = -\left(\frac{\partial F}{\partial H_z}\right)_{T,N} \,. \tag{1.122}$$

Note that the magnetic field couples to magnetic moments through Zeeman coupling,

$$\mathcal{H}(\vec{m}_1, \ldots, \vec{m}_N; \vec{H}) = \mathcal{H}_0(\vec{m}_1, \ldots, \vec{m}_N) - \vec{H} \cdots \vec{M} \,. \tag{1.123}$$

Now we discuss the equation,

$$0 = \int d\Omega_1 \cdots d\Omega_N (\langle M_z \rangle - M_z) e^{\beta(F - \mathcal{H})} \,, \tag{1.124}$$

taking the derivative with respect to the field H_z leads to

$$\begin{aligned} 0 &= \frac{\partial \langle M_z \rangle}{\partial H} - \beta \int d\Omega_1 \cdots d\Omega_N (\langle M_z \rangle - M_z) \frac{\partial}{\partial H_z} (F - \mathcal{H}) \, e^{\beta(F - \mathcal{H})} \\ &= \chi_{zz} - \beta \int d\Omega_1 \cdots d\Omega_N (\langle M_z \rangle - M_z)^2 e^{\beta(F - \mathcal{H})} = \chi_{zz} - \beta \langle (\langle M_z \rangle - M_z)^2 \rangle \,. \end{aligned} \tag{1.125}$$

This yields the convenient fluctuation-dissipation relation for magnetic susceptibility,

$$\chi_{zz} = \frac{1}{k_B T} \left\{ \langle M_z^2 \rangle - \langle M_z \rangle^2 \right\} \,. \tag{1.126}$$

Chapter 2

Quantum Statistical Physics

Quantum statistical physics opens the door to new phenomena and also provides an understanding of the third law of thermodynamics, which we had found to be often violated within classical statistical physics. Moreover, we will find that for ideal quantum gases the concept of indistinguishable particles leads to the classification of particles into two categories: Bosons and Fermions.

2.1 Basis of quantum statistical physics

Every state of a quantum mechanical system can be described by a superposition of stationary states $|\psi_n\rangle$ of the Hamiltonian $\mathcal{H}$, which form a complete orthonormal basis,

$$|\Psi\rangle = \sum_n c_n |\psi_n\rangle \tag{2.1}$$

where the complex coefficients c_n represent the wavefunction whose time dependence is determined by the Hamiltonian $\mathcal{H}$. For the stationary states the following holds:

$$\mathcal{H}|\psi_n\rangle = \varepsilon_n |\psi_n\rangle \qquad \text{with} \quad \langle\psi_n|\psi_{n'}\rangle = \delta_{nn'} \quad \text{and} \quad 1 = \sum_n |\psi_n\rangle\langle\psi_n| \ . \tag{2.2}$$

The renormalization of the state $|\Psi\rangle$ requires

$$1 = \langle\Psi|\Psi\rangle = \sum_{n,n'} c_n^* c_{n'} \langle\psi_n|\psi_{n'}\rangle = \sum_n |c_n|^2 \ . \tag{2.3}$$

The square modulus $|c_n|^2$ denotes the probability to find the state $|\psi_n\rangle$ in $|\Psi\rangle$.
Observable quantities are represented by Hermitian operators $\mathcal{A}$, and their expectation value is

$$\langle\Psi|\mathcal{A}|\Psi\rangle = \sum_{n,n'} c_n^* c_{n'} \langle\psi_n|\mathcal{A}|\psi_{n'}\rangle \ . \tag{2.4}$$

This expectation value is generally time dependent, $c_n = c_n(t)$.
Let's consider now a measurement of a macroscopic observable, which corresponds to an average (indicated here by over-bar) over a time much longer than the microscopic time scales (time between collisions, inverse energy spacing, etc.),

$$\overline{\langle\Psi|\mathcal{A}|\Psi\rangle} = \sum_{n,n'} \overline{c_n^* c_{n'}} \langle\psi_n|\mathcal{A}|\psi_{n'}\rangle \ , \tag{2.5}$$

and focus on eigenstates in a certain narrow energy range, $E \leq \epsilon_n \leq E + \delta E$ (microcanonical point of view). The quantum statistical physics is based on two key postulates:

- Equal probability:

$$\overline{c_n^* c_n} = \begin{cases} r \ , & E \leq \epsilon_n \leq E + \delta E \ , \\ 0 \ , & \text{otherwise} \ , \end{cases} \tag{2.6}$$

  where r is a real constant.

- Random phase: if $n \neq n'$ then

$$\overline{c_n^* c_{n'}} = 0 \ , \tag{2.7}$$

  i.e. the phase of the wavefunction is a random variable. Such a behavior requires an at least weak coupling to the environment in order to randomize the phases.

As a consequence averaged expectation values are given by

$$\overline{\langle \Psi | \mathcal{A} | \Psi \rangle} = \sum_n |c_n|^2 \langle \psi_n | \mathcal{A} | \psi_n \rangle \tag{2.8}$$

which corresponds to considering the state $|\Psi\rangle$ as an incoherent superposition of the eigenstates (pure versus mixed state). We may consider the drop out of interference terms as an effect of averaging over a long time whereby the phases depend on time. Alternatively, we average over an ensemble of many different states with different phases.

2.2 Density matrix

Mixed states or incoherent superpositions of states are conveniently described by density matrices $\hat{\rho}$. We define first the density matrix as an operator through its matrix elements

$$\langle \psi_n | \hat{\rho} | \psi_{n'} \rangle = \rho_{nn'} = |c_n|^2 \delta_{nn'} \ . \tag{2.9}$$

In the basis of stationary states the density matrix is diagonal. Therefore we may formally write the density matrix in spectral form as

$$\hat{\rho} = \sum_n |c_n|^2 |\psi_n\rangle \langle \psi_n| \ . \tag{2.10}$$

We may also express the average value of $\mathcal{A}$ as a trace of the form,

$$\langle \mathcal{A} \rangle = \frac{\sum_n \langle \psi_n | \mathcal{A} \hat{\rho} | \psi_n \rangle}{\sum_n \langle \psi_n | \hat{\rho} | \psi_n \rangle} = \frac{tr(\mathcal{A}\hat{\rho})}{tr\hat{\rho}} \ . \tag{2.11}$$

Note that the final expression is independent of the basis $\{|\psi_n\rangle\}$, as known from standard linear algebra. The cyclic permutation of matrices (operators) does not change the trace: $tr(ABC) = tr(BCA)$. Thus the basis transformation U yields $A' = UAU^{-1}$, such that

$$tr(A') = tr(UAU^{-1}) = tr(AU^{-1}U) = tr(A) \ . \tag{2.12}$$

In this sense the density matrix is a convenient tool to perform ensemble averages as it contains basis-free informations. In order to describe equilibrium properties $\hat{\rho}$ should not depend on time t and therefore it should commute with the Hamiltonian,

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\mathcal{H}, \hat{\rho}] = 0 \ . \tag{2.13}$$

It is obvious that the density matrix defined in (2.10) commutes with $\mathcal{H}$. Compare this with Liouville's theorem of classical mechanics.

2.3 Ensembles in quantum statistics

We now formulate the quantum statistical physics in terms of the three types of ensembles which we introduced for the classical statistical physics.

2.3.1 Microcanonical ensemble

The microcanonical ensemble is suitable for closed systems which do not exchange energy and particles with the environment. We take the density matrix in its diagonal form $\rho_{nn'} = \delta_{nn'}|c_n|^2$. In this ensemble we consider an incoherent state which consists of the equally distributed set of states within a certain narrow energy range between E and $E + \delta E$. Thus,

$$|c_n|^2 = \begin{cases} 1 & E \leq \epsilon_n \leq E + \delta E \\ \\ 0 & \text{otherwise} \ . \end{cases} \tag{2.14}$$

The energies ϵ_n are the eigenenergies of the stationary states $|\psi_n\rangle$ for the Hamiltonian $\mathcal{H}$. Formally we then write the density matrix as

$$\hat{\rho} = \sum_{E \leq \epsilon_n \leq E+\delta E} |\psi_n\rangle\langle\psi_n| \qquad \text{with} \qquad tr\hat{\rho} = \sum_n \rho_{nn} = \omega(E) \ . \tag{2.15}$$

Here $\omega(E)$ is the number of quantum states $|\psi_n\rangle$ with energy in the given energy range. Analogously to the classical case we use now $\omega(E)$ to define the entropy

$$S(E, V) = k_B \ln \omega(E) \ . \tag{2.16}$$

From this we may derive the thermodynamics. Note that $\omega(E)$ is connected with the density of states $d\Phi(E)/dE$ of the quantum system.

$$\Phi(E) = \sum_n \Theta(E - \epsilon_n) \qquad \Rightarrow \qquad \omega(E) = \frac{d\Phi(E)}{dE}\delta E \tag{2.17}$$

with $\Theta(x)$ as the step function

$$\Theta(x) = \begin{cases} 1 & x > 0 \\ 0 & x \leq 0 \end{cases} \ . \tag{2.18}$$

2.3.2 Canonical ensemble

For a system which is in thermal equilibrium with a reservoir of given temperature T we use the canoncial ensemble formulation. Analogously to the classical statistical physics we define the density matrix here as

$$\rho(p, q) = e^{-\beta\mathcal{H}(p,q)} \qquad \rightarrow \qquad \rho_{nn'} = \delta_{nn'} e^{-\beta\epsilon_n} \ , \tag{2.19}$$

and we define the partition function as

$$Z = \sum_n e^{-\beta\epsilon_n} = tr\hat{\rho} = e^{-\beta F(T,V,N)} \tag{2.20}$$

where F is the Helmholtz free energy. The density matrix can be written as an operator,

$$\hat{\rho} = \sum_n |\psi_n\rangle e^{-\beta\epsilon_n}\langle\psi_n| = e^{-\beta\mathcal{H}} \underbrace{\sum_n |\psi_n\rangle\langle\psi_n|}_{=1} = e^{-\beta\mathcal{H}} \ . \tag{2.21}$$

Thus the partition function can also be expressed as

$$Z = tre^{-\beta\mathcal{H}} \tag{2.22}$$

and average values of observables are given by

$$\langle \mathcal{A} \rangle = \frac{tr(\mathcal{A}e^{-\beta\mathcal{H}})}{tre^{-\beta\mathcal{H}}} = \frac{1}{Z} tr\left(\mathcal{A}e^{-\beta\mathcal{H}}\right) . \tag{2.23}$$

The connection to thermodynamics is given via the Helmholtz free energy,

$$F(T,V,N) = -k_B T \ln Z . \tag{2.24}$$

2.3.3 Grand canonical ensemble

Now we connect the system in addition to the heat reservoir also to the particle reservoir of given chemical potential μ. In the same spirit as for the canonical ensemble we use the analogy to the classical systems. The density matrix now reads,

$$\hat{\rho} = e^{-\beta(\mathcal{H}-\mu\hat{N})} \tag{2.25}$$

with N the particle number operator and the grandcanonical partition function is then

$$\mathcal{Z} = tre^{-\beta(\mathcal{H}-\mu\hat{N})} = \sum_N z^N Z_N \tag{2.26}$$

with $z = e^{\beta\mu}$ as the fugacity, leading to the grand potential

$$\Omega(T,V,\mu) = -k_B T \ln \mathcal{Z} . \tag{2.27}$$

2.4 Ideal quantum paramagnet - canonical ensemble

The ideal paramagnet with quantum spins represents a simple example to illustrate some aspects of quantum statistics before going to the more involved cases.

2.4.1 Spin 1/2

We consider N quantum spin 1/2 moments where for each spin the Hilbert space contains two states, $\{|\uparrow\rangle, |\downarrow\rangle\}$ for a given quantization axis which we may choose to be the z-axis. In a magnetic field these moments are described by the Hamiltonian,

$$\mathcal{H} = -\frac{\mu_B g}{\hbar} \sum_{i=1}^{N} \vec{H} \cdot \hat{\vec{S}}_i = -\frac{g\mu_B}{2} \sum_{i=1}^{N} \vec{H} \cdot \hat{\vec{\sigma}}_i \tag{2.28}$$

with μ_B the Bohr magneton and $g = 2$ the gyromagnetic ratio. The Pauli matrices are defined as

$$\hat{\sigma}^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \hat{\sigma}^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \hat{\sigma}^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} , \tag{2.29}$$

and $\hat{\sigma}^0$ is the 2×2 unit matrix. Now we use the properties[1]

$$(\vec{a} \cdot \hat{\vec{\sigma}})^{2n} = |\vec{a}|^{2n} \hat{\sigma}^0 \quad \text{and} \quad (\vec{a} \cdot \hat{\vec{\sigma}})^{2n+1} = |\vec{a}|^{2n} \vec{a} \cdot \hat{\vec{\sigma}} \tag{2.31}$$

and $tr\,\hat{\vec{\sigma}} = 0$ and $tr\hat{\sigma}^0 = 2$ in order to determine the partition function,

$$\begin{aligned} Z &= tr\left\{e^{-\beta\mathcal{H}}\right\} = tr\left\{e^{\beta\mu_B \sum_i \vec{H}\cdot\hat{\vec{\sigma}}_i}\right\} = \left(tr\left\{e^{\beta\mu_B \vec{H}\cdot\hat{\vec{\sigma}}}\right\}\right)^N \\ &= \left(tr\left\{\hat{\sigma}^0 \cosh(\beta\mu_B H) + \hat{H} \cdot \hat{\vec{\sigma}} \sinh(\beta\mu H)\right\}\right)^N = (2\cosh(\beta\mu_B H))^N , \end{aligned} \tag{2.32}$$

[1] We use the well known relation:

$$(\vec{a}\cdot\hat{\vec{\sigma}})(\vec{b}\cdot\hat{\vec{\sigma}}) = \vec{a}\cdot\vec{b}\,\hat{\sigma}^0 + i(\vec{a}\times\vec{b})\cdot\hat{\vec{\sigma}} . \tag{2.30}$$

where $H = |\vec{H}|$ and $\hat{H} = \vec{H}/H$. We obtain the free energy

$$F = -Nk_BT\ln[2\cosh(\beta\mu_BH)] = \begin{cases} -N\mu_BH & k_BT \ll \mu_BH \\ -Nk_BT\ln 2 & k_BT \gg \mu_BH \end{cases} \tag{2.33}$$

which is interpreted as $F = U - TS$ being dominated by the internal energy U at low and by the entropy $S = k_B \ln 2$ in the high-temperature limit. Note that the entropy is given by

$$S(T) = -\frac{\partial F}{\partial T} = Nk_B\ln[2\cosh(\beta\mu_BH)] - Nk_B\beta\mu_BH\tanh(\beta\mu_BH) \tag{2.34}$$

which goes to zero for $T \to 0$ satisfying the third law of thermodynamics. Now we turn to the magnetization,

$$\begin{aligned} M_n &= \mu_B\sum_{i=1}^{N}\langle\hat{n}\cdot\hat{\vec{\sigma}}_i\rangle = \mu_BN\langle\hat{n}\cdot\hat{\vec{\sigma}}_1\rangle \\ &= N\frac{tr\left\{\mu_B\hat{n}\cdot\hat{\vec{\sigma}}\left[\hat{\sigma}^0\cosh(\beta\mu_BH) + \hat{H}\cdot\hat{\vec{\sigma}}\sinh(\beta\mu H)\right]\right\}}{2\cosh(\beta\mu_BH)} = N\hat{n}\cdot\hat{H}\mu_B\tanh(\beta\mu_BH) \end{aligned} \tag{2.35}$$

where $\hat{n}$ is a normal vector. Let us calculate the magnetic susceptibility for the case that $\vec{H} \parallel \hat{z}$, first for a moment along z,

$$\begin{aligned} \chi_{zz} &= \mu_B^2\beta N\left\{\langle\hat{\sigma}^{z2}\rangle - \langle\hat{\sigma}^z\rangle^2\right\} = \mu_B^2\beta N\left\{\langle\hat{\sigma}^0\rangle - \langle\hat{\sigma}^z\rangle^2\right\} \\ &= \frac{\mu_B^2N}{k_BT}\left\{1 - \tanh^2(\beta\mu_BH)\right\} = \frac{\mu_B^2N}{k_BT}\frac{1}{\cosh^2(\beta\mu_BH)} \ . \end{aligned} \tag{2.36}$$

This yields a high-temperature behavior ($k_BT \gg \mu_BH$)

$$\chi_{zz}(T) = \frac{\mu_B^2N}{k_BT} \tag{2.37}$$

corresponding to a Curie-behavior.

2.4.2 Spin S - classical limit

We now turn to larger quantum spins with magnitude $S = \hbar s$ where s is an integer or half-integer. The Hilbert space of such a spin contains $2s+1$ basis states $\{|s, s_z\rangle\} = \{|s, -s\rangle, |s, -s+1\rangle, \ldots, |s, s-1\rangle, |s, s\rangle\}$ with $\hat{\vec{S}}^2|s, s_z\rangle = \hbar^2 s(s+1)|S, S_z\rangle$ and $\hat{S}_z|S, S_z\rangle = \hbar s_z|S, S_z\rangle$. We apply a magnetic field parallel to the z-axis of the N independent spins, leading to the Hamiltonian,

$$\mathcal{H} = -\frac{g\mu_B}{\hbar}\sum_{i=1}^{N}\hat{\vec{S}}\cdot\vec{H} = -\frac{g\mu_B}{\hbar}\sum_{i=1}^{N}\hat{S}_i^zH \ , \tag{2.38}$$

where $g = 2$ again. Note that the field direction does not matter for the following discussion. We calculate again the partition function of the canonical ensemble,

$$\begin{aligned} Z &= tr\left\{e^{-\beta\mathcal{H}}\right\} = tr\left\{\prod_{i=1}^{N}e^{\beta g\mu_BH\hat{S}_i^z/\hbar}\right\} = \left(\sum_{s_z=-s}^{s}\langle s, s_z|se^{\beta g\mu_BH\hat{S}_i^z/\hbar}|s, s_z\rangle\right)^N = \left(\sum_{s_z=-s}^{s}e^{\beta g\mu_BHs_z}\right)^N \\ &= \left(e^{-\beta g\mu_BHs}\sum_{n=0}^{2s}e^{\beta g\mu_BHn}\right)^N = \left(e^{-\beta g\mu_BHs}\frac{e^{\beta g\mu_BH(2s+1)} - 1}{e^{\beta g\mu_BH} - 1}\right)^N = \left(\frac{\sinh\left(\beta\mu_BH(2s+1)\right)}{\sinh\left(\beta\mu_BH\right)}\right)^N \ . \end{aligned} \tag{2.39}$$

We obtain the free energy

$$F = -Nk_BT \ln \left\{ \frac{\sinh\left(\beta\mu_B H(2s+1)\right)}{\sinh\left(\beta\mu_B H\right)} \right\} \tag{2.40}$$

and the internal energy

$$U = -N\mu_B H \Big\{ (2s+1)\coth\left(\beta\mu_B H(2s+1)\right) - \coth\left(\beta\mu_B H\right) \Big\} = -N\mu_B H s B_s(\beta\mu_B H) \tag{2.41}$$

where $B_s(x)$ is the "Brillouin function". In Fig.2.1 the heat capacity is depicted, which is the derivative of U with respect to temperature. Note the approach towards the classical limit with increasing spin s (see also discussion for F below). Also the magnetization can be expressed by the Brillouin function,

$$M_z = g\mu_B \sum_{i=1}^{N} \langle \hat{S}_i^z \rangle = N\mu_B 2s B_s(\beta\mu_B H) \ , \tag{2.42}$$

which also identifies the internal energy as $U = -M_z H$. The other components vanish, $M_x = M_y = 0$.
The limit of $s \gg 1$ leads us to the classical limit[2]. Let us examine this by simultaneously fixing $2s\mu_B = m$ to be finite. The free energy and entropy take the limit for $k_BT \gg mH$,

$$F = -Nk_BT \ln 2s \quad \text{and} \quad S = Nk_B \ln 2s \tag{2.47}$$

where we may identify the value of S with S_0 of the classical case in the footnote. In the low-temperature limit we distinguish two regimes:
(1) $2sk_BT \gg mH \gg k_BT$: we find

$$F = -NmH + Nk_BT \ln(\beta mH/s) \quad \text{and} \quad S = Nk_B \ln 2s - Nk_B \ln(2\beta mH) + Nk_B \tag{2.48}$$

which corresponds essentially to the low-temperature classical regime.
(2) $mH \gg 2sk_BT$: we obtain

$$F = -NmH\left(1 - \frac{1}{2s}\right) + O\left(Te^{-2\beta mH/s}\right) \quad \text{and} \quad S \to 0 \tag{2.49}$$

[2] *Classical ideal paramagnet:* We take a classical vector magnetic moment $\vec{m}$ of length m and assume a magnetic field along the z-direction. Thus, each moment possesses only the angular orientation as a degree of freedom. This leads to the partition function,

$$Z = \int \prod_{i=1}^{N} \left\{ \frac{d\Omega_i}{4\pi} e^{\beta\, \vec{m}_i \cdot \vec{H}} \right\} = \left(\int \frac{d\Omega}{4\pi} e^{\beta m H \cos\theta} \right)^N = \left(\frac{\sinh(\beta mH)}{\beta mH} \right)^N \ . \tag{2.43}$$

The free energy is given by

$$F = -Nk_BT \left\{ \ln\left(\sinh(\beta mH)\right) - \ln(\beta mH) \right\} = \begin{cases} -NmH + Nk_BT \ln(2\beta mH) & k_BT \ll mH \\ -\dfrac{Nk_BT}{3!}\left(\dfrac{mH}{k_BT}\right)^2 & k_BT \gg mH \end{cases} \tag{2.44}$$

and the entropy in the limiting cases,

$$S - S_0 = -\left(\frac{\partial F}{\partial T}\right)_{H,N} = \begin{cases} -Nk_B \ln(2\beta mH) + Nk_B & k_BT \ll mH \\ -\dfrac{N}{3}\left(\dfrac{mH}{k_BT}\right)^3 & k_BT \gg mH \end{cases} \tag{2.45}$$

where we observe that in the zero-temperature limit the classical entropy diverges logarithmically in temperature. In the high-temperature limit the entropy should reach a value connected to the phase space of each magnetic moment, such that we may choose

$$S_0 = Nk_B \ln(2s+1) \approx Nk_B \ln(2s) \ . \tag{2.46}$$

which corresponds to the quantum result. This quantum range shrinks for increasing s, see Fig.2.1 .

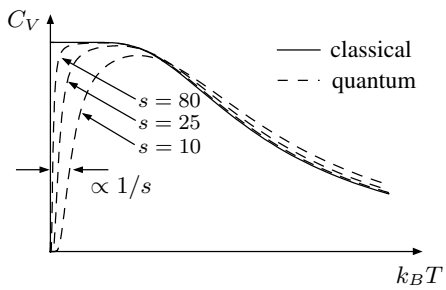

Figure 2.1: As the spin s increases, the "quantum" heat capacity approaches the classical heat capacity.

2.5 Ideal quantum gas - grand canonical ensemble

A gas of independent particles in quantum mechanics has the additional key feature that indistinguishable particles are classified in fermions (particles with half-integer spins) and bosons (particles with integer spins). The former follow the Pauli principle, i.e. we cannot find two fermions in the same quantum state. For bosons no such restriction exists. A many-particle state of bosons (fermions) is described by a wavefunction which is completely symmetric (antisymmetric) under the pair-wise exchange of particle variables. We will discuss this in detail in the next chapter when we introduce the technique of second quantization. The free particles in quantum mechanics are represented by plane waves

$$\psi_{\vec{p}}(\vec{r}) = \langle \vec{r} | \psi_{\vec{p}} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{p}\cdot\vec{r}/\hbar} \qquad \text{with} \quad \epsilon_{\vec{p}} = \frac{\vec{p}^{\,2}}{2m} \; . \tag{2.50}$$

The grand partition function for a gas of such particles is given by

$$\mathcal{Z} = \sum_{\{n_{\vec{p}}\}} g_{\{n_{\vec{p}}\}} e^{-\beta(E-\mu N)_{\{n_{\vec{p}}\}}} \; , \tag{2.51}$$

with

$$E = \sum_{\vec{p}} \epsilon_{\vec{p}} n_{\vec{p}} \qquad \text{and} \qquad N = \sum_{\vec{p}} n_{\vec{p}} \; . \tag{2.52}$$

Here $n_{\vec{p}}$ is the number of particles per state, the occupation number, whereby the sum $\sum_{\{n_{\vec{p}}\}}$ runs over all allowed configurations of occupations. The factor $g_{\{n_{\vec{p}}\}}$ is given by

$$g_{\{n_{\vec{p}}\}} = \begin{cases} 1 & \text{indistinguishable particles (fermions and bosons)} \; , \\ \displaystyle\prod_{\vec{p}} \frac{1}{n_{\vec{p}}!} & \text{classical particles (Boltzmann)} \; . \end{cases} \tag{2.53}$$

Each many-particle quantum state for indistinguishable particles includes all permutations through the total symmetrization (bosons) or antisymmetrization (fermions) of the wavefunction. For fermions we find that for each state $|\psi_{\vec{p}}\rangle$ the occupation number is $n_{\vec{p}} = 0, 1$ and for

bosons $n_{\vec{p}} = 0, 1, 2, \ldots$. Thus, calculating the partition function we obtain for fermions/bosons,

$$\begin{aligned}
\mathcal{Z} &= \sum_{n_{\vec{p}_1}, n_{\vec{p}_2}, \ldots} \left[\left\{ z e^{-\beta \epsilon_{\vec{p}_1}} \right\}^{n_{\vec{p}_1}} \left\{ z e^{-\beta \epsilon_{\vec{p}_2}} \right\}^{n_{\vec{p}_2}} \cdots \right] \\
&= \prod_{\vec{p}} \sum_{n_{\vec{p}}} \left(z e^{-\beta \epsilon_{\vec{p}}} \right)^{n_{\vec{p}}} = \begin{cases} \displaystyle\prod_{\vec{p}} \left(1 + z e^{-\beta \epsilon_{\vec{p}}} \right) & \text{fermions} \\ \displaystyle\prod_{\vec{p}} \frac{1}{1 - z e^{-\beta \epsilon_{\vec{p}}}} & \text{bosons} \end{cases}
\end{aligned} \tag{2.54}$$

with $z = e^{\beta \mu}$ as the fugacity.[3]
From the partition function we arrive at the equation of state

$$\frac{pV}{k_B T} = -\beta \Omega(T, V, \mu) = \begin{cases} \displaystyle\sum_{\vec{p}} \ln \left(1 + z e^{-\beta \epsilon_{\vec{p}}} \right) & \text{fermions} , \\ \displaystyle -\sum_{\vec{p}} \ln \left(1 - z e^{-\beta \epsilon_{\vec{p}}} \right) & \text{bosons} , \end{cases} \tag{2.56}$$

and the particle number

$$N = z \frac{\partial}{\partial z} \ln \mathcal{Z} = \begin{cases} \displaystyle\sum_{\vec{p}} \frac{1}{e^{\beta \epsilon_{\vec{p}}} z^{-1} + 1} & \text{fermions} , \\ \displaystyle\sum_{\vec{p}} \frac{1}{e^{\beta \epsilon_{\vec{p}}} z^{-1} - 1} & \text{bosons} . \end{cases} \tag{2.57}$$

These equations can be used to determine the chemical potential when N is fixed. The occupation number of a state is also easily obtained,

$$\begin{aligned}
\langle n_{\vec{p}} \rangle &= \frac{1}{\mathcal{Z}} \left\{ \prod_{\vec{p}' \neq \vec{p}} \sum_{n_{\vec{p}'}} \left(z e^{-\beta \epsilon_{\vec{p}'}} \right)^{n_{\vec{p}'}} \right\} \sum_{n_{\vec{p}}} n_{\vec{p}} (z e^{-\beta \epsilon_{\vec{p}}})^{n_{\vec{p}}} \\
&= \frac{\sum_{n_{\vec{p}}} n_{\vec{p}} (z e^{-\beta \epsilon_{\vec{p}}})^{n_{\vec{p}}}}{\sum_{n_{\vec{p}}} (z e^{-\beta \epsilon_{\vec{p}}})^{n_{\vec{p}}}} = -k_B T \frac{\partial}{\partial \epsilon_{\vec{p}}} \ln \mathcal{Z} = \begin{cases} \displaystyle\frac{1}{z^{-1} e^{\beta \epsilon_{\vec{p}}} + 1} & \text{fermions} , \\ \displaystyle\frac{1}{z^{-1} e^{\beta \epsilon_{\vec{p}}} - 1} & \text{bosons} . \end{cases}
\end{aligned} \tag{2.58}$$

These correspond to the Fermi-Dirac and the Bose-Einstein distribution, respectively.

[3] *Classical particles:* The partition function is given by

$$\mathcal{Z} = \sum_{n_{\vec{p}_1}, n_{\vec{p}_2}, \ldots} \left[\frac{1}{n_{\vec{p}_1}!} \left\{ z e^{-\beta \epsilon_{\vec{p}_1}} \right\}^{n_{\vec{p}_1}} \frac{1}{n_{\vec{p}_2}!} \left\{ z e^{-\beta \epsilon_{\vec{p}_2}} \right\}^{n_{\vec{p}_2}} \cdots \right] = \sum_{N=0}^{\infty} z^N \frac{1}{N!} \left\{ \sum_{\vec{p}} e^{-\beta \epsilon_{\vec{p}}} \right\}^N = \sum_{N=0}^{\infty} z^N Z_N^{(class)} , \tag{2.55}$$

which corresponds to the usual partition function of independent classical particles within the grand canonical ensemble.

Eventually we compare the grand potential and the internal energy. Using (2.56) we obtain

$$\begin{aligned}\Omega &= \mp k_B T \sum_{\vec{p}} \ln\left(1 \pm z e^{-\beta\epsilon_{\vec{p}}}\right) = \mp k_B T \int d\epsilon\, g(\epsilon)\, \ln\left(1 \pm z e^{-\beta\epsilon}\right) \\ &= \mp V k_B T \frac{1}{8\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon\, \epsilon^{1/2} \ln(1 \pm z e^{-\beta\epsilon}) \\ &= -\frac{2}{3} V \frac{1}{8\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{z^{-1}e^{\beta\epsilon} \pm 1}\ ,\end{aligned} \tag{2.59}$$

where the plus (minus) sign corresponds to fermions (bosons). For the second equality we performed an integration by parts. We have also introduced the density of states

$$g(\epsilon) = \sum_{\vec{p}} \delta(\epsilon - \epsilon_{\vec{p}}) = V \frac{1}{8\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}\ , \tag{2.60}$$

for the energy integration. Now we consider the internal energy

$$U = \sum_{\vec{p}} \langle n_{\vec{p}} \rangle \epsilon_{\vec{p}} = V \frac{1}{8\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\epsilon\, \frac{\epsilon^{3/2}}{z^{-1}e^{\beta\epsilon} \pm 1}\ . \tag{2.61}$$

Thus from $\Omega = -pV$ we obtain the general relation

$$U = \frac{3}{2} pV\ . \tag{2.62}$$

Note that we did not so far include the spin s of the particles in our considerations. This gives an additional factor $2s+1$ to Ω and U.

2.6 Properties of Fermi gas

We consider now fermions of spin s, i.e. there are $2s+1$ different species. The equation of state and the equation for the particle number of the Fermi gas are given by

$$\begin{aligned}\frac{p}{k_B T} &= \frac{4\pi}{h^3}(2s+1) \int_0^\infty dp\, p^2 \ln\left(1 + z e^{-\beta\epsilon_{\vec{p}}}\right)\ , \\ \frac{1}{v} = \frac{N}{V} &= \frac{4\pi}{h^3}(2s+1) \int_0^\infty dp\, p^2 \frac{1}{z^{-1}e^{\beta\epsilon_{\vec{p}}} + 1}\ ,\end{aligned} \tag{2.63}$$

where we used the relation $\sum_{\vec{p}} = \frac{V}{h^3}\int d^3p$. We rewrite these equations introducing special functions of z,

$$\begin{aligned}\frac{p}{k_B T} &= \frac{2s+1}{\lambda^3} f_{5/2}(z) \\ \frac{1}{v} &= \frac{2s+1}{\lambda^3} f_{3/2}(z)\end{aligned} \tag{2.64}$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. These functions are defined as[4]

$$
\begin{aligned}
f_{5/2}(z) &= \frac{4}{\sqrt{\pi}} \int_0^\infty dx\, x^2 \ln(1 + z e^{-x^2}) = -\sum_{l=1}^{\infty} (-1)^l \frac{z^l}{l^{5/2}} \\
f_{3/2}(z) &= z \frac{\partial}{\partial z} f_{5/2}(z) = -\sum_{l=1}^{\infty} (-1)^l \frac{z^l}{l^{3/2}} \ .
\end{aligned}
\tag{2.66}
$$

For the following it will also be important to consider the asymptotic behavior of these functions. For $z \ll 1$ we may use the expansion just given. For $z \gg 1$ we find[5]

$$
\begin{aligned}
f_{5/2}(z) &\approx \frac{8}{15\sqrt{\pi}} (\ln z)^{5/2} \left[1 + \frac{5\pi^2}{8(\ln z)^2} + \cdots \right] \\
f_{3/2}(z) &= \frac{4}{3\sqrt{\pi}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8(\ln z)^2} + \cdots \right] \ .
\end{aligned}
\tag{2.70}
$$

2.6.1 High-temperature and low-density limit

Low density (high temperature) implies $\lambda^3 \ll v = V/N$ and $z = e^{\beta\mu} \ll 1$. We can use now (2.64)

$$
\frac{\lambda^3}{v} = (2s+1) \left\{ z - \frac{z^2}{2^{3/2}} + \cdots \right\} \qquad \Rightarrow \qquad z = \frac{\lambda^3}{v} \frac{1}{2s+1} + \frac{1}{2^{3/2}(2s+1)^2} \left(\frac{\lambda^3}{v} \right)^2 + \cdots \ . \tag{2.71}
$$

This allows us to replace z in the equation of state [6],

$$
\frac{p}{k_B T} \approx \frac{2s+1}{\lambda^3} \left\{ z - \frac{z^2}{2^{5/2}} \right\} \approx \frac{N}{V} \left\{ 1 + \frac{N}{2^{5/2}(2s+1)} \frac{\lambda^3}{V} \right\} \ . \tag{2.73}
$$

[4]Expansion of $f_{5/2}(z)$:

$$
\frac{4}{\sqrt{\pi}} \int_0^\infty dx\, x^2 \ln(1 + z e^{-x^2}) = -\frac{4}{\sqrt{\pi}} \int_0^\infty dx \sum_{l=1}^{\infty} x^2 (-1)^l \frac{z^l e^{-l x^2}}{l} = -\sum_{l=1}^{\infty} (-1)^l \frac{z^l}{l^{5/2}} \ . \tag{2.65}
$$

[5]Derivation of the large-z-expansion: Use $\nu = \mu/k_B T = \ln z$ and rewrite

$$
f_{5/2}(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty dy\, y^{1/2} \ln(1 + e^{\nu - y}) = \frac{8}{15\sqrt{\pi}} \int_{-\nu}^\infty dy' (y' + \nu)^{5/2} \frac{e^{y'}}{(1 + e^{y'})^2} \ , \tag{2.67}
$$

where the second equation is obtained by twice integrating by parts. More over we extend the lower integration boundary to $-\infty$, at the expense of a small error of order $e^{-\nu} = 1/z$. We now expand $(y' + \nu)^{5/2}$ assuming ν large and find

$$
\begin{aligned}
f_{5/2}(z) &= \frac{8}{15\sqrt{\pi}} \int_{-\infty}^{+\infty} dy' \left[\nu^{5/2} + \frac{5}{2} \nu^{3/2} y' + \frac{15}{8} \nu^{1/2} y'^2 + \cdots \right] \frac{e^{y'}}{(1 + e^{y'})^2} \\
&= \frac{8}{15\sqrt{\pi}} \left[I_0 \nu^{5/2} + \frac{5}{2} I_1 \nu^{3/2} + \frac{15}{8} I_2 \nu^{1/2} + \cdots \right]
\end{aligned}
\tag{2.68}
$$

where

$$
I_n = \int_{-\infty}^{+\infty} dy \frac{y^n e^y}{(1 + e^y)^2} \qquad \Rightarrow \qquad I_0 = 1, I_1 = 0, I_2 = \frac{\pi^2}{3}, \ldots \ . \tag{2.69}
$$

Note that all $I_n = 0$ for n odd. It is easy to obtain $f_{3/2}(z)$ by taking the derivative.

[6]Note that the lowest order expansion reproduces the chemical potential of the classical ideal gas, as given in Eq.(1.51) and (1.77):

$$
z = e^{\beta\mu} \approx \frac{N}{V} \lambda^3 \quad \Rightarrow \quad \mu = -k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \ . \tag{2.72}
$$

The second term represents the first quantum correction to the classical limit of the ideal gas. This allows us also to calculate the isothermal compressibility,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{V}{Nk_BT}\frac{1}{1+\frac{\lambda^3 N}{2^{3/2}V(2s+1)}} \ . \tag{2.74}$$

The quantum correction suppresses the compressibility, as a consequence of Pauli's exclusion principle, i.e. fermions avoid each other. The occupation numbers is approximatively given by

$$\langle n_{\vec{p}}\rangle \approx \frac{\lambda^3}{v}\frac{1}{2s+1}e^{-\beta\epsilon_{\vec{p}}} = \frac{Nh^3}{V(2\pi m k_BT)^{3/2}}e^{-\beta\epsilon_{\vec{p}}} \tag{2.75}$$

corresponding to the Maxwell-Boltzmann distribution. With the general relation (2.62) we obtain immediately the internal energy and the heat capacity

$$U \approx \frac{3}{2}Nk_BT\left\{1+\frac{N\lambda^3}{2^{5/2}(2s+1)V}\right\} \quad \text{and} \quad C_V = \frac{3}{2}Nk_B\left\{1-\frac{N\lambda^3}{2^{7/2}(2s+1)V}\right\} \ , \tag{2.76}$$

including the first quantum corrections.

2.6.2 Low-temperature and high-density limit: degenerate Fermi gas

At low temperature we reach the "quantum limit" $\lambda^3 \gg v = V/N$, which implies large fugacity z. First we consider the zero-temperature situation. The occupation numbers follow a step function

$$\langle n_{\vec{p}}\rangle = \Theta(\mu-\epsilon_{\vec{p}}) = \begin{cases} 1 \ , & \epsilon_{\vec{p}} < \mu \ , \\ 0 \ , & \epsilon_{\vec{p}} > \mu \ . \end{cases} \tag{2.77}$$

The fermions occupy states within a sphere in momentum space, the Fermi sphere (Fig.2.2). The particle density n is

$$n = \frac{N}{V} = \frac{2s+1}{h^3}\int d^3p\langle n_{\vec{p}}\rangle = \frac{2s+1}{h^3}\frac{4\pi}{3}p_F^3 = \frac{(2s+1)k_F^3}{6\pi^2} \tag{2.78}$$

where p_F is the Fermi momentum ($\epsilon_{\vec{p}_F} = \mu(T=0) = \epsilon_F$), isotropic, and $k_F = p_F/\hbar$ is the Fermi wavevector. The groundstate energy is

$$U_0 = \frac{2s+1}{h^3}V\int d^3p\epsilon_{\vec{p}}\langle n_{\vec{p}}\rangle = \frac{3}{10}(2s+1)N\epsilon_F \tag{2.79}$$

where ϵ_F denotes the Fermi energy. The zero-point pressure is obtained through (2.56),

$$p_0 = \frac{2}{3}\frac{U_0}{V} = \frac{1}{5}(2s+1)\frac{N}{V}\epsilon_F \ . \tag{2.80}$$

In contrast to the classical ideal gas, a Fermi gas has finite zero-point pressure which is again a consequence of the Pauli principle and is responsible for the stability of metals, neutron stars etc.

Next we turn to finite temperatures for which the occupation number broadens the step at p_F. We use now (2.70, 2.78) to obtain the relation

$$\left(\frac{\epsilon_F}{k_BT}\right)^{3/2} = \frac{3}{4}\frac{\sqrt{\pi}\lambda^3}{2s+1}\frac{N}{V} = \left(\frac{\mu}{k_BT}\right)^{3/2} + \frac{\pi^2}{8}\left(\frac{\mu}{k_BT}\right)^{-1/2} + \cdots \ , \tag{2.81}$$

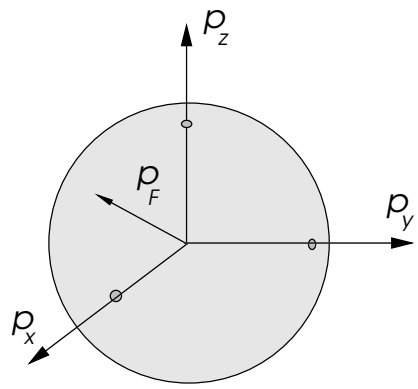

Figure 2.2: Fermi sphere of occupied single particle states. Fermi radius p_F.

which at constant density $n = N/V$ can be solved for the chemical potential,

$$\mu(T) = \epsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2 + \cdots\right) , \tag{2.82}$$

and analogously we obtain for the pressure,

$$p(T) = p_0 \left(1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2 + \cdots\right) . \tag{2.83}$$

Again we derive the internal energy from the relation (2.56)

$$U = \frac{3}{2}pV = U_0 \left(1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2 + \cdots\right) , \tag{2.84}$$

which also leads to the heat capacity for fixed N

$$C_N = k_B N \frac{\pi^2}{4}(2s+1)\frac{k_B T}{\epsilon_F} + \cdots , \tag{2.85}$$

see Fig.2.3. This is the famous linear temperature dependence of the heat capacity, which can be well observed for electrons in simple metals. Obviously now the third law of thermodynamics is satisfied, $C_N \overset{T\to 0}{\longrightarrow} 0$. Also the entropy goes to zero linearly in T.

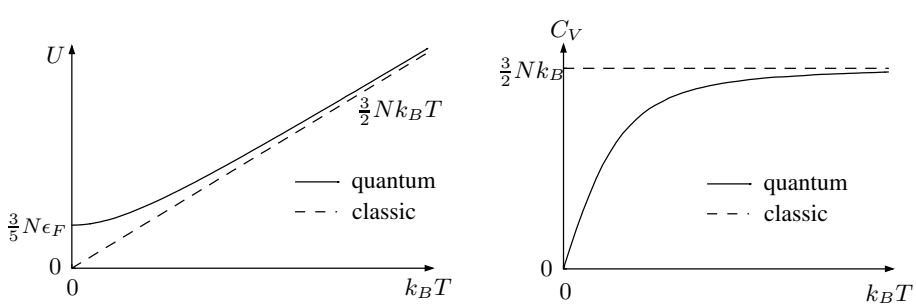

Figure 2.3: The internal energy U and the heat capacity C_V in the quantum situation compared with the classical situation.

2.6.3 Spin-1/2 Fermions in a magnetic field

We consider now the magnetic response of spin $s = 1/2$ fermions in a magnetic field (ideal paramagnetic gas). The Hamiltonian has to be extended by a Zeeman term. Taking the field along the z-axis this reads,

$$\mathcal{H}_Z = -\frac{g\mu_B}{\hbar}\sum_{i=1}^{N} s_i^z H \tag{2.86}$$

with $g = 2$ as gyromagnetic ratio and μ_B the Bohr magneton. This can be absorbed into a spin-dependent fugacity,[7]

$$z_\pm = e^{\beta\mu \pm \beta\mu_B H} \ , \tag{2.90}$$

such that the density of fermions is given by

$$n = \frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3}\left\{f_{3/2}(z_+) + f_{3/2}(z_-)\right\} = n_+ + n_- \tag{2.91}$$

and the magnetization

$$m = \frac{M}{V} = \mu_B(n_+ - n_-) = \frac{\mu_B}{\lambda^3}\left\{f_{3/2}(z_+) - f_{3/2}(z_-)\right\} \ . \tag{2.92}$$

Let us now calculation the spin susceptibility for zero magnetic field, given by

$$\chi = \left.\frac{\partial m}{\partial H}\right|_{H=0} = \frac{\mu_B^2}{\lambda^3 k_B T}\, 2z\left.\frac{\partial f_{3/2}(z)}{\partial z}\right|_{H=0} = \frac{2\mu_B^2}{\lambda^3 k_B T} f_{1/2}(z) \tag{2.93}$$

with $z = e^{\beta\mu}$. We may now again consider limiting cases.

High-temperature limit: We replace $z \ll 1$ in Eq.(2.93) using Eq.(2.71) with $n = 1/v$ and find

$$\chi = \frac{\mu_B^2 n}{k_B T}\left\{1 - \frac{\lambda^3 n}{2^{5/2}}\right\} \ . \tag{2.94}$$

The first term is the result for particles with spin and has a Curie like behavior and the second term is the first quantum correction reducing the susceptibility.

Low-temperature limit: Taking only the lowest order for $z \gg 1$ we obtain,

$$\chi = \frac{\mu_B^2}{\lambda^3 k_B T}\frac{4}{\sqrt{\pi}}(\ln z)^{1/2} = \frac{\mu_B^2}{\lambda^3 k_B T}\frac{4}{\sqrt{\pi}}\left(\frac{\epsilon_F}{k_B T}\right)^{1/2} = \mu_B^2\frac{3n}{2\epsilon_F} \ . \tag{2.95}$$

This is the famous Pauli spin susceptibility for a Fermi gas, which is temperature independent.

[7] We calculate the grand canonical partition function

$$\mathcal{Z} = \prod_{\vec{p}}\left\{\sum_{n_{\vec{p}}}\left(ze^{-\beta\epsilon_{\vec{p}}+\beta\mu_B H}\right)^{n_{\vec{p}}}\right\}\left\{\sum_{n_{\vec{p}}}\left(ze^{-\beta\epsilon_{\vec{p}}-\beta\mu_B H}\right)^{n_{\vec{p}}}\right\} = \prod_{\vec{p}}\prod_{\sigma=+,-}\sum_{n_{\vec{p}}}\left(z_\sigma e^{-\beta\epsilon_{\vec{p}}}\right)^{n_{\vec{p}}} \tag{2.87}$$

where z_σ is defined as in Eq.(2.90). The grand canonical potential is given by

$$\Omega = -k_B T\ln\mathcal{Z} = -\frac{k_B T}{\lambda^3}\left\{f_{5/2}(z_+) + f_{5/2}(z_-)\right\} \tag{2.88}$$

from which we determine the magnetization

$$\begin{aligned} m &= -\frac{1}{V}\frac{\partial\Omega}{\partial H} = \frac{k_B T}{\lambda^3}\sum_\sigma\frac{\partial}{\partial H}f_{5/2}(z_\sigma) = \frac{k_B T}{\lambda^3}\sum_\sigma\frac{\partial z_\sigma}{\partial H}\left.\frac{\partial}{\partial z}f_{5/2}(z)\right|_{z=z_\sigma} \\ &= \frac{\mu_B}{\lambda^3}\sum_\sigma\sigma z_\sigma\left.\frac{\partial}{\partial z}f_{5/2}(z)\right|_{z=z_\sigma} = \frac{\mu_B}{\lambda^3}\sum_\sigma\sigma f_{3/2}(z_\sigma) \end{aligned} \tag{2.89}$$

corresponding to Eq.(2.92).

2.7 Bose gas

There are two situations for Bosons: (1) a system with well-defined particle number, e.g. bosonic atoms, ^{4}He, ... ; (2) Bosons which results as modes of harmonic oscillators (no fixed particle number), e.g. photons, phonons, magnons, etc..

2.7.1 Bosonic atoms

We consider Bosons without spin ($S = 0$) for which ^{4}He is a good example. Analogously to the fermions we introduce functions of z to express the equation of state and the particle number,

$$\begin{aligned} \frac{p}{k_B T} &= \frac{1}{\lambda^3} g_{5/2}(z) = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}} \\ \frac{1}{v} = \frac{N}{V} &= \frac{1}{\lambda^3} g_{3/2}(z) = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}} \ . \end{aligned} \tag{2.96}$$

For small z both functions grow linearly from zero and $g_{3/2}(z)$ has a divergent derivative for $z \to 1$. We concentrate on the range $0 < z \leq 1$, such that $\mu(T) \leq 0$. For $z = 1$ we obtain

$$g_{3/2}(1) = \sum_l \frac{1}{l^{3/2}} = \zeta(3/2) \approx 2.612 \qquad \text{and} \quad g_{5/2}(1) = \sum_l \frac{1}{l^{5/2}} = \zeta(5/2) \approx 1.342 \tag{2.97}$$

where $\zeta(x)$ is Riemann's ζ-function (see Fig.2.4).

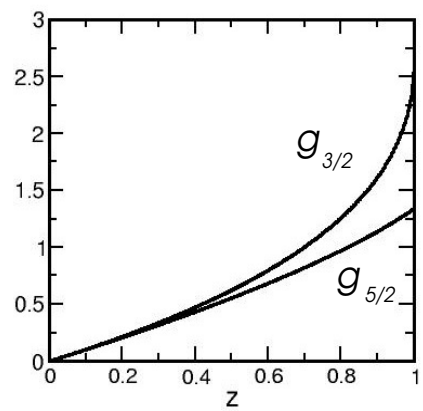

Figure 2.4: Functions $g_{3/2}(z)$ and $g_{5/2}(z)$.

2.7.2 High-temperature and low-density limit

It is easy to see that (like the fermions) the bosons behave in this limit as a classical ideal gas. An intriguing aspect occurs, however, in the quantum corrections. For the pressure we find

$$p(T) = \frac{N}{V} k_B T \left\{ 1 - \frac{N}{2^{5/2}} \frac{\lambda^3}{V} + \cdots \right\} \ . \tag{2.98}$$

The quantum correction reduces the classical ideal gas pressure and yields the compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{V}{N k_B T} \frac{1}{1 - \frac{\lambda^3 N}{2^{3/2} V}} \ . \tag{2.99}$$

In contrast to the fermions where the quantum nature of the particles diminishes the compressibility, here the compressibility is enhanced. Actually, in this approximation the compressibility even diverges if

$$2^{3/2} = \frac{N}{V}\lambda^3 \,, \tag{2.100}$$

i.e. at low enough temperature or high enough density. We will now see that this indeed indicates an instability of the Bose gas.

2.7.3 Low-temperature and high-density limit: Bose-Einstein condensation

Let us now consider Eq. (2.96) carefully. The function $g_{3/2}(z)$ is monotonically increasing with z. If T is lowered, $\lambda \propto T^{-1/2}$ increases, such that z has to increase too in order to satisfy (2.96). Therefore μ approaches the singular point at 0 ($z = 1$). The critical point is determined by

$$g_{3/2}(1) = \zeta(3/2) = \frac{N}{V}\lambda^3 \qquad \Rightarrow \qquad \begin{cases} T_c = \dfrac{h^2}{2\pi k_B m[\zeta(3/2)V/N]^{2/3}} \,, \\[2ex] V_c = \dfrac{N}{\zeta(3/2)}\dfrac{h^3}{(2\pi m k_B T)^{3/2}} \,. \end{cases} \tag{2.101}$$

This defines a critical temperature T_c and critical volume V_c below which a new state of the Bose gas occurs. Note that this equation is qualitatively very similar to (2.100) and even quantitatively not so far ($\zeta(3/2) \approx 2.612 \leftrightarrow 2^{3/2} \approx 2.85$) . The question arises what happens for $T < T_c$ or $V < V_c$. Actually the problem occurring in (2.96) and (2.101) arises in the step

$$N = \sum_{\vec{p}} \frac{1}{e^{\beta(\epsilon_{\vec{p}}-\mu)} - 1} \to \frac{V}{h^3}\int d^3p \frac{1}{e^{\beta(\epsilon_{\vec{p}}-\mu)} - 1} \,. \tag{2.102}$$

The integral does not count the occupation of the state $\vec{p} = 0$, because the momentum distribution function entering the integral,

$$\rho(p) = \frac{p^2}{e^{\beta(\epsilon_{\vec{p}}-\mu)} - 1} \qquad \Rightarrow \qquad \rho(0) = 0 \,. \tag{2.103}$$

This is fine as long as the occupation of the '$\vec{p} = 0$'-state (single-particle groundstate) is vanishingly small compared to N. However, for $T < T_c$ ($V < V_c$) the occupation becomes macroscopic, $\langle n_{\vec{p}=0}\rangle/N > 0$ and we cannot neglect this contribution in the calculation of N (see Fig.2.5). Thus, the correct density is

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) + n_0(T) = n_n(T) + n_0(T) \tag{2.104}$$

with $n_0(T)$ denoting the density of bosons in the single-particle groundstate ($\vec{p} = 0$). These particles form a condensate, the *Bose-Einstein condensate*. What happens at T_c is a phase transition. We encounter here a "two-fluid" system for which the total particle density split into a condensed fraction n_0 and a normal fraction n_n. From (2.104) we find the temperature dependence of n_0 (see Fig.2.5),

$$n_0(T) = \frac{N}{V}\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right] \,. \tag{2.105}$$

Next we also determine the equation of state,

$$p = \begin{cases} \dfrac{k_B T}{\lambda^3} g_{5/2}(z) \,, & V > V_c \\[2ex] \dfrac{k_B T}{\lambda^3} g_{5/2}(1) \,, & V < V_c \end{cases} \,. \tag{2.106}$$

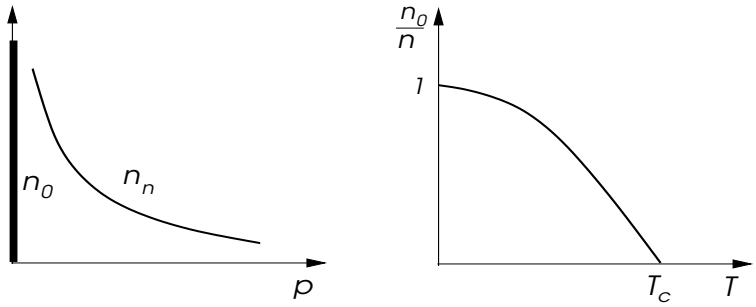

Figure 2.5: Occupation: Left panel: A macroscopic fraction of particle occupy the momentum $p = 0$-state for $T < T_c$. Right panel: Temperature dependence of the condensate fraction.

We now consider the compressibility for $V > V_c$. For this purpose we first determine

$$\frac{\partial V}{\partial z} = -N\lambda^3 \frac{g'_{3/2}(z)}{g_{3/2}(z)^2} \,, \tag{2.107}$$

and consider

$$\frac{\partial p}{\partial V} = \frac{k_B T}{\lambda^3} g'_{5/2}(z) \frac{\partial z}{\partial V} \qquad \Rightarrow \qquad \kappa_T = \frac{N\lambda^6}{V k_B T g_{3/2}(z)^2} \frac{g'_{3/2}(z)}{g'_{5/2}(z)} \,, \tag{2.108}$$

where we use the notation $g'_n(z) = dg_n(z)/dz$. As anticipated earlier the compressibility diverges at the transition $V \to V_c$ (or $T \to T_c$), since the derivative $g'_{3/2}(z) \to \infty$ for $z \to 1$. In the condensed phase the pressure is independent of V as is obvious from (2.106). Therefore the condensed phase is infinitely compressible, i.e. it does not resist to compression.
Some further thermodynamic quantities can be derived. First we consider the entropy S from the grand canonical potential

$$S(T,V,\mu) = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} = \left(\frac{\partial pV}{\partial T}\right)_{V,\mu} = \begin{cases} N k_B \left(\dfrac{5v}{2\lambda^3} g_{5/2}(z) - \ln z \right) \,, & T > T_c \,, \\[2ex] N k_B \dfrac{5}{2} \dfrac{g_{5/2}(1)}{g_{3/2}(1)} \left(\dfrac{T}{T_c}\right)^{3/2} \,, & T < T_c \,, \end{cases} \tag{2.109}$$

where we used (2.96).[8] For the heat capacity at fixed particle number N we find from the

[8]Calculation of the temperature derivatives: (1) Fixed chemical potential:

$$\frac{\partial}{\partial T} \frac{V k_B T}{\lambda^3} g_{5/2}(z) = \frac{5 V k_B}{\lambda^3} g_{5/2}(z) + \underbrace{\frac{V k_B T}{\lambda^3} \frac{g_{3/2}(z)}{z} \frac{\partial z}{\partial T}}_{= -k_B \frac{V}{\lambda^3} g_{3/2}(z) \beta\mu = -N k_B \ln z} \tag{2.110}$$

where we used $\frac{\partial}{\partial z} g_{5/2} = g_{3/2}/z$.
(2) Fixed particle number: we use

$$g_{3/2}(z) = \frac{N}{V}\lambda^3 \quad \Rightarrow \quad \frac{dg_{3/2}}{dT} = \frac{g_{1/2}(z)}{z} \frac{dz}{dT} = -\frac{3}{2} \frac{N}{V} \frac{\lambda^3}{T} \tag{2.111}$$

which leads to the relation

$$\frac{dg_{5/2}}{dT} = \frac{g_{3/2}(z)}{z} \frac{dz}{dT} = -\frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \frac{N\lambda^3}{V} \,. \tag{2.112}$$

This leads to the expression for the heat capacity.

internal energy $U = \frac{3}{2}pV$,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \begin{cases} Nk_B \left(\dfrac{15v}{4\lambda^3} g_{5/2}(z) - \dfrac{9}{4}\dfrac{g_{3/2}(z)}{g_{1/2}(z)}\right) , & T > T_c \, , \\ \\ Nk_B \dfrac{15}{4}\dfrac{g_{5/2}(1)}{g_{3/2}(1)} \left(\dfrac{T}{T_c}\right)^{3/2} , & T < T_c \, . \end{cases} \tag{2.113}$$

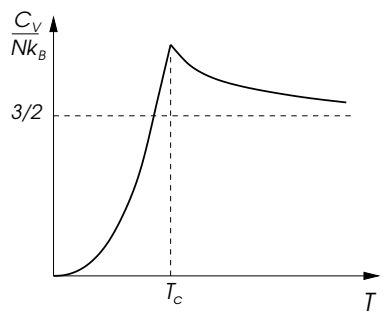

Figure 2.6: Heat capacity: C_V has a cusp at the transition and vanishes as $T^{3/2}$ towards zero-temperature. In the high-temperature limit C_v approaches $3Nk_B/2$ which corresponds to the equipartition law of a mono-atomic gas.

In accordance with the third law of thermodynamics both the entropy and the heat capacity go to zero in the zero-temperature limit. The entropy for $T < T_c$ can be viewed as

$$\frac{S}{N} = s\left(\frac{T}{T_c}\right)^{3/2} = \frac{n_n(T)}{n}s \qquad \text{with} \quad s = \frac{5}{2}k_B\frac{g_{5/2}(1)}{g_{3/2}(1)} \tag{2.114}$$

where s is the entropy per normal particle (specific entropy), i.e. a non-vanishing contribution to the entropy is only provided by the normal fraction (two-fluid model). The heat capacity has a cusp at $T = T_c$.

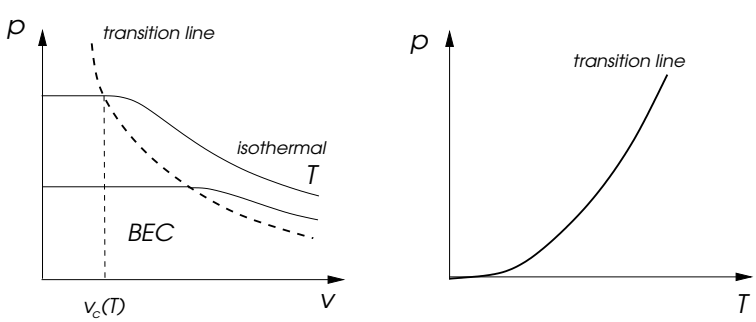

Figure 2.7: Phase diagrams; left panel: p-v-diagram; the isothermal lines reach the transition line with zero-slope, i.e. the compressibility diverges. Right panel: p-T-diagram; the condensed phase corresponds to the transition line, there is no accessible space above the transition line.

We consider now the phase diagram of various state variable.

(1) p-v-diagram: phase transition line

$$p_0 v^{5/3} = \frac{h^2}{2\pi m} \frac{g_{5/2}(1)}{[g_{3/2}(1)]^{5/3}} \ , \tag{2.115}$$

(2) p-T-diagram: phase transition line

$$p_0 = \frac{k_B T}{\lambda^3} g_{5/2}(1) \propto T^{5/2} \tag{2.116}$$

which is the vapor pressure (constant for $T < T_c$) (see Fig.2.7). We use this line to determine the latent heat l per particle via the Clausius-Clapeyron relation,

$$\frac{dp_0}{dT} = \frac{l}{T\Delta v} \quad \text{with} \qquad l = T\Delta s \ . \tag{2.117}$$

The condensate takes no specific volume compared to the normal fraction. Thus, $\Delta v = v_c$. Therefore we obtain

$$l = T v_c \frac{dp_0}{dT} = T v_c \frac{5}{2} \frac{k_B g_{5/2}(1)}{\lambda^3} = T \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \tag{2.118}$$

where we used the relation $\lambda^3 = v_c g_{3/2}(1)$. Note that this is consistent with our result on the specific entropy s. The condensed phase has no specific entropy such that $\Delta s = s$ and, consequently, $l = T\Delta s$ using (2.114).

Examples of the Bose-Einstein condensates is the quantum fluid ^{4}He which shows a condensation below $T_\lambda \approx 2.18K$ into a superfluid phase. We will discuss this in more detail in Chapt. 6. A further very modern example are ultracold atoms in optical traps, e.g. ^{87} Rb (37 electrons + 87 nucleons = 124 Fermions $\rightarrow$ Boson). For 2000 atoms in the trap the critical temperature to Bose-Einstein condensation is as low as 170 nK (for the measured momentum distribution see Fig.2.8).

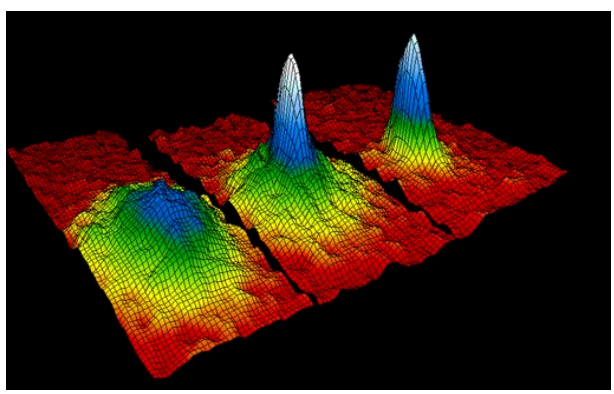

Figure 2.8: Velocity distribution of Rb-atoms: Left panel: $T > T_c$; middle panel: $T \sim T_c$; right panel $T \ll T_c$. A peak at the center develops corresponding to the fraction of particles with "zero-velocity" and at the same time the fraction of particles with finite velocity shrinks. (Source: http://www.nist.gov/public_affairs/gallery/bosein.htm)

2.8 Photons and phonons

We consider now classes of Bose gases whose particle numbers is not conserved. They are derived as normal modes of harmonic oscillators. Thus we first consider the statistical physics of the

harmonic oscillator. The most simple example is the one-dimensional harmonic oscillator whose spectrum is given by

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad \text{with} \qquad n = 0, 1, 2, \ldots \tag{2.119}$$

and the eigenstates $|n\rangle$.[9] The quantum number n is considered as the occupation number of the oscillator mode. We analyze this within the canonical ensemble formulation with a given temperature T. The partition function reads

$$Z = tre^{-\beta\mathcal{H}} = \sum_{n=0}^{\infty}\langle n|e^{-\beta\mathcal{H}}|n\rangle = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \ . \tag{2.123}$$

The internal energy is obtained through

$$U = -\frac{\partial \ln Z}{\partial\beta} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \ . \tag{2.124}$$

The heat capacity is

$$C = \frac{dU}{dT} = k_B\left(\frac{\hbar\omega}{2k_BT}\right)^2 \frac{1}{\sinh^2(\beta\hbar\omega/2)} \ , \tag{2.125}$$

with the limiting properties

$$C = \begin{cases} k_B & k_BT \gg \hbar\omega \\ k_B\left(\dfrac{\hbar\omega}{k_BT}\right)^2 e^{-\beta\hbar\omega} & k_BT \ll \hbar\omega \ . \end{cases} \tag{2.126}$$

In the high-temperature limit the heat capacity approaches the equipartition law of a one-dimensional classical harmonic oscillator. The mean quantum number is given by

$$\langle n\rangle = \frac{1}{Z}\sum_{n=0}^{\infty} ne^{-\beta\epsilon_n} = \frac{1}{e^{\beta\hbar\omega} - 1} \ . \tag{2.127}$$

This corresponds to the Bose-Einstein distribution function. Thus we interpret n as a number of bosons occupying the mode ω.

---

[9] Harmonic oscillator with the Hamiltonian

$$\mathcal{H} = \frac{\hat{P}^2}{2} + \frac{\omega^2}{2}\hat{Q}^2 = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \tag{2.120}$$

with a and $a^\dagger$ as the lowering and raising operators, respectively,

$$\left.\begin{aligned} \hat{Q} &= \sqrt{\frac{\hbar}{2\omega}}(a + a^\dagger) \\ \hat{P} &= -i\omega\sqrt{\frac{\hbar}{2\omega}}(a - a^\dagger) \end{aligned}\right\} \quad \Rightarrow \quad [a, a^\dagger] = 1 \quad \Leftrightarrow \quad [\hat{Q}, \hat{P}] = i\hbar \tag{2.121}$$

The stationary states $|n\rangle$ are defined by $\mathcal{H}|n\rangle = \epsilon_n|n\rangle$ and obey

$$a|n\rangle = \sqrt{n}|n-1\rangle \qquad \text{and} \qquad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \ . \tag{2.122}$$

We can interpret $a^\dagger$ and a as creation and annihilation operator for a particle of energy $\hbar\omega$. In the language of second quantization the commutation relation of $a^\dagger$ and a corresponds to that of bosons.

2.8.1 Blackbody radiation - photons

Electromagnetic radiation in a cavity is a good example of a discrete set of independent harmonic oscillators. Consider a cubic cavity of edge length L. The wave equation is expressed in terms of the vector potential

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \vec{\nabla}^2\right)\vec{A} = 0 \tag{2.128}$$

and the electric and magnetic field are then

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} \qquad \text{and} \qquad \vec{B} = \vec{\nabla}\times\vec{A}\,, \tag{2.129}$$

where we used the Coulomb gauge $\vec{\nabla}\cdot\vec{A} = 0$ and $\phi = 0$. This can be solved by a plane wave,

$$\vec{A}(\vec{r},t) = \frac{1}{\sqrt{V}}\sum_{\vec{k},\lambda}\left\{A_{\vec{k}\lambda}\vec{e}_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{r}-i\omega t} + A^*_{\vec{k}\lambda}\vec{e}^*_{\vec{k}\lambda}e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right\} \qquad \text{with} \qquad \begin{cases} \omega = \omega_{\vec{k}} = c|\vec{k}|\,, \\ \vec{e}_{\vec{k}\lambda}\cdot\vec{k} = 0\,, \end{cases} \tag{2.130}$$

i.e. a linear dispersion relation and a transverse polarization $\vec{e}_{\vec{k}\lambda}$ (λ: polarization index). Assuming for simplicity periodic boundary conditions in the cube we obtain the quantization of the wavevector,

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \qquad \text{with} \qquad n_i = 0, \pm1, \pm2, \ldots \tag{2.131}$$

Each of the parameter set $(\vec{k},\lambda)$ denotes a mode representing an independent harmonic oscillator. These oscillators can be quantized again in the standard way.[10] The states of a mode differ by energy quanta $\hbar\omega_{\vec{k}}$. The occupation number $n_{\vec{k}\lambda}$ is interpreted as the number of *photons* in this mode.
The partition function is then derived from that of a harmonic oscillator

$$Z = \prod_{\vec{k},\lambda}\frac{e^{-\beta\hbar\omega_{\vec{k}}/2}}{1-e^{-\beta\hbar\omega_{\vec{k}}}} = \prod_{\vec{k}}\left(\frac{e^{-\beta\hbar\omega_{\vec{k}}/2}}{1-e^{-\beta\hbar\omega_{\vec{k}}}}\right)^2 \tag{2.135}$$

where the exponent 2 originates from the two polarization directions. The internal energy follows from

$$U(T) = -\frac{\partial \ln Z}{\partial\beta} = 2\sum_{\vec{k}}\frac{\hbar\omega_{\vec{k}}}{e^{\beta\hbar\omega_{\vec{k}}}-1} = \int d\omega D(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega}-1} = V\int d\omega u(\omega,T) \tag{2.136}$$

where we have neglected the zero point motion term (irrelevant constant). The density of modes in (2.136) is denoted as

$$D(\omega) = \sum_{\vec{k},\lambda}\delta(\omega-\omega_{\vec{k}}) = \frac{2V}{(2\pi)^3}4\pi\int dk\, k^2\delta(\omega-ck) = V\frac{\omega^2}{\pi^2c^3} \tag{2.137}$$

[10] Canonical quantization of the radiation field: Introduce the variables

$$Q_{\vec{k}\lambda} = \frac{1}{\sqrt{4\pi c}}\left(A_{\vec{k}\lambda} + A^*_{\vec{k}\lambda}\right) \quad \text{and} \quad P_{\vec{k}\lambda} = \frac{i\omega_{\vec{k}}}{\sqrt{4\pi c}}\left(A_{\vec{k}\lambda} - A^*_{\vec{k}\lambda}\right) \tag{2.132}$$

which leads to the following expression for the Hamiltonian

$$\mathcal{H} = \int d^3r\frac{\vec{E}^2+\vec{B}^2}{8\pi} = \sum_{\vec{k},\lambda}\frac{\omega_{\vec{k}}}{2\pi c}\left|A_{\vec{k}\lambda}\right|^2 = \frac{1}{2}\sum_{\vec{k},\lambda}\left(P^2_{\vec{k}\lambda} + \omega^2_{\vec{k}}Q^2_{\vec{k}\lambda}\right)\,. \tag{2.133}$$

This is the Hamiltonian of a harmonic oscillator for each mode which we can quantize and obtain the new form

$$\mathcal{H} = \sum_{\vec{k},\lambda}\hbar\omega_{\vec{k}}\left(a^\dagger_{\vec{k}\lambda}a_{\vec{k}\lambda} + \frac{1}{2}\right) = \sum_{\vec{k},\lambda}\hbar\omega_{\vec{k}}\left(n_{\vec{k}\lambda} + \frac{1}{2}\right) \tag{2.134}$$

where $A_{\vec{k}\lambda} \to a_{\vec{k}\lambda}$ annihilates and $A^*_{\vec{k}\lambda} \to a^\dagger_{\vec{k}\lambda}$ creates a photon in the mode $(\vec{k},\lambda)$.

which leads to the spectral energy density

$$u(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \ , \tag{2.138}$$

which is the famous Planck formula (Fig.2.9). There are two limits

$$u(\omega, T) \approx \begin{cases} k_B T \dfrac{\omega^2}{\pi^2 c^3} & \hbar\omega \ll k_B T \quad \text{Rayleigh-Jeans-law} \\ \\ \dfrac{\hbar\omega^3}{\pi^2 c^3} e^{-\beta\hbar\omega} & \hbar\omega \gg k_B T \quad \text{Wien's law} \end{cases} \tag{2.139}$$

whereby the Rayleigh-Jeans law corresponds to the classical limit. The maximum for given T follows Wien's displacement law,

$$\hbar\omega_0 = 2.82 k_B T \ . \tag{2.140}$$

The total internal energy density leads to the Stefan-Boltzmann law

$$\frac{U}{V} = \int d\omega u(\omega, T) = \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3} \propto T^4 \ . \tag{2.141}$$

The energy current density of a blackbody is defined as

$$\frac{U}{V} c = \frac{\text{energy}}{\text{area} \cdot \text{time}} \ . \tag{2.142}$$

Thus the emission power of electromagnetic radiation per unit area for the surface of a blackbody is defined by

$$P_{em} = \frac{U}{V} c \frac{1}{4\pi} \int' d\Omega_{\vec{k}} \frac{\vec{k} \cdot \vec{n}}{|\vec{k}|} = \frac{U}{V} c \frac{1}{4\pi} \int' d\Omega_{\vec{k}} \cos\theta = \frac{Uc}{4V} = \frac{\pi^2}{60} \frac{(k_B T)^4}{\hbar^3 c^2} = \sigma T^4 \tag{2.143}$$

where for the current density the component perpendicular to the surface counts ($\vec{n}$: surface normal vector). Note that the integral $\int' d\Omega_{\vec{k}}$ only extends over the hemisphere with $\cos\theta > 0$.

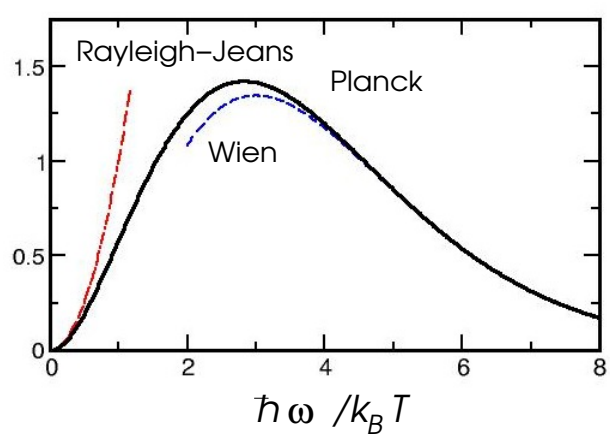

Figure 2.9: Spectral density of black body radiation.

This blackbody radiation plays an important role for the energy budget of the earth. The sun can be considered a blackbody emitting an energy current at the temperature of $T \approx 6000K$. This delivers an energy supply of $1.37kW/m^2$ to the earth. The earth, on the other hand, has to emit radiation back to the universe in order not to heat up arbitrarily. The earth is not a black body but a "gray" body as it is strongly reflecting in certain parts of the spectrum. A further example of blackbody radiation is the cosmic background radiation at a temperature 2.73 K which originates from the big bang.

2.8.2 Phonons in a solid

We consider Debye's theory of the lattice vibration and their influence on the thermodynamics of a solid. A solid consists of atoms which form a lattice. They interact with each other through a harmonic potential. Let us assume that the solid consists of N_A atoms arranged in a cube of edge length L, i.e. there are $3N_A$ degrees of freedom of motion. For our purpose it is convenient and sufficient to approximate this solid as a homogeneous isotropic elastic medium whose vibration are described by the following equations of motion:

$$\begin{aligned} &\frac{1}{c_l^2}\frac{\partial^2 \vec{u}}{\partial t^2} - \vec{\nabla}(\vec{\nabla}\cdot\vec{u}) = 0 \quad \text{longitudinal sound mode ,} \\ &\frac{1}{c_t^2}\frac{\partial^2 \vec{u}}{\partial t^2} - \vec{\nabla}^2\vec{u} = 0 \qquad\quad \text{transversal sound mode .} \end{aligned} \tag{2.144}$$

There are two independent transversal ($\vec{k}\cdot\vec{u} = 0$) and one longitudinal ($\vec{k}\times\vec{u} = 0$) sound mode. These equation can be solved by plane waves and yield linear dispersion analogous to the electromagnetic waves:

$$\omega_{\vec{k}}^{(l)} = c_l|\vec{k}| \qquad \text{and} \qquad \omega_{\vec{k}}^{(t)} = c_t|\vec{k}| \ . \tag{2.145}$$

The density of states is obtained analogously using periodic boundary conditions for the waves,

$$D(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right) \ . \tag{2.146}$$

A difference occurs due to the finite number of degrees of freedom. In the end we get $3N_A$ modes. Thus there must be a maximal value of ω and $|\vec{k}|$. We take the sum

$$3N_A = \sum_{|\vec{k}|\le k_D} 3 = \frac{3V}{(2\pi)^3}4\pi\int_0^{k_D} dk\ k^2 = \frac{Vk_D^3}{2\pi^2} \qquad \Rightarrow \quad k_D = \left(\frac{6\pi^2 N_A}{V}\right)^{1/3} \tag{2.147}$$

and define in this way the Debye wave vector k_D and the Debye frequency $\omega_D = c_{eff}k_D$ where

$$\frac{3}{c_{eff}^3} = \left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right) \ . \tag{2.148}$$

The internal energy is obtained again in the same way as for the electromagnetic radiation apart from the limit on the frequency integration,

$$\frac{U(T)}{V} = \int_0^{\omega_D} d\omega\ u(\omega, T) \ . \tag{2.149}$$

We consider first the limit of small temperatures $k_BT \ll k_B\theta_D = \hbar\omega_D$ (θ_D: Debye temperature). The internal energy is given by

$$U(T) = V\frac{(k_BT)^4}{(2\pi\hbar)^3}\frac{3}{c_{eff}^3}4\pi\underbrace{\int_0^\infty dx\frac{x^3}{e^x-1}}_{=\pi^4/15} = V\frac{\pi^2(k_BT)^4}{10\hbar^3c_{eff}^3} = \frac{3\pi^4k_BT}{5}\left(\frac{T}{\theta_D}\right)^3 N_A \tag{2.150}$$

and correspondingly the low-temperature heat capacity is

$$C_V = \frac{12\pi^4}{5}N_Ak_B\left(\frac{T}{\theta_D}\right)^3 \ , \tag{2.151}$$

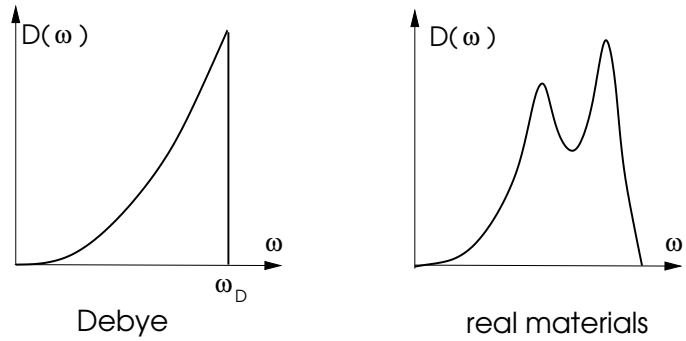

Figure 2.10: Density of states of phonons. Left panel: Debye model; right panel: more realistic spectrum. Note that the low frequency part in both cases follows an ω^2 law and leads to the T^3-behavior of the heat capacity at low temperature. This is a consequence of the linear dispersion which is almost independent of the lattice structure and coupling.

the famous Debye law. On the other hand, at high temperatures ($T \gg \theta_D$) we use

$$\frac{1}{e^{\beta\hbar\omega}-1} \approx \frac{1}{\beta\hbar\omega} - \frac{1}{2} + \frac{\beta\hbar\omega}{12} \ . \tag{2.152}$$

This yields for the internal energy

$$\begin{aligned} U(T) &= \frac{3V}{2\pi^2 c_{eff}^3} \int_0^{\omega_D} d\omega \ \left(\omega^2 k_B T - \frac{\hbar\omega^3}{2} + \frac{\hbar^2\omega^4}{12 k_B T}\right) + \cdots \\ &= 3N_A k_B T \left\{1 - \frac{3}{8}\frac{\hbar\omega_D}{k_B T} + \frac{1}{20}\left(\frac{\hbar\omega_D}{k_B T}\right)^2\right\} + \cdots \end{aligned} \tag{2.153}$$

and leads to the heat capacity

$$C_V = 3N_A k_B \left\{1 - \frac{1}{20}\frac{\theta_D^2}{T^2}\right\} + \cdots \ . \tag{2.154}$$

In the high-temperature limit the heat capacity approaches the value of the equipartition law for $3N_A$ harmonic oscillators (Fig.2.11).

The Debye temperature lies around room temperature usually. However, there also notable exception such as lead (Pb) with $\theta_D = 88K$ or diamond with $\theta_D = 1860K$.

2.9 Diatomic molecules

We now investigate the problem of the diatomic molecules (made out of N atoms) which are bound by a two-particle interaction potential $V(r) = \sum_{i<j} V_{ij}(r)$ with $V_{ij}(r) = v(|\vec{r}_i - \vec{r}_j|)$. A good approximation for the binding potential is the Lenard-Jones potential composed of an attractive and a 'hard-core' repulsive part,

$$v(r) = 4\epsilon \left[\left(\frac{\tilde{r}}{r}\right)^{12} - \left(\frac{\tilde{r}}{r}\right)^{6}\right] \tag{2.155}$$

with ϵ as the potential depth and $r_0 = 2^{1/6}\tilde{r}$ as the minimal point, see Fig.2.12 . Quantum

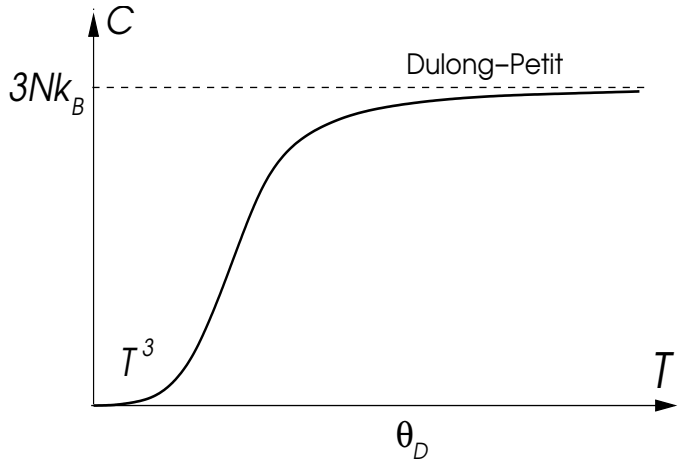

Figure 2.11: Heat capacity: Low-temperature behavior follows a T^3-law. At high-temperature the universal Dulong-Petit law recovers, which is a classical result of the equipartition law for particles in a harmonic potential.

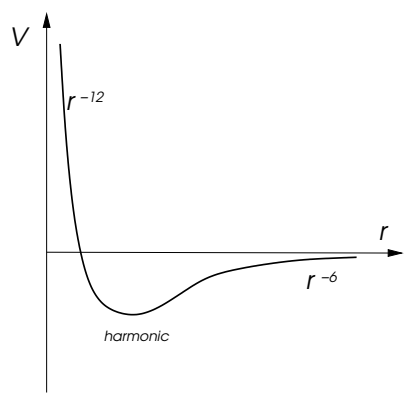

Figure 2.12: Lenard-Jones potential.

mechanical aspects appear in the low-temperature regime $k_B T \ll \epsilon$ (ϵ: depth of the Lenard-Jones potential). Under this condition we consider the Lenard-Jones potential around its minimum as a harmonic potential. Ignoring for the moment the motion of the center of mass, the Hamiltonian can be restricted to the relative coordinates r and relative momenta $\vec{p}$,

$$\mathcal{H} = \frac{\vec{p}^2}{2m^*} + v(r) = \frac{\vec{p}^2}{2m^*} + A(r-r_0)^2 - \epsilon \approx \frac{p_r^2}{2m^*} + \frac{\vec{L}^2}{2m^* r_0^2} + A(r-r_0)^2 - \epsilon \tag{2.156}$$

where the reduced mass is given by $m^* = m/2$ and p_r is radial momentum along the axis of the molecule bond. The motion separates into radial vibrational part which corresponds to a one-dimensional harmonic oscillator and the rotational motion. The two independent spectra are given by

$$E_n^{vib} = \hbar\omega\left(n + \frac{1}{2}\right) \qquad \text{and} \qquad E_l^{rot} = \frac{\hbar^2 l(l+1)}{2m^* r_0^2} \tag{2.157}$$

with $\omega = \sqrt{2A/m^*}$.

Let us now analyze the partition function of the different degrees of freedom. The translational degree of freedom (center of mass motion) corresponds to the motion of a particle of mass $2m$ in three dimensions. At low temperatures this has to be treated as a bosonic quantum liquid in

the case that the atoms are identical (not only chemically but also as an isotope, same mass m),

$$\mathcal{Z}_{trans} = \prod_{\vec{p}} \frac{1}{1 - ze^{-\beta \vec{p}^2/4m}} \ . \tag{2.158}$$

Next we have the vibrational part and the rotational part which we want to consider more carefully,

$$Z_{vib} = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^{N/2} \tag{2.159}$$

and

$$Z_{rot} = \left(\sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)/I_{rot}} \right)^{N/2} \tag{2.160}$$

where $I_{rot} = 2m^* r_0^2/\hbar^2$. Note that per angular momentum quantum number l there are $2l+1$ degenerate states. Since we know the behavior of Z_{trans} and Z_{vib} already from the previous sections, we address now only the rotational part. The partition function cannot be expressed in closed form. Thus we examine only the limiting behaviors. As a characteristic energy scale we take $k_B\theta_{rot} = 2/I_{rot}$. For $T \gg \theta_{rot}$ we obtain

$$\begin{aligned} Z_{rot} &\approx \left(\int_0^\infty dl\ (2l+1) e^{-\beta l(l+1)/I_{rot}} \right)^{N/2} = \left(-I_{rot} k_B T \int_0^\infty dl\ \frac{d}{dl} e^{-\beta l(l+1)/I_{rot}} \right)^{N/2} \\ &= (I_{rot} k_B T)^{N/2} = \left(2\frac{T}{\theta_{rot}} \right)^{N/2} \ . \end{aligned} \tag{2.161}$$

We may expand further in β/I_{rot}[11] and find

$$Z_{rot} \approx \left(2\frac{T}{\theta_{rot}} + \frac{1}{3} + \frac{\theta_{rot}}{30T} + \cdots \right)^{N/2} \ . \tag{2.163}$$

For $T \ll \theta_{rot}$,

$$Z_{rot} \approx \left(1 + 3e^{-\beta 2/I_{rot}} + \cdots \right)^{N/2} \ . \tag{2.164}$$

There is a hierarchy of temperatures in this system, $T_c \ll \theta_{rot} \ll \theta_{vib} \ll T_{dis}$, where T_c is the critical temperature for the Bose-Einstein condensation of the molecules, $k_B\theta_{vib} = \hbar\omega$ and $k_B T_{dis}$ is the molecule dissociation temperature ($\sim$ binding energy). We consider in the different regimes the behavior of the heat capacity per molecule, $C(T) = dU/dT$ (see Fig.2.13,

$$\frac{2C(T)}{N} = \begin{cases} \frac{3}{2}k_B + 3k_B \left(\frac{\theta_{rot}}{T}\right)^2 e^{-\theta_{rot}/T} & T_c \ll T \ll \theta_{rot} \\ \frac{3}{2}k_B + k_B + \frac{k_B}{180}\left(\frac{\theta_{rot}}{T}\right)^2 + k_B \left(\frac{\theta_{vib}}{2T}\right)^2 e^{-\theta_{vib}/T} & \theta_{rot} \ll T \ll \theta_{vib} \\ \frac{3}{2}k_B + k_B + k_B & \theta_{vib} \ll T \ll T_{dis} \\ 3k_B & T_{dis} \ll T \ . \end{cases} \tag{2.165}$$

[11] We use the Euler-MacLaurin sum,

$$\sum_{l=0}^{\infty} f(l) = \int_0^\infty dl f(l) + \frac{1}{2}f(0) + \sum_{k=1}^{\infty} \frac{(-1)^k B_k}{(2k)!} f^{(2k-1)}(0) + R_\infty \ , \tag{2.162}$$

with B_k the Bernoulli numbers $B_1 = 1/6$, $B_2 = 1/30$, ... and R_∞ is a small correction.

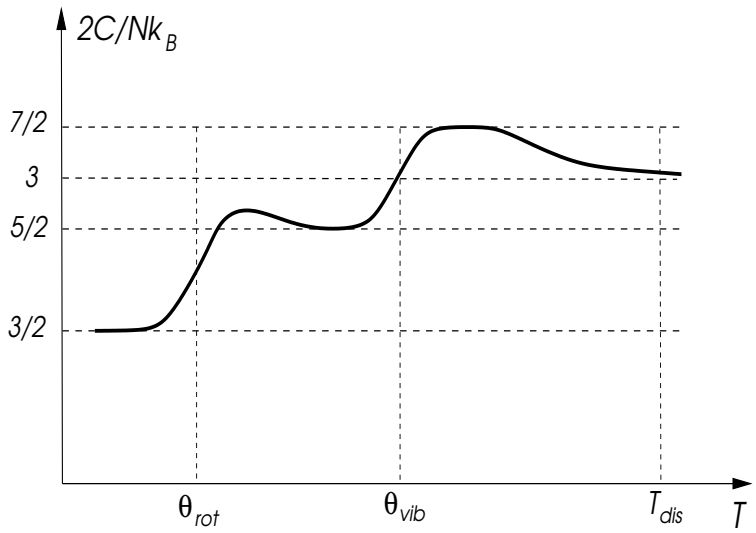

Figure 2.13: Schematic behavior of heat capacity of a diatomic molecule.

Note that due to the vibrational modes the heat capacity goes through maxima when molecules are formed. Also the rotational modes are responsible for a non-monotonic behavior. Upon lowering temperature it looses gradually in magnitude due to the quantum mechanical freezing out of degrees of freedom.
For the hydrogen molecule H_2 the energy scales are $T_{dis} \sim 50000K$, $\theta_{vib} \sim 2000K$ and $\theta_{rot} \sim 85K$. [12] There is no Bose-Einstein condensation for H_2, because it solidifies at $14K$.

[12] Note that due to the fact that the nuclear spins of the H-atom is 1/2, there is a subtlety about the degeneracies. Actually, as identical Fermions their wave function has to be totally antisymmetric under exchange. If the two spins form a spin singlet then the orbital part has to have even parity, i.e. $l = 0, 2, 4, \ldots$ (called "para-hydrogen"), while for the spin triplet configuration odd parity is required, i.e. $l = 1, 3, 5, \ldots$ (called "ortho-hydrogen"). As a consequence in the partition function (2.160) the summands of odd l should have a prefactor 3. This does not affect the heat capacity at temperatures $T \gg \theta_{rot}$ which is the classical limit of the rotator. But there is a (minor) correction at lower temperature such that

$$\frac{2C}{N} \approx \frac{3}{2}k_B + 9k_B \left(\frac{\theta_{rot}}{T}\right)^2 e^{-\theta_{rot}/T} \tag{2.166}$$

for $T_c \ll T \ll \theta_{rot}$.

Chapter 3

Identical Quantum Particles - Formalism of Second Quantization

Here we introduce the formalism of second quantization which is a convenient technical tool discussing many-body quantum systems. It is indispensable in quantum field theory as well as in solid state physics. We distinguish between fermions (half-integer spins) and bosons (integer spins) which behave quite differently, as we have seen in the previous chapter. This behavior is implemented in their many-body wave functions. While in the previous chapter we could circumvent to deal with this aspect as we considered independent indistinguishable quantum particles, it is unavoidable to implement a more careful analysis once interactions between the particles appear.

3.1 Many-body wave functions and particle statistics

Quantum mechanical systems of many identical particles are described by Hamiltonians which are formulated in such a way that they are invariant under exchange (permutation) of particle degrees of freedom (coordinate, momentum, spin etc). These particles are indistinguishable, since in quantum mechanics it is impossible to follow the trajectories of particles under general conditions, unlike in classical mechanics. Permutations play indeed an important role in characterising quantum particles. We introduce the many-body wave function of N particles,

$$\psi(\vec{r}_1, s_1; \vec{r}_2, s_2; \ldots; \vec{r}_N, s_N) \tag{3.1}$$

where each particle is labeled by the coordinate $\vec{r}$ and spin s. In the following we will use for this the short-hand notation $\psi(1, \ldots, N)$. Analogously we define many-body operators,

$$\hat{A}(1, \ldots, N) = A(\hat{\vec{r}}_1, \hat{\vec{p}}_1, \hat{\vec{S}}_1; \ldots; \hat{\vec{r}}_N, \hat{\vec{p}}_N, \hat{\vec{S}}_n) \tag{3.2}$$

with $\hat{\vec{r}}_j$, $\hat{\vec{p}}_j$ and $\hat{\vec{S}}_j$ being the operators for position, momentum and spin of particle j. Note that the Hamiltonian $\mathcal{H}$ belongs to these operators too.
We introduce the transposition (exchange) operator $\hat{P}_{ij}$ which is an element of the permutation group of N elements and exchanges the particle i and j $(1 \leq i, j \leq N)$,

$$\begin{aligned} \hat{P}_{ij}\psi(1, \ldots, i, \ldots, j, \ldots, N) &= \psi(1, \ldots, j, \ldots, i, \ldots, N) \ , \\ \hat{P}_{ij}\hat{A}(1, \ldots, i, \ldots, j, \ldots, N) &= \hat{A}(1, \ldots, j, \ldots, i, \ldots, N) \ . \end{aligned} \tag{3.3}$$

Note that $(\hat{P}_{ij})^{-1} = \hat{P}_{ij}$. As it is invariant under particle exchange, the Hamiltonian commutes with $\hat{P}_{ij}$,

$$[\mathcal{H}, \hat{P}_{ij}] = 0 \tag{3.4}$$

and, consequently, any combination of several transpositions, i.e. all elements of the permutation group S_N, commute with $\mathcal{H}$. Hence, eigenstates of $\mathcal{H}$ have the property

$$\mathcal{H}|\psi\rangle = E|\psi\rangle \quad \Rightarrow \quad \mathcal{H}\hat{P}_{ij}|\psi\rangle = \hat{P}_{ij}\mathcal{H}|\psi\rangle = E\hat{P}_{ij}|\psi\rangle \ , \tag{3.5}$$

where we define the wave function as

$$\psi(1,\ldots,N) = \langle 1,\ldots,N|\psi\rangle \ . \tag{3.6}$$

We distinguish now between fermions and bosons through their behavior under transpositions $\hat{P}_{ij}$,

$$\psi(1,\ldots,i,\ldots,j,\ldots,N) = \begin{cases} +\psi(1,\ldots,j,\ldots,i,\ldots,N) & \text{Bosons} \ , \\ -\psi(1,\ldots,j,\ldots,i,\ldots,N) & \text{Fermions} \ . \end{cases} \tag{3.7}$$

This means that bosonic wave functions are completely symmetric under exchange of particles, while fermionic wave functions are completely antisymmetric[1]. Note that the antisymmetric wave functions prevents two fermions from having the same quantum numbers. If $(\vec{r}_i, s_i)$ and $(\vec{r}_j, s_j)$ are identical, then we find

$$\psi(1,\ldots,i,\ldots,i,\ldots,N) = -\psi(1,\ldots,i,\ldots,i,\ldots,N) = 0 \ , \tag{3.8}$$

which implies the Pauli exclusion principle.

3.2 Independent, indistinguishable particles

We consider N identical particles in a potential V which are not interacting among each other. The Hamiltonian is then given by

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i \qquad \text{with} \qquad \mathcal{H}_i = \frac{\hat{\vec{p}}_i^{\,2}}{2m} + V(\hat{\vec{r}}_i) \ . \tag{3.9}$$

The states of each particle form an independent Hilbert space $\{\psi_\nu\}$ and we can find the stationary states

$$\mathcal{H}_i\psi_\nu(\vec{r}_i, s_i) = \epsilon_\nu\psi_\nu(\vec{r}_i, s_i) \ . \tag{3.10}$$

These single-particle wave functions are renormalised, i.e.

$$\sum_s \int d^3r \ |\psi(\vec{r}, s)|^2 = 1 \ . \tag{3.11}$$

We may now construct a many-body wave function as a product wave function with the corresponding exchange property.
For bosons we write

$$\langle \vec{r}_1, s_1; \ldots, \vec{r}_N, s_N|\Psi_B\rangle = \Psi_B(1,\ldots,N) = \sum_{\hat{P}\in S_N} \hat{P}\psi_{\nu_1}(\vec{r}_1, s_1)\cdots\psi_{\nu_N}(\vec{r}_N, s_N) \tag{3.12}$$

and for fermions

$$\langle \vec{r}_1, s_1; \ldots, \vec{r}_N, s_N|\Psi_F\rangle = \Psi_F(1,\ldots,N) = \sum_{\hat{P}\in S_N} \mathrm{sgn}(\hat{P})\hat{P}\psi_{\nu_1}(\vec{r}_1, s_1)\cdots \ , \psi_{\nu_N}(\vec{r}_N, s_N) \tag{3.13}$$

[1] *Composite particles:* Note that this property is valid also for composite particles. Any particle composed of an even number of particles would be a Boson, e.g. ^{4}He which contains 2 protons + 2 neutrons + 2 electrons = 6 fermions, as exchange two such particles leaves the sign of wave function unchanged. In the same way a particle with an odd number of fermions is a fermions, e.g. ^{3}He with 2 protons + 1 neutron + 2 electrons = 5 fermions.

where the operator $\hat{P}$ permutes the state indices ν_i of the wave functions and $\mathrm{sgn}(\hat{P})$ is the sign of the permutation $\hat{P}$ which is $+1$ (-1) if $\hat{P}$ is composed of an even (odd) number of transpositions. Interestingly the fermionic wave function can be represented as a determinant, the so-called *Slater determinant*,

$$\Psi_F(1,\ldots,N) = \mathrm{Det}\begin{bmatrix} \psi_{\mu_1}(1) & \cdots & \psi_{\mu_1}(N) \\ \vdots & & \vdots \\ \psi_{\mu_N}(1) & \cdots & \psi_{\mu_N}(N) \end{bmatrix} . \tag{3.14}$$

Obviously the determinant vanishes if two rows or columns are identical, enforcing the Pauli principle. These wave functions are not renormalized so that

$$\begin{aligned} \langle\Psi_B|\Psi_B\rangle &= N! n_{\nu_1}! \cdots n_{\nu_N}! \ , \\ \langle\Psi_F|\Psi_F\rangle &= N! \ , \end{aligned} \tag{3.15}$$

where n_{ν_j} denotes the number of particles in the stationary single particle state labeled by ν_j. For fermions it is $n_{\nu_j} = 0, 1$ only.

3.3 Second Quantization Formalism

It is in principle possible to investigate many-body states using many-body wave functions. However, we will introduce here a formalism which is in many respects much more convenient and efficient. It is based on the operators which "create" or "annihilate" particles and act on states in the Fock space $\mathcal{F}$ which is an extended space of states combining Hilbert space $\mathcal{Q}_n$ of different particle numbers n,

$$\mathcal{F} = \bigoplus_{n=0}^{\infty} \mathcal{Q}_n \ . \tag{3.16}$$

Note that the name "second quantization" does not imply a new quantum mechanics.
We can express a many-body state of independent particles in the particle *occupation number representation*s,

$$|n_{\nu_1}, n_{\nu_2}, \ldots\rangle \tag{3.17}$$

which is a state in $\mathcal{F}$ whose particle number is given by $N = n_{\nu_1} + n_{\nu_2} + \cdots$.

3.3.1 Creation- and annihilation operators

We define operators $\hat{a}_\nu$ and $\hat{a}_\nu^\dagger$ which connect Hilbertspaces of different particle number,

$$\hat{a}_\nu : \mathcal{Q}_n \to \mathcal{Q}_{n-1} \qquad \text{and} \qquad \hat{a}_\nu^\dagger : \mathcal{Q}_n \to \mathcal{Q}_{n+1} \ . \tag{3.18}$$

The first we call annihilation and the second creation operator whose action is best understood in the particle number or occupation representation.

<u>Bosons:</u> Let us first consider bosons which, for simplicity, do not possess a spin. The two operators have to following property,

$$\begin{aligned} \hat{a}_\nu|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots\rangle &= \sqrt{n_\nu}|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu - 1, \ldots\rangle \ , \\ \hat{a}_\nu^\dagger|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots\rangle &= \sqrt{n_\nu + 1}|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu + 1, \ldots\rangle \ , \end{aligned} \tag{3.19}$$

and

$$\begin{aligned} \langle n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots|\hat{a}_\nu^\dagger &= \sqrt{n_\nu}\langle n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu - 1, \ldots| \ , \\ \langle n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots|\hat{a}_\nu &= \sqrt{n_\nu + 1}\langle n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu + 1, \ldots| \ . \end{aligned} \tag{3.20}$$

It is obvious that

$$\hat{a}_\nu|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu = 0, \ldots\rangle = 0 \quad \text{and} \quad \langle n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu = 0, \ldots|\hat{a}_\nu^\dagger = 0 \; . \tag{3.21}$$

The operators satisfy the following commutation relations,

$$[\hat{a}_\nu, \hat{a}_{\nu'}^\dagger] = \delta_{\nu\nu'} \quad \text{and} \quad [\hat{a}_\nu, \hat{a}_{\nu'}] = [\hat{a}_\nu^\dagger, \hat{a}_{\nu'}^\dagger] = 0 \; . \tag{3.22}$$

Note that these relations correspond to those of the lowering and raising operators of a harmonic oscillator. Indeed we have seen previously that the excitation spectrum of a harmonic oscillator obeys bosonic statistics.
The creation operators can also be used to construct a state from the vacuum, denoted as $|0\rangle$, where there are no particles, such that $\hat{a}_\nu|0\rangle = 0$. A general state in occupation number representation can be written as,

$$|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots\rangle = \frac{\cdots(\hat{a}_\nu^\dagger)^{n_\nu}\cdots(\hat{a}_{\nu_2}^\dagger)^{n_{\nu_2}}(\hat{a}_{\nu_1}^\dagger)^{n_{\nu_1}}}{\sqrt{n_{\nu_1}!n_{\nu_2}!\cdots}} \; |0\rangle \; . \tag{3.23}$$

The number operator is defined as

$$\hat{n}_\nu = \hat{a}_\nu^\dagger\hat{a}_\nu \qquad \text{with} \qquad \hat{n}_\nu|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots\rangle = n_\nu|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots\rangle \tag{3.24}$$

and the total number of particles is obtain through the operator

$$\hat{N} = \sum_i \hat{n}_{\nu_i} \; . \tag{3.25}$$

Knowing the spectrum of the Hamiltonian of independent particles as given in Eq.(3.10) we may express the Hamiltonian as

$$\mathcal{H} = \sum_\nu \epsilon_\nu \hat{a}_\nu^\dagger\hat{a}_\nu = \sum_\nu \epsilon_\nu \hat{n}_\nu \; . \tag{3.26}$$

<u>Fermions:</u> Now we turn to fermions with spin 1/2 (half-integer spin). Again the single-particle state shall be labelled by ν including the spin index for $\uparrow$ and $\downarrow$. Analogously to the case of bosons we introduce operators $\hat{a}_\nu^\dagger$ and $\hat{a}_\nu$ which obey anti-commutation rules,

$$\{\hat{a}_\nu, \hat{a}_{\nu'}^\dagger\} = \delta_{\nu\nu'} \quad \text{and} \quad \{\hat{a}_\nu, \hat{a}_{\nu'}\} = \{\hat{a}_\nu^\dagger, \hat{a}_{\nu'}^\dagger\} = 0 \; , \tag{3.27}$$

where $\{\ldots\}$ is defined as $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$. In particular this implies that

$$\hat{a}_\nu^\dagger\hat{a}_\nu^\dagger = 0 \quad \text{and} \quad \hat{a}_\nu\hat{a}_\nu = 0 \tag{3.28}$$

such that $n_\nu = 0, 1$, i.e. each single-particle state labelled by ν can only be occupied by at most one particle, because

$$\hat{a}_\nu^\dagger|\ldots, n_\nu = 1, \ldots\rangle = \hat{a}_\nu^\dagger\hat{a}_\nu^\dagger|\ldots, n_\nu = 0, \ldots\rangle = 0 \; . \tag{3.29}$$

A general state may be written as

$$|n_{\nu_1}, n_{\nu_2}, \ldots, n_\nu, \ldots\rangle = \cdots(\hat{a}_\nu^\dagger)^{n_\nu}\cdots(\hat{a}_{\nu_2}^\dagger)^{n_{\nu_2}}(\hat{a}_{\nu_1}^\dagger)^{n_{\nu_1}} \; |0\rangle \tag{3.30}$$

which restricts n_ν to 0 or 1. The order of the creation operators plays an important role as the exchange of two operators yields a minus sign. We consider an example here,

$$|n_1, n_2, n_3, n_4\rangle = |1, 1, 1, 1\rangle = \hat{a}_4^\dagger\hat{a}_3^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger \; |0\rangle \; . \tag{3.31}$$

Removing now one particle yields

$$\begin{aligned}\hat{a}_2|1,1,1,1\rangle &= \hat{a}_2[\hat{a}_4^\dagger\hat{a}_3^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger]\,|0\rangle = \hat{a}_4^\dagger\hat{a}_3^\dagger\hat{a}_2\hat{a}_2^\dagger\hat{a}_1^\dagger\,|0\rangle = \hat{a}_4^\dagger\hat{a}_3^\dagger(1-\hat{a}_2^\dagger\hat{a}_2)\hat{a}_1^\dagger\,|0\rangle \\ &= \hat{a}_4^\dagger\hat{a}_3^\dagger\hat{a}_1^\dagger\,|0\rangle = |1,1,0,1\rangle\end{aligned} \tag{3.32}$$

and now analogously

$$\begin{aligned}\hat{a}_3|1,1,1,1\rangle &= \hat{a}_3[\hat{a}_4^\dagger\hat{a}_3^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger]\,|0\rangle = -\hat{a}_4^\dagger\hat{a}_3\hat{a}_3^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger\,|0\rangle = -\hat{a}_4^\dagger(1-\hat{a}_3^\dagger\hat{a}_3)\hat{a}_2^\dagger\hat{a}_1^\dagger\,|0\rangle \\ &= -\hat{a}_4^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger\,|0\rangle = -|1,0,1,1\rangle\ .\end{aligned} \tag{3.33}$$

Clearly the order of the operators is important and should not be ignored when dealing with fermions.

3.3.2 Field operators

We consider now independent free particles whose states are characterized by momentum $\vec{p} = \hbar\vec{k}$ and spin s with an energy $\epsilon_{\vec{k}} = \hbar^2\vec{k}^{\,2}/2m$. The wave function has a plane wave shape,

$$\psi_{\vec{k}} = \frac{1}{\sqrt{\Omega}}e^{i\vec{k}\cdot\vec{r}} \qquad \text{with} \qquad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)\ , \tag{3.34}$$

where we used periodic boundary conditions in a cube of edge length L (volume $\Omega = L^3$). On this basis we write field operators

$$\widehat{\Psi}_s(\vec{r}) = \frac{1}{\sqrt{\Omega}}\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\,\hat{a}_{\vec{k}\,s} \qquad \text{and} \qquad \widehat{\Psi}_s^\dagger(\vec{r}) = \frac{1}{\sqrt{\Omega}}\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}\,\hat{a}_{\vec{k}\,s}^\dagger \tag{3.35}$$

and the inverse,

$$\hat{a}_{\vec{k}}^\dagger = \int d^3r\frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}}\,\widehat{\Psi}^\dagger(\vec{r}) \qquad \text{und} \qquad \hat{a}_{\vec{k}} = \int d^3r\frac{e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{\Omega}}\,\widehat{\Psi}(\vec{r}) \tag{3.36}$$

Also these operators $\widehat{\Psi}_s(\vec{r})$ and $\widehat{\Psi}_s^\dagger(\vec{r})$ act as annihilation or creation operators, respectively, in the sense,

$$\widehat{\Psi}_s(\vec{r})^\dagger|0\rangle = |\vec{r}, s\rangle \qquad \text{and} \qquad \phi_s(\vec{r}) = \langle\vec{r}, s|\phi\rangle = \langle 0|\,\widehat{\Psi}_s(\vec{r})|\phi\rangle\ . \tag{3.37}$$

Moreover we have the condition

$$\widehat{\Psi}_s(\vec{r})|0\rangle = 0 \qquad \text{and} \qquad \langle 0|\,\widehat{\Psi}_s^\dagger(\vec{r}) = 0\ . \tag{3.38}$$

The field operators also satisfy (anti-)commuation relations,

$$\widehat{\Psi}_s(\vec{r})\,\widehat{\Psi}_{s'}^\dagger(\vec{r}\,') \mp \widehat{\Psi}_{s'}^\dagger(\vec{r}\,')\,\widehat{\Psi}_s(\vec{r}) = \frac{1}{\Omega}\sum_{\vec{k},\vec{k}\,'} e^{i\vec{k}\cdot\vec{r}-i\vec{k}\,'\cdot\vec{r}\,'}\underbrace{(\hat{a}_{\vec{k}\,s}\hat{a}_{\vec{k}\,'s'}^\dagger \mp \hat{a}_{\vec{k}\,'s'}^\dagger\hat{a}_{\vec{k}\,s})}_{=\,\delta_{\vec{k}\,\vec{k}\,'}\delta_{ss'}} = \delta(\vec{r}-\vec{r}\,')\delta_{ss'} \tag{3.39}$$

and analogously

$$\widehat{\Psi}_s(\vec{r})\,\widehat{\Psi}_{s'}(\vec{r}\,') \mp \widehat{\Psi}_{s'}(\vec{r}\,')\,\widehat{\Psi}_s(\vec{r}) = 0 \quad \text{and} \quad \widehat{\Psi}_s^\dagger(\vec{r})\,\widehat{\Psi}_{s'}^\dagger(\vec{r}\,') \mp \widehat{\Psi}_{s'}^\dagger(\vec{r}\,')\,\widehat{\Psi}_s^\dagger(\vec{r}) = 0 \tag{3.40}$$

for bosons $(-)$ and fermions $(+)$. Taking these relations it becomes also clear that

$$\begin{aligned}\langle\vec{r}\,', s'|\,\vec{r}, s\rangle &= \langle 0|\,\widehat{\Psi}_{s'}(\vec{r}\,')\,\widehat{\Psi}_s(\vec{r})^\dagger|0\rangle \\ &= \langle 0|\delta(\vec{r}-\vec{r}\,')\delta_{ss'}|0\rangle \mp \underbrace{\langle 0|\,\widehat{\Psi}_s(\vec{r})^\dagger\,\widehat{\Psi}_{s'}(\vec{r}\,')|0\rangle}_{=0} = \delta(\vec{r}-\vec{r}\,')\delta_{ss'}\ .\end{aligned} \tag{3.41}$$

Applying a field-operator to a N-particle state yields,

$$\widehat{\Psi}^{\dagger}_{s}(\vec{r})|\vec{r}_1, s_1; \ldots; \vec{r}_N, s_N\rangle = \sqrt{N+1}|\vec{r}_1, s_1; \ldots; \vec{r}_N, s_N; \vec{r}, s\rangle \ , \tag{3.42}$$

such that

$$|\vec{r}_1, s_1; \vec{r}_2, s_2; \ldots; \vec{r}_N, s_N\rangle = \frac{1}{\sqrt{N!}} \widehat{\Psi}^{\dagger}_{s_N}(\vec{r}_N) \cdots \widehat{\Psi}^{\dagger}_{s_1}(\vec{r}_1)|0\rangle \ . \tag{3.43}$$

Note that particle statistics leads to the following relation under particle exchange,

$$|\vec{r}_1, s_1; \vec{r}_2, s_2; \ldots; \vec{r}_N, s_N\rangle = \pm|\vec{r}_2, s_2; \vec{r}_1, s_1; \ldots; \vec{r}_N, s_N\rangle \tag{3.44}$$

where $+$ is for bosons and $-$ is for fermions. The renormalisation of the real space states have to be understood within the projection to occupation number states, yielding many-body wave functions analogous to those introduced Eqs.(3.12, 3.13),

$$\Phi(1, \ldots, N) = \langle \vec{r}_1, s_1; \ldots, \vec{r}_N, s_N|n_{\vec{k}_1, s_1'}, n_{\vec{k}_2, s_2'}, \ldots, n_{\vec{k}_N, s_N'}\rangle \ . \tag{3.45}$$

Taking care of the symmetry / antisymmetry of the many-body wave function we recover the renormalization behavior in Eqs.(3.42, 3.43).

3.4 Observables in second quantization

It is possible to express Hermitian operators in the second quantization language. We will show this explicitly for the density operator by calculating matrix elements. The particle density operator is given by

$$\widehat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \widehat{\vec{r}}_i) \ . \tag{3.46}$$

Now we take two states $|\phi\rangle, |\phi'\rangle \in \mathcal{Q}_N$ with the fixed particle number N and examine the matrix element

$$\begin{aligned}
\langle\phi'|\widehat{\rho}(\vec{r})|\phi\rangle &= \int d^3r_1 \cdots d^3r_N \langle\phi'|\vec{r}_1, \ldots, \vec{r}_N\rangle\langle\vec{r}_1, \ldots, \vec{r}_N|\sum_i \delta(\vec{r} - \widehat{\vec{r}}_i)|\phi\rangle \\
&= \int d^3r_1 \cdots d^3r_N \sum_i \delta(\vec{r} - \vec{r}_i)\langle\phi'|\vec{r}_1, \ldots, \vec{r}_N\rangle\langle\vec{r}_1, \ldots, \vec{r}_N|\phi\rangle \\
&= N \int d^3r_1 \cdots d^3r_{N-1}\langle\phi'|\vec{r}_1, \ldots, \vec{r}_{N-1}, \vec{r}\rangle\langle\vec{r}_1, \ldots, \vec{r}_{N-1}, \vec{r}|\phi\rangle \ ,
\end{aligned} \tag{3.47}$$

where we suppress spin indices for the time being. Here we used in the last equality that we can relabel the coordinate variables and permute the particles. Since we have the product of two states under the same perturbation, fermion sign changes do not appear and N identical integrals follow. We claim now that the density operator can also be written as

$$\widehat{\rho}(\vec{r}) = \widehat{\Psi}^{\dagger}(\vec{r})\widehat{\Psi}(\vec{r}), \tag{3.48}$$

which leads to

$$\begin{aligned}
\langle\phi'|\widehat{\Psi}^{\dagger}(\vec{r})\widehat{\Psi}(\vec{r})|\phi\rangle &= \int d^3r_1 \cdots d^3r_{N-1}\langle\phi'|\widehat{\Psi}^{\dagger}(\vec{r})|\vec{r}_1, \ldots, \vec{r}_{N-1}\rangle\langle\vec{r}_1, \ldots, \vec{r}_{N-1}|\widehat{\Psi}(\vec{r})|\phi\rangle \\
&= N \int d^3r_1 \cdots d^3r_{N-1}\langle\phi'|\vec{r}_1, \ldots, \vec{r}_{N-1}, \vec{r}\rangle\langle\vec{r}_1, \ldots, \vec{r}_{N-1}, \vec{r}|\phi\rangle
\end{aligned} \tag{3.49}$$

which is obviously identical to Eq.(3.47).
According to Eq.(3.26) the kinetic energy can be expressed as

$$\mathcal{H}_{kin} = \sum_{\vec{k}} \frac{\hbar^2 \vec{k}^{\,2}}{2m} \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}} = \sum_{\vec{k}} \frac{\hbar^2 \vec{k}^{\,2}}{2m} \hat{n}_{\vec{k}} \tag{3.50}$$

which, using Eq.(3.36), may also be expressed in field operator language as

$$\begin{aligned} \widehat{T} &= \frac{1}{2m\Omega} \sum_{\vec{k}} \int d^3r d^3r' \, \left(\hbar \vec{\nabla} e^{i\vec{k}\cdot\vec{r}}\right) \left(\hbar \vec{\nabla}' e^{-i\vec{k}\cdot\vec{r}'}\right) \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r}') \\ &= \frac{\hbar^2}{2m} \int d^3r \, (\vec{\nabla} \widehat{\Psi}^\dagger(\vec{r})) \cdot (\vec{\nabla} \widehat{\Psi}(\vec{r})). \end{aligned} \tag{3.51}$$

Note the formal similarity with the expectation value of the kinetic energy using single-particle wave functions, $\frac{\hbar^2}{2m} \int d^3r \; \vec{\nabla} \varphi^*(\vec{r}) \cdot \vec{\nabla} \varphi(\vec{r})$. In an analogous way we represent the potential energy,

$$\widehat{H}_{pot} = \int d^3r U(\vec{r}) \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r}) = \int d^3r U(\vec{r}) \widehat{\rho}(\vec{r}) \, . \tag{3.52}$$

Beside the particle density operator $\hat{\rho}(\vec{r})$ also the current density operators can be expressed by field operators,

$$\widehat{\vec{J}}(\vec{r}) = \frac{\hbar}{2mi} \left(\widehat{\Psi}^\dagger(\vec{r})(\vec{\nabla} \widehat{\Psi}(\vec{r})) - (\vec{\nabla} \widehat{\Psi}^\dagger(\vec{r})) \widehat{\Psi}(\vec{r}) \right) \tag{3.53}$$

and the spin density operator for spin-1/2 fermions (writing spin indices again),

$$\widehat{\vec{S}}(\vec{r}) = \frac{\hbar}{2} \sum_{ss'} \widehat{\Psi}^\dagger_s(\vec{r}) \vec{\sigma}_{ss'} \widehat{\Psi}_{s'}(\vec{r}), \tag{3.54}$$

where $\vec{\sigma}_{ss'}$ are the Pauli matrices. In momentum space the operators read,

$$\widehat{\rho}_{\vec{q}} = \int d^3r e^{-i\vec{q}\cdot\vec{r}} \widehat{\rho}(\vec{r}) = \sum_{\vec{k},s} \hat{a}^\dagger_{\vec{k},s} \hat{a}_{\vec{k}+\vec{q},s} \tag{3.55}$$

$$\widehat{\vec{S}}_{\vec{q}} = \frac{\hbar}{2} \sum_{\vec{k},s,s'} \hat{a}^\dagger_{\vec{k},s} \vec{\sigma}_{ss'} \hat{a}_{\vec{k}+\vec{q},s'} \tag{3.56}$$

$$\widehat{\vec{J}}_{\vec{q}} = \frac{\hbar}{m} \sum_{\vec{k},s} \left(\vec{k} + \frac{\vec{q}}{2} \right) \hat{a}^\dagger_{\vec{k},s} \hat{a}_{\vec{k}+\vec{q},s} \, . \tag{3.57}$$

Finally we turn to the genuine many-body feature of particle-particle interaction,

$$\begin{aligned} \widehat{H}_{int} &= \frac{1}{2} \sum_{s,s'} \int d^3r \, d^3r' \; \widehat{\Psi}^\dagger_s(\vec{r}) \widehat{\Psi}^\dagger_{s'}(\vec{r}') V(\vec{r} - \vec{r}') \widehat{\Psi}_{s'}(\vec{r}') \widehat{\Psi}_s(\vec{r}) \\ &= \frac{1}{2\Omega} \sum_{\vec{k},\vec{k}'\vec{q}} \sum_{s,s'} V_{\vec{q}} \hat{a}^\dagger_{\vec{k}+\vec{q},s} \hat{a}^\dagger_{\vec{k}'-\vec{q},s'} \hat{a}_{\vec{k}',s'} \hat{a}_{\vec{k},s}, \end{aligned} \tag{3.58}$$

where the factor 1/2 corrects for double counting and

$$V(\vec{r}) = \frac{1}{\Omega} \sum_{\vec{q}} V_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \, . \tag{3.59}$$

Note that the momentum space representation has the simple straightforward interpretation that two particles with momentum $\hbar\vec{k}$ and $\hbar\vec{k}'$ are scattered into states with momentum $\hbar(\vec{k} + \vec{q})$ and $\hbar(\vec{k}' - \vec{q})$, respectively, by transferring the momentum $\hbar\vec{q}$.

3.5 Equation of motion

For simplicity we discuss here again a system of independent free quantum particles described by the Hamiltonian

$$\mathcal{H} = \sum_{\vec{k}} \epsilon_{\vec{k}} \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}} \tag{3.60}$$

where we suppress again the spin index. We turn now to the Heisenberg representation of time dependent operators,

$$\hat{a}_{\vec{k}}(t) = e^{i\mathcal{H}t/\hbar} \hat{a}_{\vec{k}} e^{-i\mathcal{H}t/\hbar} \ . \tag{3.61}$$

Thus, we formulate the equation of motion for this operator,

$$\begin{aligned} i\hbar \frac{d}{dt} \hat{a}_{\vec{k}} &= -[\mathcal{H}, \hat{a}_{\vec{k}}] = -\sum_{\vec{k}'} \epsilon_{\vec{k}'} [\hat{a}^\dagger_{\vec{k}'} \hat{a}_{\vec{k}'}, \hat{a}_{\vec{k}}] \\ &= -\sum_{\vec{k}'} \epsilon_{\vec{k}'} \begin{cases} \hat{a}^\dagger_{\vec{k}'} \underbrace{[\hat{a}_{\vec{k}'}, \hat{a}_{\vec{k}}]}_{=0} + \underbrace{[\hat{a}^\dagger_{\vec{k}'}, \hat{a}_{\vec{k}}]}_{=-\delta_{\vec{k},\vec{k}'}} \hat{a}_{\vec{k}'} & \text{for bosons} \\ \hat{a}^\dagger_{\vec{k}'} \underbrace{\{\hat{a}_{\vec{k}'}, \hat{a}_{\vec{k}}\}}_{=0} - \underbrace{\{\hat{a}^\dagger_{\vec{k}'}, \hat{a}_{\vec{k}}\}}_{=\delta_{\vec{k},\vec{k}'}} \hat{a}_{\vec{k}'} & \text{for fermions} \end{cases} \\ &= \sum_{\vec{k}'} \epsilon_{\vec{k}'} \hat{a}_{\vec{k}'} \delta_{\vec{k},\vec{k}'} = \epsilon_{\vec{k}} \hat{a}_{\vec{k}} \ , \end{aligned} \tag{3.62}$$

and analogously

$$i\hbar \frac{d}{dt} \hat{a}^\dagger_{\vec{k}} = -[\mathcal{H}, \hat{a}^\dagger_{\vec{k}}] = -\epsilon_{\vec{k}} \hat{a}^\dagger_{\vec{k}} \ . \tag{3.63}$$

A further important relation in the context of statistical physics is

$$e^{-\beta\mathcal{H}} \hat{a}^\dagger_{\vec{k}} e^{\beta\mathcal{H}} = e^{-\beta\epsilon_{\vec{k}}} \hat{a}^\dagger_{\vec{k}} \ . \tag{3.64}$$

Analogously we find for the number operator $\hat{N} = \sum_{\vec{k}} \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}}$,

$$e^{\beta\mu\hat{N}} \hat{a}^\dagger_{\vec{k}} e^{-\beta\mu\hat{N}} = e^{\beta\mu} \hat{a}^\dagger_{\vec{k}} \ . \tag{3.65}$$

Both relations are easily proven by examining the action of this operator on a eigenstate of the Hamiltonian $|\Phi\rangle = |n_{\vec{k}_1}, \ldots, n_{\vec{k}}, \ldots\rangle$,

$$\begin{aligned} e^{-\beta\mathcal{H}} \hat{a}^\dagger_{\vec{k}} e^{\beta\mathcal{H}} |\Phi\rangle &= e^{\beta E} e^{-\beta\mathcal{H}} \hat{a}^\dagger_{\vec{k}} |\Phi\rangle = \sqrt{n_{\vec{k}} + 1} e^{\beta E} e^{-\beta\mathcal{H}} |n_{\vec{k}_1}, \ldots, n_{\vec{k}} + 1, \ldots\rangle \\ &= \sqrt{n_{\vec{k}} + 1} e^{\beta(E-E')} |n_{\vec{k}_1}, \ldots, n_{\vec{k}} + 1, \ldots\rangle = e^{\beta(E-E')} \hat{a}^\dagger_{\vec{k}} |\Phi\rangle \end{aligned} \tag{3.66}$$

where $E = \sum_{\vec{k}'} \epsilon_{\vec{k}'} n_{\vec{k}'}$ and $E' = \sum_{\vec{k}'} \epsilon_{\vec{k}'} n_{\vec{k}'} + \epsilon_{\vec{k}}$ such that $E - E' = -\epsilon_{\vec{k}}$. Note that for fermions the operation of $\hat{a}^\dagger_{\vec{k}}$ on $|\Phi\rangle$ is only finite, if $n_{\vec{k}} = 0$ otherwise we have a zero. Still the relation remains true for both types of quantum particles. The analogous proof applies to Eq.(3.65).

<u>Fermi-Dirac and Bose-Einstein distribution:</u> Let us look at the thermal average,

$$\langle \hat{n}_{\vec{k}} \rangle = \langle \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}} \rangle = \frac{tr\{e^{-\beta\mathcal{H}'} \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}}\}}{tr e^{-\beta\mathcal{H}'}} \ , \tag{3.67}$$

where we use the Hamiltonian $\mathcal{H}' = \mathcal{H} - \mu\hat{N}$. We can rearrange the numerator of (3.67) using Eqs.(3.64) and (3.65),

$$\begin{aligned} tr\{e^{-\beta\mathcal{H}'}\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\} &= tr\{e^{-\beta\mathcal{H}'}\hat{a}^\dagger_{\vec{k}}e^{\beta\mathcal{H}'}e^{-\beta\mathcal{H}'}\hat{a}_{\vec{k}}\} = e^{-\beta(\epsilon_{\vec{k}}-\mu)}tr\{\hat{a}^\dagger_{\vec{k}}e^{-\beta\mathcal{H}'}\hat{a}_{\vec{k}}\} \\ &= e^{-\beta(\epsilon_{\vec{k}}-\mu)}tr\{e^{-\beta\mathcal{H}'}\hat{a}_{\vec{k}}\hat{a}^\dagger_{\vec{k}}\} = e^{-\beta(\epsilon_{\vec{k}}-\mu)}tr\{e^{-\beta\mathcal{H}'}[1 \pm \hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}]\} \ , \end{aligned} \tag{3.68}$$

where '+' and '−' stand for bosons and fermions, respectively. Inserting this into Eq.(3.67) we find,

$$\langle\hat{n}_{\vec{k}}\rangle = e^{-\beta(\epsilon_{\vec{k}}-\mu)}(1 \pm \langle\hat{n}_{\vec{k}}\rangle) \qquad \Rightarrow \qquad \langle\hat{n}_{\vec{k}}\rangle = \begin{cases} \dfrac{1}{e^{\beta(\epsilon_{\vec{k}}-\mu)}-1} & \text{bosons} \\[2ex] \dfrac{1}{e^{\beta(\epsilon_{\vec{k}}-\mu)}+1} & \text{fermions} \end{cases} \tag{3.69}$$

which corresponds to the standard Bose-Einstein and Fermi-Dirac distribution.

3.6 Correlation functions

Independent classical particles do not have any correlation among each other. This is different for quantum particles. The second quantization language is very suitable for the formulation of correlation functions and to show that fermion and bose gases behave rather differently.

3.6.1 Fermions

First let us write the ground state of a free Fermi gas of spin-1/2 fermions as we have introduced it already in Sect.2.6.2. Starting from the vacuum $|0\rangle$ we fill successively all low lying states with a fermion of both spins s until all fermions are placed. This defines the Fermi sphere in k-space with the radius k_F, the Fermi wave vector. The ground state is then,

$$|\Phi_0\rangle = \prod_{\vec{k}}^{|\vec{k}|\leq k_F} \prod_{s=\uparrow,\downarrow} \hat{a}^\dagger_{\vec{k}s}|0\rangle \tag{3.70}$$

and $n_{\vec{k}} = \langle\Phi_0|\hat{n}_{\vec{k}}|\Phi_0\rangle = \Theta(k_F - |\vec{k}|)$ is a step function with $\hat{n}_{\vec{k}} = \sum_s \hat{a}^\dagger_{\vec{k}s}\hat{a}_{\vec{k}s}$.
First we formulate the *one-particle correlation function* in real space using field operators,

$$\frac{n}{2}g_s(\vec{r}-\vec{r}\,') = \langle\Phi_0|\,\widehat{\Psi}^\dagger_s(\vec{r})\,\widehat{\Psi}_s(\vec{r}\,')|\Phi_0\rangle \ , \tag{3.71}$$

which measure the probability amplitude to be able to insert a Fermion at place $\vec{r}$ after having removed one at $\vec{r}\,'$ with the same spin s. We evaluate this expression by going to k-space,

$$\begin{aligned} \frac{n}{2}g_s(\vec{r}-\vec{r}\,') &= \frac{1}{\Omega}\sum_{\vec{k},\vec{k}\,'} e^{-i\vec{k}\cdot\vec{r}+i\vec{k}\,'\cdot\vec{r}\,'} \underbrace{\langle\Phi_0|\,\widehat{a}^\dagger_{\vec{k}s}\,\widehat{a}_{\vec{k}\,'s}|\Phi_0\rangle}_{=n_{\vec{k}s}\delta_{\vec{k},\vec{k}\,'}} = \int_{|\vec{k}|\leq k_F}\frac{d^3k}{(2\pi)^3}e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \\ &= \frac{1}{(2\pi)^2}\int_0^{k_F} dk\ k^2 \int_{-1}^{+1} d\cos\theta\ e^{ik|\vec{r}-\vec{r}\,'|\cos\theta} = \frac{1}{2\pi^2|\vec{r}-\vec{r}\,'|}\int_0^{k_F} dk\ k\sin(k|\vec{r}-\vec{r}\,'|) \\ &= \frac{3n}{2}\frac{\sin x - x\cos x}{x^3}\bigg|_{x=k_F|\vec{r}-\vec{r}\,'|} \ . \end{aligned} \tag{3.72}$$

Note the limits: $g_s(\vec{r}\to 0)=n/2$ and $g_s(\vec{r}\to\infty)=0$ where $g_s(\vec{r}-\vec{r}\,')$ corresponds to the overlap of the two states

$$\sqrt{\frac{2}{n}}\,\widehat{\Psi}_s(\vec{r})|\Phi_0\rangle \quad \text{and} \quad \sqrt{\frac{2}{n}}\,\widehat{\Psi}_s(\vec{r}\,')|\Phi_0\rangle\ . \tag{3.73}$$

Next we turn to the *pair correlation function* which we define as

$$\left(\frac{n}{2}\right)^2 g_{ss'}(\vec{r}-\vec{r}\,') = \langle\Phi_0|\,\widehat{\Psi}^\dagger_s(\vec{r})\,\widehat{\Psi}^\dagger_{s'}(\vec{r}\,')\,\widehat{\Psi}_{s'}(\vec{r}\,')\,\widehat{\Psi}_s(\vec{r})|\Phi_0\rangle \tag{3.74}$$

being the probability to be able to pick two fermions at the different places, $\vec{r}$ and $\vec{r}\,'$, with the spins s and s', respectively. Again we switch to the more convenient k-space,

$$\left(\frac{n}{2}\right)^2 g_{ss'}(\vec{r}-\vec{r}\,') = \frac{1}{\Omega^2}\sum_{\vec{k},\vec{k}\,',\vec{q},\vec{q}\,'} e^{-i(\vec{k}-\vec{k}\,')\cdot\vec{r}}e^{-i(\vec{q}-\vec{q}\,')\cdot\vec{r}\,'}\langle\Phi_0|\,\widehat{a}^\dagger_{\vec{k}\,s}\,\widehat{a}^\dagger_{\vec{q}\,s'}\,\widehat{a}_{\vec{q}\,'s'}\,\widehat{a}_{\vec{k}\,'s}|\Phi_0\rangle\ . \tag{3.75}$$

Note that the expectation bracket only remains finite, if every particle annihilated is created by these operators again, otherwise we get zero.
We start with the simpler case $s\neq s'$ which implies that in Eq.(3.75) the wave vectors satisfy $\vec{k}=\vec{k}\,'$ and $\vec{q}=\vec{q}\,'$. This leads to

$$\left(\frac{n}{2}\right)^2 g_{ss'}(\vec{r}-\vec{r}\,') = \frac{1}{\Omega^2}\sum_{\vec{k},\vec{q}}\langle\Phi_0|\,\widehat{n}_{\vec{k}\,s}\,\widehat{n}_{\vec{q}\,s'}|\Phi_0\rangle = \left(\frac{n}{2}\right)^2, \tag{3.76}$$

such that $g_{ss'}(\vec{r}-\vec{r}\,')=1$ independent of position. Fermions of different spin are uncorrelated. Now we consider $s=s'$ where the expectation value in Eq.(3.75) has to be rearranged carefully,

$$\begin{aligned}
\langle\Phi_0|\,\widehat{a}^\dagger_{\vec{k}\,s}\,\widehat{a}^\dagger_{\vec{q}\,s}\,\widehat{a}_{\vec{q}\,'s}\,\widehat{a}_{\vec{k}\,'s}|\Phi_0\rangle &= \delta_{\vec{k}\,\vec{k}\,'}\delta_{\vec{q}\,\vec{q}\,'}\langle\Phi_0|\,\widehat{a}^\dagger_{\vec{k}\,s}\,\widehat{a}^\dagger_{\vec{q}\,s}\,\widehat{a}_{\vec{q}\,s}\,\widehat{a}_{\vec{k}\,s}|\Phi_0\rangle \\
&\quad +\delta_{\vec{k}\,\vec{q}\,'}\delta_{\vec{q}\,\vec{k}\,'}\langle\Phi_0|\,\widehat{a}^\dagger_{\vec{k}\,s}\,\widehat{a}^\dagger_{\vec{q}\,s}\,\widehat{a}_{\vec{k}\,s}\,\widehat{a}_{\vec{q}\,s}|\Phi_0\rangle \\
&= (\delta_{\vec{k}\,\vec{k}\,'}\delta_{\vec{q}\,\vec{q}\,'}-\delta_{\vec{k}\,\vec{q}\,'}\delta_{\vec{q}\,\vec{k}\,'})\langle\Phi_0|\,\widehat{a}^\dagger_{\vec{k}\,s}\,\widehat{a}_{\vec{k}\,s}\,\widehat{a}^\dagger_{\vec{q}\,s}\,\widehat{a}_{\vec{q}\,s}|\Phi_0\rangle \\
&= (\delta_{\vec{k}\,\vec{k}\,'}\delta_{\vec{q}\,\vec{q}\,'}-\delta_{\vec{k}\,\vec{q}\,'}\delta_{\vec{q}\,\vec{k}\,'})n_{\vec{k}\,s}n_{\vec{q}\,s}\ .
\end{aligned} \tag{3.77}$$

From this it follows straightforwardly,

$$\left(\frac{n}{2}\right)^2 g_{ss}(\vec{r}-\vec{r}\,') = \frac{1}{\Omega^2}\sum_{\vec{k},\vec{q}}\left(1-e^{-i(\vec{k}-\vec{q})\cdot(\vec{r}-\vec{r}\,')}\right)n_{\vec{k}\,s}n_{\vec{q}\,s} = \left(\frac{n}{2}\right)^2[1-g_s(\vec{r}-\vec{r}\,')^2], \tag{3.78}$$

and we can write,

$$g_{ss}(\vec{r}-\vec{r}\,') = 1-\left.\frac{9(\sin x - x\cos x)^2}{x^6}\right|_{x=k_F|\vec{r}-\vec{r}\,'|}\ . \tag{3.79}$$

In Fig.3.1 we see that the equal-spin correlation function goes to zero as the two positions approach which is called the exchange hole with a radius of the order of k_F^{-1}. On long distances there is no correlation apart from weak ripples of the wave length k_F^{-1}. The probability to find another fermion around the position of a fermion at $\vec{r}$ corresponds to

$$g(\vec{r}) = \frac{1}{2}[g_{\uparrow\uparrow}(\vec{r})+g_{\uparrow\downarrow}(\vec{r})]. \tag{3.80}$$

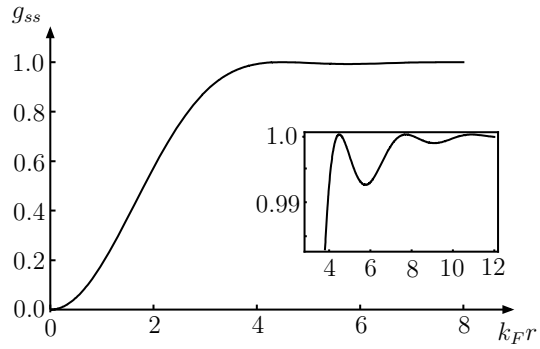

Figure 3.1: The equal-spin pair correlation function for fermions.

The density depletion around such a fermion is then,

$$\begin{aligned} n\int d^3r\,(g(\vec{r})-1) &= -\frac{n}{2}\int d^3r\,\{g_s(\vec{r})\}^2 = -\frac{2}{n}\int d^3r\,\frac{1}{\Omega^2}\sum_{\vec{k},\vec{k}'} n_{\vec{k}s}n_{\vec{k}'s}e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} \\ &= -\frac{2}{n\Omega}\sum_{\vec{k}} n_{\vec{k}s} = -1, \end{aligned} \tag{3.81}$$

which means that the exchange hole expels one fermion such that each fermion "defends" a given volume against other fermions of the same spin.

3.6.2 Bosons

We consider a general occupation number state for free spinless bosons ($S=0$),

$$|\Phi\rangle = |n_{\vec{k}_0}, n_{\vec{k}_1}, \ldots\rangle = \cdots(\widehat{a}^\dagger_{\vec{k}_1})^{n_{\vec{k}_1}}(\widehat{a}^\dagger_{\vec{k}_0})^{n_{\vec{k}_0}}|0\rangle\ . \tag{3.82}$$

The ground state would be the state with all bosons occupying the lowest-energy single-particle state. For such a state $|\Phi\rangle$ the one-particle correlation function looks similar to the fermionic case,

$$\langle\Phi|\,\widehat{\Psi}^\dagger(\vec{r})\,\widehat{\Psi}(\vec{r}\,')|\Phi\rangle = \frac{1}{\Omega}\sum_{\vec{k},\vec{k}'} e^{-i\vec{k}\cdot\vec{r}+i\vec{k}'\cdot\vec{r}'}\underbrace{\langle\Phi|\,\widehat{a}^\dagger_{\vec{k}}\,\widehat{a}_{\vec{k}'}|\Phi\rangle}_{n_{\vec{k}}\delta_{\vec{k}\vec{k}'}} = \frac{1}{\Omega}\sum_{\vec{k}} n_{\vec{k}}e^{-\vec{k}\cdot(\vec{r}-\vec{r}\,')}, \tag{3.83}$$

which in the limit $\vec{r}\,'\to\vec{r}$ approaches the constant density n and vanishes at very large distances. The pair correlation functions is given by

$$\begin{aligned} n^2 g(\vec{r}-\vec{r}\,') &= \langle\Phi|\,\widehat{\Psi}^\dagger(\vec{r})\,\widehat{\Psi}^\dagger(\vec{r}\,')\,\widehat{\Psi}(\vec{r}\,')\,\widehat{\Psi}(\vec{r})|\Phi\rangle \\ &= \frac{1}{\Omega^2}\sum_{\vec{k},\vec{k}',\vec{q},\vec{q}'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}-i(\vec{q}-\vec{q}')\cdot\vec{r}'}\langle\Phi|\,\widehat{a}^\dagger_{\vec{k}}\,\widehat{a}^\dagger_{\vec{q}}\,\widehat{a}_{\vec{q}'}\,\widehat{a}_{\vec{k}'}|\Phi\rangle\ , \end{aligned} \tag{3.84}$$

where we have to evaluate the expectation value again

$$\begin{aligned} &\langle\Phi|\,\widehat{a}^\dagger_{\vec{k}}\,\widehat{a}^\dagger_{\vec{q}}\,\widehat{a}_{\vec{q}'}\,\widehat{a}_{\vec{k}'}|\Phi\rangle \\ &\quad= (1-\delta_{\vec{k}\vec{q}})\left\{\delta_{\vec{k}\vec{k}'}\delta_{\vec{q}\vec{q}'}+\delta_{\vec{k}\vec{q}'}\delta_{\vec{q}\vec{k}'}\right\}\underbrace{\langle\Phi|\,\widehat{a}^\dagger_{\vec{k}}\,\widehat{a}^\dagger_{\vec{q}}\,\widehat{a}_{\vec{q}}\,\widehat{a}_{\vec{k}}|\Phi\rangle}_{=n_{\vec{k}}n_{\vec{q}}} \\ &\qquad+\delta_{\vec{k}\vec{q}}\delta_{\vec{k}\vec{k}'}\delta_{\vec{q}\vec{q}'}\underbrace{\langle\Phi|\,\widehat{a}^\dagger_{\vec{k}}\,\widehat{a}^\dagger_{\vec{k}}\,\widehat{a}_{\vec{k}}\,\widehat{a}_{\vec{k}}|\Phi\rangle}_{=n_{\vec{k}}(n_{\vec{k}}-1)}\ . \end{aligned} \tag{3.85}$$

This leads to

$$
\begin{aligned}
n^2 g(\vec{r}-\vec{r}\,') &= \frac{1}{\Omega^2}\left[\sum_{\vec{k},\vec{q}}(1-\delta_{\vec{k}\,\vec{q}})\left(1+e^{-i(\vec{k}-\vec{q})\cdot(\vec{r}-\vec{r}\,')}\right)n_{\vec{k}}n_{\vec{q}}+\sum_{\vec{k}}n_{\vec{k}}(n_{\vec{k}}-1)\right] \\
&= \frac{1}{\Omega^2}\left[\sum_{\vec{k},\vec{q}}n_{\vec{k}}n_{\vec{q}}-\sum_{\vec{k}}n_{\vec{k}}^2-\sum_{\vec{k}}n_{\vec{k}}+\left|\sum_{\vec{k}}e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}n_{\vec{k}}\right|^2\right] \qquad (3.86) \\
&= n^2+\left|\frac{1}{\Omega}\sum_{\vec{k}}e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}n_{\vec{k}}\right|^2-\frac{1}{\Omega^2}\sum_{\vec{k}}n_{\vec{k}}(n_{\vec{k}}+1)\ .
\end{aligned}
$$

Let us now consider two cases. (1) All particles are in the same momentum state $n_{\vec{k}}=N\delta_{\vec{k},\vec{k}_0}$ which, for a Bose-Einstein condensate, is the ground state $\vec{k}_0=0$. In this case,

$$
n^2 g(\vec{r}-\vec{r}\,')=2n^2-\frac{1}{\Omega^2}N(N+1)=\frac{N(N-1)}{\Omega^2}, \qquad (3.87)
$$

no correlation is observed. The probability to pick the first particle is $n=N/\Omega$ and a second one $(N-1)/\Omega$ ($\approx n$ for large N). (2) We broaden the distribution into a Gaussian

$$
n_{\vec{k}}=\frac{(2\pi)^3 n}{(A\sqrt{\pi})^3}e^{-(\vec{k}-\vec{k}_0)^2/A^2}\ , \qquad (3.88)
$$

which corresponds to the classical Maxwell-Boltzmann distribution, if we write $A^2=2mk_BT/\hbar^2=4\pi/\lambda^2$ (λ: thermal wave length). Then the correlation function is calculated as follows,

$$
\begin{aligned}
n^2 g(\vec{r}-\vec{r}\,') &= n^2+\left|\underbrace{\int\frac{d^3k}{(2\pi)^3}e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}n_{\vec{k}}}_{ne^{-A^2(\vec{r}-\vec{r}\,')^2/4}e^{-i\vec{k}_0(\vec{r}-\vec{r}\,')}}\right|^2+\mathcal{O}\left(\frac{1}{\Omega}\right) \qquad (3.89) \\
&= n^2\left(1+e^{-A^2(\vec{r}-\vec{r}\,')^2/2}\right)+\mathcal{O}\left(\frac{1}{\Omega}\right).
\end{aligned}
$$

The probability of finding two bosons at the same position is twice as large as for long distances, see Fig. 3.2 . Thus, in contrast to fermions, bosons like to cluster together.

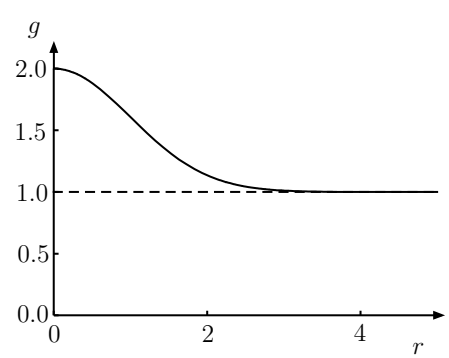

Figure 3.2: The pair correlation function for bosons.

3.7 Selected applications

We consider here three examples applying second quantization to statistical physics systems.

3.7.1 Spin susceptibility

We calculate the spin susceptibility of spin-1/2 fermions using the fluctuation-dissipation relation.

$$\chi = \frac{1}{\Omega k_B T}\left\{\langle \hat{M}_z^2\rangle - \langle \hat{M}_z\rangle^2\right\} , \tag{3.90}$$

where

$$\hat{M}_z = \frac{g\mu_B}{\hbar}\int d^3r\ \widehat{S}_z(\vec{r}) = \mu_B \sum_{\vec{k}}\sum_{ss'} \hat{a}^\dagger_{\vec{k}\,s}\sigma^z_{ss'}\hat{a}_{\vec{k}\,s'} = \mu_B \sum_{\vec{k},s} s\hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s} \tag{3.91}$$

using Sect.3.4. Moreover, $g = 2$ and $s = \pm 1$. First we calculate the magnetization in zero magnetic field,

$$\langle \hat{M}_z\rangle = \mu_B \sum_{\vec{k},s} s\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle = \mu_B \sum_{\vec{k},s} s n_{\vec{k}} = 0 . \tag{3.92}$$

Now we turn to

$$\langle \hat{M}_z^2\rangle = \mu_B^2 \sum_{\vec{k},s}\sum_{\vec{k}',s'} ss'\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\rangle , \tag{3.93}$$

which we determine by applying the scheme used in Sect.3.5 to calculate the Fermi-Dirac distribution. Thus, we write

$$\begin{aligned}
\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\rangle &= \frac{1}{Z} tr\left\{e^{-\beta\mathcal{H}'}\hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\right\} = \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z} tr\left\{e^{-\beta\mathcal{H}'}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\hat{a}^\dagger_{\vec{k}\,s}\right\} \\
&= \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z}\left[tr\left\{e^{-\beta\mathcal{H}'}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\right\}\delta_{\vec{k}\,\vec{k}'}\delta_{ss'} + tr\left\{e^{-\beta\mathcal{H}'}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\right\}\right] \\
&= e^{-\beta(\epsilon_{\vec{k}}-\mu)}\left\{\left(1-\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle\right)\delta_{\vec{k}\,\vec{k}'}\delta_{ss'} + \langle \hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\rangle\right\} \\
&\quad - e^{-\beta(\epsilon_{\vec{k}}-\mu)}\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\rangle
\end{aligned} \tag{3.94}$$

which leads straightforwardly to

$$\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\rangle = \langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle\left(1-\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle\right)\delta_{\vec{k}\,\vec{k}'}\delta_{ss'} + \langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle\langle \hat{a}^\dagger_{\vec{k}'s'}\hat{a}_{\vec{k}'s'}\rangle . \tag{3.95}$$

We now insert this result into Eq.(3.93) and obtain

$$\begin{aligned}
\langle \hat{M}_z^2\rangle &= 2\mu_B^2 \sum_{\vec{k}}\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle\left(1-\langle \hat{a}^\dagger_{\vec{k}\,s}\hat{a}_{\vec{k}\,s}\rangle\right) = 2\mu_B^2\sum_{\vec{k}} n_{\vec{k}\,s}(1-n_{\vec{k}\,s}) \\
&= 2\mu_B^2 \sum_{\vec{k}} \frac{1}{4\cosh^2(\beta(\epsilon_{\vec{k}}-\mu)/2)} ,
\end{aligned} \tag{3.96}$$

where the second term cancels due to the spin summation. In the low-temperature limit this is confined to a narrow region ($\sim k_B T$) around the Fermi energy, such that we approximate

$$\langle \hat{M}_z^2\rangle \approx \mu_B^2\Omega\int_{-\infty}^{+\infty} d\epsilon N(\epsilon_F)\frac{1}{4\cosh^2(\beta\epsilon/2)} = \Omega\mu_B^2 k_B T N(\epsilon_F) , \tag{3.97}$$

where the density of states is defined as

$$N(\epsilon) = \frac{1}{\Omega} \sum_{\vec{k},s} \delta(\epsilon - \epsilon_{\vec{k}}) \; . \tag{3.98}$$

Then the spin susceptibility is given as the Pauli susceptibility,

$$\chi = \mu_B^2 N(\epsilon_F) = \mu_B^2 \frac{3n}{2\epsilon_F} \; , \tag{3.99}$$

where the expression with the density of states at ϵ_F is general and the second equality is valid for free fermions. The Pauli susceptibility is independent of temperature, because only $N(\epsilon_F)k_BT$ fermions can be spin polarised (thermal softening of the Fermi sea). Thus, the factor $(k_BT)^{-1}$ is compensated by the shrinking density of polarisable spins as temperature decreases.[2]

3.7.2 Bose-Einstein condensate and coherent states

Our aim here is to characterise the Bose-Einstein condensate further beyond what we did in the last chapter. Here, we consider the concepts of both the off-diagonal long-range order and the order parameter for the condensate. We start with the discussion of the single-particle correlation function for a homogeneous gas of spin-0 bosons,

$$g(\vec{r} - \vec{r}\,') = \langle \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r}\,')\rangle = \frac{1}{\Omega} \sum_{\vec{k},\vec{k}\,'} \langle \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}\,'}\rangle e^{i(\vec{k}\,'\cdot\vec{r}\,' - \vec{k}\cdot\vec{r})} = \frac{1}{\Omega} \sum_{\vec{k}} \langle \hat{n}_{\vec{k}}\rangle e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \; , \tag{3.103}$$

where $\langle \hat{n}_{\vec{k}}\rangle$ is the Bose-Einstein distribution. For independent free bosons we may write

$$g(\vec{R}) = \int \frac{d^3k}{(2\pi)^3} \frac{e^{-i\vec{k}\cdot\vec{R}}}{e^{\beta(\epsilon_{\vec{k}}-\mu)} - 1} \; , \tag{3.104}$$

with $\epsilon_{\vec{k}} = \hbar^2 \vec{k}^{\,2}/2m$ and $\vec{R} = \vec{r} - \vec{r}\,'$. Let us look at the two limits $\vec{R} \to 0$ and $\vec{R} \to \infty$. For the first limit we may expand

$$g(\vec{R}) = \int \frac{d^3k}{(2\pi)^3} \frac{1 + i\vec{k}\cdot\vec{R} - (\vec{k}\cdot\vec{R})^2/2 + \cdots}{e^{\beta(\epsilon_{\vec{k}}-\mu)} - 1} = n\left(1 - \frac{\vec{R}^{\,2}}{6}\langle \vec{k}^{\,2}\rangle + \cdots\right) \; , \tag{3.105}$$

where $n = N/\Omega$ is the particle density and

$$\langle \vec{k}^{\,2}\rangle \sim \frac{4\pi}{\lambda^2} \tag{3.106}$$

where $\lambda = (2\pi m k_B T/h^2)^{1/2}$ is the thermal wave length providing the characteristic length scale. The correlation falls off quadratically for finite, but small $\vec{R}$. For the long-distance limit we

[2] *Classical limit:* The classical limit can be discussed using the Maxwell-Boltzmann distribution function,

$$n_{\vec{k}\,s} = \frac{n\lambda^3}{2} e^{-k^2\lambda^2/4\pi} \; , \tag{3.100}$$

with λ as the thermal wavelength. Inserting into Eq.(3.96) we obtain

$$\langle \hat{M}_z^2\rangle = 2\mu_B^2\Omega \int \frac{d^3k}{(2\pi)^3} n_{\vec{k}\,s}(1 - n_{\vec{k}\,s}) = 2\mu_B^2\Omega \int \frac{d^3k}{(2\pi)^3} \left\{ \frac{n\lambda^3}{2} e^{-k^2\lambda^2/4\pi} - \frac{n^2\lambda^6}{4} e^{-k^2\lambda^2/2\pi} \right\} = \mu_B^2 \Omega n \left(1 - \frac{\lambda^3 n}{2^{5/2}}\right) \; , \tag{3.101}$$

which using Eq.(3.90) leads to the susceptibility found earlier in Eq.(2.94).

$$\chi = \frac{\mu_B^2 n}{k_B T}\left(1 - \frac{\lambda^3 n}{2^{5/2}}\right) \tag{3.102}$$

The factor $1 - n_{\vec{k}\,s}$ in Eq.(3.96) introduces the quantum correction in the second term.

note that only the small wave vectors contribute to the integral so that we may expand the integrand in the following way,

$$g(\vec{R}) \approx \int \frac{d^3k}{(2\pi)^3} \frac{e^{-i\vec{k}\cdot\vec{R}}}{\beta(\epsilon_{\vec{k}} - \mu)} = \frac{2mk_BT}{\hbar^2} \int \frac{d^3k}{(2\pi)^3} \frac{e^{-i\vec{k}\cdot\vec{R}}}{\vec{k}^{\,2} + k_0^2} \tag{3.107}$$

where $k_0^2 = -\frac{2m\mu}{\hbar^2} > 0$. This form we know from the Yukawa potential,

$$g(\vec{R}) \approx \frac{mk_BT}{(2\pi)^4\hbar^2} \frac{e^{-k_0|\vec{R}|}}{|\vec{R}|} = \frac{e^{-k_0|\vec{R}|}}{(2\pi)^3\lambda^2|\vec{R}|} \ . \tag{3.108}$$

The single-particle correlation function decays exponentially for large distances (Fig.3.3). This behavior is valid for $T > T_c$ where $\mu < 0$.

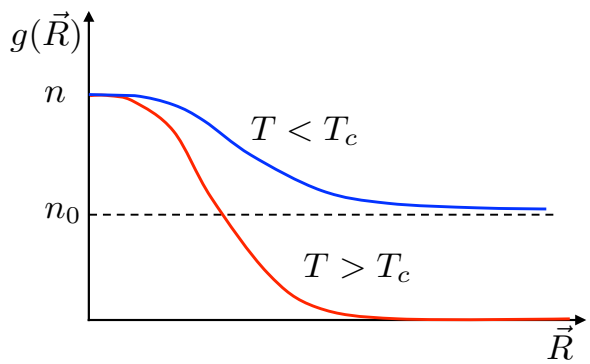

Figure 3.3: Schematic behavior of the single-particle correlation function in the normal($T > T_c$) and the Bose-Einstein condensed phase ($T < T_c$). n is the overall particle density and n_0 the density of condensed particles.

For $T < T_c$ the chemical potential lies at the lowest single-particle state, i.e. $\mu = 0$, such that $k_0 = 0$. The short-distance behavior is still described by Eq.(3.105). For the long-distance behavior we conclude from Eq.(3.108) that the correlation function goes to zero like $|\vec{R}|^{-1}$. However, this is not true, since our integral approach neglects the macroscopic occupation of the $\vec{k} = 0$ state. Thus, we should use

$$\langle \hat{n}_{\vec{k}} \rangle = n_0\delta(\vec{k}) + \frac{1}{(2\pi)^3} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1} \ , \tag{3.109}$$

such that for $|\vec{R}| \to \infty$,

$$g(\vec{R}) = n_0 + \frac{1}{(2\pi)^3\lambda^2|\vec{R}|} \ . \tag{3.110}$$

The correlation function approaches a finite value on long distances in the presence of a Bose-Einstein condensate (Fig.3.3).

Bogolyubov approximation:

We consider this now from the view point of the field operator for free bosons,

$$\widehat{\Psi}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{k}} \hat{a}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} = \frac{\hat{a}_0}{\sqrt{\Omega}} + \frac{1}{\sqrt{\Omega}} \sum_{\vec{k}\neq 0} \hat{a}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \ . \tag{3.111}$$

The correlation function in Eq.(3.110) suggests the following approximation: $\hat{a}_0 \to a_0 = \sqrt{N_0}$. For a Bose-Einstein condensate we may replace the operator $\hat{a}_0$ simply by a complex number, such that

$$\widehat{\Psi}(\vec{r}) \to \widehat{\Psi}(\vec{r}) = \psi_0(\vec{r}) + \delta\widehat{\Psi}(\vec{r}) , \tag{3.112}$$

with $\psi_0(\vec{r}) = \sqrt{n_0}e^{i\phi}$, where ϕ is an arbitrary phase and $n_0 = N_0/\Omega$. In a uniform system this phase does not affect the physical properties. This so-called Bogolyubov approximation is, of course, incompatible with the occupation number representation. On the other hand, it is possible for a condensate state whose particle number is not fixed. Indeed a state incorporating this property is a coherent state.

Coherent state:

We introduce a coherent state as an eigenstate of the annihilation operator $\hat{a}_\nu$ of a bosonic state of energy ϵ_ν. Let us call this state $|\Psi_\alpha\rangle$ with

$$\hat{a}_\nu|\Psi_\alpha\rangle = \alpha|\Psi_\alpha\rangle , \tag{3.113}$$

with α a complex number. Such a state is given by

$$|\Psi_\alpha\rangle = e^{-|\alpha|^2/2}\sum_{N_\nu}\frac{\alpha^{N_\nu}}{\sqrt{N_\nu!}}|N_\nu\rangle;, \tag{3.114}$$

with $\hat{a}_\nu|N_\nu\rangle = \sqrt{N_\nu}|N_\nu - 1\rangle$. The expectation value for $\hat{n}_\nu = \hat{a}_\nu^\dagger\hat{a}_\nu$ is

$$\langle\hat{n}_\nu\rangle = \langle\Psi_\alpha|\hat{a}_\nu^\dagger\hat{a}_\nu|\Psi_\alpha\rangle = \langle\Psi_\alpha|\alpha^*\alpha|\Psi_\alpha\rangle = \alpha^*\alpha = |\alpha|^2 \tag{3.115}$$

and the variance is

$$\langle\hat{n}_\nu^2\rangle - \langle\hat{n}_\nu\rangle^2 = \langle\hat{a}_\nu^\dagger\hat{a}_\nu\hat{a}_\nu^\dagger\hat{a}_\nu\rangle - |\alpha|^4 = \langle\hat{a}_\nu^\dagger\hat{a}_\nu\rangle + \langle\hat{a}_\nu^\dagger\hat{a}_\nu^\dagger\hat{a}_\nu\hat{a}_\nu\rangle - |\alpha|^4 = |\alpha|^2 + |\alpha|^4 - |\alpha|^4 = |\alpha|^2 \tag{3.116}$$

such that

$$\frac{\langle\hat{n}_\nu^2\rangle - \langle\hat{n}_\nu\rangle^2}{\langle\hat{n}_\nu\rangle^2} = \frac{1}{|\alpha|^2} = \frac{1}{\langle\hat{n}_\nu\rangle} . \tag{3.117}$$

Taking now the $\vec{k} = 0$ state as coherent we identify

$$\hat{a}_0|\Psi\rangle = \alpha_0|\Psi\rangle = \sqrt{N_0}e^{i\phi}|\Psi\rangle . \tag{3.118}$$

In this spirit we find that the mean value is

$$\langle\widehat{\Psi}(\vec{r})\rangle = \psi_0(\vec{r}) , \tag{3.119}$$

which does not vanish for the condensed state. Note, however, $\langle\hat{a}_{\vec{k}}\rangle = 0$, if $\vec{k} \neq 0$. The finite value of $\langle\hat{a}_0\rangle$ requires states of different number of particles in the $\vec{k} = 0$ state for the matrix elements making up this mean value. This is an element of spontaneous symmetry breaking. The condensate can be considered as a reservoir with on average $N_0 \gg 1$ particles, to which we can add or from which we can remove particles without changing the properties of the system. The coherent state satisfies this condition. We also can define an *order parameter* characterizing the condensate, the *condensate wavefunction* of Eq.(3.119),

$$\psi_0(\vec{r}) = |\psi_0(\vec{r})|e^{i\phi(\vec{r})} = \sqrt{n_0}e^{i\phi} . \tag{3.120}$$

Spontaneous symmetry breaking occurs via the (arbitrary) choice of the phase of the condensate wave function.
The number of particles and the phase ϕ are conjugate in the sense that a state with fixed particle number has no definite phase (also no order parameter like Eq.(3.120)) and a state

with fixed phase has no definite particle number. [3] First we consider the wave function of the coherent state in the number representation,

$$\Psi_N = \langle N|\Psi_\alpha\rangle = e^{-|\alpha|^2/2}\frac{\alpha^N}{\sqrt{N!}} \tag{3.125}$$

with $\alpha = \sqrt{N_0}e^{i\phi_0}$. Thus, the probability for the particle number N is given by

$$P_N = |\Psi_N|^2 = e^{N_0}\frac{N_0^N}{N!} \approx \frac{1}{\sqrt{2\pi N_0}}e^{-(N-N_0)^2/2N_0} \tag{3.126}$$

for large N_0. On the other hand, projecting into the phase representation,

$$\begin{aligned}\Psi_\phi &= \langle\phi|\Psi_\alpha\rangle = \sum_{N=0}^{\infty}\langle\phi|N\rangle\langle N|\Psi_\alpha\rangle = \frac{e^{-|\alpha|^2/2}}{\sqrt{2\pi}}\sum_{N=0}^{\infty}\frac{\alpha^N e^{-i\phi N}}{\sqrt{N!}} \\ &\approx \frac{1}{\sqrt{2\pi}}\int_0^\infty dN\frac{e^{-(N-N_0)^2/4N_0}}{(2\pi N_0)^{1/4}}e^{-iN(\phi-\phi_0)} = \left(\frac{N_0}{2\pi}\right)^{1/4} e^{-(\phi-\phi_0)^2 N_0/4}\end{aligned} \tag{3.127}$$

such that

$$P_\phi = |\langle\phi|\Psi_\alpha\rangle|^2 \approx \sqrt{\frac{N_0}{2\pi}}e^{-(\phi-\phi_0)^2 N_0/2}\ . \tag{3.128}$$

The Gaussian approximation is in both representations only valid, if $N_0 \gg 1$. The coherent state is neither an eigenstate of $\hat{N}$ nor $e^{i\hat{\phi}}$. But for both the distributions are well localized around the corresponding mean values, N_0 and ϕ_0. The uncertainty relation is obtained by considering the deviations from the mean values,

$$\left.\begin{aligned}\Delta\phi^2 &= \langle\Psi_\alpha|(\hat{\phi}-\phi_0)^2|\Psi_\alpha\rangle = \frac{1}{N_0} \\ \Delta N^2 &= \langle\Psi_\alpha|(\hat{N}-N_0)^2|\Psi_\alpha\rangle = N_0\end{aligned}\right\} \quad\Rightarrow\quad \Delta N\ \Delta\phi = 1\ , \tag{3.129}$$

compatible with a commutation relation of the form $[\hat{N},\hat{\phi}] = i$.

[3] *Phase and number operator eigenstates:* The define the number operator and the phase operator and their corresponding eigenstates.

$$\hat{N}|N\rangle = N|N\rangle \qquad \text{and} \qquad e^{i\hat{\phi}}|\phi\rangle = e^{i\phi}|\phi\rangle \tag{3.121}$$

where the two states are connected by the Fourier transform

$$|\phi\rangle = \frac{1}{\sqrt{2\pi}}\sum_{N=0}^{\infty}e^{iN\phi}|N\rangle \qquad \text{with} \qquad \langle N|\phi\rangle = \frac{e^{iN\phi}}{\sqrt{2\pi}} \tag{3.122}$$

analogous to the relation between real and momentum space states. In this context care has to be taken to ensure that the states $|\phi\rangle$ form an orthogonal complete set of the Hilbert space. A way to construct this is to start with an finite Hilbert space $\{|N\rangle\}$ assuming that $0 \le N \le L-1 \gg 1$. Then we can restrict ourselves to a discrete set of phases $\phi = \phi_k = 2\pi k/L$ with $k = 0,\ldots,L-1$ (analog to wave vectors in a finite system with periodic boundary conditions). Now it is easy to see that

$$\langle\phi_k|\phi_{k'}\rangle = \delta_{k,k'}\ . \tag{3.123}$$

Keeping this in mind we take the limit $L\to\infty$.

Based on this above operators can be represented as

$$\hat{N} = \sum_{N=0}^{\infty}N|N\rangle\langle N| \qquad \text{and} \qquad e^{i\hat{\phi}} = \sum_{N=0}^{\infty}|N\rangle\langle N+1|\ ;. \tag{3.124}$$

Thus for both $\hat{N}$ and $e^{i\hat{\phi}}$ the coherent state does not represent an eigenstate, but rather the best localized in either basis.

3.7.3 Phonons in an elastic medium

We consider here vibrations of an elastic media using a simplified model of longitudinal waves only. As in Sect.2.8.2 we describe deformation of the elastic medium by means of the displacement field $\vec{u}\,(\vec{r},t)$. The kinetic and elastic energy are then given by

$$E_{\rm kin} = \frac{\rho_m}{2}\int d^3r\,\left(\frac{\partial\,\vec{u}\,(\vec{r},t)}{\partial t}\right)^2 \qquad \text{and} \qquad E_{\rm el} = \frac{\lambda}{2}\int d^3r(\vec{\nabla}\cdot\vec{u}\,(\vec{r},t))^2\,, \tag{3.130}$$

where ρ_m is the mass density of the medium and λ denotes the elastic modulus. Note that we use a simplified elastic term which is only based on density fluctuations, corresponding to $\vec{\nabla}\cdot\vec{u}$, and does not include the contributions of shear distortion. This two energies are now combined to the Lagrange functional $L[\,\vec{u}\,] = E_{\rm kin} - E_{\rm el}$, whose variation with respect to $\vec{u}\,(\vec{r},t)$ yields the wave equation,

$$\frac{1}{c_l^2}\frac{\partial^2}{\partial t^2}\,\vec{u} - \vec{\nabla}\,(\vec{\nabla}\cdot\vec{u}\,) = 0\,, \tag{3.131}$$

for longitudinal waves with the sound velocity $c_l = \sqrt{\lambda/\rho_m}$. The general solution can be represented as a superposition of plane waves,

$$\vec{u}\,(\vec{r},t) = \frac{1}{\sqrt{\Omega}}\sum_{\vec{k}}\vec{e}_{\,\vec{k}}\,\left(q_{\vec{k}}(t)e^{i\,\vec{k}\cdot\vec{r}} + q_{\vec{k}}(t)^*e^{-i\,\vec{k}\cdot\vec{r}}\right)\,, \tag{3.132}$$

with polarization vector $\vec{e}_{\,\vec{k}} = \vec{k}\,/|\,\vec{k}\,|$ and the amplitudes $q_{\vec{k}}(t)$ satisfy the equation,

$$\frac{d^2}{dt^2}q_{\vec{k}} + \omega_{\vec{k}}^2\,q_{\vec{k}} = 0\,, \tag{3.133}$$

with the frequency $\omega_{\vec{k}} = c_l|\,\vec{k}\,| = c_l k$. We may rewrite the energy, $E = E_{\rm kin} + E_{\rm el}$, in terms of $q_{\vec{k}}$,

$$E = \sum_{\vec{k}}\rho_m\omega_{\vec{k}}^2\,\left[q_{\vec{k}}(t)q_{\vec{k}}^*(t) + q_{\vec{k}}(t)^*q_{\vec{k}}(t)\right]\,. \tag{3.134}$$

which we express in a symmetrized form. Now we introduce new variables

$$Q_{\vec{k}} = \sqrt{\rho_m}(q_{\vec{k}} + q_{\vec{k}}^*) \qquad \text{and} \qquad P_{\vec{k}} = \frac{d}{dt}Q_{\vec{k}} = -i\omega_{\vec{k}}\sqrt{\rho_m}(q_{\vec{k}} - q_{\vec{k}}^*)\,, \tag{3.135}$$

leading to the energy

$$E = \frac{1}{2}\sum_{\vec{k}}\left(P_{\vec{k}}^2 + \omega_{\vec{k}}^2Q_{\vec{k}}^2\right)\,. \tag{3.136}$$

This corresponds to a set of independent harmonic oscillators labelled by the wave vectors $\vec{k}$, as we have seen in Sect.2.8. We now turn to the step of canonical quantization replacing the variables $(P_{\vec{k}}, Q_{\vec{k}}) \to (\widehat{P}_{\vec{k}}, \widehat{Q}_{\vec{k}})$ which satisfy the standard commutation relation,

$$[\,\widehat{Q}_{\vec{k}}\,,\,\widehat{P}_{\vec{k}'}] = i\hbar\delta_{\vec{k},\vec{k}'}\,. \tag{3.137}$$

This can be reexpressed in terms of lowering and raising operators,

$$\begin{aligned}\hat{b}_{\vec{k}} &= \frac{1}{\sqrt{2\hbar\omega_{\vec{k}}}}\left(\omega_{\vec{k}}\,\widehat{Q}_{\vec{k}} + i\,\widehat{P}_{\vec{k}}\right)\,,\\ \hat{b}_{\vec{k}}^\dagger &= \frac{1}{\sqrt{2\hbar\omega_{\vec{k}}}}\left(\omega_{\vec{k}}\,\widehat{Q}_{\vec{k}} - i\,\widehat{P}_{\vec{k}}\right)\,,\end{aligned} \tag{3.138}$$

which obey the following commutation relations due to Eq.(3.137),

$$[\hat{b}_{\vec{k}}, \hat{b}^\dagger_{\vec{k}'}] = \delta_{\vec{k},\vec{k}'} \ , \quad [\hat{b}_{\vec{k}}, \hat{b}_{\vec{k}'}] = [\hat{b}^\dagger_{\vec{k}}, \hat{b}^\dagger_{\vec{k}'}] = 0 \ . \tag{3.139}$$

Therefore $\hat{b}^\dagger_{\vec{k}}$ and $\hat{b}_{\vec{k}}$ can be viewed as creation and annihilation operators, respectively, for bosonic particles, called phonons. The Hamiltonian can be now written as

$$\mathcal{H} = \sum_{\vec{k}} \hbar\omega_{\vec{k}} \left(\hat{b}^\dagger_{\vec{k}} \hat{b}_{\vec{k}} + \frac{1}{2} \right) = \sum_{\vec{k}} \hbar\omega_{\vec{k}} \left(\hat{n}_{\vec{k}} + \frac{1}{2} \right) \tag{3.140}$$

whose eigenstates are given in the occupation number representation, $|n_{\vec{k}_1}, n_{\vec{k}_2}, \ldots\rangle$.
We can now also introduce the corresponding field operator using Eq.(3.132),

$$\widehat{\vec{u}}\,(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{k}} \vec{e}_{\vec{k}} \sqrt{\frac{\hbar}{2\rho_m \omega_{\vec{k}}}} \left[\hat{b}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \hat{b}^\dagger_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} \right] \tag{3.141}$$

which is not an eigen operator for the occupation number states. Actually the thermal mean value of the field vanishes $\langle\, \widehat{\vec{u}}\,(\vec{r})\rangle = 0$.

Correlation function:

The correlation function is given by

$$\begin{aligned} g(\vec{r} - \vec{r}\,') &= \langle\, \widehat{\vec{u}}\,(\vec{r}) \cdot \widehat{\vec{u}}\,(\vec{r}\,')\rangle - \langle\, \widehat{\vec{u}}\,(\vec{r})\rangle \cdot \langle\, \widehat{\vec{u}}\,(\vec{r}\,')\rangle = \langle\, \vec{u}\,(\vec{r}) \cdot \vec{u}\,(\vec{r}\,')\rangle \\ &= \frac{1}{\Omega} \sum_{\vec{k},\vec{k}'} \frac{\hbar\, \vec{e}_{\vec{k}} \cdot \vec{e}_{\vec{k}'}}{2\rho_m \sqrt{\omega_{\vec{k}}\omega_{\vec{k}'}}} \left\langle \left[\hat{b}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \hat{b}^\dagger_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} \right] \left[\hat{b}_{\vec{k}'} e^{i\vec{k}'\cdot\vec{r}'} + \hat{b}^\dagger_{\vec{k}'} e^{-i\vec{k}'\cdot\vec{r}'} \right] \right\rangle \ . \end{aligned} \tag{3.142}$$

Note that

$$\langle \hat{b}^\dagger_{\vec{k}} \hat{b}_{\vec{k}'} \rangle = \langle \hat{n}_{\vec{k}} \rangle \delta_{\vec{k},\vec{k}'} \ , \quad \langle \hat{b}_{\vec{k}} \hat{b}^\dagger_{\vec{k}'} \rangle = \left\{ 1 + \langle \hat{n}_{\vec{k}} \rangle \right\} \delta_{\vec{k},\vec{k}'} \ , \langle \hat{b}^\dagger_{\vec{k}} \hat{b}^\dagger_{\vec{k}'} \rangle = \langle \hat{b}_{\vec{k}} \hat{b}_{\vec{k}'} \rangle = 0 \ , \tag{3.143}$$

such that

$$\begin{aligned} g(\vec{r} - \vec{r}\,') &= \frac{\hbar}{2\rho_m \Omega} \sum_{\vec{k}} \frac{1}{\omega_{\vec{k}}} \left\{ \left(1 + \langle \hat{n}_{\vec{k}} \rangle \right) e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} + \langle \hat{n}_{\vec{k}} \rangle e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')} \right\} \\ &= \frac{\hbar}{(2\pi)^2 \rho_m c_l} \int dk \frac{\sin(k|\vec{r} - \vec{r}\,'|)}{|\vec{r} - \vec{r}\,'|} \left(1 + 2\langle \hat{n}_{\vec{k}} \rangle \right) \ , \end{aligned} \tag{3.144}$$

where we turn the $\vec{k}$-sum into an integral and performed the angular integration[4]. With $\langle \hat{n}_{\vec{k}} \rangle = (e^{\beta\hbar\omega_k} - 1)^{-1}$ and abbreviating $\vec{R} = \vec{r} - \vec{r}\,'$, we obtain

$$g(\vec{R}) = \frac{\hbar}{(2\pi)^2 \rho_m c_l R} \int_0^{k_D} dk \ \sin kR \ \coth\left(\frac{\beta\hbar c_l k}{2} \right) \ , \tag{3.146}$$

where we include the cut-off at the Debye wave vector to account for the finite number of degrees of freedom. Note $k_D \sim \pi/a$ with a being the lattice constant. We focus on length scales much

[4] *Angular integral:*

$$\int d\Omega_{\vec{k}}\, e^{\pm i\vec{k}\cdot\vec{r}} = \int_0^{2\pi} d\phi \int_{-1}^{+1} d\cos\theta e^{\pm ikr\cos\theta} = 2\pi \left. \frac{e^{\pm ikr\cos\theta}}{\pm ikr} \right|_{\cos\theta=-1}^{\cos\theta=+1} = 4\pi \frac{\sin(kr)}{kr} \ . \tag{3.145}$$

larger than the lattice constant, we consider the limit $k_D R \gg 1$, for which we rewrite the above expression to

$$g(R) \approx \frac{\hbar}{(2\pi)^2 \rho_m c_l R^2} \underbrace{\int_0^{k_D R \to \infty} dy \ \sin y \ \coth(\gamma y)}_{= h(\gamma)} \qquad \text{with} \quad \gamma = \frac{\theta_D}{2 T k_D R} \ , \tag{3.147}$$

where we find

$$h(\gamma) = \lim_{\eta \to 0_+} \int_0^\infty dy \ \sin y \ \coth(\gamma y) e^{-\eta y} = \begin{cases} \dfrac{\pi}{2\gamma} & , \ \gamma \ll 1 \ , \\ 1 & , \ \gamma \gg 1 \ . \end{cases} \tag{3.148}$$

This leads to

$$g(R) \approx \frac{k_B \Theta_D}{(2\pi)^2 \lambda k_D} \times \begin{cases} R^{-2} & T \ll T^*(R) \\ \dfrac{\pi T}{\Theta_D} k_D R^{-1} & T \gg T^*(R) \end{cases} \tag{3.149}$$

where the Debye temperature is defined by $k_B \Theta_D = \hbar c_l k_D$ and $T^*(R) = \Theta_D / 2 k_D R$.

Melting:

Next we consider the local fluctuations of the displacement field, i.e. $\vec{r} \to \vec{r}\,'$, leading to

$$\langle \vec{u}(\vec{r})^2 \rangle = \frac{\hbar}{(2\pi)^2 \rho_m c_l} \int_0^{k_D} dk \ k \ \coth\left(\frac{\beta \hbar c_l k}{2}\right) = \begin{cases} \dfrac{k_D k_B T}{2\pi^2 \lambda} & T \gg \Theta_D \ , \\ \dfrac{k_D k_B \Theta_D}{8\pi^2 \lambda} & T \ll \Theta_D \ , \end{cases} \tag{3.150}$$

which are at high (low) temperature thermal (quantum) fluctuations. As $\vec{u}$ denotes the deviation of the position of an atom from its equilibrium position, we can apply Lindemann's criterion for melting of the systems. We introduce the lattice constant a with $k_D \approx \pi/a$. If $\langle \vec{u}^{\,2} \rangle$ is a sizeable fraction of a^2 then a crystal would melt. Thus we define the Lindemann number L_m with

$$L_m = \frac{\langle \vec{u}^{\,2} \rangle}{a^2} = \frac{k_B T}{2\pi \lambda a^3} \qquad \Rightarrow \qquad k_B T_m = 2\pi \lambda a^3 L_m = 2\pi \rho_m a^3 c_l^2 L_m = 2\pi M_i c_l^2 L_m \ , \tag{3.151}$$

where $M_i = \rho_m a^3$ is the atomic mass per unit cell. Note that usually $L_m \approx 0.1$ give a reasonable estimate for a melting temperature T_m.

Coherent state:

We introduce the following coherent phonon state,

$$|\Phi_{\vec{Q}}\rangle = e^{-|\tilde{u}|^2/2} \sum_{n=0}^{\infty} \frac{(\tilde{u} b^\dagger_{\vec{Q}})^n}{\sqrt{n!}} |0\rangle \tag{3.152}$$

with $\tilde{u} = |\tilde{u}| e^{-i\varphi}$ and $\vec{Q}$ a finite wave vector. Now we consider the expectation value of $\widehat{\vec{u}}\,(\vec{r})$,

$$\langle \Phi_{\vec{Q}} | \, \widehat{\vec{u}}\,(\vec{r}) | \Phi_{\vec{Q}} \rangle = \sqrt{\frac{\hbar}{2\Omega \rho_m \omega_{\vec{Q}}}} \frac{\vec{Q}}{|\vec{Q}|} 2|\tilde{u}| \cos(\vec{Q} \cdot \vec{r} - \varphi) \ . \tag{3.153}$$

The coherent state describes a density wave state, where $|\tilde{u}|$ determines the amplitude and φ the global shift of the wave. The density modulation is obtained by $\vec{\nabla} \cdot \vec{u}(\vec{r}) = \delta\rho(\vec{r})/\rho$.

The density wave state may be interpreted as the Bose-Einstein condensation of phonons with wave vector $\vec{Q}$, which yields an obvious breaking of the translational symmetry and the phase $(0 \leq \varphi < 2\pi)$ leads to all degenerate states, one of which has to be chosen spontaneously by the system.

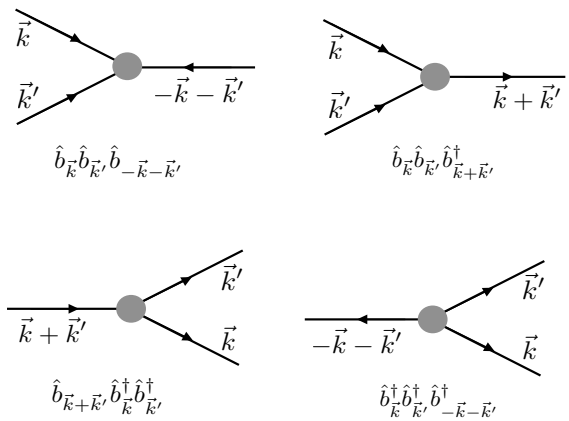

Figure 3.4: Diagrams of the three-phonon coupling terms. Arrows entering the circle denote annihilation and arrows leaving the circle denote creation of phonons.

Anharmonic elastic energy - phonon-phonon interaction:

In order to illustrate the emergence of interaction terms we consider a straightforward extension of the elastic energy in Eq.(3.130), restricting to density-density coupling, i.e.

$$E'_{\text{el}} = \frac{C'}{3} \int d^3r (\vec{\nabla} \cdot \vec{u})^3 \, . \tag{3.154}$$

We turn now to the quantized version inserting $\widehat{\vec{u}}\,(\vec{r})$ of Eq.(3.141),

$$\begin{aligned}
\mathcal{H}'_{\text{el}} &= \frac{C}{3}\left(\frac{\hbar}{2\rho_m\Omega}\right)^{3/2} \sum_{\vec{k},\vec{k}'} \frac{(\vec{e}_{\vec{k}} \cdot \vec{k})(\vec{e}_{\vec{k}'} \cdot \vec{k}')(\vec{e}_{\vec{k}+\vec{k}'} \cdot (\vec{k}+\vec{k}'))}{\left(\omega_{\vec{k}}\omega_{\vec{k}'}\omega_{\vec{k}+\vec{k}'}\right)^{1/2}} \\
&\qquad \times \left\{ \hat{b}_{\vec{k}}\hat{b}_{\vec{k}'}\hat{b}_{-\vec{k}-\vec{k}'} + 3\,\hat{b}_{\vec{k}}\hat{b}_{\vec{k}'}\hat{b}^{\dagger}_{\vec{k}+\vec{k}'} + 3\,\hat{b}_{\vec{k}+\vec{k}'}\hat{b}^{\dagger}_{\vec{k}}\hat{b}^{\dagger}_{\vec{k}'} + \hat{b}^{\dagger}_{\vec{k}}\hat{b}^{\dagger}_{\vec{k}'}\hat{b}^{\dagger}_{-\vec{k}-\vec{k}'} \right\} \\
&= \frac{C}{3}\left(\frac{\hbar}{2\rho_m c_l\Omega}\right)^{3/2} \sum_{\vec{k},\vec{k}'} \left(|\vec{k}|\,|\vec{k}'|\,|\vec{k}+\vec{k}'|\right)^{1/2} \\
&\qquad \times \left\{ \hat{b}_{\vec{k}}\hat{b}_{\vec{k}'}\hat{b}_{-\vec{k}-\vec{k}'} + 3\,\hat{b}_{\vec{k}}\hat{b}_{\vec{k}'}\hat{b}^{\dagger}_{\vec{k}+\vec{k}'} + 3\,\hat{b}_{\vec{k}+\vec{k}'}\hat{b}^{\dagger}_{\vec{k}}\hat{b}^{\dagger}_{\vec{k}'} + \hat{b}^{\dagger}_{\vec{k}}\hat{b}^{\dagger}_{\vec{k}'}\hat{b}^{\dagger}_{-\vec{k}-\vec{k}'} \right\} \, .
\end{aligned} \tag{3.155}$$

This interaction term can be interpreted as "scattering" processes involving three phonons. The expression contains three types of processes:

$$
\begin{aligned}
&\hat{b}_{\vec{k}}\hat{b}_{\vec{k}'}\hat{b}_{-\vec{k}-\vec{k}'} && \text{3 phonons are annihilated ,} \\
&\hat{b}_{\vec{k}}\hat{b}_{\vec{k}'}\hat{b}^{\dagger}_{\vec{k}+\vec{k}'} && \text{2 phonons are annihilated and 1 phonon is created ,} \\
&\hat{b}_{\vec{k}+\vec{k}'}\hat{b}^{\dagger}_{\vec{k}}\hat{b}^{\dagger}_{\vec{k}'} && \text{1 phonon is annihilated and 2 phonon are created ,} \\
&\hat{b}^{\dagger}_{\vec{k}}\hat{b}^{\dagger}_{\vec{k}'}\hat{b}^{\dagger}_{-\vec{k}-\vec{k}'} && \text{3 phonons are created .}
\end{aligned}
\tag{3.156}
$$

Note that in all processes the momentum is conserved, but the phonon number is not conserved. As shown in Fig.3.4, these processes can also be represented as diagrams, so-called Feynman diagrams.
Usually interaction terms are difficult to handle. But various approximative techniques are available.

Chapter 4

One-dimensional systems of interacting degrees of freedom

So far we considered almost exclusively ideal systems of non-interacting degrees of freedom, which we could treat with reasonable effort. Systems with interactions are considerably more complex to handle and in most cases no exact analytical discussion is possible. Notably in one spatial dimension we find a number of models which can be treated exactly and give us some interesting new aspects. Here we consider two classical systems, the spin chain and the lattice gas in one-dimension. Note, however, that in principle there are exact solutions also for quantum spin chains and other one-dimensional quantum models whose statistical physics, nevertheless, is rather complex to address.

4.1 Classical spin chain

We consider here a chain of spins (magnetic moments) $\{\vec{s}_i\}$ which are represented by freely rotating vectors of fixed length S. They interact with each other via nearest-neighbor coupling in the following way:

$$\mathcal{H}(\vec{s}_i) = J \sum_{i=1}^{N} \vec{s}_i \cdot \vec{s}_{i+1} \tag{4.1}$$

where J is the coupling strength. Note that this model has a global spin rotation symmetry, i.e. the Hamiltonian remains invariant, if we rotate all the spin in the same way. It is known as the Heisenberg Hamiltonian. For $J < 0$ the spins tend to align parallel (ferromagnetic) and for $J > 0$ they tend to be antiparallel, alternating (antiferromagnetic). We require that the chain is open and occupied by $N + 1$ spins (N bonds).

4.1.1 Thermodynamics

First we tackle the thermodynamics of the system using the canonical ensemble. Interestingly the topology of the coupling allows to calculate the partition function exactly.[1] We consider the spins as vectors of fixed length whose degree of freedom is the angular orientation and we write the partition function as

$$Z = \int d\Omega_1 \, \cdots d\Omega_{N+1} \, e^{-\beta J \sum_i \vec{s}_i \cdot \vec{s}_{i+1}} \, , \tag{4.2}$$

which decays into a product form, if we consider the reference polar axis ("z-axis") for the spin $\vec{s}_i$ given by the direction of the spin $\vec{s}_{i+1}$ (θ_i is defined as the angle between $\vec{s}_i$ and $\vec{s}_{i+1}$). Therefore

[1] We follow here M.E. Fisher, American Journal of Physics **32**, 343 (1964).

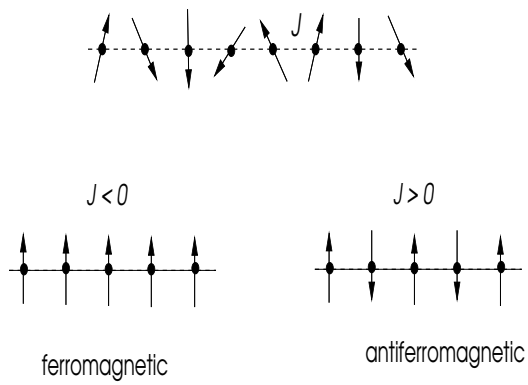

Figure 4.1: Spin chain: Coupling J between spins of arbitrary orientation. $J < 0$: ferromagnetic alignment preferred; $J > 0$: antiferromagnetic alignment preferred.

we may write

$$\begin{aligned} Z &= \prod_{i=1}^{N} \left\{ \int e^{-\beta J \vec{s}_i \cdot \vec{s}_{i+1}} d\Omega_i \right\} \int d\Omega_{N+1} = \prod_{i=1}^{N} \left\{ \int e^{-\beta J S^2 \cos\theta_i} d\Omega_i \right\} \int d\Omega_{N+1} \\ &= 4\pi \left\{ 2\pi \int_{-1}^{+1} dx e^{-\beta J S^2 x} \right\}^N = 4\pi \left\{ 4\pi \frac{\sinh(\beta J S^2)}{\beta J S^2} \right\}^N \end{aligned} \tag{4.3}$$

which looks similar to the expression obtained for the classical ideal paramagnet (see Sect.2.4.2). We may actually consider each spin being subject to a Zeeman field induced via the coupling by the neighboring spins, a feature which we will use later in the context of the mean field approximation. It is interesting to see that Z does not depend on the sign of J. Thus, the thermodynamics is the same for a ferromagnetic and an antiferromagnetic chain.
Easily we can determine the free and the internal energy,

$$\begin{aligned} F(T,N) &= N k_B T \ln(\beta J S^2) - N k_B T \ln\left\{\sinh(\beta J S^2)\right\} - N k_B T \ln 4\pi \ , \\ U(T,N) &= N k_B T - N J S^2 \coth(\beta J S^2) \ . \end{aligned} \tag{4.4}$$

In the low-temperature limit, $\beta J S^2 \gg 1$, the internal energy approaches the ground state energy, $U \to -N|J|S^2$, i.e. all spins are parallel ($J < 0$) or alternating ($J > 0$). The heat capacity is obtained through the derivative of U with respect to T,

$$C = N k_B \left\{ 1 - \left(\frac{\beta J S^2}{\sinh(\beta J S^2)} \right)^2 \right\} \tag{4.5}$$

with a similar form as for the ideal paramagnet. Note, that $C \to N k_B$ in the zero-temperature limit and, consequently, the third law of thermodynamic is not satisfied (see Fig.4.2).

4.1.2 Correlation function

We now discuss the correlation among the spins along the chain. Due to the spin-spin interaction, a spin influences the orientation of other spins over larger distances. We define the correlation function

$$\begin{aligned} \Gamma_l &= \langle \vec{s}_i \cdot \vec{s}_{i+l} \rangle = \langle s_i^x s_{i+l}^x \rangle + \langle s_i^y s_{i+l}^y \rangle = \langle s_i^z s_{i+l}^z \rangle = 3 \langle s_i^z s_{i+l}^z \rangle \\ &= \frac{3}{Z} \int d\Omega_1 \ \cdots d\Omega_{N+1} S^2 \cos\Theta_i \cos\Theta_{i+l} e^{-\beta J S^2 \sum_i \cos\theta_i} \ . \end{aligned} \tag{4.6}$$

where Θ_i is the angle of spin i with respect to the general z-axis (e.g. along the chain). We can perform all integrations for the spin $\vec{s}_j$ with $j < i$ and $j > i + l$ which can be decomposed into the same product form as discussed above. The remaining integrals are now

$$\begin{aligned}\Gamma_l = 3S^2 \left(\frac{\beta J S^2}{4\pi \sinh(\beta J S^2)}\right)^{l+1} \int d\Omega_i \cos\Theta_i e^{-\beta J S^2 \cos\theta_i} \\ \times \int d\Omega_{i+1} e^{-\beta J S^2 \cos\theta_{i+1}} \cdots \int d\Omega_{i+l} \cos\Theta_{i+l}\end{aligned} \tag{4.7}$$

Taking again the direction of spin $\vec{s}_{i+1}$ as the reference for the spin $\vec{s}_i$ we find the relation[2]

$$\cos\Theta_i = \cos\Theta_{i+1}\cos\theta_i + \sin\Theta_{i+1}\sin\theta_i\cos\phi_i \ . \tag{4.10}$$

Inserting this we notice that the averages $\langle\cos\theta_i\rangle \neq 0$ and $\langle\sin\theta_i\cos\phi_i\rangle = 0$. Thus

$$\begin{aligned}\Gamma_l &= 3S^2 \left(\frac{\beta J S^2}{4\pi \sinh(\beta J S^2)}\right)^{l+1} \int d\Omega_i \cos\theta_i e^{-\beta J S^2 \cos\theta_i} \\ &\quad \times \int d\Omega_{i+1} \cos\Theta_{i+1} e^{-\beta J S^2 \cos\theta_{i+1}} \cdots \int d\Omega_{i+l} \cos\Theta_{i+l} \\ &= \Gamma_{l-1} \frac{\beta J S^2}{4\pi \sinh(\beta J S^2)} \int d\Omega_i \cos\theta_i e^{-\beta J S^2 \cos\theta_i} = \Gamma_{l-1} u(\beta J S^2)\end{aligned} \tag{4.11}$$

with

$$u(x) = \frac{1}{x} - \coth x \ . \tag{4.12}$$

If we take into account that $\Gamma_{l=0} = S^2$ we find

$$\Gamma_l = S^2 \left[u(\beta J S^2)\right]^l = S^2 e^{-l/\xi}(-sign(J))^l \quad \text{with} \quad \xi^{-1} = -\ln\{|u(\beta J S^2)|\} \ . \tag{4.13}$$

Note that $0 < |u| < 1$ for all finite temperatures and couplings. The correlation function decays exponentially for all finite temperature and allows us to introduce a characteristic length scale, the correlation length ξ:

$$\xi(T) = \begin{cases} [\ln(3k_B T/|J|S^2)]^{-1} & k_B T \gg |J|S^2 \\ \dfrac{|J|S^2}{k_B T} & k_B T \ll |J|S^2 \end{cases} \tag{4.14}$$

For large temperature the correlation length shrinks rather slowly to zero and in the zero-temperature limit it diverges indicating an infinitely extending correlation at $T = 0$. Indeed we find for $T = 0$ that $u \to 1$ such that

$$\Gamma_l(T = 0) = S^2(-\text{sign}J)^l \tag{4.15}$$

for all l. This means that the spins order either ferromagnetically for $J < 0$ or antiferromagnetically for $J > 0$ at $T = 0$. However, for any finite temperature we find $\Gamma_l \to 0$ for $l \to \infty$.

[2]Consider $\vec{s}_1$ and $\vec{s}_2$ and take $\hat{y}' \perp \hat{z}, \vec{s}_2$ with $|\hat{y}'| = |\hat{z}| = 1$:

$$\vec{s}_1 = \vec{s}_2\cos\theta_1 + (\hat{y}' \times \vec{s}_2)\sin\theta_1\cos\phi_1 + \hat{y}' S \sin\theta_1 \sin\phi_1 \tag{4.8}$$

and multiply by $\hat{z}$:

$$\underbrace{\hat{z}\cdot\vec{s}_1}_{=S\cos\Theta_1} = \cos\theta_1 \underbrace{\hat{z}\cdot\vec{s}_2}_{=S\cos\Theta_2} + \hat{y}' \cdot \underbrace{(\vec{s}_2 \times \hat{z})}_{=\hat{y}' S \sin\Theta_2} \sin\theta_1\cos\phi_1 \ . \tag{4.9}$$

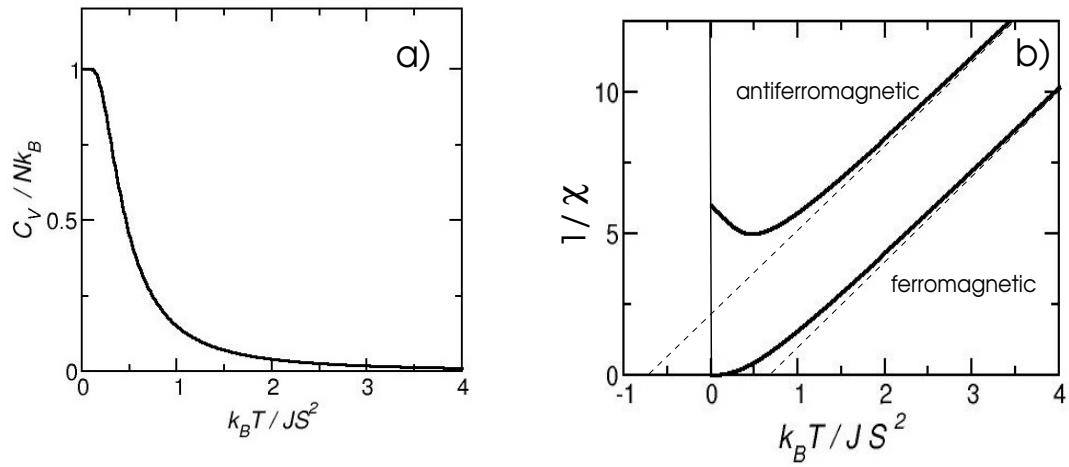

Figure 4.2: Thermodynamic properties of spin chain: a) heat capacity: saturates at low temperature to Nk_B like the potential energy of a two-dimensional harmonic oscillator; b) Susceptibility plotted inversely: ferromagnetic case show divergence at $T = 0$ and antiferromagnetic case approaches non-monotonically a finite value at $T = 0$. Extrapolations from high-temperature region cut horizontal axis at positive (ferromagnetic) and negative (antiferromagnetic) axis, indicating effective energy scales for the corresponding correlations.

4.1.3 Susceptibility

Finally we want to study the susceptibility by assuming a coupling to the magnetic field of the form

$$\mathcal{H}' = \mathcal{H} - g \sum_{i=1}^{N+1} \vec{s}_i \cdot \vec{H} \ . \tag{4.16}$$

Since it is impossible to use the above scheme to calculate the partition function for $\mathcal{H}'$ with a finite magnetic field, we will use the relation derived earlier (1.126) based on the fluctuations of the magnetization, which does not require the knowledge of the partition function at finite fields. In this way we obtain the susceptibility in the zero-field limit (linear response). The magnetic moment is give by $\vec{m} = g \sum_{i=1}^{N+1} \vec{s}_i$. Thus, the susceptibility per spin is given by

$$\chi_{zz} = \frac{1}{Nk_BT} \left\{ \langle m_z^2 \rangle - \langle m_z \rangle^2 \right\} = \frac{g^2}{Nk_BT} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \left\{ \langle s_i^z s_j^z \rangle - \langle s_i^z \rangle \langle s_j^z \rangle \right\} \ . \tag{4.17}$$

The second term on the right hand side vanishes, since $\langle s_i^z \rangle = 0$ for all i in zero magnetic field. For the first term we can use our result for the correlation function. In the limit of very large N we obtain

$$\begin{aligned} \chi_{zz} &= \frac{g^2}{3Nk_BT} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \Gamma_{|i-j|} \approx \frac{g^2}{3Nk_BT} \sum_{i=1}^{N} \left(\Gamma_{l=0} + 2S^2 \sum_{l=1}^{\infty} u^l \right) \\ &= \frac{g^2}{3k_BT} S^2 \left(1 + \frac{2u}{1-u} \right) = \frac{g^2 S^2}{3k_BT} \frac{1 + u(\beta J S^2)}{1 - u(\beta J S^2)} \ . \end{aligned} \tag{4.18}$$

Here we use that for large systems ($N \to \infty$) the corrections due to boundary contributions is negligible. This susceptibility at high temperature ($k_BT \gg |J|S^2$) follows the Curie behavior

$$\chi_{zz} = \frac{g^2 S^2}{3k_BT} \tag{4.19}$$

irrespective of the sign of J. For the antiferromagnetic coupling χ_{zz} goes through a maximum at $k_B T_{max} \approx 0.238 J S^2$ to a finite zero-temperature value. On the other hand, in the ferromagnetic case χ_{zz} diverges at low temperatures

$$\chi_{zz} = \frac{g^2 S^2}{3} \frac{2|J|S^2}{(k_B T)^2} \,, \tag{4.20}$$

more strongly than the Curie $1/T$ behavior.
Let us now also look at the first lowest order correction in the high-temperature limit,

$$\frac{1}{\chi_{zz}} \approx \frac{3k_B T}{g^2 S^2}\left(1 + \frac{2JS^2}{3k_B T}\right) = \frac{3k_B}{g^2 S^2}(T - \Theta_W) \quad \Rightarrow \quad \chi_{zz} = \frac{C}{T - \Theta_W} \tag{4.21}$$

where $\Theta_W = -2JS^2/3k_B$ defines the so-called Weiss temperature. Thus the extrapolation from the high-temperature limit of $1/\chi_{zz}$ allows to determine Θ_W from the intersection on the temperature axis and consequently the sign and magnitude of the J (see dashed lines in Fig. 4.2).
The Weiss temperature indicates the relevant energy scale of interaction among the spins. However, it does not imply that we would find a phase transition to a long-range ordered state (see Sect.4.3). As our discussion in this section shows, there is no ordering at any finite temperature.

4.2 Interacting lattice gas

We consider a simple model of a gas of hard-core particles which occupy sites on a lattice.[3] "Hard-core" means that it is not allowed to place two or more particles on the same site, i.e. there is an infinite repulsive onsite interaction or the Pauli principle is in action. We introduce nearest-neighbor interaction and neglect the kinetic energy. Then the Hamiltonian can be formulated as

$$\mathcal{H} = V \sum_{i=1}^{L} n_i n_{i+1} - \mu \sum_{i=1}^{L+1} \left(n_i - \frac{1}{2}\right) \tag{4.22}$$

where the lattice has $L+1$ sites and the coupling strength V for the interaction can be attractive ($V < 0$) or repulsive ($V > 0$). The chemical potential is introduced because we do not want to fix the particle number, but work within a grand-canonical ensemble which makes the problem more easy to solve. The variables n_i can only take the values 0 and 1 due to the hard-core constraint. We assume periodic boundary conditions such that $i = L + 1 \to i = 1$. The particles may represent spinless (or spin polarized) fermions or hard-core bosons. The statistics of the particles cannot be determined, since on a chain they cannot pass each other. In the given form the Hamiltonian describes also classical particles.

4.2.1 Transfer matrix method

Let us immediately determine the partition function,

$$\mathcal{Z} = \sum_{\{n_i\}} e^{-\beta \mathcal{H}} \,. \tag{4.23}$$

We introduce the 2×2-matrix (transfer matrix) for the bonds $(i, i+1)$,

$$P_{n_i, n_{i+1}} = e^{-\beta[V n_i n_{i+1} - \mu(n_i + n_{i+1} - 1)/2]}$$

$$\Rightarrow \quad \hat{P} = \begin{pmatrix} P_{00} & P_{01} \\ P_{10} & P_{11} \end{pmatrix} = \begin{pmatrix} e^{-\beta\mu/2} & 1 \\ 1 & e^{-\beta V + \beta\mu/2} \end{pmatrix} \,. \tag{4.24}$$

[3] In the exercise we will show the connection of the lattice gas model to the Ising spin model. The corresponding discussion will make the similarity of the two systems clear.

When we have one bond with periodic boundary condition it is obvious that the partition function is given by four terms

$$\begin{aligned}\mathcal{Z}_2 &= \sum_{n_1,n_2} e^{-\beta\mathcal{H}(n_1,n_2)} = \sum_{n_1,n_2} P_{n_1,n_2}P_{n_2,n_1} = tr\{\hat{P}^2\} \\ &= P_{00}P_{00} + P_{01}P_{10} + P_{10}P_{01} + P_{11}P_{11} = e^{-\beta\mu} + 1 + 1 + e^{-2\beta V+\beta\mu}\end{aligned} \tag{4.25}$$

This allows us to rewrite the sum in the partition function as

$$\mathcal{Z} = \sum_{n_1=0,1}\sum_{n_2=0,1}\cdots\sum_{n_L=0,1} P_{n_1,n_2}P_{n_2,n_3}\cdots P_{N_{L-1},n_L}P_{n_L,n_1} = tr\{\hat{P}^L\} = \sum_{n_1=0,1} P^L_{n_1,n_1}\ , \tag{4.26}$$

where we performed the matrix multiplication. Interestingly, we have now to analyse P^L which can easily be done in the eigenbasis of the matrix $\hat{P}$. For the trace we actually only need the eigenvalues,

$$\lambda_\pm = e^{-\beta V/2}\cosh\left(\beta\frac{V-\mu}{2}\right) \pm \sqrt{e^{-\beta V}\sinh^2\left(\beta\frac{V-\mu}{2}\right)+1} \tag{4.27}$$

and

$$\mathcal{Z} = \lambda_+^L + \lambda_-^L \approx \lambda_+^L \qquad \text{for} \quad L \gg 1\ . \tag{4.28}$$

Then the grand canonical potential and internal energy are given by

$$\Omega(T,\mu) = -k_BT\ln\lambda_+^L = -Lk_BT\ln\left[e^{-\beta V/2}\cosh\left(\beta\frac{V-\mu}{2}\right) + \sqrt{e^{-\beta V}\sinh^2\left(\beta\frac{V-\mu}{2}\right)+1}\right]\ . \tag{4.29}$$

The particle number and the isothermal compressibility of the system can then be calculated easily,

$$N = L\langle n_i\rangle = \frac{L}{2} - \left(\frac{\partial\Omega}{\partial\mu}\right)_T \qquad \text{and} \qquad \kappa_T = \frac{L}{N^2}\left(\frac{\partial N}{\partial\mu}\right)_T\ . \tag{4.30}$$

We start with the high-temperature limit ($k_BT \gg |\mu|, |V|$) where we obtain the following expansion,

$$N \approx \frac{L}{2}\left\{1 - \frac{\beta}{2}(V-\mu) + \frac{\beta^2 V}{4}(V-\mu) + \cdots\right\}\ . \tag{4.31}$$

In this limit it is equally probable to find or not to find a particle on a site ($N \to L/2$). The particle number increases (decreases) upon lowering temperature, if V is attractive, $V < 0$, (repulsive, $V > 0$), or the chemical potential is positive (negative). The compressibility for $\mu = 0$ is then given by

$$\kappa_T \approx \frac{1}{2k_BT}\left(1 - \frac{\beta V}{2} + \cdots\right) \tag{4.32}$$

which is enhanced (reduced) for attractive (repulsive) interaction V, as we would expect simply by noticing that it is easier to add particles, if they attract each other than when they repel each other.

At low temperatures we obtain for the particle number with $\mu = 0$,

$$N = \frac{L}{2}\left[1 + \frac{e^{-\beta V/2}\sinh(\beta V/2)}{\sqrt{1+e^{-\beta V}\sinh^2(\beta V/2)}}\right] \to \begin{cases} \frac{L}{2}\left(1+\frac{1}{\sqrt{5}}\right) & V > 0\ , \\ L & V < 0\ , \end{cases} \tag{4.33}$$

where the case $V > 0$ yields a partial filling optimizing the free energy for a given chemical potential. On the other hand, $V < 0$ tends towards complete filling. The compressibility

remains in both cases finite,

$$\kappa_T = \begin{cases} \dfrac{1}{k_B T} \dfrac{5^{5/2}}{(1+\sqrt{5})^2} & V > 0 \, , \\ \\ \dfrac{1}{4 k_B T} & V < 0 \, . \end{cases} \tag{4.34}$$

Case $\mu = V$

Analogously to the case of the classical spin chain also the one-dimensional lattice gas does not show a phase transition at finite temperature. However, obvious trends towards order are visible. It is interesting to consider this system for a special value of the chemical potential, namely $\mu = V$ where we have no bias concerning the particle number. This choice looks "fine-tuned", as the particle number at all temperatures and V is fixed to $N = L/2$. It is also particularly easy to follow the calculations through, which gives the compressibility,

$$\kappa_T = \frac{1}{2 k_B T} e^{-\beta V/2} \tag{4.35}$$

which indicates that for low temperatures the compressibility goes to zero for $V > 0$ showing that repulsive interaction yields an incompressible (crystalline) state of particles (one particle every second site). On the other hand, attractive interaction yields a diverging compressibility, indicating that the gas tends to get strongly compressible, i.e. it goes towards a "liquid" phase with much reduced effective volume per particle.
We may consider this also from the point of view of the fluctuation-dissipation theorem which connects the response function κ_T with the fluctuations of the particle number,

$$\langle N^2 \rangle - \langle N \rangle^2 = \frac{k_B T \langle N \rangle^2}{L} \kappa_T(T) \propto L e^{-\beta V/2} \, . \tag{4.36}$$

The message of this relation is that for the repulsive case the particle number fluctuations go rapidly to zero for $k_T < |V|$, as expected, if the system "solidifies" with the particle density $n = N/L = 1/2$. On the other hand, for attractive interaction the fluctuations strongly increase in the same low-temperature regime for the given density ($n = 1/2$) at finite temperature, indicating that particles can be further "condensed".

4.2.2 Correlation function

The transfer matrix method is also very convenient to obtain the correlation function,

$$\Gamma_l = \langle n_i n_{i+l} \rangle - \langle n_i \rangle \langle n_{i+l} \rangle \, . \tag{4.37}$$

We consider first

$$\begin{aligned} \langle n_i \rangle &= \frac{1}{\mathcal{Z}} \sum_{n_1, \ldots, n_L} P_{n_1,n_2} P_{n_2,n_3} \cdots P_{n_{i-1},n_i} n_i P_{n_i,n_{i+1}} \cdot P_{n_L,n_1} \\ &= \frac{1}{\mathcal{Z}} tr \left\{ \hat{P}^{i-1} \hat{w} \hat{P}^{L-i} \right\} = \frac{1}{\mathcal{Z}} tr \left\{ \hat{w} \hat{P}^L \right\} \end{aligned} \tag{4.38}$$

with $\hat{w}$ defined as $w_{n,n'} = n \delta_{n,n'}$. Let us transform this to the basis in which $\hat{P}$ is diagonal through the unitary transformation

$$\hat{U} \hat{P} \hat{U}^{-1} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} = \hat{P}' \qquad \text{and} \qquad \hat{U} \hat{w} \hat{U}^{-1} = \begin{pmatrix} w'_{00} & w'_{01} \\ w'_{10} & w'_{11} \end{pmatrix} = \hat{w}' \, . \tag{4.39}$$

This leads to

$$\langle n_i \rangle = \frac{1}{\mathcal{Z}} tr \left\{ \hat{w}' \hat{P}' \right\} = \frac{w'_{00}\lambda_+^L + w'_{11}\lambda_-^L}{\lambda_+^L + \lambda_-^L} \longrightarrow w'_{00} \ . \tag{4.40}$$

In the same way we treat now

$$\begin{aligned} \langle n_i n_{i+l} \rangle &= \frac{1}{\mathcal{Z}} tr \left\{ \hat{P}^i \hat{w} \hat{P}^l \hat{w} \hat{P}^{L-i-l} \right\} = \frac{1}{\mathcal{Z}} tr \left\{ \hat{w} \hat{P}^l \hat{w} \hat{P}^{L-l} \right\} = \frac{1}{\mathcal{Z}} tr \left\{ \hat{w}' (\hat{P}')^l \hat{w}' (\hat{P}')^{L-l} \right\} \\ &= \frac{w'^2_{00}\lambda_+^L + w'_{01}w'_{10}(\lambda_+^l \lambda_-^{L-l} + \lambda_-^l \lambda_+^{L-l}) + w'^2_{11}\lambda_-^L}{\lambda_+^L + \lambda_-^L} \quad \longrightarrow \quad w'^2_{00} + w'_{01}w'_{10} \left(\frac{\lambda_-}{\lambda_+} \right)^l \ . \end{aligned} \tag{4.41}$$

The correlation function is given by

$$\Gamma_l = w'_{01}w'_{10} \left(\frac{\lambda_-}{\lambda_+} \right)^l = n^2 e^{-l/\xi} [\mathrm{sign}(\lambda_-/\lambda_+)]^l \tag{4.42}$$

where we identify $\Gamma_{l=0}$ with n^2 and the correlation length

$$\xi = \frac{1}{\ln |\lambda_+/\lambda_-|} \ . \tag{4.43}$$

For $V > 0$ the correlation function shows alternating sign due to the trend to charge density modulation. In the special case $\mu = V$ we obtain

$$\Gamma_l = \frac{1}{2} (\tanh(\beta V/4))^l \qquad \text{and} \qquad \xi = \frac{1}{\ln |\coth(\beta V/4)|} \ . \tag{4.44}$$

In the zero-temperature limit ξ diverges, but is finite for any $T > 0$.

It is important that both the thermodynamics as well as the correlation functions are determined through the eigenvalues of the transfer matrix $\hat{P}$.

4.3 Long-range order versus disorder

We find in the one-dimensional spin chain no phase transition to any *long-range ordered* state at finite temperatures. The term "long-range order" is easiest understood through the correlation function. We consider here again the example of a spin chain. The correlation function has the property,

$$\tilde{\Gamma}_l = \langle \vec{s}_i \cdot \vec{s}_{i+l} \rangle - \langle \vec{s}_i \rangle \cdot \langle \vec{s}_{i+l} \rangle \quad \stackrel{l \to \infty}{\longrightarrow} \quad 0 \tag{4.45}$$

which is true for a spin system with or without order. By rewriting

$$\lim_{l \to \infty} \langle \vec{s}_i \cdot \vec{s}_{i+l} \rangle = \langle \vec{s}_i \rangle \cdot \langle \vec{s}_{i+l} \rangle \ , \tag{4.46}$$

we see that the left hand side is finite only with a finite mean value of $\langle \vec{s}_i \rangle$. Note that for the classical spin chain only at $T = 0$ long-range order is realized. All spins are parallel for $J < 0$ (ferromagnet) or alternating for $J > 0$ (antiferromagnet) such that

$$\langle \vec{s}_i \rangle = \begin{cases} \hat{z} S & J < 0 \\ \hat{z} (-1)^i S & J > 0 \end{cases} \tag{4.47}$$

assuming that the spin align parallel to the z-axis ($\hat{z}$ is the unit vector along the z-axis). Naturally the limit in Eq.(4.46) is then finite. [4] Also the lattice gas in one dimension does not show long-range order except at $T = 0$.

[4] Previously we encountered long-range order in a Bose-Einstein condensate looking at the correlation function in Eqs.(3.103) and (3.110). Extending the correlation function to

$$\tilde{g}(\vec{R}) = \langle \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r} + \vec{R}) \rangle - \langle \widehat{\Psi}^\dagger(\vec{r}) \rangle \langle \widehat{\Psi}(\vec{r} + \vec{R}) \rangle \ , \tag{4.48}$$

Interestingly, in the case of quantum systems quantum phase transitions can destroy long-range order even at $T = 0$. An important example is the antiferromagnetic spin chain with a Heisenberg Hamiltonian. In contrast the ferromagnetic Heisenberg chain has an ordered ground state with all spins aligned, because the state with all spins parallel is an eigenstate of the total spin operator, $\hat{\vec{S}}_{\rm tot} = \sum_{i=1}^{N+1} \hat{\vec{s}}_i$ and $\hat{\vec{S}}_{\rm tot}$ commutes with the Hamiltonian, since it has full spin rotation symmetry as in the classical case ($N+1$: number of spins on the chain),

$$|\Psi_{\rm FM}\rangle = |\uparrow\uparrow\uparrow\cdots\rangle \qquad \Rightarrow \qquad \hat{S}^z_{\rm tot}|\Psi_{\rm FM}\rangle = (N+1)\hbar s|\Psi_{\rm FM}\rangle\ . \tag{4.50}$$

In case of the antiferromagnetic chain the (classical) state with alternating spins $|\Psi_{\ cAF}\rangle = |\uparrow\downarrow\uparrow\downarrow\cdots\rangle$, is not an eigenstate of the quantum Heisenberg Hamiltonian and consequently not the ground state of the quantum antiferromagnetic chain.

Our discussion of the melting transition in Sect. 3.7.3 is suitable to shed some light on the problem of quantum fluctuation. Also a crystal lattice of atoms is a long-range ordered state. Considering the melting transition based on the Lindemann criterion for the displacement fields, we tackle the stability of the lattice from the ordered side. Thus, we use again the language of the elastic medium as in Sect.3.7.3 and rewrite the fluctuation of the displacement field in Eq.(3.150),

$$\langle\, \vec{u}\,(\,\vec{r}\,)^2\rangle = \frac{\hbar}{\rho_m}\int \frac{d^Dk}{(2\pi)^D}\frac{1}{\omega_{\vec{k}}}\coth\left(\frac{\beta\hbar c_l k}{2}\right) \tag{4.51}$$

with D, the dimension. For $D = 1$ we find

$$\langle u^2\rangle = \frac{\hbar}{2\pi\rho_n c_l}\int_0^{k_D} dk\,\frac{1}{k}\coth\left(\frac{\beta\hbar c_l k}{2}\right) \quad \stackrel{T\to 0}{\longrightarrow} \quad \frac{\hbar}{2\pi\rho_n c_l}\int_0^{k_D} dk\,\frac{1}{k}\ . \tag{4.52}$$

This integral diverges even at $T = 0$ and, thus, exceeds the Lindemann criterion in Eq.(3.151), $L_m \gg \langle u^2\rangle/a^2$. At $T = 0$ only quantum fluctuations can destroy long range order. We call this also quantum melting of the lattice. For $D \geq 2$ we find a converging integral at $T = 0$. Nevertheless, also here quantum melting is possible, if the lattice is "soft" enough, i.e. the elastic modulus is small enough. Note that He is such a case, as we will discuss later. At zero temperature He is solid only under pressure which leads to an increase of the elastic modulus λ, i.e. under pressure the lattice becomes stiffer.

At finite temperature also in two-dimensions an ordered atomic lattice is not stable,

$$\langle\, \vec{u}\,(\,\vec{r}\,)^2\rangle = \frac{\hbar}{2\pi\rho_m c_l}\int_0^{k_D} dk\coth\left(\frac{\beta\hbar c_l k}{2}\right) \tag{4.53}$$

which diverges at the lower integral boundary due to the fact that for $k \to 0$ we expand $\coth(\beta\hbar c_l k/2) \approx 2k_BT/\hbar c_l k$ yielding a logarithmic divergence. That two-dimensional are rather subtle can be seen for the case of graphene, a single layer of graphite (honeycomb lattice of carbon) which is stable.

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we find that always $\lim_{\vec{R}\to\infty}\tilde{g}(\vec{R}) = 0$, since with the Bogolyubov approximation,

$$\lim_{\vec{R}\to\infty}\langle\,\widehat{\Psi}^\dagger(\,\vec{r}\,)\,\widehat{\Psi}\,(\,\vec{r}\,+\,\vec{R}\,)\rangle = \lim_{\vec{R}\to\infty}\langle\,\widehat{\Psi}^\dagger(\,\vec{r}\,)\rangle\langle\,\widehat{\Psi}\,(\,\vec{r}\,+\,\vec{R}\,)\rangle = \lim_{\vec{R}\to\infty}\psi_0^*(\,\vec{r}\,)\psi_0(\,\vec{r}\,+\,\vec{R}\,) = n_0 \tag{4.49}$$

for $T < T_c$ and a constant phase ϕ of $\psi_0(\,\vec{r}\,)$.

Chapter 5

Phase transitions

Phase transitions in macroscopic systems are ubiquitous in nature and represent a highly important topic in statistical physics and thermodynamics. Phase transitions define a change of state of a system upon changing external parameters. In many cases this kind of change is obvious, e.g. transition between liquid and gas or between paramagnetic and ferromagnetic phase, and in most cases it is accompanied by anomalies in measurable macroscopic quantities.
In the previous chapter we have seen a phase transition, the Bose-Einstein condensation. This transition is special in the sense that it occurs for non-interacting particles. Generally, phase transitions require an interaction favoring an ordered phase. Then the phase transition occurs as a competition between the internal energy (or enthalpy) which is lowered by the order and the entropy which at finite temperature favors disorder. The relevant thermodynamic potentials to describe phase transitions are the Helmholtz free energy $F(T, V, N)$ and the Gibbs free energy $G(T, p, N)$,

$$F = U - TS \qquad \text{and} \qquad G = H - TS \; . \tag{5.1}$$

These potentials show anomalies (singularities) at the phase transition.

5.1 Ehrenfest classification of phase transitions

The type of singularity in the thermodynamic potential defines the order of the phase transition. According to Ehrenfest classification we call a phase transition occurring at a critical temperature T_c (different phase for $T > T_c$ and $T < T_c$) to be of nth order, if the following properties hold:

$$\left(\frac{\partial^m G}{\partial T^m}\right)_p\bigg|_{T=T_{c+}} = \left(\frac{\partial^m G}{\partial T^m}\right)_p\bigg|_{T=T_{c-}} \quad \text{and} \quad \left(\frac{\partial^m G}{\partial p^m}\right)_{T=T_{c+}} = \left(\frac{\partial^m G}{\partial p^m}\right)_{T=T_{c-}} \tag{5.2}$$

for $m \leq n-1$, and

$$\left(\frac{\partial^n G}{\partial T^n}\right)_p\bigg|_{T=T_{c+}} \neq \left(\frac{\partial^n G}{\partial T^n}\right)_p\bigg|_{T=T_{c-}} \quad \text{and} \quad \left(\frac{\partial^n G}{\partial p^n}\right)_{T=T_{c+}} \neq \left(\frac{\partial^n G}{\partial p^n}\right)_{T=T_{c-}} \tag{5.3}$$

The same definition is used for the free energy. In practice this classification is rarely used beyond $n = 2$.

<u>$n = 1$:</u> A discontinuity is found in the entropy and in the volume:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \qquad \text{and} \qquad V = \left(\frac{\partial G}{\partial p}\right)_T \tag{5.4}$$

The discontinuity of the entropy is experimentally the *latent heat*. The change in volume is connected with the difference in the density of the substance. A well-known example is the

transition between the liquid and the gas phase, for which the former is much denser than the latter and accordingly takes a much smaller volume.

$\underline{n=2}$: The discontinuities are not in the first derivatives but in the second derivatives of the Helmholtz free energy or Gibbs free energy, i.e. in the response functions. Some such quantities are the heat capacity, the compressibility or the thermal expansion coefficient:

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p , \kappa_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_T , \alpha = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T \partial p}\right) \tag{5.5}$$

As we will see later, second order phase transitions are usually connected with spontaneous symmetry breaking and can be associated with the continuous growth of an order parameter. Such transitions show also interesting fluctuation features which lead to the so-called critical phenomena and universal behavior at the phase transition.

Ehrenfest relations: Interesting relations between various discontinuities at the phase transition exist. They are generally known at Ehrenfest relations. We consider first a *first-order* transition such as the gas-liquid transition. The phase boundary line in the p-T-phase diagram describes the relation between temperature and vapor pressure in the case of liquid-gas transition. For the differentials of the Gibbs free energy in the two phases, the following equality holds:

$$dG_l = dG_g \qquad \Rightarrow \qquad -S_l dT + V_l dp = -S_g dT + V_g dp \ . \tag{5.6}$$

This allows us to get from the vapor pressure curve ($p(T)$ at the phase boundary in the p-T-plane) the relation

$$\frac{dp}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T\Delta V} \tag{5.7}$$

where $L = T(S_g - S_l)$ is the *latent heat* and $\Delta V = V_g - V_l$ is the change of the volume. This relation is known as the *Clausius-Clapeyron* equation.
If the transition is of *second order* then the both the entropy and the volume are continuous through the transition between two phase A and B:

$$S_A(T,p) = S_B(T,p) \quad \text{and} \quad V_A(T,p) = V_B(T,p) \ , \tag{5.8}$$

which yields the relations through the equality of their differentials,

$$\begin{aligned} dS_A &= \left(\frac{\partial S_A}{\partial T}\right)_p dT + \left(\frac{\partial S_A}{\partial p}\right)_T dp = \left(\frac{\partial S_B}{\partial T}\right)_p dT + \left(\frac{\partial S_B}{\partial p}\right)_T dp = dS_B \ , \\ dV_A &= \left(\frac{\partial V_A}{\partial T}\right)_p dT + \left(\frac{\partial V_A}{\partial p}\right)_T dp = \left(\frac{\partial V_B}{\partial T}\right)_p dT + \left(\frac{\partial V_B}{\partial p}\right)_T dp = dV_B \ . \end{aligned} \tag{5.9}$$

We now use the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha \tag{5.10}$$

and obtain

$$\frac{dp}{dT} = -\frac{\left(\frac{\partial S_B}{\partial T}\right)_p - \left(\frac{\partial S_A}{\partial T}\right)_p}{\left(\frac{\partial S_B}{\partial p}\right)_T - \left(\frac{\partial S_A}{\partial p}\right)_T} = \frac{\Delta C_p}{TV\Delta\alpha} \tag{5.11}$$

and analogously

$$\frac{dp}{dT} = -\frac{\left(\frac{\partial V_B}{\partial T}\right)_p - \left(\frac{\partial V_A}{\partial T}\right)_p}{\left(\frac{\partial V_B}{\partial p}\right)_T - \left(\frac{\partial V_A}{\partial p}\right)_T} = \frac{\Delta\alpha}{\Delta\kappa_T} \ . \tag{5.12}$$

Various other relations exist and are of experimental importance.

5.2 Phase transition in the Ising model

The Ising model is the simplest model of a magnetic system. We consider magnetic moments or spins with two possible states, $s_i = \pm s$ (Ising spins). Sitting on a lattice they interact with their nearest neighbors (analogously to the spin chain in the Chapter 3). We write the model Hamiltonian as

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j - \sum_i s_i H \ . \tag{5.13}$$

The sum $\sum_{\langle i,j \rangle}$ denotes summation over nearest neighbors on the lattice, counting each bond only once. J is the coupling constant which we assume to be positive. The second term corresponds to a Zeeman term due to an external magnetic field. The Ising spins are classical variables, unlike quantum spins $\vec{s}$ whose different components do not commute with each other. Ising spins represent only one component of a quantum spin.
The interaction favors the parallel alignment of all spins such that this model describes a ferromagnetic system. The ferromagnetic phase is characterized by a finite uniform mean value $\langle s_i \rangle = m \neq 0$, the magnetization, even in the absence of an external magnetic field.

5.2.1 Mean field approximation

The analysis of many coupled degrees of freedom is in general not simple. For the Ising model we have exact solutions for the one- and two-dimensional case. For three dimensions only numerical simulations or approximative calculations are possible. One rather frequently used method is the so-called mean field approximation. In the lattice model we can consider each spin s_i as being coupled to the reservoir of its neighboring spins. These neighboring spins act then like a fluctuating field on the spin. In case of order they form a net directed field on s_i, a mean field. Since this conditions applies to all spins equally, the scheme can be closed by having a self-consistency in the mean field.
Let us now tackle the problem in a more systematic way. We rewrite the spin for each site

$$s_i = \langle s_i \rangle + (s_i - \langle s_i \rangle) = m + (s_i - m) = m + \delta s_i \tag{5.14}$$

and insert it into the Hamiltonian, where we approximate $\langle s_i \rangle = m$ uniformly.

$$\begin{aligned} \mathcal{H} &= -J \sum_{\langle i,j \rangle} \{m + (s_i - m)\} \{m + (s_j - m)\} - \sum_i s_i H \\ &= -J \sum_{\langle i,j \rangle} \left\{ m^2 + m(s_i - m) + m(s_j - m) + \delta s_i \delta s_j \right\} - \sum_i s_i H \\ &= -J \sum_i \left(z m s_i - \frac{z}{2} m^2 \right) - \sum_i s_i H - J \sum_{\langle i,j \rangle} \delta s_i \delta s_j \ . \end{aligned} \tag{5.15}$$

Here z is the number of nearest neighbors (for a hypercubic lattice in d dimensions $z = 2d$). In the mean field approximation we neglect the last term assuming that it is small. This means that the fluctuations around the mean value would be small,

$$E_{ij} = \frac{\langle \delta s_i \delta s_j \rangle}{\langle s_i \rangle \langle s_j \rangle} = \frac{\langle \delta s_i \delta s_j \rangle}{m^2} \ll 1 \ , \tag{5.16}$$

to guarantee the validity of this approximation. We will see later that this condition is not satisfied very near the phase transition and that its violation is the basis for so-called critical phenomena. We now write the mean field Hamiltonian

$$\mathcal{H}_{mf} = -\sum_i s_i h_{\text{eff}} + N J \frac{z}{2} m^2 \qquad \text{with} \qquad h_{\text{eff}} = J z m + H \ , \tag{5.17}$$

which has the form of an ideal paramagnet in a magnetic field $h_{\rm eff}$. It is easy to calculate the partition function and the free energy as a function of the parameter m,

$$Z_N(T,m,H) = e^{-\beta J z m^2 N/2} \left\{2\cosh(\beta s h_{\rm eff})\right\}^N \tag{5.18}$$

and

$$F(T,H,m) = -k_BT \ln Z_N = NJ\frac{z}{2}m^2 - Nk_BT \ln\left\{2\cosh(\beta s h_{\rm eff})\right\} \ . \tag{5.19}$$

The equilibrium condition is reached when we find the minimum of F for given T and H. To this end we minimize F with respect to m as the only free variable,

$$0 = \frac{\partial F}{\partial m} = NJzm - NJzs\tanh(\beta s h_{\rm eff}) \ . \tag{5.20}$$

This equation is equivalent to the self-consistence equation for the mean value of s_i:

$$m = \langle s_i\rangle = \frac{e^{-\beta J z m^2 N/2}}{Z_N}\sum_{\{s_j\}} s_i e^{\sum_{i'=1}^N s_{i'} h_{eff}} = \frac{\sum_{s_i=\pm s} s_i e^{\beta s_i h_{\rm eff}}}{\sum_{s_i=\pm s} e^{\beta s_i h_{\rm eff}}} = s\tanh(\beta s h_{\rm eff}) = -\frac{1}{N}\left(\frac{\partial F}{\partial H}\right)_{T,m} \tag{5.21}$$

This is a non-linear equation whose solution determines m and eventually through the free energy all thermodynamic properties. [1]

5.2.2 Instability of the paramagnetic phase

The disordered phase above a certain critical temperature T_c is called paramagnetic phase. For this phase we consider first the magnetic susceptibility $\chi(T)$ at zero magnetic field, which is obtained from

$$\chi(T) = N\frac{d\langle s_i\rangle}{dH}\bigg|_{H=0} = -\frac{d^2F}{dH^2}\bigg|_{H=0} = -\frac{d}{dH}\left\{\frac{\partial F}{\partial H} + \frac{\partial F}{\partial m}\frac{\partial m}{\partial H}\right\}\bigg|_{H=0} = -\frac{d}{dH}\frac{\partial F}{\partial H}\bigg|_{H=0} \tag{5.26}$$

[1] *Variational approach:* Consider the Ising model (5.13) without magnetic field. We now determine the free energy on a variational level assuming a distribution of N independent spin with a net magnetization $M = N_+ - N_-$ ($N = N_+ + N_-$). The probability that a certain spin is "+s" or "-s" is given by $w_\pm = \frac{1}{2}(1 \pm \tilde m)$ with $\tilde m = M/N$. There are

$$\omega(M) = \frac{N!}{\left[\frac{1}{2}(N+M)\right]!\left[\frac{1}{2}(N-M)\right]!} \ . \tag{5.22}$$

configurations corresponding to a given M. We may now determine the free energy as $F = U - TS = \langle H\rangle_M - k_BT\ln\omega(M)$ in the following way:

$$U = \langle H\rangle_M = -J\sum_{\langle i,j\rangle}\langle s_i s_j\rangle = -\frac{JNzs^2}{2}(w_+w_+ + w_-w_- - w_+w_- - w_-w_+) = -\frac{JNzs^2}{2}\tilde m^2 \tag{5.23}$$

where we use for $\langle s_i s_j\rangle$ simply the configurational average for pairs of completely independent spins for given M, i.e. $w_+w_+ + w_-w_-$ ($w_+w_- + w_+w_-$) is the probability that neighboring spins are parallel (antiparallel). In this approach there is no correlation between the neighboring spins. For the entropy term we use Stirling approximation and keep only extensive terms,

$$TS = k_BT\ln\omega(M) \approx Nk_BT\left[\ln 2 - \frac{1}{2}(1+\tilde m)\ln(1+\tilde m) - \frac{1}{2}(1-\tilde m)\ln(1-\tilde m)\right] \ . \tag{5.24}$$

Thus, we have expressed the free energy by a variational phase represented by independent spins whose variational parameter is the mean moment $m = \langle s\rangle = s(w_+ - w_-) = s\tilde m$. We minimize F with respect to $\tilde m$,

$$0 = \frac{\partial F}{\partial \tilde m} = -Jzs^2N\tilde m + \frac{Nk_BT}{2}\ln\left(\frac{1+\tilde m}{1-\tilde m}\right) \quad\Rightarrow\quad \tilde m = \tanh\left(\frac{Jzs^2\tilde m}{k_BT}\right) \tag{5.25}$$

which corresponds to Eq.(5.21) in the absence of a magnetic field. Thus, this variational approach and mean field are equivalent and give the same thermodynamic properties. As we will see, the mean field approach is more easily improved. In many cases similar variational calculations of the free energy based on independent degrees of freedom yield thermodynamics equivalent to a mean field approach.

where we used the equilibrium condition (5.20). Thus we obtain

$$\begin{aligned}\chi(T) &= N\left.\frac{dm}{dH}\right|_{H=0} = Ns\frac{d}{dH}\tanh\left[\beta(Jzsm(H)+sH)\right]\Big|_{H=0} \\ &= \frac{Ns}{k_BT}\left\{Jzs\left.\frac{dm}{dH}\right|_{H=0}+s\right\} = \frac{s}{k_BT}Jzs\chi(T)+\frac{Ns^2}{k_BT}\,.\end{aligned} \tag{5.27}$$

where we used that for a paramagnet $m(H=0)=0$. This leads to the susceptibility

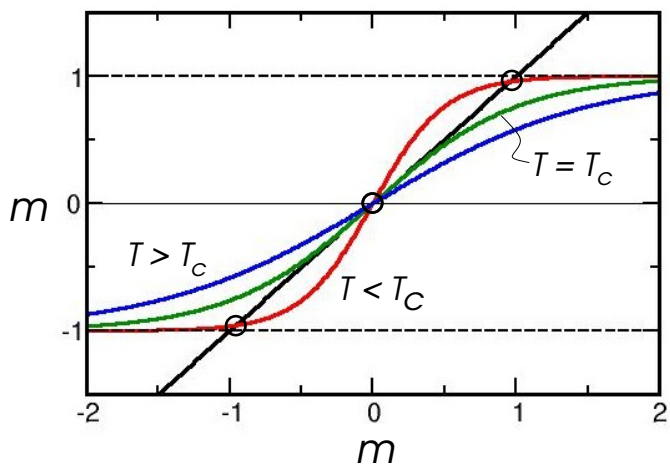

Figure 5.1: Graphical solution of the self-consistence equation (5.21). The crossing points of the straight line and the step-like function gives the solution. There is only one solution at $m=0$ for $T \geq T_c$ and three solutions for $T < T_c$.

$$\chi(T) = \frac{Ns^2}{k_BT - Jzs^2} \tag{5.28}$$

which is modified compared to that of the ideal paramagnet. If $k_BT \to Jzs^2$ from above $\chi(T)$ is singular. We define this as the critical temperature

$$T_c = \frac{Jzs^2}{k_B}\,. \tag{5.29}$$

As the system approaches $T=T_c$ it becomes more and more easy to polarize its spin by a tiny magnetic field. This indicates an instability of the system which we now analyze in terms of the self-consistence equation (5.21) in the absence of a magnetic field. Looking at Fig. 5.1 we find that indeed the critical temperature T_c plays an important role in separating two types of solutions of equations (5.21). For $T \geq T_c$ there is one single solution at $m=0$ and for $T<T_c$ there are three solutions including $m=0, m(T), -m(T)$. The physically relevant solution is then the one with finite value of m, as we will show below. It is obvious that below $T=T_c$ the mean field m grows continuously from zero to a finite value. In order to see which of the solutions is a minimum of the free energy we expand F in m assuming that m and H are small.

$$F(T,H,m) \approx NJz\left[\frac{m^2}{2} - \frac{k_BT}{Jz}\left\{\frac{(\beta sh_{\text{eff}})^2}{2} - \frac{(\beta sh_{\text{eff}})^4}{12}\right\}\right] - Nk_BT\ln 2 \tag{5.30}$$

For $H = 0$ we find

$$\begin{aligned} F(T, H = 0, m) &\approx F_0(T) + NJz \left[\left(1 - \frac{T_c}{T}\right) \frac{m^2}{2} + \frac{1}{12s^2} \left(\frac{T_c}{T}\right)^3 m^4 \right] \\ &\approx F_0(T) + NJz \left[\left(\frac{T}{T_c} - 1\right) \frac{m^2}{2} + \frac{m^4}{12s^2} \right] \end{aligned} \tag{5.31}$$

where for the last step we took into account that our expansion is only valid for $T \approx T_c$. Moreover, $F_0 = -Nk_BT \ln 2$. This form of the free energy expansion is the famous Landau theory of a continuous phase transition.

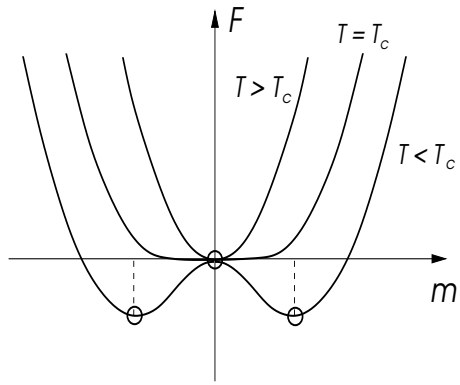

Figure 5.2: Landau free energy: $T > T_c$: 2nd-order term is positive and minimum of F at $m = 0$; $T = T_c$, 2nd vanishes and free energy minimum at $m = 0$ becomes very shallow; $T < T_c$: 2nd-order term is negative and minimum of F is at finite value of m, bounded by the 4th-order term.

It is obvious that for $T > T_c$ the minimum lies at $m = 0$. For $T < T_c$ the coefficient of the m^2-term (2nd-order) changes sign and a finite value of m minimizes F (see Fig. 5.2). The minimization leads to

$$m(T) = \begin{cases} \pm s\sqrt{3\tau} & T < T_c \\ 0 & T \geq T_c \end{cases} \tag{5.32}$$

with $\tau = 1 - T/T_c$ as a short-hand notation. There are two degenerate minima and the system chooses spontaneously one of the two (spontaneous symmetry breaking).
Next we analyze the behavior of the free energy and other thermodynamic quantities around the phase transition. The temperature dependence of the free energy and the entropy is given by

$$F(T) = F_0(T) - \frac{3Nk_BT_c\tau^2}{4}\Theta(\tau) \qquad \text{and} \qquad S(T) = -\frac{\partial F(T)}{\partial T} = Nk_B \ln 2 - \frac{3Nk_B\tau}{2}\Theta(\tau)\ , \tag{5.33}$$

and eventually we obtain for the heat capacity,

$$\frac{C}{T} = \frac{\partial S}{\partial T} = \frac{3Nk_B}{2T_c}\Theta(\tau) + C_0 \tag{5.34}$$

where C_0 is zero in the present approximation for $H = 0$. While the free energy and the entropy are continuous through the transition, the heat capacity shows a jump indicating the release of entropy through ordering. Thus, we conclude that this phase transition is of second order.
Within mean field approximation the region close to T_c is described by the Landau expansion. However, taking the solution of the complete mean field equations leads to the thermodynamic

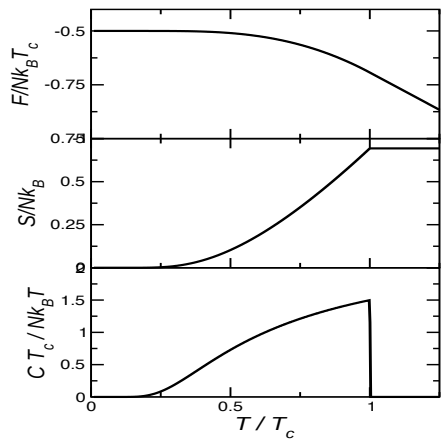

Figure 5.3: Thermodynamic quantities within mean field theory. Free energy, entropy and heat capacity.

behavior for the whole temperature range as shown in Fig. 5.3. Note that in this mean field approximation the entropy is $Nk_B \ln 2$ in the paramagnetic phase, the maximal value the entropy can reach.

5.2.3 Phase diagram

So far we have concentrated on the situation without magnetic field. In this case the phase transition goes to one of two degenerate ordered phases. Either the moments order to $m = +|m|$ or $m = -|m|$. An applied magnetic field lifts the degeneracy by introducing a bias for one of the two states. The order with m parallel to the field is preferred energetically. In a finite field the transition turns into a crossover, since there is already a moment m for temperatures above T_c. This is also reflected in the thermodynamic properties which show broad features around T_c and not anymore the sharp transition, e.g. the heat capacity is turned into a broadened anomaly (see Fig. 5.4).

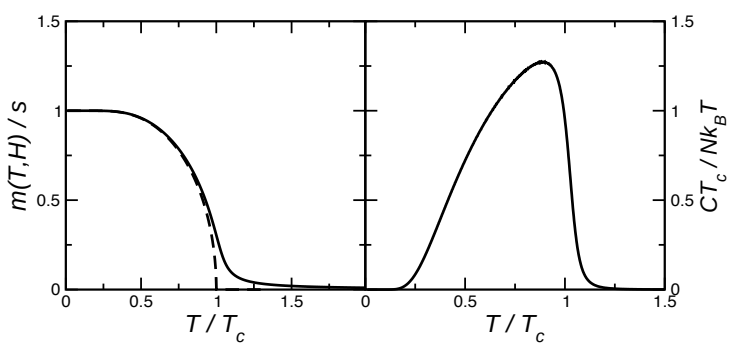

Figure 5.4: Ising system in a finite magnetic field: (left panel) Magnetization as a function of temperature in a fixed magnetic field (solid line) and in zero field (dashed line); (right panel) heat capacity for a fixed magnetic field. In a magnetic field no sharp transition exists.

Next we turn to the behavior of the magnetization m as a function of the magnetic field and temperature (illustrated in Fig. 5.5 and 5.6). At $H = 0$ going from high to low temperatures the slope of $m(H)|_{H=0}$ is linear and diverges as we approach T_c. This reflects the diverging susceptibility as a critical behavior.

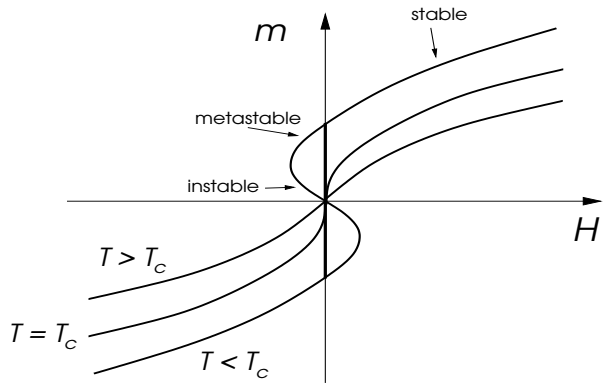

Figure 5.5: Magnetization as a function of magnetic field for different temperatures.

For all temperatures $T > T_c$ $m(H)$ is a single-valued function in Fig. 5.5 . Below T_c, however, $m(H)$ is triply valued as a solution of the self-consistence equation. The part with $dm/dH > 0$ is stable or metastable representing local minima of the free energy. The part of $dm/dH < 0$ corresponds to a local maximum of the free energy and is unstable. Considering for $T < T_c$ the magnetic field running from negative to positive values, we find for $H < 0$ the state with $m < 0$ has lowest free energy. At $H = 0$ there is a degeneracy between $+|m|$ and $-|m|$ as both minima have the same energy and for $H > 0$, $m > 0$ is the lowest energy phase. Thus we encounter a level-crossing of the free energy for the two states at $H = 0$ and magnetization jumps from negative to positive direction. This represents a first-order transition, since the free energy as a function of H is singular, i.e. it has a sharp slope change (a discontinuity in the first derivative of F with respect to H).[2]
This may be visualized also in a three-dimensional graph in m, H and T (Fig. 5.6). The shaded region appearing for $T < T_c$ is a coexistence region of two degenerate phases. As m is changed in this region, the fraction of the two degenerate finite magnetization phases is changed continuously following a Maxwell construction.

$$m(q) = q|m(H = 0, T)| + (1 - q)\{-|m(H = 0, T)|\} = (2q - 1)|m(H = 0, T)| \tag{5.35}$$

where q can change continuously with $0 \leq q \leq 1$. This may be viewed as domains of the two states changing in size.
In the H-T-plane this shaded region is simply a line for the first order transition of a discontinuously changing magnetization.

5.3 Gaussian transformation

We analyze the mean field approximation from a different point of view, using the Gaussian transformation. The partition function of the Ising model can be rewritten by introducing an

[2]Note that in reality ramping H through 0 does not necessarily lead to a sharp transition. Flipping all magnetic moments at once is not a trivial matter. Thus the system may stay trapped in the metastable free energy minimum for a certain range of positive H. The transition may happen through the nucleation of reversed magnetic bubbles (domains) and the subsequent expansion of the reversed region by means of domain wall motion. (Similar to the nucleation and expansion of droplets in undercooled vapor.) There is a certain field where the metastable minimum becomes a saddle point and thus unstable for infinitesimally higher fields. Varying the magnetic field periodically can lead to hysteretic loops.

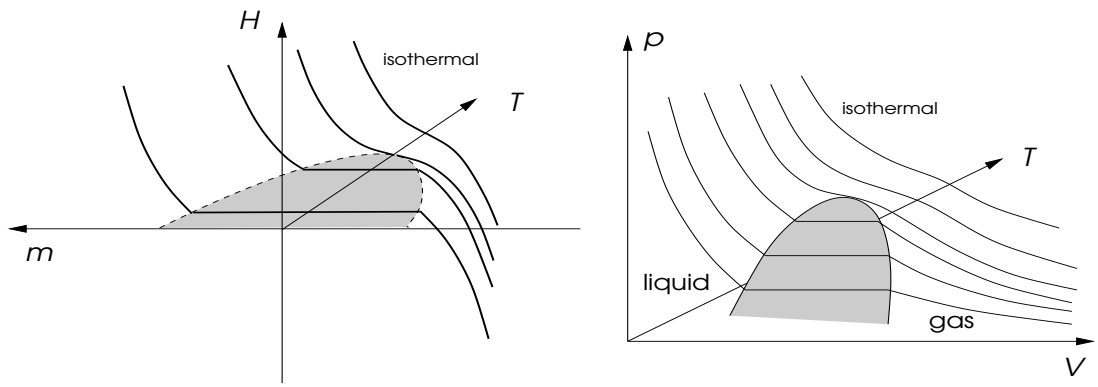

Figure 5.6: Left panel: phase diagram of ferromagnetic Ising model in (H, m, T); right panel: phase diagram of the liquid-gas transition in (p, V, T). In both cases the shaded region represents a coexistence region.

auxiliary field ϕ_i:

$$\begin{aligned} Z &= \sum_{\{s_i\}} e^{-\frac{\beta}{2}\sum_{i,j} J_{ij} s_i s_j + \beta \sum_i s_i H_i} \\ &= \frac{1}{(2\pi k_B T)^{N/2}\sqrt{detJ}} \int_{-\infty}^{+\infty} \left(\prod_{i'} d\phi_{i'}\right) e^{\frac{\beta}{2}\sum_{i,j}(J^{-1})_{ij}(\phi_i - H_i)(\phi_j - H_j)} \prod_i \sum_{s_i = \pm s} e^{\beta \phi_i s_i} \\ &= \frac{1}{(2\pi k_B T)^{N/2}\sqrt{detJ}} \int_{-\infty}^{+\infty} \left(\prod_{i'} d\phi_{i'}\right) e^{\frac{\beta}{2}\sum_{i,j}(J^{-1})_{ij}(\phi_i - H_i)(\phi_j - H_j) + \sum_i \ln[2\cosh(\beta s \phi_i)]} \end{aligned} \tag{5.36}$$

where we use the $N \times N$-matrix

$$J_{ij} = \begin{cases} -J & (i,j) \text{ nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \tag{5.37}$$

and $(J^{-1})_{ij}$ is the inverse of J_{ij}. We take the magnetic field as site dependent, which will be convenient later. We used the identity

$$\begin{aligned} &\int_{-\infty}^{+\infty} d\phi\, e^{-\frac{\phi^2}{2a} + s\phi} = e^{\frac{a}{2}s^2} \int_{-\infty}^{+\infty} d\phi\, e^{-\frac{1}{2a}(\phi - sa)^2} = \sqrt{2\pi a} e^{\frac{a}{2}s^2} \\ \Rightarrow \quad &\int_{-\infty}^{+\infty} \left(\prod_i d\phi_i\right) e^{-\frac{1}{2}\sum_{i,j}\phi_i (A^{-1})_{ij}\phi_j + \sum_i \phi_i s_i} = (2\pi)^{N/2}\sqrt{detA}\, e^{\frac{1}{2}\sum_{ij} s_i A_{ij} s_j} \end{aligned} \tag{5.38}$$

with A being a positive definite $N \times N$-matrix. This exact rewriting of the partition function is called Gaussian transformation (sometimes also called Hubbard-Stratonovich transformation).[3] We replaced here the discrete variable s_i by a continuous field ϕ_i.
We introduce the potential $S(\phi_i, H_i)$ and write

$$Z = C \int_{-\infty}^{+\infty} \left(\prod_{i'} d\phi_{i'}\right) e^{-\beta S(\phi_i, H_i)} = e^{-\beta F} \tag{5.39}$$

[3] *Reference:* "Field Theory, the Renormalization Group, and Critical Phenomena", Daniel J. Amit, World Scientific.

with $C = 1/(2\pi k_B T)^{N/2}\sqrt{detJ}$ and

$$S(\phi_i, H_i) = -\frac{1}{2}\sum_{i,j}(J^{-1})_{ij}(\phi_i - H_i)(\phi_j - H_j) - \frac{1}{\beta}\sum_i \ln[2\cosh(\beta s\phi_i)] \tag{5.40}$$

From this we can derive the mean field result by the saddle point approximation (sometimes also called method of steepest descent) which is based on the idea that one set replaces the auxiliary field by the value $\bar{\phi}_i$ which dominates the integral for the partition function.[4] This is analogous to discussions we had earlier when we tested the equivalence of different ensembles. This method relies on the fact that the fluctuations of the field ϕ_i are small - something which has to be tested. Therefore we look for the maximum of S now and approximate Z then by

$$Z \approx Ce^{-\beta S(\bar{\phi}_i, H_i)} \qquad \text{with} \quad 0 = \left.\frac{\partial S}{\partial \phi_i}\right|_{\phi_i = \bar{\phi}_i} = -\sum_j (J^{-1})_{ij}(\bar{\phi}_j - H_j) - s\tanh(\beta s\bar{\phi}_i) \tag{5.44}$$

which leads to the saddle-point equation

$$\bar{\phi}_i = H_i - s\sum_j J_{ij}\tanh(\beta s\bar{\phi}_j) \tag{5.45}$$

For $H_i = 0$ the saddle point is given by the uniform solution $\bar{\phi}_i = \bar{\phi}$, satisfying

$$\bar{\phi} = -s\sum_j J_{ij}\tanh(\beta s\bar{\phi}) = Jzs\tanh(\beta s\bar{\phi})\ . \tag{5.46}$$

This yields the same critical temperature for the onset of a finite solution for $\bar{\phi}$ as the mean field solution. The relation to m of the mean field approximation is given by the condition

$$\langle s_i\rangle = k_B T\frac{\partial \ln Z}{\partial H_i} = -\frac{dS(\bar{\phi}_i, H_i)}{dH_i} = -\frac{\partial S}{\partial H_i} = -\sum_j (J^{-1})_{ij}(\bar{\phi}_j - H_j) = s\tanh(\beta s\bar{\phi}_i) \tag{5.47}$$

such that

$$m = s\tanh(\beta s\bar{\phi}) \qquad \Rightarrow \qquad \bar{\phi} = Jzm\ . \tag{5.48}$$

The discussion of the thermodynamic properties are in this formulation analogous to the ordinary mean field treatment and give exactly the same behavior. We are, however, now in a position to go beyond the mean field level and, in particular, to test the validity of the mean field approximation.

[4] *Method of steepest descent:* We consider the integral

$$I = \int_a^b e^{Ng(x)}dx \tag{5.41}$$

and $N \gg 1$ and $g(x)$ a function with a unique maximum at $x = \bar{x}$ in the interval $[a, b]$, i.e.

$$g(x) = g(\bar{x}) + g'(\bar{x})(x - \bar{x}) + \frac{1}{2}g''(\bar{x})(x - \bar{x})^2 + \cdots\ . \tag{5.42}$$

For the maximum, the conditions $g'(\bar{x}) = 0$ and $g''(\bar{x}) < 0$ holds. We approximate the integral

$$I \approx e^{Ng(\bar{x})}\int_a^b dx\, e^{-\frac{1}{2}N|g''(\bar{x})|(x-\bar{x})^2} \approx e^{Ng(\bar{x})}\int_{-\infty}^{+\infty} dx\, e^{-\frac{1}{2}N|g''(\bar{x})|(x-\bar{x})^2} = \left(\frac{2\pi}{N|g''(\bar{x})|}\right)^{1/2} e^{Ng(\bar{x})} \tag{5.43}$$

which is exact in the limit $N \to \infty$. Considering $\ln I$ we find that $\ln I \approx Ng(\bar{x}) + O(\ln N)$.

5.3.1 Correlation function and susceptibility

We consider first the correlation function

$$\Gamma_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle = (k_B T)^2 \frac{\partial^2 \ln Z}{\partial H_i \partial H_j} \approx -k_B T \frac{d^2 S(\bar{\phi}_i, H_i)}{dH_i dH_j} \ . \tag{5.49}$$

With (5.47) we obtain

$$\beta \Gamma_{ij} = \frac{d}{dH_j} s \tanh(\beta s \bar{\phi}_i) = \beta s^2 \cosh^{-2}(\beta s \bar{\phi}) \frac{d\bar{\phi}_i}{dH_j} \tag{5.50}$$

which if inverted yields

$$\Gamma_{ij}^{-1} = \frac{1}{s^2} \cosh^2(\beta s \bar{\phi}) \frac{dH_j}{d\bar{\phi}_i} = \frac{1}{s^2} \cosh^2(\beta s \bar{\phi}) \left\{ \delta_{ij} + \frac{\beta s^2 J_{ij}}{\cosh^2(\beta s \bar{\phi})} \right\} \tag{5.51}$$

where we use (5.45)

$$H_j = \bar{\phi}_j + s \sum_{j'} J_{jj'} \tanh(\beta s \bar{\phi}_{j'}) \quad \Rightarrow \quad \frac{dH_j}{d\bar{\phi}_i} = \delta_{ij} + \frac{\beta s^2 J_{ij}}{\cosh^2(\beta s \bar{\phi})} \ . \tag{5.52}$$

The following Fourier-transformations lead to a simple form for (5.51), [5]

$$J_{ij} = \frac{1}{N} \sum_{\vec{q}} J(\vec{q}) e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} \ , \quad \Gamma_{ij} = \frac{1}{N} \sum_{\vec{q}} \Gamma(\vec{q}) e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} \ , \quad \delta_{ij} = \frac{1}{N} \sum_{\vec{q}} e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} \tag{5.57}$$

with

$$\Gamma(\vec{q}) = \frac{k_B T \Gamma_0}{1 + \Gamma_0 J(\vec{q})} \qquad \text{with} \qquad \Gamma_0 = \frac{\beta s^2}{\cosh^2(\beta s \bar{\phi})} = \beta s^2 \left\{ 1 - \tanh^2(\beta s \bar{\phi}) \right\} = \beta (s^2 - m^2) \ , \tag{5.58}$$

using (5.48). On a d-dimensional hypercubic lattice with only nearest-neighbor coupling, we obtain for the Fourier transformed coupling strength,

$$J(\vec{q}) = \frac{1}{N} \sum_{i,j} J_{ij} e^{-i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} = -2J \sum_{\alpha=1}^{d} \cos q_\alpha a \tag{5.59}$$

with the lattice constant a. As we will see below, if we focus on the long-distance correlations only, we can restrict ourselves to the small $\vec{q}$ range and we expand $J(\vec{q})$ as

$$J(\vec{q}) \approx -Jz + Jq^2 a^2$$

$$\Rightarrow \qquad \Gamma(\vec{q}) \approx \frac{k_B T}{\frac{k_B T}{s^2 - m^2} - Jz + Jq^2 a^2} \approx \frac{k_B T s^2}{k_B (T - T_c) + J s^2 q^2 a^2 + k_B T m^2 / s^2} \tag{5.60}$$

[5] For the inversion of Γ_{ij} it is important to realize that $\Gamma_{ij} = \Gamma(\vec{r}_i - \vec{r}_j)$ is translation invariant. We use now the linear equation

$$a_i = \sum_j \Gamma_{ij}^{-1} b_j \quad \Rightarrow \quad \sum_j \Gamma_{ij} a_j = b_i \ . \tag{5.53}$$

We perform now the Fourier transform of the second equation,

$$\frac{1}{N} \sum_i \sum_j \Gamma_{ij} a_j e^{-i\vec{q}\cdot\vec{r}_i} = \frac{1}{N} \sum_i \sum_j \Gamma_{ij} a_j e^{-i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} e^{-i\vec{q}\cdot\vec{r}_j} = \Gamma(\vec{q}) a(\vec{q}) = \frac{1}{N} \sum_i b_i e^{-\vec{q}\cdot\vec{r}_i} = b(\vec{q}) \ . \tag{5.54}$$

On the other hand, we find

$$\frac{1}{N} \sum_i \sum_j \Gamma_{ij}^{-1} b_j e^{-i\vec{q}\cdot\vec{r}_i} = \frac{1}{N} \sum_i \sum_j \Gamma_{ij}^{-1} b_j e^{-i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} e^{-i\vec{q}\cdot\vec{r}_j} = \Gamma^{-1}(\vec{q}) b(\vec{q}) = \frac{1}{N} \sum_i a_i e^{-\vec{q}\cdot\vec{r}_i} = a(\vec{q}) \ , \tag{5.55}$$

leading to the relation

$$\Gamma^{-1}(\vec{q}) = \frac{1}{\Gamma(\vec{q})} \ , \tag{5.56}$$

which is a convenient way to handle the inverted matrix Γ_{ij}^{-1}.

where for the last approximation, we assumed $m \ll s$ as is the case in ordered phase close to T_c and for $T > T_c$. This correlation function has then the famous Ornstein-Zernike form,

$$\Gamma(\vec{q}) = \frac{A}{1+\xi^2 q^2} \tag{5.61}$$

where ξ is the correlation length, as introduced in (4.13).
First let us use this result to determine the susceptibility. For this purpose we take the earlier derived connection of the susceptibility with the fluctuations.

$$\chi = \beta \sum_{i,j} \{\langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle\} = \beta \sum_{i,j} \Gamma_{ij} = N\beta\Gamma(\vec{q}=0) = \frac{Ns^2}{k_B(T-T_c) + k_B T m^2/s^2} \tag{5.62}$$

We use now the earlier mean field result for $m^2 = 3s^2\tau$ in (5.32) and obtain for the regime very close to T_c the behavior,

$$\chi(T) = \begin{cases} \dfrac{Ns^2}{k_B(T-T_c)} & T > T_c \ , \\[2ex] \dfrac{Ns^2}{2k_B|T-T_c|} & T < T_c \ , \end{cases} \tag{5.63}$$

showing that the susceptibility is singular approaching T_c from both sides of the phase transition with the same exponent for $|\tau|$.
Now return to the correlation function in the paramagnetic phase ($T > T_c$) and represent the correlation function in real space, where we restrict ourselves to the long-distance behavior $r \to \infty$. Thus we have the Fourier-transform $\Gamma(\vec{q})$. For large $|\vec{r}|$ the phase factor $e^{i\vec{q}\cdot\vec{r}}$ rapidly oscillates for for large $\vec{q}$ such that in $\Gamma(\vec{q})$ only small $\vec{q}$ are important.
For simplicity we consider only the three-dimensional case,

$$\begin{aligned} \Gamma_{\vec{r}} &= \int \frac{d^3q}{(2\pi)^3} \Gamma(\vec{q}) e^{i\vec{q}\cdot\vec{r}} \approx \frac{A}{4\pi^2} \int_0^\infty dq\, q^2 \int d\theta\ \sin\theta\ \frac{e^{iqr\cos\theta}}{1+\xi^2 q^2} = \frac{A}{4\pi^2 ir} \int_0^\infty dq\, q \frac{e^{iqr} - e^{-iqr}}{1+\xi^2 q^2} \\ &= \frac{A}{4\pi^2 ir} \int_{-\infty}^{+\infty} dq\, q \frac{e^{iqr}}{1+\xi^2 q^2} = \frac{A}{4\pi} \frac{e^{-r/\xi}}{r\xi^2} = \frac{k_B T}{4\pi J} \frac{e^{-r/\xi}}{r} \end{aligned} \tag{5.64}$$

where we used residue calculation for the last integral and introduced the parametrization,

$$A = \frac{s^2}{1-T_c/T} = \frac{k_B T \xi^2}{J a^2} \qquad \text{and} \qquad \xi^2 = \frac{J s^2 a^2}{k_B(T-T_c)} \ . \tag{5.65}$$

The general form of the correlation function for other dimensions d is

$$\Gamma_{\vec{r}} \propto \frac{e^{-r/\xi}}{r^{(d-1)/2}} \tag{5.66}$$

if $T > T_c$.[6] In all cases there is a correlation length which diverges as we approach $T \to T_{c+}$. At T_c we find

$$\Gamma_{\vec{r}} = \frac{k_B T}{J a^2} \int \frac{d^d q}{(2\pi)^d} \frac{e^{i\vec{q}\cdot\vec{r}}}{q^2} \propto \begin{cases} \ln r & d = 2 \\[2ex] r^{2-d} & d \neq 2 \end{cases} \tag{5.70}$$

[6]Note that the correlation function in $\vec{q}$-space

$$\Gamma(\vec{q}) = \frac{A}{1+\xi^2\vec{q}^2} \qquad \Leftrightarrow \qquad (1+\xi^2\vec{q})\Gamma(\vec{q}) = A \tag{5.67}$$

is the Fourier transform of the differential equation

$$A\delta(\vec{r}) = \{1 - \xi^2 \vec{\nabla}^2\}\Gamma_{\vec{r}} = \left\{1 - \frac{1}{r^{d-1}} \frac{\partial}{\partial r} r^{d-1} \frac{\partial}{\partial r}\right\} \Gamma_{\vec{r}} \ . \tag{5.68}$$

With the ansatz $\Gamma_{\vec{r}} = r^b e^{-r/\xi}$ we obtain easily, $b = (1-d)/2$ as given in (5.66). At the transition point we have

This suggests that for $T \to T_{c+}$ the correlation function should rather behave as

$$\Gamma_{\vec{r}} \propto \begin{cases} \ln r \; e^{-r/\xi} & d = 2 \\ \\ \dfrac{e^{-r/\xi}}{r^{d-2}} & d \neq 2 \end{cases} \tag{5.71}$$

which we will encounter later in the context of scaling again.
Eventually we may characterize the ordered phase ($T < T_c$), also through the behavior of the correlation function, which has the property

$$\lim_{r \to \infty} \Gamma_{\vec{r}} = 0 \tag{5.72}$$

for $T > T_c$ as well as $T < T_c$. In the latter case ξ plays the role of "healing length" over which any distortion of the mean field recovers to its uniform value $\langle s_i \rangle = m$. This means now that

$$\lim_{|\vec{r}_i - \vec{r}_j| \to \infty} \langle s_i s_j \rangle = \langle s_i \rangle \langle s_j \rangle = \begin{cases} 0 & T > T_c \; , \\ \\ m^2 & T < T_c \; . \end{cases} \tag{5.73}$$

Thus in the ordered phase spins are correlated of "infinite" distances (defined only in the thermodynamic limit of infinitely large systems) and are called long range ordered in contrast to short range order which means correlations over short distances only.

5.4 Ginzburg-Landau theory

We have used the Landau expansion of the free energy above to discuss phase transitions in the vicinity of the critical temperature where m was small. This method can be extended to a highly convenient scheme which allows us to discuss phase transition more generally, in particular, those of second order. Landau's concept is based on symmetry and spontaneous symmetry breaking. The disordered high-temperature phase has a certain symmetry which is characterized by a group $\mathcal{G}$ of all symmetry operations leaving the system invariant. At the second order phase transition a form of order appears reducing this symmetry such that the low-temperature phase obeys a symmetry group $\mathcal{G}'$ which is a subgroup of $\mathcal{G}$. This change of symmetry is called *spontaneous symmetry breaking*. This symmetry lowering is described by the appearance of an *order parameter*, a quantity which does not possess all symmetries of the group $\mathcal{G}$.
A further important aspect emerges when long-length scale variations of the order parameter are taken into account. This can be easily incorporated in the Ginzburg-Landau theory and allows to discuss spatial variations of the ordered phase as well as fluctuations.

5.4.1 Ginzburg-Landau theory for the Ising model

For the Ising model of the previous section we can identify m as the order parameter. The order parameter m is not invariant under time reversal symmetry $\hat{K}$,

$$\hat{K} m = -m \; . \tag{5.74}$$

$\xi^{-1} = 0$ such that the differential equation has then the form,

$$\vec{\nabla}^2 \Gamma_{\vec{r}} = \tilde{A} \delta(\vec{r}) \qquad \Rightarrow \quad \Gamma_{\vec{r}} \propto \begin{cases} r & d = 1 \\ \ln r & d = 2 \\ r^{2-d} & d \geq 3 \end{cases} \; , \tag{5.69}$$

as given in (5.70).

The two states with positive and negative m are degenerate. The relevant symmetry group above the phase transition is

$$\mathcal{G} = G \times \mathcal{K} \tag{5.75}$$

with G as the space group of the lattice (simple cubic) and $\mathcal{K}$, the group $\{E, \hat{K}\}$ (E denotes the identity operation). As for the space group we consider the magnetic moment here detached from the crystal lattice rotations such that G remains untouched through the transition so that the corresponding subgroup is

$$\mathcal{G}' = G \subset \mathcal{G} \tag{5.76}$$

The degeneracy of the ordered phase is given by the order of $\mathcal{G}/\mathcal{G}'$ which is 2 in our case.
The Ginzburg-Landau free energy functional has in d dimensions the general form

$$\begin{aligned} F[m;H,T] &= F_0(H,T) + \int d^d r \, \left\{ \frac{A}{2} m(\vec{r})^2 + \frac{B}{4} m(\vec{r})^4 - H(\vec{r}) m(\vec{r}) + \frac{\kappa}{2} [\vec{\nabla} m(\vec{r})]^2 \right\} \\ &= F_0(H,T) + \int d^d r \; f(m, \vec{\nabla} m; H, T) \end{aligned} \tag{5.77}$$

where we choose the coefficients according to the expansion done in (5.31) as

$$A = \frac{Jz}{a^d} \left(\frac{T}{T_c} - 1 \right) = -\frac{Jz}{a^d} \tau \quad \text{and} \quad B = \frac{Jz}{3 s^2 a^d} \; . \tag{5.78}$$

Here a is the lattice constant. We have introduced the spatial continuum limit for the order parameter m which is based on the procedure of *coarse graining*. We take a block of sites with the volume L_b^d with L_b much larger than the lattice constant a and define

$$m(\vec{r}) = \frac{1}{N_b} \sum_{i \in \Lambda_b(\vec{r})} \langle s_i \rangle \qquad \text{with} \qquad N_b = \frac{a^d}{L_b^d} \tag{5.79}$$

and $\Lambda_b(\vec{r})$ is the set of sites in the block around the center position $\vec{r}$. Here we assume that $\langle s_i \rangle$ is changing slowly in space on the length scale L_b.
Under this condition we can now also determine κ from the model Hamiltonian using the following consideration. The variational equation of the free energy functional is given by

$$0 = \frac{\delta F}{\delta m} \quad \Rightarrow \quad 0 = \frac{\partial f}{\partial m} - \vec{\nabla} \cdot \frac{\partial f}{\partial \vec{\nabla} m} = -\kappa \vec{\nabla}^2 m + A m + B m^3 - H \tag{5.80}$$

Let us compare this equation with the saddle-point equation (5.45,5.46) assuming $H = 0$. It is sufficient to keep only the terms of first order in m. We then take the equations (5.45,5.48) and expand the self-consistence equation to linear order

$$\begin{aligned} \bar{\phi}_i &= \bar{\phi}(\vec{r}_i) \approx -\beta s^2 \sum_j J_{ij} \bar{\phi}(\vec{r}_j) = \beta s^2 \sum_{\{\vec{a}\}_{n.n.}} J \bar{\phi}(\vec{r}_i + \vec{a}) \\ &= \beta s^2 J \left[z \bar{\phi}(\vec{r}_i) + \sum_{\{\vec{a}\}_{n.n.}} \vec{a} \cdot \vec{\nabla} \bar{\phi}(\vec{r}_i) + \frac{1}{2} \sum_{\{\vec{a}\}_{n.n.}} \sum_{\mu,\nu = x,y\ldots} a_\mu a_\nu \frac{\partial^2}{\partial r_\mu \partial r_\nu} \bar{\phi}(\vec{r}_i) \right] \; . \end{aligned} \tag{5.81}$$

The sum $\sum_{\{\vec{a}\}_{n.n.}}$ runs over nearest-neighbor sites. Note that the second term in the bracket $[\ldots]$ vanishes due to symmetry. Now using the coarse graining procedure we may replace $\bar{\phi}(\vec{r}_i) = Jzm(\vec{r})$ and obtain

$$0 = Jz \left(\frac{T}{T_c} - 1 \right) m(\vec{r}) - J a^2 \vec{\nabla}^2 m(\vec{r}) \; , \tag{5.82}$$

and the comparison of coefficients leads to

$$\kappa = Ja^{2-d} \ . \tag{5.83}$$

We may rewrite the equation (5.82) as

$$0 = m - \xi^2 \vec{\nabla}^2 m \qquad \text{with} \qquad \xi^2 = \frac{a^2 k_B T_c}{z k_B (T - T_c)} = \frac{J s^2 a^2}{k_B (T - T_c)} \tag{5.84}$$

where we introduced the length ξ which is exactly equal to the correlation length for $T > T_c$ in (5.65).

5.4.2 Critical exponents

Close to the phase transition at T_c various quantities have a specific temperature or field dependence which follows powerlaws in $\tau = 1 - T/T_c$ with characteristic exponents, so-called critical exponents. We introduce here the exponents relevant for a magnetic system like the Ising model. The heat capacity C and the susceptibility χ follow the behavior

$$C(T) \propto |\tau|^{-\alpha} \qquad \text{and} \qquad \chi(T) \propto |\tau|^{-\gamma} \tag{5.85}$$

for both $\tau > 0$ and $\tau < 0$. Also the correlation length displays a powerlaw

$$\xi(T) \propto |\tau|^{-\nu} \ . \tag{5.86}$$

For $\tau > 0$ (ordered phase) the magnetization grows as

$$m(T) \propto |\tau|^{\beta} \ . \tag{5.87}$$

At $T = T_c$ ($\tau = 0$) the magnetization has the field dependence

$$m \propto H^{1/\delta} \tag{5.88}$$

and the correlation function has a powerlaw dependence on the distance r

$$\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2+\eta}} \ . \tag{5.89}$$

These exponents are not completely independent but are related by means of so-called scaling laws:

- Rushbrooke scaling: $\alpha + 2\beta + \gamma = 2$
- Widom scaling: $\gamma = \beta(\delta - 1)$
- Fisher scaling: $\gamma = (2 - \eta)\nu$
- Josephson scaling: $\nu d = 2 - \alpha$

We do not derive all relations, but restrict to Fisher's result in order to show the basic idea. We consider the correlation function for $\tau < 0$ but very close to T_c. Then using (5.89) we assume that we can write $\Gamma_{\vec{r}}$ as

$$\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2+\eta}} g(r/\xi) \ . \tag{5.90}$$

According to our previous discussion the susceptibility is given by the integral of $\Gamma_{\vec{r}}$ over space

$$\chi \propto \int d^d r \ \Gamma_{\vec{r}} \propto \int d^d r \ \frac{1}{r^{d-2+\eta}} g(r/\xi) \propto \xi^{2-\eta} \int d^d y \frac{1}{y^{d-2+\eta}} g(y) \propto |\tau|^{-\nu(2-\eta)} \propto |\tau|^{-\gamma} \tag{5.91}$$

which leads to $\gamma = \nu(2 - \eta)$.

Let us now determine the exponents within mean field theory. The only one we have not determined so far is δ. Using the Ginzburg-Landau equations for $\tau = 0$ leads to

$$Bm^3 = H \qquad \Rightarrow \qquad \delta = 3 \tag{5.92}$$

Thus the list of exponents is

$$\alpha = 0\ , \quad \beta = \frac{1}{2}\ , \quad \gamma = 1 \quad \delta = 3\ , \quad \nu = \frac{1}{2} \quad \eta = 0 \tag{5.93}$$

These exponents satisfy the scaling relations apart from the Josephson scaling which depends on the dimension d.
The critical exponents arise from the specific fluctuation (critical) behavior around a second-order phase transition. They are determined by dimension, structure of order parameter and coupling topology, and are consequently identical for equivalent phase transitions. Therefore, the critical exponents incorporate *universal* properties.

5.4.3 Range of validity of the mean field theory - Ginzburg criterion

In Eq. (5.16) we gave a condition for the validity of the mean field approximation. The fluctuations around the mean field should be small. We formulate this statement more precisely here. In previous chapters we have found that for large systems the fluctuations are very small compared to the mean value (e.g. energy, particle number, ...). Looking at the fluctuations of the magnetic moments, the question arises what is the "system size". The natural length scale for fluctuations here is the correlation length which we know from the correlation function Γ_{ij}. Thus, the relevant "system size" corresponds to the volume $V_\xi = \xi^d$. Looking at the ratio

$$E_{ij} = \frac{\langle (s_i - \langle s_i \rangle)(s_j - \langle s_j \rangle) \rangle}{\langle s_i \rangle \langle s_j \rangle} \qquad \Rightarrow \qquad E_{GL} = \frac{\sum_{j \in \Lambda_\xi} \Gamma_{0j}}{\sum_{j \in \Lambda_\xi} \langle s_0 \rangle \langle s_j \rangle}\ , \tag{5.94}$$

where Λ_ξ denotes the set of lattice points around 0 covered by the volume V_ξ. We first look at the numerator and use the fact that $\Gamma_{\vec{r}}$ decays on the length ξ quickly. Thus we use

$$\int_{V_\xi} d^d r\ \Gamma_{\vec{r}} = f k_B T \frac{\chi(T)}{N}\ . \tag{5.95}$$

where the factor f is independent of ξ and temperature and gives the fraction to which integral limited to V_ξ corresponds to the susceptibility $\chi k_B T = \sum_{i,j} \Gamma_{ij}$. We can estimate it by using the scaling form of $\Gamma_{\vec{r}}$,

$$\int_0^\xi dr \frac{r^{d-1}}{r^{d-2}} g(r/\xi) = f \int_0^\infty dr \frac{r^{d-1}}{r^{d-2}} g(r/\xi) \qquad \Rightarrow \qquad \xi^2 \int_0^1 dx\ x g(x) = f \xi^2 \int_0^\infty dx\ x g(x)\ , \tag{5.96}$$

which leads indeed to f independent of ξ and of order one. Next we consider the denominator of E_{GL} and we restrict to $T < T_c$ so that we immediately find

$$\sum_{j \in V_\xi} \langle s_0 \rangle \langle s_j \rangle = m(T)^2 N_\xi \tag{5.97}$$

with $N_\xi = (\xi/a)^d$ as the number of lattice sites within the volume V_ξ. The criterion for the mean field theory to be applicable is then given by

$$f k_B T_c \frac{\chi(T)}{N} \ll \left(\frac{\xi}{a}\right)^d m(T)^2 \quad \Rightarrow \quad \frac{f s^2}{\tau} \ll 3 s^2 \tau \left(\frac{\xi_0}{a}\right)^d \tau^{-d/2} \tag{5.98}$$

with ξ_0 as the correlation length at zero-temperature. From these we obtain the range of validity

$$\tau^{\frac{4-d}{2}} \gg \frac{f}{3}\left(\frac{a}{\xi_0}\right)^d \tag{5.99}$$

which excludes obviously a narrow range of temperature close to T_c for dimensions $d \leq 3$. For dimensions $d > 4$ there is no limitations and the mean field theory including the Ginzburg-Landau theory is valid also close to T_c. The temperature region

$$\Delta T = T_c - T \sim T_c \left\{\frac{f}{3}\left(\frac{a}{\xi_0}\right)^d\right\}^{\frac{2}{4-d}} \tag{5.100}$$

is called the critical region and grows with shrinking ξ_0 as the number of spins in the correlation volume V_ξ becomes smaller.
One important result is the fact that the dimension $d_c = 4$ has been identified as an upper critical dimension. For $d > d_c$ the mean field exponents are valid. This does, however, not mean that the mean field approximation delivers the exact thermodynamics.

5.5 Self-consistent field approximation

Fluctuation effects affect not only the critical exponents, they also alter the condition for the instability. The mean field approximation overestimates the tendency to order by ignoring fluctuations. The functional integral formulation based on the Gaussian transformation allows us to tackle the discussion of fluctuation effects in a systematic way. A good insight into some aspects of the fluctuation effects is obtained by the so-called self-consistent field approximation which is used to analyze the instability condition. We consider the fluctuations around the mean order parameter value by looking at the partition function in Eq.(5.39)

$$Z = C\int_{-\infty}^{+\infty}\left(\prod_i d\phi_i\right) e^{-\beta S(\phi_i, H_i)} \ . \tag{5.101}$$

Our aim in the following will be to examine the instability condition of the paramagnetic state in the absence of a magnetic field, i.e. $H_i = 0$. Including thermal fluctuations we find that the mean square of the field ϕ_i is finite above the transition temperature, while the simple mean value vanishes, i.e. $\langle\phi_i^2\rangle \neq 0$ while $\langle\phi_i\rangle = 0$.

5.5.1 Renormalization of the critical temperature

We take now advantage of the fact that in the paramagnetic phase only small values of ϕ_i are important. Therefore, we expand to $S(\phi_i)$ to second order in the fields ϕ_i in the following way,

$$\begin{aligned} S(\phi) &\approx S_0 + \frac{1}{2}\left\{\sum_{i,j}(J^{-1})_{ij}\phi_i\phi_j + k_B T\sum_{i,j}\left\langle\frac{\partial^2 \ln[2\cosh(\beta s\phi_i]}{\partial\phi_i\partial\phi_j}\right\rangle\phi_i\phi_j\right\} \\ &= S_0 + \frac{1}{2}\sum_{i,j}\left\{(J^{-1})_{ij} + \beta s^2\delta_{ij}\left\langle\frac{1}{\cosh^2(\beta s\phi_i)}\right\rangle\right\}\phi_i\phi_j \\ &\approx S_0 + \frac{1}{2}\sum_{i,j}\left\{(J^{-1})_{ij} + \beta s^2\delta_{ij}(1-\beta s^2\langle\phi_i^2\rangle\right\}\phi_i\phi_j \ . \end{aligned} \tag{5.102}$$

We take $\langle\phi_i^2\rangle = \langle\phi^2\rangle$ independent of position. Now we turn to Fourier space,

$$\phi_i = \frac{1}{N}\sum_{\vec{q}}\phi_{\vec{q}}\, e^{i\vec{q}\cdot\vec{r}_i} \qquad \text{with} \qquad \phi^*_{\vec{q}} = \phi_{-\vec{q}} \ , \tag{5.103}$$

and we obtain

$$
\begin{aligned}
S(\phi) &= S_0 + \frac{1}{2N}\sum_{\vec{q}}\left\{\frac{1}{J(\vec{q})} + \beta s^2(1-\beta^2 s\langle\phi^2\rangle)\right\}\phi_{\vec{q}}\phi_{-\vec{q}} \\
&\approx S_0 - \frac{1}{2JzN}\sum_{\vec{q}}\left\{\frac{q^2a^2}{z} + 1 - Jzs^2\beta - Jzs^4\beta^3\langle\phi^2\rangle\right\}\phi_{\vec{q}}\phi_{-\vec{q}} \\
&= S_0 + \frac{a^d}{2J^2z^2N}\sum_{\vec{q}}\left\{\kappa q^2 + A + 3Bs^6\beta^3\langle\phi^2\rangle\right\}\phi_{\vec{q}}\phi_{-\vec{q}}
\end{aligned}
\tag{5.104}
$$

A slightly more compact form is reached by taking the relation $\phi_{\vec{q}} = Jzm_{\vec{q}}$ following Eq.(5.48) and $k_BT_c = Jzs^2$ such that

$$
S = S_0 + \frac{a^d}{2N}\sum_{\vec{q}}\left\{\kappa q^2 + A + 3B\langle m^2\rangle\right\}m_{\vec{q}}m_{-\vec{q}} = S_0 + \frac{1}{2}\sum_{\vec{q}}G^{-1}(\vec{q})m_{\vec{q}}m_{-\vec{q}} \tag{5.105}
$$

taking the coefficients from the above Ginzburg-Landau formulation.
Now we may rewrite the partition function in this approximation as

$$
\begin{aligned}
Z' &= Z_0\prod_{\vec{q}}{}' \int dm_{\vec{q}}\, dm_{-\vec{q}}\, \exp\left\{-\beta G^{-1}(\vec{q})m_{\vec{q}}m_{-\vec{q}}/2\right\} \\
&= Z_0\prod_{\vec{q}}{}' \int dm'_{\vec{q}}\, dm''_{\vec{q}}\, \exp\left\{-\beta G^{-1}(\vec{q})({m'_{\vec{q}}}^2 + {m''_{-\vec{q}}}^2)/2\right\}
\end{aligned}
\tag{5.106}
$$

where we used the parametrization $m_{\pm\vec{q}} = m'_{\vec{q}} \pm im''_{\vec{q}}$. The product $\prod'$ runs only over the half-space of $\vec{q}$, e.g. $\{\vec{q} \mid q_z \geq 0\}$, because the full product $\prod_{\vec{q}} dm_{\vec{q}}dm_{-\vec{q}}$ would constitute a doubling of integrals compared to $\prod_i d\phi_i$. Using this we calculate the mean value

$$
\begin{aligned}
\langle m^2\rangle &= \frac{1}{L^d}\int d^dr\, \langle m(\vec{r})^2\rangle = \frac{1}{N^2}\sum_{\vec{q}}\langle m_{\vec{q}}m_{-\vec{q}}\rangle \\
&= \frac{1}{N^2}\sum_{\vec{q}}\langle {m'_{\vec{q}}}^2 + m''^2_{\vec{q}}\rangle = \frac{k_BT}{N^2}\sum_{\vec{q}}G(\vec{q}) = \frac{1}{L^d}\sum_{\vec{q}}\frac{k_BT}{A + 3B\langle m^2\rangle + \kappa q^2}
\end{aligned}
\tag{5.107}
$$

which represents a self-consistent equation for $\langle m^2\rangle$. Note that the $G(\vec{q})$ corresponds to a renormalized correlation function, analogous to $\Gamma_{\vec{q}}$ in (5.60).
On the other hand, we can determine the susceptibility using the fluctuations,

$$
\begin{aligned}
\chi(T) &= \beta\frac{1}{L^d}\int d^dr\, d^dr'\left\{\langle m(\vec{r})m(\vec{r}')\rangle - \langle m(\vec{r})\rangle\langle m(\vec{r}')\rangle\right\} \\
&= \beta\langle m^2_{\vec{q}=0}\rangle = G(\vec{q}=0) = \frac{1}{A + 3B\langle m^2\rangle}\ .
\end{aligned}
\tag{5.108}
$$

The fact that the susceptibility diverges at the phase transition can now be used to determine the instability temperature T_c^* which is different from the "bare" T_c defining the zero of A. Thus we analyze the equation

$$
\chi^{-1} = [A + 3B\langle m^2\rangle] = A + \frac{3Bk_BT}{L^d}\sum_{\vec{q}}\frac{1}{\chi^{-1} + \kappa q^2}\ , \tag{5.109}
$$

where $\chi^{-1} = 0$ determines T_c^*. For the sum over $\vec{q}$ we have to be careful because the form we have chosen for the expansion in small powers of q is not valid at large q. We correct for this by introducing an upper cutoff Λ for q, which is of the order a^{-1}, the inverse lattice constant. Then going to integral form $L^{-d}\sum_{\vec{q}} \to \int d^dq/(2\pi)^d$ and setting $\chi^{-1} = 0$ we reach at equation

$$A_c = Jza^{-d}\left(\frac{T_c^*}{T_c} - 1\right) = -\frac{Jza^{-d}}{s^2}\frac{C_d k_B T_c^*}{(2\pi)^d}\int_0^\Lambda dq\,\frac{q^{d-1}}{\kappa q^2} \tag{5.110}$$

where $C_d = \int d\Omega$ is the surface area of a unit-sphere in d dimensions as defined in Eq.(1.39). Thus the renormalized transition temperature is

$$T_c^* = \frac{T_c}{1 + \dfrac{C_d z}{(2\pi)^d}\dfrac{(\Lambda a)^{d-2}}{d-2}} \quad < T_c\,. \tag{5.111}$$

Therefore the transition temperature is reduced by the fluctuations. The dimension $d = d_L = 2$ appears as a lower critical dimension. For dimension $d < d_L$ the integral diverges at the lower boundary (infrared divergence) such that no finite transition temperature is possible. The dimension d_L is more subtle. Below we will comment from a different point of view on this result.

5.5.2 Renormalized critical exponents

Now we turn to the behavior of the susceptibility at the new critical temperature. For this purpose we rewrite (5.109) with the help of (5.110) and obtain for $T \to T_{c+}^*$

$$\begin{aligned}\chi^{-1} &= (A - A_c) + \frac{3BC_d}{(2\pi)^d}\int_0^\Lambda dq\, q^{d-1}\left[\frac{k_BT}{\chi^{-1} + \kappa q^2} - \frac{k_BT_c^*}{\kappa q^2}\right] \\ &\approx (A - A_c) - \frac{3BC_d k_BT_c^*}{(2\pi)^d\kappa}\int_0^\Lambda dq\frac{q^{d-3}}{1 + \chi\kappa q^2} \\ &= (A - A_c) - \frac{3BC_d k_BT_c^*}{(2\pi)^d\kappa}\{\kappa\chi\}^{(2-d)/2}\int_0^{\Lambda\sqrt{\kappa\chi}} dx\frac{x^{d-3}}{1 + x^2}\,.\end{aligned} \tag{5.112}$$

Note that $\kappa\chi = \xi^2$. We distinguish now two cases. First choose the dimension larger than the upper critical dimension $d > d_c = 4$ and obtain

$$\begin{aligned}\chi^{-1} &\approx (A - A_c) - \frac{3BC_d k_BT_c^*}{(2\pi)^d\kappa}\{\kappa\chi\}^{(2-d)/2}\frac{\{\Lambda(\kappa\chi)^{1/2}\}^{d-4}}{d-4} \\ &= (A - A_c) - \frac{3BC_d k_BT_c^*}{(2\pi)^d\kappa^2}\frac{\Lambda^{d-4}}{d-4}\chi^{-1} = \frac{k_B}{a^d s^2}(T - T_c^*) - \frac{C_d z^2}{2(2\pi)^d}\frac{T_c^*}{T_c}\frac{(\Lambda a)^{d-4}}{d-4}\chi^{-1}\end{aligned} \tag{5.113}$$

$$\Rightarrow \qquad \chi(T) = \frac{a^d s^2}{k_B(T - T_c^*)}\left\{1 + \frac{C_d z^2}{2(2\pi)^d}\frac{T_c^*}{T_c}\frac{(\Lambda a)^{d-4}}{d-4}\right\}^{-1} \propto |T - T_c^*|^{-1}\,.$$

We observe that this corresponds to the behavior found in mean field calculation. Indeed above the critical dimension d_c the mean field exponents are correct, and the only effect of fluctuations is to renormalize certain quantities such as the critical temperature.
Next we consider $d < d_c = 4$. In this case the integral over x in (5.112) converges and the upper bound does not enter in the limit $T \to T_c^*$. The integral only depends on d and is given by $K_d = \Gamma[(d-2)/2]\Gamma[(4-d)/2]$. Therefore, we obtain

$$\chi^{-1} = (A - A_c) - \frac{3BC_d k_BT_c^*}{(2\pi)^d\kappa^{d/2}}K_d\chi^{(2-d)/2}\,. \tag{5.114}$$

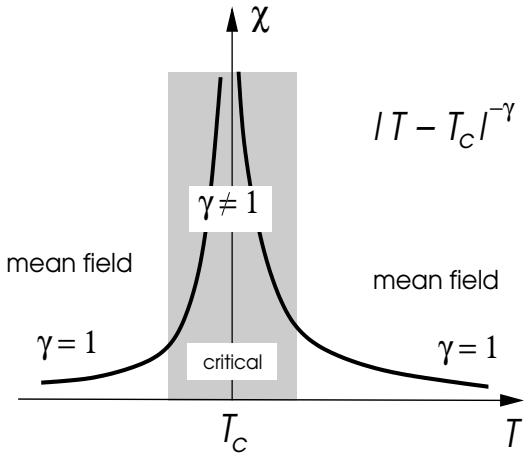

Figure 5.7: Critical region.

This equation has two regimes. For large χ the second term on the right hand side is dominating over χ^{-1}. On the other hand, if χ is small, χ^{-1} is dominant. The first case applies for T very close to T_c^* such that we arrive at the behavior

$$\chi(T) \propto |T - T_c^*|^{-\gamma} \qquad \text{with} \quad \gamma = \frac{2}{d-2} \; . \tag{5.115}$$

Away from T_c^* the second case holds and we return back to the usual mean field behavior,

$$\chi(T) \propto |T - T_c^*|^{-1} \; . \tag{5.116}$$

The crossover happens roughly at the boundary defined by the Ginzburg criterion. It is now also obvious that the critical exponent γ depends on the dimension. The critical dimensions $d_L = 2$ and $d_c = 4$ need a special care in this discussion as the expression we have obtained do not straightforwardly apply to them.
We can now also use this result to determine the exponent of the correlation length ν. We may use $\xi^2 = \kappa\chi$ such that we find immediately

$$\nu = \frac{\gamma}{2} \; . \tag{5.117}$$

5.6 Long-range order - Peierls' argument

We have seen in the previous section that the critical temperature is reduced from its mean field value by thermal fluctuations. The lower the dimension (the coordination number) the more severe thermal fluctuations act against order. We consider here the case of the Ising model in one and two dimensions. In one dimension no magnetic order is possible at any finite temperature, while in two dimensions there is a finite-temperature phase transition.

5.6.1 Absence of finite-temperature phase transition in the 1D Ising model

We consider the ground state of the ferromagnetic Ising chain. All spins are aligned. The lowest energy excitation is a domain wall for which the spins point up on the left and down on the right hand side of the domain wall. The energy for such a wall is $2Js^2$. With N spins on the Ising chain, there would be $N-1$ positions possible for this wall and would yield an entropy $S = k_B \ln(N-1)$ accounting for the uncertainty of the configuration of the state. Therefore a simple estimate of the free energy for the presence of a domain wall leads to

$$\Delta F = 2Js^2 - k_B T \ln(N-1) \; . \tag{5.118}$$

Taking now the thermodynamic limit $N \to \infty$ would yield for any finite temperature a negative ΔF such that the ordered phase (without domain wall) would be unfavorable.

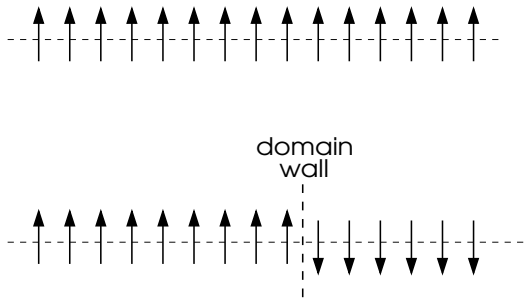

Figure 5.8: Domain wall as the lowest excitation.

In the one-dimensional Ising chain long-range order exists only at zero temperature analogously to the classical spin chain discussed earlier.

5.6.2 Long-range order in the 2D Ising model

The argument given by Peierls to proof long-range order for the 2D Ising model is also based on domains. We consider a square lattice and assume that all spins at the boundary are pointing up. This requirement is not relevant, if the thermodynamic limit is considered, i.e. the number of site or spins $N \to \infty$. However, it implies that all domain walls on the lattice are closed. The energy cost for a domain wall of the length L compared to the completely aligned configuration is

$$E(L) = 2Js^2 L \; . \tag{5.119}$$

Now choose a site j somewhere in the interior of the system. We define $P_\pm$ as the probability that this spin s_j is $\pm s$. Thus the mean value of the spin is

$$\langle s_j \rangle = s(P_+ - P_-) \tag{5.120}$$

where in the case of long range order $\langle s_j \rangle > 0$ due to the boundary condition. Moreover the correlation function satisfies for $|i - j| \to \infty$,

$$\langle s_i s_j \rangle \to \langle s_i \rangle \langle s_j \rangle = s^2 (P_+ - P_-)^2 \tag{5.121}$$

which is finite for the long-range ordered system, if $P_+ \neq P_-$. Thus our proof has to address this point.
In case $s_j = -s$ we find an odd number of domain walls encircling the site j. The relative probability that the shortest domain wall around j (closest to site j) has the length L is given by

$$P_{L,j} = \frac{e^{-KL}}{Z} \sum_{L'} e^{-KL'} \tag{5.122}$$

where the sum $\sum_{L'}$ runs over all other domain walls and $K = 2\beta J s^2$. If we consider $s_j = +s$ this shortest domain wall is absent. Thus we may write

$$P_+ = \frac{1}{Z} \sum_{L'} e^{-KL'} \qquad \text{and} \qquad P_- = \sum_L g(L) e^{-KL} P_+ \; . \tag{5.123}$$

Here $g(L)$ is the number of domain wall shapes of length L around j.

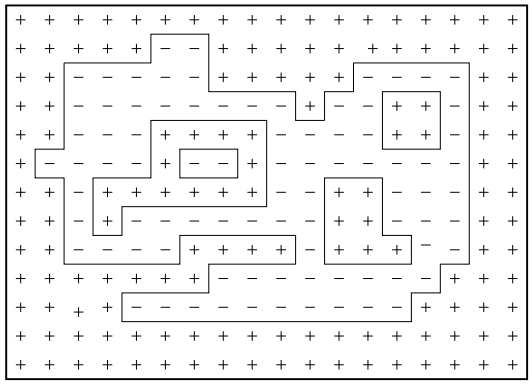

Figure 5.9: Domain wall configurations.

From topological point of view the domain wall should not cut itself. If we ignore this condition and in addition the requirement that the domain wall is closed, we can derive a simple upper bound for $g(L)$,

$$g(L) < 4 \times 3^{L-1} \times \frac{1}{L} \times \frac{1}{2} \times \left(\frac{L}{4}\right)^2 = \frac{L^2}{24L} e^{L \ln 3} \ , \tag{5.124}$$

which can be understood as a walk of length L through the lattice. From the starting point, we may start in 4 directions and every following step has 3 possible directions. On the contour there are L equivalent starting points (assuming close contour) and 2 directions. Then there are maximally $(L/4)^2$ sites enclosed by the domain and the starting point may be shift on any of them (for given circumference the square has the largest area among all rectangles). Therefore we can write

$$P_- < \sum_{L \geq 4} \frac{L^2}{24L} e^{L(\ln 3 - K)} P_+ < \sum_{L=4,6,8,\ldots} \frac{L^2}{96} e^{L(\ln 3 - K)} \tag{5.125}$$

since $P_+ < 1$. For sufficiently low temperature $\ln 3 - K = \ln 3 - 2Js^2\beta < 0$ so that the sum converges very well. By making the temperature small enough, also the condition $P_- < \frac{1}{2}$ can be reached. With the condition $P_+ + P_- = 1$ it follows that

$$P_+ - P_- > 0 \qquad \Rightarrow \qquad \lim_{|i-j| \to \infty} \langle s_i s_j \rangle = const. \tag{5.126}$$

which means that we have long- range order at a finite temperature.

Chapter 6

Superfluidity

Only the nobel gas Helium remains a liquid down to zero temperature at ambient pressure. After liquefaction it is a quantum liquid which involves two isotopes, with bosonic (fermionic) character for ^{4}He (^{3}He). Note that the nucleus of ^{4}He consists of two protons and two neutrons, resulting in a boson, while ^{3}He has only one neutron and forms a fermionic atom. Only under pressure eventually solidification occurs (Fig. 6.1). Both quantum liquids undergo a phase transition to the miraculous state of superfluidity, characterized by the frictionless or dissipationless flow of the fluid through constrictions and narrow capillaries, beside a few other amazing properties. Considering their phase diagrams in Fig.6.1, we recognize a profound difference for the superfluid phase between ^{4}He (left panel) and ^{3}He (right panel). The bosonic atoms undergo a Bose-Einstein condensation to become a superfluid below $T_\lambda \approx 2.18$K at ambient pressure. The fermionic atoms, on the other hand, become superfluid only around 10^{-3}K, when they form so-called Cooper pairs, in many aspects resembling the superconducting phase of electrons. Here we will discuss only the case of superfluid ^{4}He.

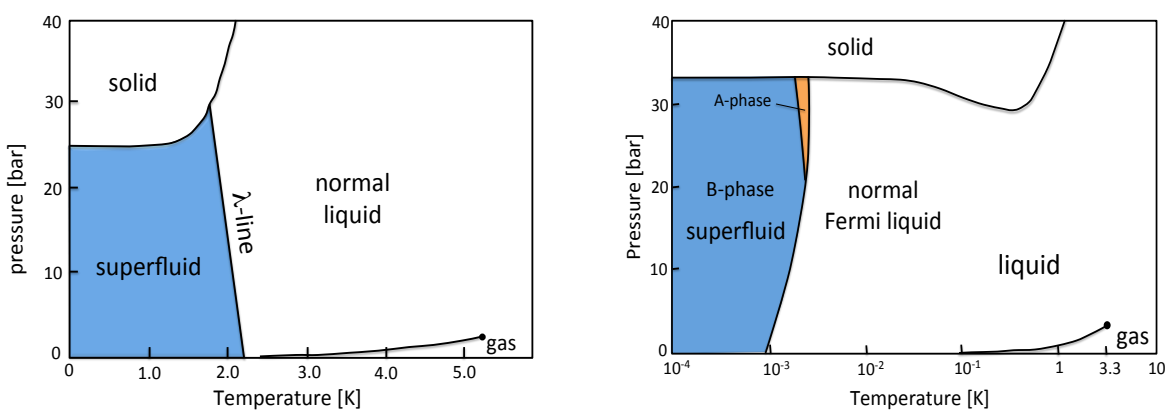

Figure 6.1: Phase diagrams of Helium. Left panel: bosonic ^{4}He. Right panel: fermionic ^{3}He. Note the logarithmic temperature scale in the right panel. While ^{4}He has one superfluid phase, there are two, the A- and B-phase, for ^{3}He.

6.1 Quantum liquid Helium

We consider now the quantum liquid ^{4}He.[1] The first question we ask is why Helium remains liquid even in its ground state. A classical system of interacting particles would form a solid

[1]The quantum liquid ^{3}He is a so-called Fermi liquid well described by Landau's phenomenological theory based on the concept of fermionic quasiparticles. This concept can be extended to other interacting fermions, most notably to electrons in metals, as will be discussed in the course "Solid State Theory".

lattice in order to minimize the potential energy, as the kinetic energy vanishes at zero temperature. This is not the case when we consider quantum particles which are subject to zero-point motion. Let us consider here a simple argument on why Helium is liquid while other noble gases solidify.

The interaction between Helium atoms consists of two components. There is a strongly repulsive interaction on short range, since the closed electron shells (two 1s electrons) repel each other when the atoms come close. On long distances the atoms attract each other through the rather weak van der Waals force. A good fit of the potential is given by[2]

$$V(r) = Ae^{-r/r_1} - B\left(\frac{r_2}{r}\right)^6 \tag{6.1}$$

with $A = 489\text{eV}$, $B = 9.3 \times 10^{-5}\text{eV}$, $r_1 = 0.22$ Å and $r_2 = 4.64$ Å. Qualitatively this resembles the Lenard-Jones potential we introduced earlier, with a negative minimum and a vanishing potential for large distances r. It has a minimum at $r_0 \approx 3$Å with a potential energy $V = -7.8 \times 10^{-4}\text{eV}$. The mean distance between Helium atoms towards zero temperature at ambient pressure is $d \approx 4.4$Å. Assuming that Helium is a solid with this lattice constant, the condition for melting is that position fluctuations of the atoms acquire a "considerable" fraction of the lattice spacing d. The Lindemann criterion for melting request the mean displacement of the atom from its equilibrium position,

$$\frac{\Delta r}{d} \leq L_m \qquad \text{with} \qquad L_m \approx 0.1\ , \tag{6.2}$$

such that for the solid the atom would have to be confined with a range of linear size $\Delta r \approx 0.5$Å. Taking Heisenberg's uncertainty principle, $\Delta r \times \Delta p \approx \hbar$ we obtain for the zero-point energy,

$$\Delta E = \frac{\Delta p^2}{2m} \approx \frac{1}{2m}\left(\frac{\hbar}{\Delta r}\right)^2 \approx 8.6 \times 10^{-4}\text{eV}\ , \tag{6.3}$$

which is slightly larger than the potential depth. Thus, the Helium atoms dissociate due to the zero-point motion. Only pressure beyond 25 bar opens the way to solidifications at low temperatures ($T < 5$K). We encounter "quantum melting" at very low temperatures, when we lower the pressure isothermally through the critical pressure $p_c \sim 25$bar (see also in Sect. 3.7.3). Classical thermally driven melting is observed for isobar increase of temperature from the solid phase with the pressure clearly above 25 bar.

6.1.1 Superfluid phase

Around $T_\lambda \approx 2.17$K the quantum liquid undergoes a phase transition between a normal and superfluid phase. This transition is called "λ-transition" due to the peculiar shape of the specific heat as a function of temperature. (Fig.6.2). There is an obvious similarity with the specific heat of bosons as shown in Fig.2.6, which suggest that the superfluid phase is based on Bose-Einstein condensation. There are, however, also clear differences such as the low-temperature behavior of the specific heat, which has a power law $T^{3/2}$ for the ideal Bose gas and T^3 for ^{4}He. This is connected with the difference in the excitation spectrum.

We examine here the property of a superfluid to flow frictionless. First we ask the question whether the ideal Bose-Einstein condensate is a superfluid. For this purpose we study an ideal Bose gas of particles flowing in a capillary tube with a velocity $-\vec{v}$ relative to the capillary walls. We can view the same situation in the rest frame of the superfluid, such that the tube is moving with velocity $\vec{v}$. The former inertial system we call K', the latter K. Then the following relations for the momentum and energy of the superfluid hold,

$$\begin{aligned} K: &\quad \vec{P} && E \\ K': &\quad \vec{P}\,' = \vec{P} - M\,\vec{v} && E' = E - \vec{P}\cdot\vec{v} + \frac{M}{2}\,\vec{v}^{\,2} \end{aligned} \tag{6.4}$$

[2]Reference: J.C. Slater and J.G. Kirkwood, Phys. Rev. 37, 682 (1931).

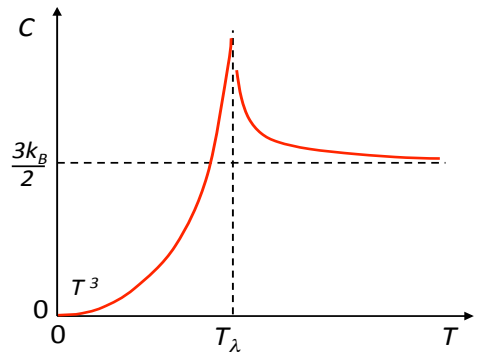

Figure 6.2: Specific heat at the superfluid transition T_λ.

where M is the total mass of all particles of the superfluid. Initially all particles have the same velocity $\vec{v}$ such that $\vec{P} = 0$ and $E = 0$ in system K (rest frame of superfluid). Let us assume one particle scatters with the wall and transfers the momentum $\vec{p}$ to the wall. Such an excitation of the superfluid costs the energy $\epsilon(\vec{p})$, viewed in system K. For this situation we obtain $E = \epsilon(\vec{p})$ and $\vec{P} = -\vec{p}$. Thus, the energy difference between the initial and the final state in the rest frame of the superfluid, K', is given by

$$\Delta E' = \epsilon(\vec{p}) + \vec{p} \cdot \vec{v} \ . \tag{6.5}$$

The minimal energy drop is obtained by choosing $\vec{p}$ antiparallel to $\vec{v}$, such that the superfluid overall slows down. The scattering process can only happen, if the energy of the superfluid is reduced, $\Delta E' < 0$. For an ideal Bose gas the energy of an excitation is given by $\epsilon(\vec{p}) = \vec{p}^{\,2}/2m$. There is always a momentum $\vec{p}$ with

$$\Delta E' = \frac{\vec{p}^{\,2}}{2m} + \vec{p} \cdot \vec{v} = \frac{p2}{2m} - vp < 0 \qquad \Rightarrow \qquad p < 2mv \ . \tag{6.6}$$

Consequently the condensed ideal Bose gas is not a superfluid and is subject to friction, as we can always find a scattering channel which slows the superfluid down by transferring momentum to the capillary.

Real Bose gases have interaction. This leads in the superfluid phase to a different form of elementary excitations with a linear dispersion,

$$\epsilon(\vec{p}) = c_s |\vec{p}| = c_s p \ , \tag{6.7}$$

corresponding to a sound-like excitation. Inserting this in Eq.(6.6) we find that the inequality can only be satisfied for $v \geq c_s$. Therefore there is a critical velocity v_c below which the fluid flows frictionless (dissipationless).

The real excitation spectrum of the superfluid has a more complex structure as shown in Fig. 6.3. At small energy and momentum the spectrum is linear as assumed above. However, with growing momentum it turns non-monotonic with a local minimum around p_0. This part of the spectrum is called *roton*. For these two parts of $\epsilon(p)$ we write

$$\epsilon(p) = \begin{cases} c_s p & p \ll p_0 \\ \Delta + \dfrac{(p-p_0)^2}{2m^*} & p \approx p_0 \end{cases} \tag{6.8}$$

where for ^{4}He the parameters are

$$c_s = 240\,\mathrm{ms}^{-1} \ , \quad \frac{p_0}{\hbar} = 1.9\,\text{Å}^{-1} \ , \quad \frac{\Delta}{k_B} = 8.7\,\mathrm{K} \ , \quad m^* = 0.16\,m_{\mathrm{He}} \ . \tag{6.9}$$

The critical velocity is now given by the lowest possible excitation within Eq.(6.5), corresponding to the dashed line in Fig.6.3,

$$v_c \approx \frac{\epsilon(p_0)}{p_0} = \frac{\Delta}{p_0} = 60\,\mathrm{ms}^{-1}\,. \tag{6.10}$$

Note that the roton minimum is a precursor of solid He. Under pressure Δ shrinks and eventually

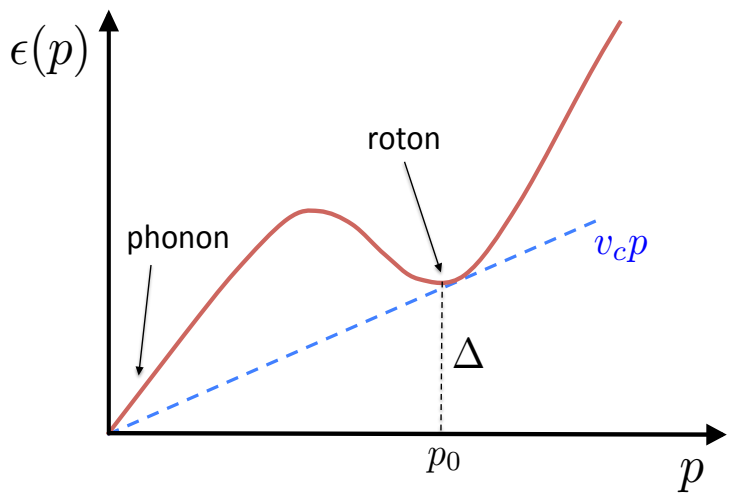

Figure 6.3: Spectrum of a real superfluid with a linear sound-like behavior at low energy and a local minimum around p_0, the rotons. The dashed line ($v_c p$) indicates the maximal velocity of the superfluid to sustain frictionless flow, i.e. flow without generating elementary excitations which would lead to a slow down.

reaches zero at a critical pressure where the rotons condense forming a coherent state with specific momentum corresponding to a crystalline (hexagonal closed packed) lattice.

6.1.2 Collective excitations - Bogolyubov theory

In this section we discuss the low-energy excitations of a Bose gas of weakly interacting particles. For this purpose we follow the theory developed by Bogolyubov. We write the Hamiltonian in the second-quantization language for spinless bosons,

$$\mathcal{H} = \mathcal{H}_{\mathrm{kin}} + \mathcal{H}_{\mathrm{int}} \tag{6.11}$$

with

$$\begin{aligned} \mathcal{H}_{\mathrm{kin}} &= \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu)\hat{a}^{\dagger}_{\vec{k}}\hat{a}_{\vec{k}} \\ \mathcal{H}_{\mathrm{int}} &= \frac{1}{2}\int d^3r\, d^3r'\; \widehat{\Psi}^{\dagger}(\vec{r})\,\widehat{\Psi}^{\dagger}(\vec{r}\,')V(\vec{r}-\vec{r}\,')\,\widehat{\Psi}(\vec{r}\,')\,\widehat{\Psi}(\vec{r}) \end{aligned} \tag{6.12}$$

where $\epsilon_{\vec{k}} = \hbar^2\vec{k}^{\,2}/2m$ and $V(\vec{r}-\vec{r}\,') = U\delta(\vec{r}-\vec{r}\,')$ denotes a contact interaction, i.e. the particles repel each other when they are on the same position. We transform the interaction part into the occupation number representations using Eq.(3.35),

$$\mathcal{H}_{\mathrm{int}} = \frac{U}{2\Omega}\sum_{\vec{k},\vec{k}\,',\vec{q}} \hat{a}^{\dagger}_{\vec{k}+\vec{q}}\hat{a}^{\dagger}_{\vec{k}\,'-\vec{q}}\hat{a}_{\vec{k}\,'}\hat{a}_{\vec{k}}\,. \tag{6.13}$$

Now we turn to the Bogolyubov approximation introduced in Sect. 3.7.2, by identifying the $\hat{a}^{\dagger}_0$ and $\hat{a}_0$ by $\sqrt{N_0}$ (phase $\phi = 0$ for simplicity). This is justified when $N_0 \gg N - N_0$. We can

then approximate the Hamiltonian by keeping only the leading terms in N_0 obtained through the following combinations of momenta:

$\vec{k}\,,\,\vec{k}\,',\,\vec{q}$	$\hat{a}^\dagger_{\vec{k}+\vec{q}}\hat{a}^\dagger_{\vec{k}\,'-\vec{q}}\hat{a}_{\vec{k}\,'}\hat{a}_{\vec{k}}$	$\vec{k}\,,\,\vec{k}\,',\,\vec{q}$	$\hat{a}^\dagger_{\vec{k}+\vec{q}}\hat{a}^\dagger_{\vec{k}\,'-\vec{q}}\hat{a}_{\vec{k}\,'}\hat{a}_{\vec{k}}$
$\vec{k}\,=\,\vec{k}\,'=\,\vec{q}\,=0$	N_0^2	$\vec{k}\,=\,\vec{k}\,'=0,\;\vec{q}\,\neq 0$	$N_0\hat{a}^\dagger_{\vec{q}}\hat{a}^\dagger_{-\vec{q}}$
$\vec{q}\,=-\vec{k}\,\neq 0,\,\vec{k}\,'=0$	$N_0\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}$	$\vec{q}\,=\,\vec{k}\,'\neq 0,\,\vec{k}\,=0$	$N_0\hat{a}^\dagger_{\vec{k}\,'}\hat{a}_{\vec{k}\,'}$
$\vec{k}\,=-\vec{k}\,'=-\vec{q}\,\neq 0$	$N_0\hat{a}_{\vec{k}}\hat{a}_{-\vec{k}}$	$\vec{q}\,=\,\vec{k}\,=0,\,\vec{k}\,'\neq 0$	$N_0\hat{a}^\dagger_{\vec{k}\,'}\hat{a}_{\vec{k}\,'}$
$\vec{q}\,=\,\vec{k}\,'=0,\,\vec{k}\,\neq 0$	$N_0\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}$		

Terms of order $N_0^{3/2}$ do not exist and terms of order $N_0^{1/2}$ and lower in N_0 are neglected. Collecting these terms we obtain to this order,

$$\begin{aligned}\mathcal{H}' \;&=-\mu N_0+\frac{UN_0^2}{2\Omega}+\sum_{\vec{k}\neq 0}\left\{\epsilon_{\vec{k}}-\mu+\frac{UN_0}{\Omega}\right\}\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\\ &+\frac{UN_0}{2\Omega}\sum_{\vec{k}\neq 0}\left\{\hat{a}^\dagger_{\vec{k}}\hat{a}^\dagger_{-\vec{k}}+\hat{a}_{-\vec{k}}\hat{a}_{\vec{k}}+\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}+\hat{a}^\dagger_{-\vec{k}}\hat{a}_{-\vec{k}}\right\}\;.\end{aligned} \tag{6.14}$$

The requirement that the total particle number remains constant at lowest temperature leads to $\mu = Un_0$,

$$\mathcal{H}'=-N_0\frac{Un_0}{2}+\frac{1}{2}\sum_{\vec{k}\neq 0}\left[\left\{\epsilon_{\vec{k}}+Un_0\right\}(\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}+\hat{a}^\dagger_{-\vec{k}}\hat{a}_{-\vec{k}})+Un_0(\hat{a}^\dagger_{\vec{k}}\hat{a}^\dagger_{-\vec{k}}+\hat{a}_{-\vec{k}}\hat{a}_{\vec{k}})\right]\;. \tag{6.15}$$

This Hamiltonian has a single-particle form, but does not conserve the number of particles, as terms like $\hat{a}_{-\vec{k}}\hat{a}_{\vec{k}}$ and $\hat{a}^\dagger_{\vec{k}}\hat{a}^\dagger_{-\vec{k}}$ describe how particles from excited states are absorbed by the condensate and emitted from the condensate, respectively. We search a set of bosonic annihilation and creation operators which *diagonalize* this Hamiltonian into a form

$$\mathcal{H}'=\frac{1}{2}\sum_{\vec{k}\neq 0}E_{\vec{k}}(\hat{\gamma}^\dagger_{\vec{k}}\hat{\gamma}_{\vec{k}}+\hat{\gamma}^\dagger_{-\vec{k}}\hat{\gamma}_{-\vec{k}})+E_0-\mu N_0\;. \tag{6.16}$$

where the operators $\hat{\gamma}^\dagger_{\vec{k}}$ ($\hat{\gamma}_{\vec{k}}$) create (annihilate) independent *Bogolyubov quasiparticles*. The following *Bogolyubov transformation* allows us to reach this form,

$$\hat{a}_{\vec{k}}=\hat{\gamma}_{\vec{k}}u_{\vec{k}}-\hat{\gamma}^\dagger_{-\vec{k}}v_{\vec{k}}\qquad\text{and}\qquad\hat{a}_{-\vec{k}}=\hat{\gamma}_{-\vec{k}}u_{\vec{k}}-\hat{\gamma}^\dagger_{\vec{k}}v_{\vec{k}}\;, \tag{6.17}$$

where the new operators satisfy the relation,

$$[\hat{\gamma}_{\vec{k}},\hat{\gamma}^\dagger_{\vec{k}}]=[\hat{\gamma}_{-\vec{k}},\hat{\gamma}^\dagger_{-\vec{k}}]=1\quad\Rightarrow\quad[\hat{a}_{\vec{k}},\hat{a}^\dagger_{\vec{k}}]=u^2_{\vec{k}}-v^2_{\vec{k}}=1\;. \tag{6.18}$$

The diagonalization leads to

$$E_{\vec{k}}=\sqrt{\epsilon^2_{\vec{k}}+2Un_0\epsilon_{\vec{k}}}\qquad\text{and}\qquad E_0=\frac{1}{2}\sum_{\vec{k}\neq 0}\left[E_{\vec{k}}-\epsilon_{\vec{k}}-Un_0\right]-N_0\frac{Un_0}{2} \tag{6.19}$$

and the transformation coefficients,

$$\left.\begin{aligned} u_{\vec{k}} &= \frac{1}{\sqrt{1-\chi_{\vec{k}}^2}} \\ v_{\vec{k}} &= \frac{\chi_{\vec{k}}}{\sqrt{1-\chi_{\vec{k}}^2}} \end{aligned}\right\} \quad \Rightarrow \quad \left\{\begin{aligned} \chi_{\vec{k}} &= 1 + \frac{\epsilon_{\vec{k}}}{Un_0} - \sqrt{\left(1+\frac{\epsilon_{\vec{k}}}{Un_0}\right)^2 - 1} \\ &= 1 + \frac{\epsilon_{\vec{k}}}{Un_0} - \frac{E_{\vec{k}}}{Un_0} \, . \end{aligned}\right. \tag{6.20}$$

The spectrum of the elementary excitations is linear in the small momentum limit, $\vec{k} \to 0$,

$$E_{\vec{k}} \approx c_s p = \sqrt{\frac{Un_0}{m}}\hbar k \, , \tag{6.21}$$

corresponding to a phonon spectrum of compressive waves. Thus, for small $\vec{k}$ the Bogolyubov quasiparticles represent phonons. In the large momentum region, $\epsilon_{\vec{k}} \gg Un_0$ the spectrum merges gradually with $\epsilon_{\vec{k}}$,

$$E_{\vec{k}} \approx \epsilon_{\vec{k}} + Un_0 \tag{6.22}$$

with a shift of Un_0 (see Fig.6.4). In $E_{\vec{k}}$ rotons are not included as they are beyond the simple approximation applied here. Therefore, within the Bogolyubov theory the critical velocity is determined by the slope of the phonon spectrum, i.e. by the speed of sound,

$$v_c = c_s = \sqrt{\frac{Un_0}{m}} \tag{6.23}$$

which is higher than the real v_c discussed above. The constant E_0 is the ground state energy.

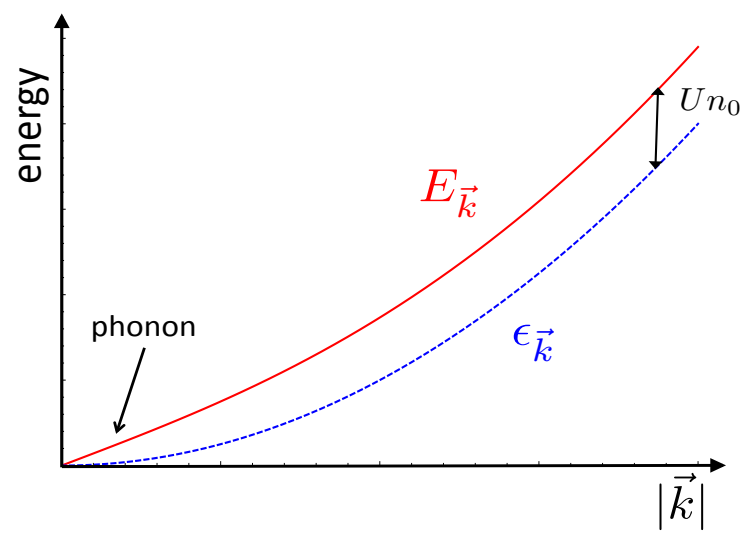

Figure 6.4: Spectrum of the Bogolyubov quasiparticles in Eqs.(6.16) and (6.19). The solid line displays $E_{\vec{k}}$ with a linear dispersion for small momenta $\vec{p} = \hbar\vec{k}$ and the dashed line shows $\epsilon_{\vec{k}}$. There are no rotons in this simple approach.

Note that in the approximation done here the sum in E_0 diverges at large $\vec{k}$. This is an artefact of taking the potential as an infinitely sharp contact interaction, i.e. U is independent of $\vec{k}$. [3]

[3] *Groundstate energy:* It is rather easy to see that in the large-$\vec{k}$ limit the integrand in E_0 (Eq.(6.19)) behaves like

$$E_{\vec{k}} - \epsilon_{\vec{k}} - Un_0 \to -\frac{m(Un_0)^2}{p^2} \, , \tag{6.24}$$

Now we turn to the condensate fraction of the interacting system. How many particles condense? This can be straightforwardly calculated,

$$n_0 = n - \frac{1}{\Omega}\sum_{\vec{k}\neq 0}\langle \hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\rangle \ . \tag{6.26}$$

This is advantageous when we want to calculate now mean values for which we insert the Bogolyubov transformation in Eq.(6.17),

$$\begin{aligned}\langle \hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\rangle &= \langle(\hat{\gamma}^\dagger_{\vec{k}}u^*_{\vec{k}} - \hat{\gamma}_{-\vec{k}}v^*_{\vec{k}})(\hat{\gamma}_{\vec{k}}u_{\vec{k}} - \hat{\gamma}^\dagger_{-\vec{k}}v_{\vec{k}})\rangle \\ &= |u_{\vec{k}}|^2\langle\hat{\gamma}^\dagger_{\vec{k}}\hat{\gamma}_{\vec{k}}\rangle + |v_{\vec{k}}|^2\langle\hat{\gamma}_{-\vec{k}}\hat{\gamma}^\dagger_{-\vec{k}}\rangle - u^*_{\vec{k}}v_{\vec{k}}\langle\hat{\gamma}^\dagger_{\vec{k}}\hat{\gamma}^\dagger_{-\vec{k}}\rangle - u_{\vec{k}}v^*_{\vec{k}}\langle\hat{\gamma}_{-\vec{k}}\hat{\gamma}_{\vec{k}}\rangle \ .\end{aligned} \tag{6.27}$$

Then we use the fact that the Bogolyubov quasiparticles are independent, described by the Hamiltonian in Eq.(6.16),

$$\begin{aligned}&\langle\hat{\gamma}^\dagger_{\vec{k}}\hat{\gamma}_{\vec{k}}\rangle = \frac{1}{e^{\beta E_{\vec{k}}}-1}\ , \quad \langle\hat{\gamma}_{-\vec{k}}\hat{\gamma}^\dagger_{-\vec{k}}\rangle = 1 + \langle\hat{\gamma}^\dagger_{-\vec{k}}\hat{\gamma}_{-\vec{k}}\rangle = 1 + \frac{1}{e^{\beta E_{\vec{k}}}-1}\ , \\ &\langle\hat{\gamma}_{-\vec{k}}\hat{\gamma}_{\vec{k}}\rangle = \langle\hat{\gamma}^\dagger_{\vec{k}}\hat{\gamma}^\dagger_{-\vec{k}}\rangle = 0\ .\end{aligned} \tag{6.28}$$

Note that $E_{\vec{k}} = E_{-\vec{k}}$. The momentum distribution of the bosons for $\vec{k}\neq 0$ is obviously,

$$n_{\vec{k}} = \langle\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\rangle = (|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2)\frac{1}{e^{\beta E_{\vec{k}}}-1} + |v_{\vec{k}}|^2 = \frac{1+\chi^2_{\vec{k}}}{1-\chi^2_{\vec{k}}}\frac{1}{e^{\beta E_{\vec{k}}}-1} + \frac{\chi^2_{\vec{k}}}{1-\chi^2_{\vec{k}}}\ . \tag{6.29}$$

The first term vanishes at $T=0$ while the second remains finite. Thus, unlike for the ideal Bose gas for which all particles condense into the $\vec{k}=0$ state, here we have an interaction induced reduction. Let us discuss this aspect. The zero-temperture distribution function has the following behavior,

$$\langle\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\rangle_{T=0} = \frac{\chi^2_{\vec{k}}}{1-\chi^2_{\vec{k}}} \approx \begin{cases} \dfrac{\sqrt{mUn_0}}{2\hbar k} & \hbar k \ll \sqrt{2mUn_0} \\[2ex] \dfrac{(mUn_0)^2}{4(\hbar k)^4} & \hbar k \gg \sqrt{2mUn_0}\end{cases} \tag{6.30}$$

which represents the depletion of the condensate due to particle-particle interaction. We calculate now the total reduction of n_0 at $T=0$ integrating over all $\vec{k}$,

$$n_0 = n - \frac{1}{\Omega}\sum_{\vec{k}\neq 0}\frac{\chi^2_{\vec{k}}}{1-\chi^2_{\vec{k}}} = n - \int\frac{d^3k}{(2\pi)^3}\frac{\chi^2_{\vec{k}}}{1-\chi^2_{\vec{k}}} = n - \frac{1}{3\pi^2}\left(\frac{mUn_0}{\hbar^2}\right)^{3/2} \tag{6.31}$$

which is valid only for sufficient weak interactions. This can be measured in terms of the characteristic length ξ, defined as

$$\frac{\hbar^2 k'^2}{2m} = Un_0 \quad \text{with} \quad k'\xi = 1 \quad \Rightarrow \quad \xi^2 = \frac{\hbar^2}{2mUn_0} \tag{6.32}$$

---

and leads to a divergence of the sum. A careful and more extensive analysis of the problem shows that this singular part can be extracted such that the renormalised ground state energy is given by

$$E_0' = \sum_{\vec{k}\neq 0}\left[E_{\vec{k}} - \epsilon_{\vec{k}} - Un_0 + \frac{m(Un_0)^2}{p^2}\right] + N_0\frac{Un_0}{2} = N_0\frac{Un_0}{2}\left[1 + \frac{16}{15\pi^2 n_0}\left(\frac{Un_0 m}{\hbar^2}\right)^{3/2}\right]\ . \tag{6.25}$$

The approximation for the ground state energy used here relies on the assumption that we are dealing with a Bose gas. This is, however, not guaranteed even for weak interactions.

which leads to the condition

$$3\pi^2 n \gg \left(\frac{mUn_0}{\hbar^2}\right)^{3/2} \qquad \Rightarrow \qquad n\xi^3 \gg 1\ . \tag{6.33}$$

The characteristic length is much larger than the mean distance between particles.
If we apply the same scheme to a one-dimensional interacting Bose gas, we find that the integral

$$\int \frac{dk}{2\pi} \frac{\chi^2_{\vec{k}}}{1-\chi^2_{\vec{k}}} \quad \longrightarrow \quad \infty \tag{6.34}$$

diverges due to the k^{-1} dependence of the integrand for small k (see Eq.(6.30). This leads to the conclusion that in one dimension quantum fluctuations destroy the Bose-Einstein condensate, as soon as interaction is present.
The phonon spectrum determines the low-temperature behavior of the superfluid. Let us consider the heat capacity as an example. For this purpose we calculate the low-temperature internal energy through the Hamiltonian $\mathcal{H}'$ in Eq.(6.16),

$$U = \langle \mathcal{H}' \rangle = E_0 - \mu N_0 + \sum_{\vec{k}\neq 0} E_{\vec{k}} \langle \hat{\gamma}^\dagger_{\vec{k}} \hat{\gamma}_{\vec{k}} \rangle = E_0 - \mu N_0 + \sum_{\vec{k}\neq 0} \frac{E_{\vec{k}}}{e^{\beta E_{\vec{k}}}-1} \approx N \frac{\pi^2}{30n} \left(\frac{m}{Un_0\hbar^2}\right)^{3/2} (k_B T)^4 \tag{6.35}$$

for $k_B T \ll Un_0$. The heat capacity is then

$$C = \frac{dU}{dT} = N \frac{2\pi^2}{15n} k_B \left(\frac{m}{Un_0\hbar^2}\right)^{3/2} (k_B T)^3 \tag{6.36}$$

which is different from the Bose-Einstein condensate with $C \propto T^{3/2}$.

6.1.3 Gross-Pitaevskii equations

We would like to introduce now a description of the Bose-Einstein condensate which allows us to take also spatial variations into account. For this purpose we write the Hamiltonian of interacting bosons entirely in the language of field operators,

$$\begin{aligned} \mathcal{H} \ &= \int d^3r \left\{ \frac{\hbar^2}{2m} (\vec{\nabla}\, \widehat{\Psi}^\dagger(\vec{r}))(\vec{\nabla}\, \widehat{\Psi}(\vec{r})) + [V(\vec{r}) - \mu]\, \widehat{\Psi}^\dagger(\vec{r})\, \widehat{\Psi}(\vec{r}) \right\} \\ &+ \frac{1}{2} \int d^3r\, d^3r'\ \widehat{\Psi}^\dagger(\vec{r})\, \widehat{\Psi}^\dagger(\vec{r}))U\delta(\vec{r} - \vec{r}')\, \widehat{\Psi}(\vec{r})\, \widehat{\Psi}(\vec{r}) \end{aligned} \tag{6.37}$$

where $V(\vec{r})$ is a potential (shifted by the chemical potential μ) acting on the bosons which are interacting by a contact interaction. We derive now the equation of motion for the field operator,

$$i\hbar \frac{\partial}{\partial t} \widehat{\Psi}(\vec{r},t) = [\widehat{\Psi}(\vec{r},t), \mathcal{H}] = \left[-\frac{\hbar^2 \vec{\nabla}^2}{2m} + V(\vec{r}) - \mu + U\, \widehat{\Psi}^\dagger(\vec{r},t)\, \widehat{\Psi}(\vec{r},t) \right] \widehat{\Psi}(\vec{r},t)\ . \tag{6.38}$$

If the external potential varies very slowly or is even constant we will replace the field operator by the Bogolyubov approximation discussed in Sect. 3.7.2 and obtain the equation

$$i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r},t) = \left(-\frac{\hbar^2 \vec{\nabla}^2}{2m} + V(\vec{r}) - \mu + U|\psi_0(\vec{r},t)|^2 \right) \psi_0(\vec{r},t)\ , \tag{6.39}$$

which is called *Gross-Pitaevskii equation.* This equation is obtained by variation from the energy functional

$$E = \int d^3r\ \left[\frac{\hbar^2}{2m} |\vec{\nabla}\, \psi_0(\vec{r})|^2 + \{V(\vec{r}) - \mu\} |\psi_0(\vec{r})|^2 + \frac{U}{2} |\psi_0(\vec{r})|^4 \right] \tag{6.40}$$

through

$$i\hbar\frac{\partial}{\partial t}\psi_0(\vec{r},t) = \frac{\delta E}{\delta\psi_0(\vec{r},t)} \ . \tag{6.41}$$

We have also introduced the chemical potential μ which can be absorbed in the potential $V(\vec{r})$. In the homogeneous equilibrium (time independent) phase we require that $\psi_0(\vec{r}) = \sqrt{n_0}$ and fix $V(\vec{r}) = 0$. In order to get the right magnitude for $|\psi_0|$ we have to choose $\mu = Un_0$ as in Eq.(6.14).

Spatial variation:

Let us consider here some properties. First we address the characteristic length scale for the recovery of the equilibrium phase near a local perturbation. For this purpose we assume a small deviation,

$$\psi_0(\vec{r}) = \sqrt{n_0} + \eta(\vec{r}) \ , \tag{6.42}$$

with $|\eta(\vec{r})|^2 \ll n_0$. Inserted into the Gross-Pitaevskii equation (Eq.(6.39)) we obtain to linear order in $\eta(\vec{r})$,

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\eta(\vec{r}) + 2Un_0\eta(\vec{r}) = 0 \tag{6.43}$$

which yields the long distance behavior around a point-like perturbation,

$$\eta(\vec{r}) = \eta_0\frac{e^{-r/\sqrt{2}\xi}}{r} \qquad \text{with} \qquad \xi^2 = \frac{\hbar^2}{2mUn_0} \tag{6.44}$$

the same length as introduced in Eq.(6.32).

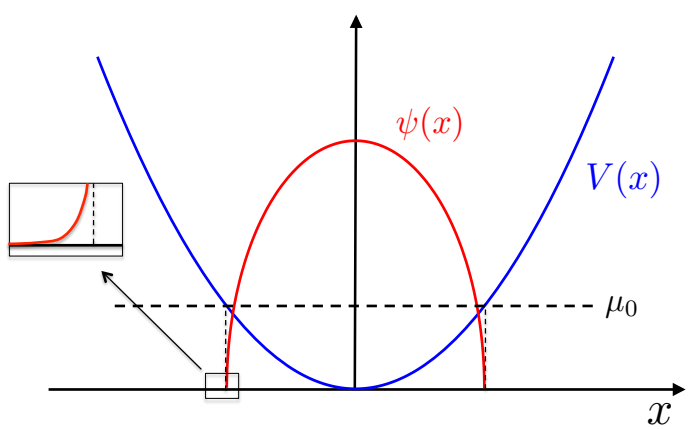

Figure 6.5: Bose-Einstein condensate trapped in a harmonic potential $V(x) \propto x^2$. The Thomas-Fermi approximation yields a condensate concentrated around the center of the potential well. Note that the approximation is only justified for large condensate densities ($n_0\xi^3 \gg 1$). Thus, near the region where the condensate density vanishes a more accurate analysis shows a smoother vanishing than the Thomas-Fermi approximation.

For very slow variations of the potential where the kinetic part (differential part) of the Gross-Pitaevskii equation can be neglected, the solution is rather simple,

$$\psi(\vec{r}) = n_0\left(\frac{\mu_0 - V(\vec{r})}{Un_0}\right)^{1/2} \tag{6.45}$$

with $\mu_0 = Un_0$ the chemical potential where $V(\vec{r}) = 0$. This is called the *Thomas-Fermi approximation*. The approximation breaks down when $|\psi(\vec{r})|$ approaches zero. Then the full problem has to be solved.

Continuity equation and currents:

We multiply now the Gross-Pitaevskii equation by $\psi_0^*(\vec{r},t)$ and subtract the complex conjugate of the resulting equation. From this we obtain,

$$\begin{aligned}\frac{\partial}{\partial t}|\psi_0(\vec{r},t)|^2 &= -\frac{\hbar}{2mi}[\psi_0^*(\vec{r},t)\vec{\nabla}^2\psi_0(\vec{r},t) - \psi_0(\vec{r},t)\vec{\nabla}^2\psi_0^*(\vec{r},t)] \\ &= -\vec{\nabla}\cdot\frac{\hbar}{2mi}[\psi_0^*(\vec{r},t)\vec{\nabla}\psi_0(\vec{r},t) - \psi_0(\vec{r},t)\vec{\nabla}\psi_0^*(\vec{r},t)]\end{aligned} \tag{6.46}$$

which we may rewrite as

$$\frac{\partial\rho(\vec{r},t)}{\partial t} + \vec{\nabla}\cdot\vec{j}(\vec{r},t) = 0 \quad \text{with} \quad \begin{cases} \rho(\vec{r},t) = |\psi_0(\vec{r},t)|^2 \\ \vec{j}(\vec{r},t) = \dfrac{\hbar}{2mi}[\psi_0^*(\vec{r},t)\vec{\nabla}\psi_0(\vec{r},t) - \psi_0(\vec{r},t)\vec{\nabla}\psi_0^*(\vec{r},t)]\,. \end{cases} \tag{6.47}$$

The current density is connected with the phase of the condensate wave function, $\psi(\vec{r}) = \sqrt{n_0}e^{i\phi(\vec{r})}$ when the condensate density is constant.

$$\vec{j}(\vec{r}) = \frac{\hbar}{m}n_0\vec{\nabla}\phi(\vec{r}) = n_0\vec{v}_s(\vec{r}) \tag{6.48}$$

which we use also to define the superfluid velocity $\vec{v}_s$. The energy of the homogeneous system ($V(\vec{r}) = 0$) is then given by

$$E(\vec{v}_s) = \Omega\left[\frac{m}{2}\vec{v}_s^{\,2}n_0 - \frac{Un_0^2}{2}\right] \tag{6.49}$$

with which we determine the critical velocity by $E(v_c) = 0$, i.e. there is no energy gain in forming a condensate. The critical current is obtained as $v_c = \sqrt{Un_0/m} = c_s$ as found in the Bogolyubov theory in Eq.(6.23).

Frictionless current and quantized vortices:

An important aspect of the condensate wave function is its property to be single-valued. This gives rise to spectacular properties, for example, for the current flow in a torus. In this multiply connected system the phase of the wave function can show a *winding* of the phase under the constraint that $\psi_0(\vec{r})$ has to match on a path around the torus. Thus the phase ϕ can only change by an integer multiple of 2π (de Broglie condition). If we assume a regular torus the current flow would be homogeneous with a constant velocity $|\vec{v}_s|$. We find that the circular integral of the velocity around the torus is quantized, because

$$\oint \vec{v}_s\cdot d\vec{s} = \frac{\hbar}{m}\oint\vec{\nabla}\phi\cdot d\vec{s} = \frac{\hbar}{m}2\pi n_\phi \tag{6.50}$$

with n_ϕ being an integer. Thus the current $j = n_0v_s$ can only take discrete values in the torus, such that a decay of current would mean an unwinding of the phase ϕ. This constitutes a frictionless flow of the superfluid as it will flow eternally.
A phase winding can occur within the superfluid also when the superfluid density forms a singularity, a zero along a line. The solution of the Gross-Pitaevskii equations then has form

$$\psi_0(r_\perp,\theta,z) = \sqrt{n_0}f(r_\perp)e^{i\theta n_\phi} \tag{6.51}$$

for zero line along the z-axis with $(r_\perp,\theta)$ being the cylindrical coordinates perpendicular to z. The function $f(r_\perp)$ goes to zero on the line $r_\perp = 0$ and recovers to 1 with the length scale ξ. This structure represents a vortex with winding number n_ϕ and is a topological defect in the superfluid. This means that it cannot be simply created or destroyed, but can only enter or leave

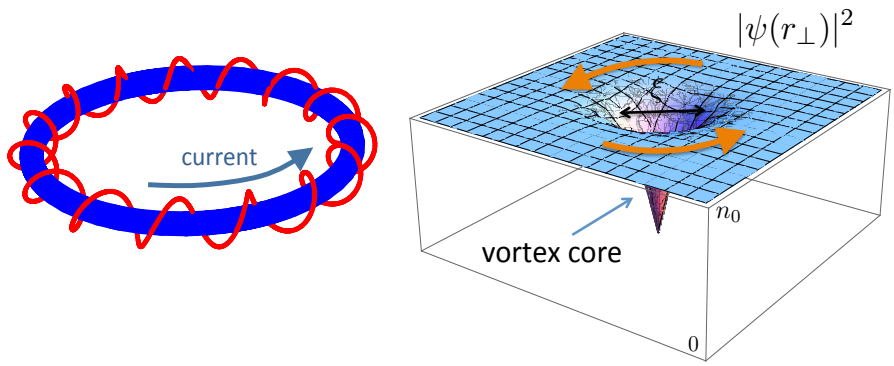

Figure 6.6: Phase winding and vortex: Left panel: phase winding (red line) around the torus leads to a current. As the phase has close the current is quantized. Right panel: Vortex structure of $|\psi(r_\perp)|^2$ with a core of linear extension $\sim \xi$.

the superfluid at the boundary. Two vortices with opposite winding numbers can annihilate each other.

The energy of a vortex consists of the core energy due to the local depletion of the condensate and the contribution of the circular flow of superfluid. The former can usually be neglected as it takes only of order of $E_{\rm core} \sim U n_0^2 \pi \xi^2/2 = \hbar^2 n_0 \pi/4m$ per unit length of the vortex. The latter, however, is larger. To be concrete we place the vortex along the rotation axis of a cylindrical vessel of radius R. Then the energy per unit length is given by

$$\Delta E = \int_\xi^R dr_\perp\, r_\perp \int_0^{2\pi} d\theta\, \frac{\hbar^2}{2m}\frac{1}{r_\perp^2}\left|\frac{\partial\psi(r_\perp,\theta)}{\partial\theta}\right|^2 + E_{\rm core} = \frac{\hbar^2 n_0}{2m} 2\pi n_\phi^2 \ln\left(\frac{R}{\xi}\right) + E_{\rm core}\,, \tag{6.52}$$

where the lower integral boundary of $r_\perp$ has been set to ξ as for the superfluid density is suppressed on smaller distances from the core. Indeed the amazing result is that the energy scales logarithmically with the system size, i.e. radius of the cylinder in our example, although the condensate density is only damaged on a comparatively small volume.

6.2 Berezinskii-Kosterlitz-Thouless transition

A peculiar behavior can be found in the two-dimensional superfluids, e.g. a ^{4}He film on a substrate. How does superfluid order establish in this case? We will see that due to phase fluctuations of the condensate wave function here a new type of phase transition appears.

6.2.1 Correlation function

First let us examine the correlation functions of the two-dimensional film. For the bosonic system we can do this the same way as we did previously in Sect.3.7.2. The correlation function is given

$$g(\vec{R}) = \langle \widehat{\Psi}^\dagger(\vec{r})\,\widehat{\Psi}(\vec{r}+\vec{R})\rangle\,. \tag{6.53}$$

In the high-temperature limit we have approximated the long-distance behavior by

$$\begin{aligned} g(\vec{R}) &= \int \frac{d^2k}{(2\pi)^2}\,\frac{e^{i\vec{k}\cdot\vec{R}}}{e^{\beta(\epsilon_{\vec{k}}-\mu)}-1} \approx \frac{2mk_BT}{\hbar^2}\int\frac{d^2k}{(2\pi)^2}\,\frac{e^{i\vec{k}\cdot\vec{R}}}{k^2+k_0^2} \\ &= \frac{2}{\lambda^2}K_0(k_0R) \approx \frac{1}{\lambda^2}\sqrt{\frac{2\pi}{k_0R}}e^{-k_0R} \end{aligned} \tag{6.54}$$

with $k_0^2 = -2m\mu/\hbar^2$, $\lambda = h/\sqrt{2\pi m k_B T}$ (thermal wavelength) and $K_0(x)$ is the modified Bessel function (also known as MacDonalds function). Thus, we find exponential decay of the correlation.

The low-temperature limit can be conveniently discussed by taking advantage of the simple formulation of the energy in Eq.(6.40), where we keep n_0 constant and restrict to the phase fluctuations. Then we obtain

$$E[\phi] = U n_0^2 \int d^2 r \ \left[\xi^2 (\vec{\nabla}\phi)^2 - \frac{1}{2}\right] = U n_0^2 \left[\sum_{\vec{q}} \xi^2 q^2 \phi_{\vec{q}} \phi_{-\vec{q}} - \frac{\Omega}{2}\right] \tag{6.55}$$

with the Fourier transform

$$\phi(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \tag{6.56}$$

and Ω here as the area of the system. Now turn to the calculation of the correlation function

$$g(\vec{R}) = n_0 \langle e^{i(\phi(0)-\phi(\vec{R}))}\rangle = n_0 e^{-\langle(\phi(0)-\phi(\vec{R}))^2\rangle} = \left(\frac{\pi R}{r_0}\right)^{-\eta(T)} \tag{6.57}$$

where the last equality is connected with the fact that with the above energy the averaging is Gaussian. [4] Here the correlation function still decays, but now algebraically with $\eta(T) = 2/n_0\lambda^2$ being a function linear in T and $r_0^{-3} = n$ being a characteristic length. At all temperatures there is no real long-range order, but it looks like we are for all low enough temperatures always on a critical point, since the correlation length is obviously infinitely larger.

[4] *Averaging:* In order to calculate the correlation function in Eq.(6.57) we turn the Fourier space for the phase:

$$\phi(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \tag{6.58}$$

and rewrite the energy

$$E[\phi] = U n_0^2 \xi^2 \sum_{\vec{q}} q^2 \phi_{\vec{q}} \phi_{-\vec{q}} = U n_0^2 \xi^2 \sum_{\vec{q}} q^2 (\phi_{1,\vec{q}}^2 + \phi_{2,\vec{q}}^2) \tag{6.59}$$

ignoring the constant term and separating real and imaginary part, $\phi_{\vec{q}} = \phi_{1,\vec{q}} + i\phi_{2,\vec{q}}$. The partition function is given by

$$Z = \int \prod_{\vec{q}} d\phi_{1,\vec{q}} \ d\phi_{2,\vec{q}} \ e^{-\beta U n_0^2 \xi^2 \sum_{\vec{q}} q^2 (\phi_{1,\vec{q}}^2 + \phi_{2,\vec{q}}^2)} \tag{6.60}$$

and the correlation function can be calculated by

$$g(\vec{R}) = \frac{1}{Z} \int \prod_{\vec{q}} d\phi_{1,\vec{q}} \ d\phi_{2,\vec{q}} \ \exp\left\{\frac{i}{\sqrt{\Omega}} \sum_{\vec{q}} (\phi_{1,\vec{q}} + i\phi_{2,\vec{q}})(1 - e^{i\vec{k}\cdot\vec{R}}) - \beta U n_0^2 \xi^2 \sum_{\vec{q}} q^2 (\phi_{1,\vec{q}}^2 + \phi_{2,\vec{q}}^2)\right\} \tag{6.61}$$

which can be evaluated by completing the square.

$$g(\vec{R}) = \exp\left\{-\frac{k_B T}{U n_0^2 \xi^2} \frac{1}{\Omega} \sum_{\vec{q}} \frac{1 - \cos\vec{q}\cdot\vec{R}}{q^2}\right\} = \exp\left\{-\frac{k_B T}{U n_0^2 \xi^2 (2\pi)^2} \int d^2 q \ \frac{1 - \cos\vec{q}\cdot\vec{R}}{q^2}\right\} . \tag{6.62}$$

We can again use the relation connection with the Bessel function used above and obtain

$$\begin{aligned} g(\vec{R}) \ &= \exp\left\{-\frac{k_B T}{U n_0^2 \xi^2 2\pi} \int_0^{\pi/r_0} dq \ \frac{1 - J_0(qR)}{q}\right\} = \exp\left\{-\eta(T) \int_0^{\pi R/r_0} dx \ \frac{1 - J_0(x)}{x}\right\} \\ &\approx \exp\left\{-\eta(T) \ln\left(\frac{\pi R}{r_0}\right)\right\} = \left(\frac{\pi R}{r_0}\right)^{-\eta(T)} \end{aligned} \tag{6.63}$$

where we introduce a cutoff for large q with $r_0 \approx n^{-1/3}$ the mean distance between the bosons.

6.2.2 Topological excitations and BKT transition

This qualitative change of the correlation function indicates a phase transition which does not fit into the picture of suppression of order due to collective modes of the phonon type. Phonons are, however, not the only excitations possible. Kosterlitz and Thoulouss realized that in a two dimensional superfluid (and also in other phases mentioned below) vortices play an important role for this change of behavior. Vortices constitute a *topological excitation*.
A conceptual argument for the occurrence of transition can be derived through the free energy of a single vortex. As we have seen above the energy of a vortex with $n_\phi = 1$ is given by

$$E = \frac{\hbar^2 n_0}{2m} 2\pi \ln\left(\frac{R}{\xi}\right) \tag{6.64}$$

where R a linear extension of the of the two-dimensional system. The entropy of the vortex is given through the phase space of the vortex which is given by number of distinct vortex positions in the system $\sim R^2/\xi^2$ (number of cells of size ξ^2 where we can place the vortex), leading to $S = k_B \ln(R/\xi)^2$. Thus the free energy of the vortex is

$$F = E - TS = \left\{\frac{\hbar^2 n_0}{2m} 2\pi - 2k_B T\right\} \ln\left(\frac{R}{\xi}\right) \tag{6.65}$$

which suggests a phase transition at

$$k_B T_{\mathrm{KT}} = \frac{\hbar^2 n_0}{2m}\pi \tag{6.66}$$

where the prefactor changes sign. Above T_{KT} vortices are favored below they are suppressed. Note that this argument does not depend on the system size as both contributions in F scale the same way.
The transition can be understood in terms of vortex-anti-vortex pairs being bound or dissociated (anti-vortex: has the same structure as the vortex but with opposite winding of the phase). The high temperature phase corresponds to unbound free vortices destroying the phase coherence, while at low temperatures vortices bind into pairs of opposite winding number such that there is no phase winding of bound pairs. A vortex and anti-vortex pair behave like particle and antiparticle. They can be created spontaneously at the expense of the energy of two vortices, without changing the overall phase winding of the system. For the same reason they can annihilate each other releasing the vortex energies. Thus the number of vortex pairs is not conserved. Only the totel winding number of all vortices is conserved,

$$n_\psi^{(tot)} = \sum_i n_\phi^{(i)} \ . \tag{6.67}$$

We can discuss the gas of vortices in terms of the grand canonical ensemble.
Two vortices interact with each other by an energy

$$E_{ij} = -2\frac{\hbar^2}{2m} 2\pi n_\phi^{(i)} n_\phi^{(j)} \ln\left|\frac{\vec{r}_i - \vec{r}_j}{\xi}\right| \ , \tag{6.68}$$

which is formally equivalent to the Coulomb energy of two charged particles (winding number as charge). Note this expression is only true if the vortex cores do not overlap, i.e. $|\vec{r}_i - \vec{r}_j| \gg \xi$.
The grand canonical partition function is given by

$$\mathcal{Z}_v = \sum_{N=0}^{\infty} \frac{z^N}{[(N/2)!]^2} \frac{1}{\xi^{2N}} \sum_{\{n_\phi\}} \int d^2 r_1 \cdots d^2 r_N \ \exp\left[2\beta \frac{\hbar^2}{2m} 2\pi \sum_{i<j} n_\phi^{(i)} n_\phi^{(j)} \ln\left|\frac{\vec{r}_i - \vec{r}_j}{\xi}\right|\right] \tag{6.69}$$

where the first sum runs only over even numbers N (vortex pairs) such that $\sum_{\{n_\phi\}}$ restricts to winding numbers adding up to $n_\psi^{(tot)} = 0$. The fugacity z includes the energy of each vortex.

Considering the very dilute vortex system with $z \to 0$ we can restrict to $N = 0, 2$ and discuss only a single vortex-anti-vortex pair ($n_\phi^{(1)} = -n_\phi^{(2)} = 1$). In view of the transition of the vortex system it is now interesting to examine the vortex spacing. The mean square distance is given by

$$\langle |\vec{r}_1 - \vec{r}_2| \rangle = \frac{1}{2\pi\Omega\xi^2 \mathcal{Z}_v} \int_{|\vec{r}_1 - \vec{r}_2| \geq \xi} d^2r_1 \, d^2r_2 |\vec{r}_1 - \vec{r}_2|^2 \left| \frac{\vec{r}_1 - \vec{r}_2}{\xi} \right|^{-\frac{2\pi\beta\hbar^2}{m}} \tag{6.70}$$

where we renormalize by the volume (area) Ω of the system. The partition function can be approximated by $\mathcal{Z}_v \approx 1$. Then decomposing the two positions $\vec{r}_1$ and $\vec{r}_2$ into center of mass and relative coordinates, $\vec{r}_{vp} = (\vec{r}_1 + \vec{r}_2)/2$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$ we obtain

$$\langle |\vec{r}|^2 \rangle = \xi^{\frac{2\pi\beta\hbar^2}{2m} - 2} \int_\xi^\infty dr \, r^{3 - \frac{2\pi\beta\hbar^2}{2m}} = -\frac{\xi^2}{4 - \frac{2\pi\hbar^2}{mk_BT}} = \frac{\xi^2}{4} \left(\frac{T_{\mathrm{KT}}}{T} - 1 \right)^{-1} \tag{6.71}$$

which shows that the vortex-anti-vortex separation is finite for $T < T_{\mathrm{KT}}$ but diverges as $T \to T_{\mathrm{KT}}$. Note that here the same transition temperature T_{KT} is found as in Eq.(6.66).
The dissociated vortices move freely and destroy the phase coherence, while the moving bound pair is not detrimental for the phase, as it does not carry a net phase winding. There are similar two-dimensional systems which contain topological excitations. In a crystal lattice the topological excitations are dislocations which have also a topological nature characterized by means of the Burger's vector. Another example is the two-dimensions XY-spin system with the Hamiltonian,

$$\mathcal{H}_{\mathrm{XY}} = J \sum_{\langle i,j \rangle} (S_i^x S_j^+ S_i^y S_j^y) = JS^2 \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j) \tag{6.72}$$

considering classical spins with $\vec{S}_i = S(\cos\theta_i, \sin\theta_i)$ where the in-plane angle plays a similar role as the phase of the condensate wave function discussed above.

Chapter 7

Linear Response Theory

Much information about a macroscopic system can be gained through the observation of its response to a small external perturbation. If the perturbation is sufficiently small we can consider the response of the system in lowest order, linear to the perturbing field, as a so-called linear response. We are familiar with this concept from our previous discussion of magnetism where in a paramagnet the magnetization is proportional to the applied magnetic field. The magnetic susceptibility as a linear response function incorporates important information about the magnetic system. We may extend our discussion by considering the response on time and space dependent perturbations into account in order to observe dynamical properties of a system.
If we knew all stationary states of a macroscopic quantum system with many degrees of freedom we could calculate essentially any desired quantity. As we mentioned earlier this full information is hard to store and is also unnecessary in view of our real experimental interests. The linear response functions are an efficient way to provide in a condensed form some of the most important and relevant information of the system, accessible in an experiment. The linear response function is one element of quantum field theory of solid state physics. We will introduce it here on an elementary level.

7.1 Linear Response function

Some of the well-known examples of linear response functions are the dielectric and the magnetic susceptibilities which describe the dielectric and magnetic response of a macroscopic system to an external field, respectively. Including spatial and time dependence we can write the relation between response and field as,

$$\begin{aligned} \vec{P}(\vec{r},t) &= \int d^3r' \int dt' \; \chi_e(\vec{r}-\vec{r}\,',t-t')\vec{E}(\vec{r}\,',t') \\ \vec{M}(\vec{r},t) &= \int d^3r' \int dt' \; \chi_m(\vec{r}-\vec{r}\,',t-t')\vec{H}(\vec{r}\,',t') \end{aligned} \tag{7.1}$$

where we consider here a homogeneous, isotropic medium. It is obvious from this form that the response functions $\chi_{e,m}$ describes how a field at the position $\vec{r}\,'$ at time t' influences the system at $\vec{r}$ at a later time t (causality). Causality actually requires that $\chi(\vec{r},t) = 0$ for $t < 0$. The response functions are non-local in space and time. The convolution of Eq.(7.1) can be converted into a simple product - a "local" form - by going to momentum-frequency space,

$$\vec{P}(\vec{q},\omega) = \chi_e(\vec{q},\omega)\vec{E}(\vec{q},\omega) \quad \text{and} \quad \vec{M}(\vec{q},\omega) = \chi_m(\vec{q},\omega)\vec{H}(\vec{q},\omega) \tag{7.2}$$

where the Fourier transformation is performed as follows,

$$f(\vec{r},t) = \frac{1}{V}\sum_{\vec{q}} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} f(\vec{q},\omega) e^{-i(\omega t - \vec{q}\cdot\vec{r})} \; . \tag{7.3}$$

We now determine the response function for a general external field and response quantity.

7.1.1 Kubo formula - retarded Green's function

We consider here a quantum system described by the Hamiltonian $\mathcal{H}_0$ and analyze its response to an external field $h(\vec{r},t)$ which couples to the field operator $\hat{A}(\vec{r})$,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'(t) = \mathcal{H}_0 + \int d^3r\ \hat{A}(\vec{r})h(\vec{r},t)e^{\eta t} \tag{7.4}$$

where $\eta = 0_+$ is a small positive parameter allowing to switch the perturbation adiabatically on, i.e. at time $t \to -\infty$ there is no perturbation. The behavior of the system can now be determined by the density matrix $\hat{\rho}(t)$. Possessing $\hat{\rho}$ we are able to calculate interesting mean values of operators, $\langle \hat{B}(t)\rangle = tr(\hat{\rho}(t)\hat{B})$. We find the density matrix by means of the equation of motion,

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = -[\hat{\rho},\mathcal{H}] = -[\hat{\rho},\mathcal{H}_0+\mathcal{H}'] \ . \tag{7.5}$$

We proceed using the concept of time-dependent perturbation theory, $\hat{\rho} = \hat{\rho}_0 + \delta\hat{\rho}(t)$, with

$$\hat{\rho}_0 = \frac{1}{Z}e^{-\beta\mathcal{H}_0} \qquad \text{and} \qquad Z = tre^{-\beta\mathcal{H}_0} \tag{7.6}$$

Then we insert this separated form and truncate the equation in linear order in $\mathcal{H}'$,

$$i\hbar\frac{\partial}{\partial t}\delta\hat{\rho} = -[\delta\hat{\rho},\mathcal{H}_0] - [\hat{\rho}_0,\mathcal{H}'] + \cdots \ . \tag{7.7}$$

We introduce now the interaction representation (time-dependent perturbation theory),

$$\delta\hat{\rho}(t) = e^{-i\mathcal{H}_0t/\hbar}\hat{y}(t)e^{i\mathcal{H}_0t/\hbar} \quad \Rightarrow \quad i\hbar\frac{\partial}{\partial t}\delta\hat{\rho} = -[\delta\hat{\rho},\mathcal{H}_0] + e^{-i\mathcal{H}_0t/\hbar}\left\{i\hbar\frac{\partial\hat{y}(t)}{\partial t}\right\}e^{i\mathcal{H}_0t/\hbar} \ . \tag{7.8}$$

Comparing Eqs. (7.7) and (7.8) and using (7.5) we arrive at the equation for $\hat{y}$,

$$i\hbar\frac{\partial\hat{y}(t)}{\partial t} = -[\hat{\rho}_0,\mathcal{H}'_{int}(t)] \qquad \text{with} \qquad \mathcal{H}'_{int}(t) = e^{i\mathcal{H}_0t/\hbar}\mathcal{H}'e^{-i\mathcal{H}_0t/\hbar} \tag{7.9}$$

which is formally solved by

$$\hat{y}(t) = \frac{i}{\hbar}\int_{-\infty}^{t} dt'\ [\hat{\rho}_0,\mathcal{H}'_{int}(t')] \ . \tag{7.10}$$

We now look at the mean value of the observable $\hat{B}(\vec{r})$. For simplicity we assume that the expectation value of $\hat{B}$ vanishes, if there is no perturbation, i.e. $\langle\hat{B}\rangle_0 = tr\{\hat{\rho}_0\hat{B}\} = 0$. We determine

$$\begin{aligned}\langle\hat{B}(\vec{r})\rangle(t) &= tr\left\{\delta\hat{\rho}(\vec{r},t)\hat{B}(\vec{r})\right\} \\ &= tr\left\{\frac{i}{\hbar}e^{-i\mathcal{H}_0t/\hbar}\int_{-\infty}^{t} dt'\ [\hat{\rho}_0,\mathcal{H}'_{int}(t')]e^{i\mathcal{H}_0t/\hbar}\hat{B}(\vec{r})\right\} \ .\end{aligned} \tag{7.11}$$

By means of cyclic permutation of the operators in $\{\ldots\}$, which does not affect the trace, we arrive at the form

$$\begin{aligned}\langle\hat{B}(\vec{r})\rangle(t) &= -\frac{i}{\hbar}\int_{-\infty}^{t} dt'\int d^3r'\ tr\left\{\hat{\rho}_0[\hat{B}_{int}(\vec{r},t),\hat{A}_{int}(\vec{r}\,',t')]\right\}h(\vec{r}\,',t')e^{\eta t'} \\ &= \int dt'\int d^3r'\ \chi_{BA}(\vec{r}-\vec{r}\,',t-t')h(\vec{r}\,',t') \ ,\end{aligned} \tag{7.12}$$

which defines the response function. Notably, it is entirely determined by the properties of the unperturbed system.

Recipe for the linear response function: We arrive at the following recipe to obtain a general linear response function: From now on we denote the Hamiltonian of the (unperturbed) system $\mathcal{H}$. Then the linear response function of the pair of operators $\hat{A}, \hat{B}$ (they are often in practice conjugate operators, $\hat{A} = \hat{B}^\dagger$) is given by

$$\chi_{BA}(\vec{r}-\vec{r}\,', t-t') = -\frac{i}{\hbar}\Theta(t-t')\langle[\hat{B}_H(\vec{r},t), \hat{A}_H(\vec{r}\,',t')]\rangle_{\mathcal{H}} \tag{7.13}$$

where $\langle\ldots\rangle_{\mathcal{H}}$ is the thermal mean value with respect to the Hamiltonian $\mathcal{H}$,

$$\langle\hat{C}\rangle_{\mathcal{H}} = \frac{tr\{\hat{C}e^{-\beta\mathcal{H}}\}}{tr\{e^{-\beta\mathcal{H}}\}}\ , \tag{7.14}$$

$\hat{A}_H(t) = e^{i\mathcal{H}t/\hbar}\hat{A}e^{-i\mathcal{H}t/\hbar}$ is the Heisenberg representation of the operator $\hat{A}$ (analog for $\hat{B}$). Note that the temporal step function $\Theta(t-t')$ ensures the causality, i.e. there is no response for the system before there is a perturbation. The form (7.13) is often called *Kubo formula* or *retarded Green's function.*

Frequently used examples are:

- *magnetic susceptibility:*

$$\begin{aligned}
&\text{perturbation} && \mathcal{H}' = -\int d^3r\ \mu_B\hat{S}^z(\vec{r})h(\vec{r},t) \\
&\text{conjugate magnetization} && \hat{M}(\vec{r}) = \mu_B\hat{S}^z(\vec{r}) \\
&\text{response function} && \chi_{zz}(\vec{r}-\vec{r}\,',t-t') = \frac{i}{\hbar}\Theta(t-t')\mu_B^2\langle[\hat{S}^z_H(\vec{r},t), \hat{S}^z_H(\vec{r}\,',t')]\rangle_{\mathcal{H}}\ .
\end{aligned} \tag{7.15}$$

- *dielectric susceptibility:*

$$\begin{aligned}
&\text{perturbation} && \mathcal{H}' = \int d^3r\ e\hat{n}(\vec{r})\phi(\vec{r},t) \\
&\text{conjugate density} && e\hat{n}(\vec{r}) \\
&\text{response function} && \chi_e(\vec{r}-\vec{r}\,',t-t') = -\frac{i}{\hbar}\Theta(t-t')e^2\langle[\hat{n}_H(\vec{r},t), \hat{n}_H(\vec{r}\,',t')]\rangle_{\mathcal{H}}\ .
\end{aligned} \tag{7.16}$$

7.1.2 Information in the response function

The information stored in the response function can be most easily visualized by assuming that we know the complete set of stationary states of the system Hamiltonian $\mathcal{H}$: $\mathcal{H}|n\rangle = \epsilon_n|n\rangle$. For simplicity we will from now on assume that $\hat{A} = \hat{B}^\dagger$ which is the case in many practical examples, and will simplify our notation. We can then rewrite the response function χ as

$$\begin{aligned}
\chi(\vec{r}-\vec{r}\,',t-t') &= -\frac{i}{\hbar}\Theta(t-t')\sum_n \frac{e^{-\beta\epsilon_n}}{Z}\Big\{\langle n|e^{i\mathcal{H}t/\hbar}\hat{B}(\vec{r})e^{-i\mathcal{H}t/\hbar}e^{i\mathcal{H}t'/\hbar}\hat{B}(\vec{r}\,')^\dagger e^{-i\mathcal{H}t'/\hbar}|n\rangle \\
&\qquad -\langle n|e^{i\mathcal{H}t'/\hbar}\hat{B}(\vec{r}\,')^\dagger e^{-i\mathcal{H}t'/\hbar}e^{i\mathcal{H}t/\hbar}\hat{B}(\vec{r})e^{-i\mathcal{H}t/\hbar}|n\rangle\Big\} \\
&= -\frac{i}{\hbar}\Theta(t-t')\sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z}\Big\{\langle n|\hat{B}(\vec{r})|n'\rangle\langle n'|\hat{B}(\vec{r}\,')^\dagger|n\rangle e^{i(\epsilon_n-\epsilon_{n'})(t-t')/\hbar} \\
&\qquad -\langle n|\hat{B}(\vec{r}\,')^\dagger|n'\rangle\langle n'|\hat{B}(\vec{r})|n\rangle e^{i(\epsilon_{n'}-\epsilon_n)(t-t')/\hbar}\Big\}\ ,
\end{aligned} \tag{7.17}$$

where we inserted $1 = \sum_{n'} |n'\rangle\langle n'|$. It is convenient to work in momentum and frequency space. Thus, we perform now the Fourier transform

$$\begin{aligned}\chi(\vec{q},\omega) &= \int d^3\tilde{r} \int_{-\infty}^{+\infty} d\tilde{t}\, \chi(\tilde{\vec{r}},\tilde{t}) e^{i\omega\tilde{t} - i\vec{q}\cdot\tilde{\vec{r}}} \\ &= -\frac{i}{\hbar}\sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z} |\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2 \int_0^{\infty} d\tilde{t}\, \left\{ e^{i(\epsilon_n - \epsilon_{n'} + \hbar\omega)\tilde{t}/\hbar} - e^{i(\epsilon_{n'} - \epsilon_n + \hbar\omega)\tilde{t}/\hbar} \right\} e^{-\eta\tilde{t}}\end{aligned} \tag{7.18}$$

where we introduce

$$\hat{B}_{\vec{q}} = \int d^3\tilde{r} \hat{B}(\tilde{\vec{r}}) e^{-i\vec{q}\cdot\tilde{\vec{r}}} \quad \text{and} \quad \hat{B}^{\dagger}_{\vec{q}} = \int d^3\tilde{r} \hat{B}(\tilde{\vec{r}})^{\dagger} e^{i\vec{q}\cdot\tilde{\vec{r}}} \,. \tag{7.19}$$

Performing the time integral in (7.18) we obtain

$$\begin{aligned}\chi(\vec{q},\omega) &= \sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z} |\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2 \left\{ \frac{1}{\hbar\omega - \epsilon_{n'} + \epsilon_n + i\hbar\eta} - \frac{1}{\hbar\omega - \epsilon_n + \epsilon_{n'} + i\hbar\eta} \right\} \\ &= \int_0^{\infty} d\omega'\, S(\vec{q},\omega') \left\{ \frac{1}{\omega - \omega' + i\eta} - \frac{1}{\omega + \omega' + i\eta} \right\} \,.\end{aligned} \tag{7.20}$$

In the last line we write the response function in a spectral form with $S(\vec{q},\omega)$ as the spectral function,

$$S(\vec{q},\omega) = \sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z} |\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2 \delta(\hbar\omega - \epsilon_{n'} + \epsilon_n) \tag{7.21}$$

We call $S(\vec{q},\omega)$ also *dynamical structure factor* which comprises information about the excitation spectrum associated with $\hat{B}$. It represents a correlation function[1] ,

$$S(\vec{r} - \vec{r}', t - t') = \frac{1}{h} \left\langle \hat{B}_H(\vec{r},t) \hat{B}_H(\vec{r}',t')^{\dagger} \right\rangle_{\mathcal{H}} \,, \tag{7.23}$$

and contains the spectrum of the excitations which can be coupled to by the external perturbation.

7.1.3 Analytical properties

The representation of the linear response function in (7.20) shows that $\chi_{BA}(\vec{q},\omega)$ has poles only in the lower half of the complex ω-plane. This property reflects causality ($\chi(\vec{r},t) = 0$ for $t < 0$). We separate now $\chi = \chi' + i\chi''$ in real and imaginary part and use the relation

$$\lim_{\eta\to 0_+} \frac{1}{x + i\eta} = \mathcal{P}\frac{1}{x} - i\pi\delta(x) \,. \tag{7.24}$$

[1] Consider the Fourier transform

$$\begin{aligned}S(\vec{q},\omega) &= \int d^3\tilde{r} \int_{-\infty}^{+\infty} dt S(\tilde{\vec{r}},t) e^{i\omega t - i\vec{q}\cdot\tilde{\vec{r}}} \\ &= \frac{1}{Vh} \int d^3\tilde{r} d^3r' \int_{-\infty}^{+\infty} dt \sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z} \langle n|e^{i\mathcal{H}t/\hbar} \hat{B}(\tilde{\vec{r}} + \vec{r}') e^{-i\mathcal{H}t/\hbar}|n'\rangle\langle n'|\hat{B}(\vec{r}')^{\dagger}|n\rangle e^{-i\vec{q}\cdot(\tilde{\vec{r}}+\vec{r}') + i\vec{q}'\cdot\vec{r}' + i\omega t} \\ &= \frac{1}{h} \int_{-\infty}^{+\infty} dt \sum_{n,n'} \frac{e^{-\beta\epsilon_n}}{Z} |\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2 e^{i(\epsilon_n - \epsilon_{n'} + \hbar\omega)t/\hbar} \\ &= \sum_{n.,n'} \frac{e^{-\beta\epsilon_n}}{Z} |\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2 \delta(\hbar\omega - \epsilon_{n'} + \epsilon_n) \,,\end{aligned} \tag{7.22}$$

as given in (7.21).

with $\mathcal{P}$ denoting the principal part. This relation leads to

$$\begin{aligned}\chi'(\vec{q},\omega) &= \int_0^\infty d\omega'\; S(\vec{q},\omega')\left\{\mathcal{P}\frac{1}{\omega-\omega'} - \mathcal{P}\frac{1}{\omega+\omega'}\right\}\;, \\ \chi''(\vec{q},\omega) &= -\pi\left\{S(\vec{q},\omega) - S(\vec{q},-\omega)\right\}\;.\end{aligned} \tag{7.25}$$

Therefore the imaginary part of χ corresponds to the excitation spectrum of the system. Finally, it has to be noted that $\chi(\vec{q},\omega)$ follows the Kramers-Kronig relations:[2]

$$\begin{aligned}\chi'(\vec{q},\omega) &= -\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega'\; \mathcal{P}\frac{\chi''(\vec{q},\omega')}{\omega-\omega'}\;, \\ \chi''(\vec{q},\omega) &= \frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega'\; \mathcal{P}\frac{\chi'(\vec{q},\omega')}{\omega-\omega'}\;.\end{aligned} \tag{7.27}$$

7.1.4 Fluctuation-Dissipation theorem

First we consider the aspect of dissipation incorporated in the response function. For this purpose we ignore for simplicity the spatial dependence and consider a perturbative part of the Hamiltonian which only depends on time.

$$\mathcal{H}' = h(t)\hat{B} \qquad \Rightarrow \qquad \langle\hat{B}\rangle(t) = \int_0^\infty dt'\; \chi(t-t')h(t') \tag{7.28}$$

with $\hat{B} = \hat{B}^\dagger$. We assume now a monochromatic external field,

$$\begin{aligned}h(t) &= \frac{1}{2}(h_0 e^{-i\omega t} + h_0^* e^{i\omega t}) \\ \Rightarrow \qquad \langle\hat{B}\rangle(t) &= \int_0^\infty dt'\chi(t-t')\frac{1}{2}(h_0 e^{-i\omega t'} + h_0^* e^{i\omega t'}) = \frac{1}{2}\left\{\chi(\omega)^* h_0 e^{-i\omega t} + \chi(\omega)h_0^* e^{i\omega t}\right\}\;.\end{aligned} \tag{7.29}$$

[2] *Kramers-Kronig relation:* This relation results from the analytic structure of χ. Consider a contour in the upper half-plane of ω' where $\chi(\vec{q},\omega')$ has no poles due to causality.

$$\begin{aligned}&\oint_C d\omega' \frac{\chi(\vec{q},\omega')}{\omega-\omega'-i\eta'} = 0 \\ &\qquad \Rightarrow \quad \textstyle\int_{-\infty}^{+\infty} d\omega'\; \chi(\vec{q},\omega')\mathcal{P}\frac{1}{\omega-\omega'} + i\pi\chi(\vec{q},\omega) = 0\;.\end{aligned} \tag{7.26}$$

Separating this equation into real and imaginary part yields the Kramers-Kronig relation.

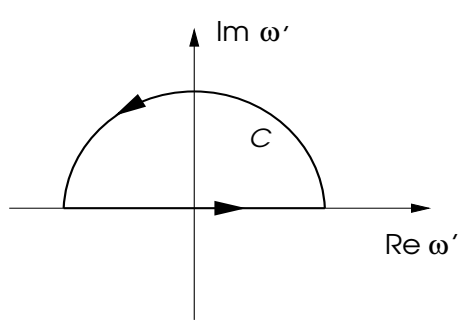

Fig. 6.1: Contour C close in the upper half of the ω'-plane.

The energy dissipation rate is determined by[3]

$$\begin{aligned}\frac{dE}{dt} &= \langle\frac{\partial}{\partial t}\mathcal{H}\rangle = \langle\hat{B}\rangle\frac{\partial h}{\partial t} = \frac{i\omega}{4}[\chi(\omega)^* - \chi(\omega)]|h_0|^2 - \frac{i\omega}{4}[\chi^*(\omega)h_0^2 e^{-2i\omega t} - \chi(\omega)h_0^* e^{2i\omega t}] \\ \Rightarrow \qquad \overline{\frac{dE}{dt}} &= \frac{\omega}{2}\chi''(\omega)|h_0|^2 < 0\end{aligned} \tag{7.31}$$

where for the time averaged rate we drop oscillating terms with the time dependence $e^{\pm i2\omega t}$. The imaginary part of the dynamical susceptibility describes the dissipation of the system.
From the definition of the dynamical structure factor it follows that

$$S(\vec{q},-\omega) = e^{-\beta\hbar\omega}S(\vec{q},\omega) \tag{7.32}$$

because

$$\begin{aligned}S(\vec{q},-\omega) &= \sum_{n,n'}\frac{e^{-\beta\epsilon_n}}{Z}|\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2\delta(-\hbar\omega - \epsilon_{n'} + \epsilon_n) \\ &= \sum_{n,n'}\frac{e^{-\beta\epsilon_{n'}-\beta\hbar\omega}}{Z}|\langle n'|\hat{B}_{-\vec{q}}|n\rangle|^2\delta(\hbar\omega - \epsilon_n + \epsilon_{n'}) = e^{-\beta\hbar\omega}S(\vec{q},\omega)\ .\end{aligned} \tag{7.33}$$

This is a statement of detailed balance. The transition matrix element between two states is the same whether the energy is absorbed or emitted. For emitting, however, the thermal occupation of the initial state has to be taken into account.
Using (7.25) we can derive the following relation

$$\chi''(\vec{q},\omega) = -\pi\left[S(\vec{q},\omega) - S(\vec{q},-\omega)\right] = -\pi[1 - e^{-\beta\hbar\omega}]S(\vec{q},\omega) \tag{7.34}$$

which is known as the *fluctuation-dissipation theorem*. Let us consider here some consequences and find the relation to our earlier simplified formulations.

$$\begin{aligned}\int_{-\infty}^{+\infty} d\omega\ S(\vec{q},\omega) &= \int_{-\infty}^{+\infty} d\omega \sum_{n,n'}\frac{e^{-\beta\epsilon_n}}{Z}|\langle n|\hat{B}_{\vec{q}}|n'\rangle|^2\delta(\hbar\omega - \epsilon_{n'} + \epsilon_n) \\ &= \frac{1}{\hbar}\sum_{n,n'}\frac{e^{-\beta\epsilon_n}}{Z}\langle n|\hat{B}_{\vec{q}}|n'\rangle\langle n'|\hat{B}^\dagger_{\vec{q}}|n\rangle \\ &= \frac{1}{\hbar}\langle\hat{B}_{\vec{q}}(0)\hat{B}^\dagger_{\vec{q}}(0)\rangle = -\frac{1}{\pi}\int_{-\infty}^{+\infty} d\omega\frac{\chi''(\vec{q},\omega)}{1 - e^{-\beta\hbar\omega}}\end{aligned} \tag{7.35}$$

This corresponds to the equal-time correlation function (assuming $\langle\hat{B}\rangle = 0$).
Now we turn to the classical case of the fluctuation-dissipation theorem and consider the the limit $k_BT \gg \hbar\omega$. Then we may approximate this equation by

$$\langle|\hat{B}_{\vec{q}}|^2\rangle \approx -\frac{k_BT}{\pi}\int_{-\infty}^{+\infty} d\omega\frac{\chi''(\vec{q},\omega)}{\omega} = -k_BT\chi'(\vec{q},0) = -k_BT\chi(\vec{q},0)\ . \tag{7.36}$$

[3]The time-derivative of the Hamiltonian is given by

$$\frac{d\mathcal{H}}{dt} = \frac{\partial\mathcal{H}}{\partial t} + \frac{i}{\hbar}[\mathcal{H},\mathcal{H}] = \frac{\partial\mathcal{H}}{\partial t} \tag{7.30}$$

for a quantum mechanical problem. The analogous relation is obtained for classical systems.

This is valid, if $\chi''(\vec{q},\omega)$ essentially vanishes for frequencies comparable and larger than the temperature.[4] For a uniform field we find

$$\int d^3r d^3r' \, \langle \hat{B}(\vec{r},t=0)\hat{B}^\dagger(\vec{r}\,',t=0)\rangle = \langle \hat{B}_{\vec{q}=0}\hat{B}^\dagger_{\vec{q}=0}\rangle = -k_BT\chi(\vec{q}=0) = -k_BT\chi \; , \tag{7.40}$$

i.e. the static uniform susceptibility is related to the integration of the equal-time correlation function as we had used previously several times. Note the minus sign results from the sign of coupling to the external field.

7.2 Example - Heisenberg ferromagnet

In this section we apply the concept of linear response function to discuss the ferromagnetic Heisenberg quantum spin model with $s = \hbar/2$. Like in the Ising model the spins reside on a hypercubic lattice and are coupled via nearest-neighbor interaction. The Heisenberg model has the full $SU(2)$ spin rotation symmetry.

$$\begin{aligned}\mathcal{H} &= -J\sum_{\langle i,j\rangle}\hat{\vec{S}}_i\cdot\hat{\vec{S}}_j = -J\sum_{\langle i,j\rangle}\left[\hat{S}^z_i\hat{S}^z_j + \frac{1}{2}\left\{\hat{S}^+_i\hat{S}^-_j + \hat{S}^-_i\hat{S}^+_j\right\}\right] \\ &= -\frac{J}{V}\sum_{\vec{q}}\gamma_{\vec{q}}\hat{\vec{S}}_{\vec{q}}\cdot\hat{\vec{S}}_{-\vec{q}} = -\frac{J}{V}\sum_{\vec{q}}\gamma_{\vec{q}}\left[\hat{S}^z_{\vec{q}}\hat{S}^z_{-\vec{q}} + \frac{1}{2}\left\{\hat{S}^+_{\vec{q}}\hat{S}^-_{-\vec{q}} + \hat{S}^-_{\vec{q}}\hat{S}^+_{-\vec{q}}\right\}\right]\end{aligned} \tag{7.41}$$

with $\gamma_{\vec{q}} = 2\sum_{\alpha=x,y,\ldots}\cos(q_\alpha)$ (lattice constant $a = 1$, unit of length). The exchange coupling $-J$ is negative so that the ground state is ferromagnetic (all spins aligned). This ground state has maximal spin $\hat{\vec{S}}_{tot} = \sum_i \hat{\vec{S}}_i$ which is a symmetry operator of the Hamiltonian. In the second line we have introduced the Fourier transformed Hamiltonian with

$$\hat{\vec{S}}_i = \frac{1}{V}\sum_{\vec{q}}\hat{\vec{S}}_{\vec{q}}e^{i\vec{q}\cdot\vec{r}_i} \tag{7.42}$$

where we use again periodic boundary conditions with a hypercube of edge length L. The quantum spins satisfy the following commutation relations:

$$\begin{aligned}\left[\hat{S}^z_i,\hat{S}^\pm_j\right] &= \pm\hbar\delta_{ij}\hat{S}^\pm_i \; , \quad \left[\hat{S}^+_i,\hat{S}^-_j\right] = 2\hbar\delta_{ij}\hat{S}^z_i \; , \\ \left[\hat{S}^z_{\vec{q}},\hat{S}^\pm_{\vec{q}'}\right] &= \pm\hbar\hat{S}^\pm_{\vec{q}+\vec{q}'} \; , \quad \left[\hat{S}^+_{\vec{q}},\hat{S}^-_{\vec{q}'}\right] = 2\hbar\hat{S}^z_{\vec{q}+\vec{q}'} \; .\end{aligned} \tag{7.43}$$

It is possible to discuss the ferromagnetic state by means of mean field approximation which is formally the same as for the Ising model leading to the same critical temperature $k_BT_c = Jzs^2 = Jd\hbar^2/2$.

[4] *Static response function:* We consider a system with

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' = \mathcal{H}_0 + \int d^3r\, h(\vec{r})\hat{B}(\vec{r}) = \mathcal{H}_0 + \frac{1}{V}\sum_{\vec{q}}h_{-q}\hat{B}_{\vec{q}} = \mathcal{H}_0 + \sum_{\vec{q}}H_{-\vec{q}}\hat{B}_{\vec{q}} \tag{7.37}$$

where we assume for the following $\hat{B}_{-\vec{q}} = \hat{B}^\dagger_{\vec{q}}$. The mean value

$$\langle\hat{B}_{\vec{q}}\rangle = \frac{\partial F}{\partial H_{-\vec{q}}} = -\frac{\partial}{\partial H_{-\vec{q}}}k_BT\ln Z = tr(\hat{\rho}\hat{B}_{\vec{q}}) \tag{7.38}$$

with $\hat{\rho} = \exp[\beta(F-\mathcal{H})]$ and $\langle\hat{B}_{\vec{q}}\rangle = 0$ for $H_{\vec{q}} = 0$. The static response function is obtain from

$$\chi(\vec{q}) = \left.\frac{\partial\langle B_{\vec{q}}\rangle}{\partial H_{\vec{q}}}\right|_{H_{\vec{q}}=0} = tr\left\{\hat{B}_{\vec{q}}\frac{\partial}{\partial H_{\vec{q}}}e^{\beta(F-\mathcal{H})}\right\}\Big|_{H_{\vec{q}}=0} = tr\left\{\hat{B}_{\vec{q}}\beta(\langle\hat{B}_{-\vec{q}}\rangle - \hat{B}_{-\vec{q}})\hat{\rho}\right\}\Big|_{H_{\vec{q}}=0} = -\beta\langle\hat{B}_{\vec{q}}\hat{B}^\dagger_{\vec{q}}\rangle \tag{7.39}$$

which is the classical form of the fluctuation dissipation theorem for spatially modulated perturbative fields.

7.2.1 Tyablikov decoupling approximation

Here we would like to go beyond mean field theory using the response function for the Heisenberg model. We introduce the transverse dynamical spin susceptibility,

$$\chi(\vec{q}, t-t') = \frac{i}{\hbar}\Theta(t-t')\langle[\hat{S}^-_{\vec{q}}(t), \hat{S}^+_{-\vec{q}}(t')]\rangle \ . \tag{7.44}$$

We use now a method based on the equation of motion to find this response function.

$$\begin{aligned} i\hbar\frac{d}{dt}\chi(\vec{q}, t-t') &= -\delta(t-t')\langle[\hat{S}^-_{\vec{q}}, \hat{S}^+_{-\vec{q}}]\rangle + \frac{i}{\hbar}\Theta(t-t')\langle[[\hat{S}^-_{\vec{q}}, \mathcal{H}](t), \hat{S}^+_{-\vec{q}}(t')]\rangle \\ &= 2\delta(t-t')\hbar\langle\hat{S}^z_{\vec{q}=0}\rangle \\ &\quad -\frac{i}{\hbar}\Theta(t-t')\frac{J\hbar}{V}\sum_{\vec{q}'}(\gamma_{\vec{q}'} - \gamma_{\vec{q}+\vec{q}'})\left\{\left\langle\left[\hat{S}^z_{\vec{q}'}(t)\hat{S}^-_{\vec{q}-\vec{q}'}(t), \hat{S}^+_{-\vec{q}}(t')\right]\right\rangle\right. \\ &\quad \left. +\langle\left[\hat{S}^-_{\vec{q}+\vec{q}'}(t)\hat{S}^z_{-\vec{q}'}(t), \hat{S}^+_{-\vec{q}}(t')\right]\rangle\right\} \ . \end{aligned} \tag{7.45}$$

On the right-hand side this equation leads to new retarded Green's functions containing three spin operators of the form,

$$\frac{i}{\hbar}\Theta(t-t')\left\langle\left[\hat{S}^z_{\vec{q}'}(t)\hat{S}^-_{\vec{q}-\vec{q}'}(t), \hat{S}^+_{-\vec{q}}(t')\right]\right\rangle \ . \tag{7.46}$$

Thus we have also to set up equations of motion for them which in turn lead to Green's functions with four spin operators and so on. The resulting hierarchy of equation is intractable.
Therefore, we introduce here an approximation which truncates the hierarchy and leads to a closed equation system, a scheme known as Tyablikov decoupling,

$$\begin{aligned} \hat{S}^z_{\vec{q}'}(t)\hat{S}^-_{\vec{q}-\vec{q}'}(t) &\to \langle\hat{S}^z_0\rangle\hat{S}^-_{\vec{q}}(t)\delta_{0,\vec{q}'} \\ \hat{S}^-_{\vec{q}+\vec{q}'}(t)\hat{S}^z_{\vec{q}'}(t) &\to \langle\hat{S}^z_0\rangle\hat{S}^-_{\vec{q}}(t)\delta_{0,\vec{q}'} \end{aligned} \tag{7.47}$$

Replacing the corresponding terms on the right-hand side of the equation of motion we obtain

$$i\hbar\frac{\partial}{\partial t}\chi(\vec{q}, t-t') = 2\delta(t-t')\hbar\langle\hat{S}^z_{\vec{q}=0}\rangle - \frac{J\hbar}{V}\langle\hat{S}^z_{\vec{q}=0}\rangle(\gamma_0 - \gamma_{\vec{q}})\chi(\vec{q}, t-t') \ . \tag{7.48}$$

We now perform a Fourier transform, replacing $t - t' = \tilde{t}$:

$$\int d\tilde{t}\ e^{i\omega\tilde{t}-\eta\tilde{t}}\left[i\frac{\partial}{\partial\tilde{t}} + \frac{J}{V}\langle\hat{S}^z_{\vec{q}=0}\rangle(\gamma_0 - \gamma_{\vec{q}})\right]\chi(\vec{q}, \tilde{t}) = \int d\tilde{t}\ e^{i\omega\tilde{t}-\eta\tilde{t}}2\delta(t-t')\langle\hat{S}^z_{\vec{q}=0}\rangle \tag{7.49}$$

which leads to

$$\left\{\omega + i\eta + 2\frac{J}{V}\langle\hat{S}^z_0\rangle(\gamma_0 - \gamma_{\vec{q}})\right\}\chi(\vec{q}, \omega) = 2\langle\hat{S}^z_0\rangle \tag{7.50}$$

which leads immediately to the solution

$$\chi(\vec{q}, \omega) = \frac{2\langle\hat{S}^z_0\rangle}{\omega + 2\frac{J}{V}\langle\hat{S}^z_0\rangle(\gamma_0 - \gamma_{\vec{q}}) + i\eta} \ . \tag{7.51}$$

Here we define now the mean field $\langle\hat{S}^z_0\rangle = -Vm$ with $0 \leq m \leq \hbar/2$. We have introduced the small imaginary part $i\eta$ in order to guarantee the causality.

First let us look at the spectrum of excitations if $m \neq 0$. This is given by the imaginary part of χ.

$$\begin{aligned} \chi''(\vec{q},\omega) &= 2\pi V m \delta[\omega - 2Jm(\gamma_0 - \gamma_{\vec{q}})] \\ \Rightarrow \quad \omega_{\vec{q}} &= 2Jm(\gamma_0 - \gamma_{\vec{q}}) = 4Jm \sum_\alpha (1 - \cos q_\alpha) \end{aligned} \tag{7.52}$$

This is the dispersion of a collective magnetic mode, a *magnon* or spin wave, which corresponds analogous to the phonons in a solid to a bosonic mode. This mode appears as an excitation with well-defined momentum-energy relation. For small energy the dispersion is quadratic, $\omega_{\vec{q}} = 2Jm\vec{q}^2$.

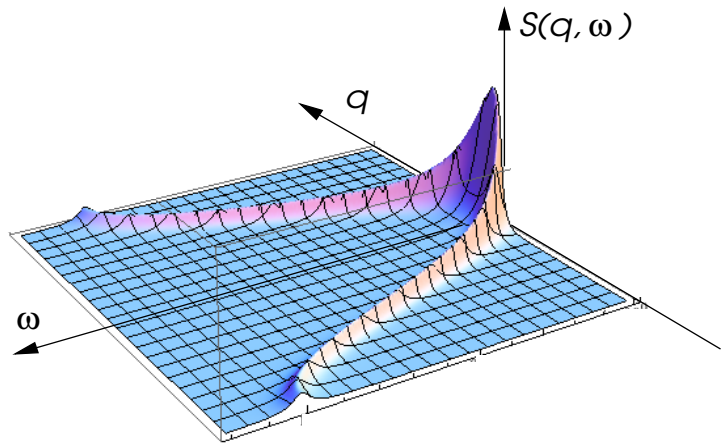

Fig. 6.2: Dynamical structure factor for the spin excitation spectrum in the ferromagnetic phase.

7.2.2 Instability condition

Now we construct the self-consistence equation for the mean field $\langle \hat{S}_0^z \rangle$. In principle we could use the previous mean field approximation solution. However, we may also require that the fluctuation-dissipation theorem is satisfied in order to take the effects of fluctuations into account. Thus, we consider the dynamical structure factor,

$$S(\vec{q},\omega) = \int dt\, e^{i\omega t} \frac{1}{\hbar} \langle \hat{S}^-_{\vec{q}}(t) \hat{S}^+_{-\vec{q}}(0) \rangle \ . \tag{7.53}$$

Taking the $\vec{q}$-sum and ω integral provides an onsite equal time correlation function:

$$\frac{1}{V^2} \sum_{\vec{q}} \int d\omega\, S(\vec{q},\omega) = \frac{1}{\hbar} \langle \hat{S}_i^-(0) \hat{S}_i^+(0) \rangle = \frac{1}{\hbar} \left\{ \langle \hat{\vec{S}}_i^2 \rangle - \langle \hat{S}_i^{z2} \rangle - \langle \hat{S}_i^z \rangle \hbar \right\} = \frac{\hbar}{2} + m \ . \tag{7.54}$$

Now we express $S(\vec{q},\omega)$ by means of the fluctuation-dissipation theorem (7.34).

$$\frac{\hbar}{2} + m = -\frac{1}{\pi} \int d\omega \frac{1}{1 - e^{-\beta\hbar\omega}} \frac{1}{V^2} \sum_{\vec{q}} \chi''(\vec{q},\omega) = \frac{1}{V} \sum_{\vec{q}} \frac{2m}{1 - e^{-\beta\hbar\omega_{\vec{q}}}} \tag{7.55}$$

The instability condition defining the critical temperature is obtained from the limit $m \to 0$, assuming it to be a second order (continuous) phase transition. Then we expand the denominator on the right-hand side and obtain the equation

$$\frac{\hbar}{2} = \frac{k_B T_c}{J\hbar} \frac{1}{V} \sum_{\vec{q}} \frac{1}{\gamma_0 - \gamma_{\vec{q}}} \tag{7.56}$$

For the three-dimensional system a numerical solution shows $k_B T_c \approx 1.1 J\hbar^2$ which is considerably smaller than the mean field result of $1.5 J\hbar^2$. The reduction is, analogous to the self-consistent fluctuation approximation, caused by thermal fluctuations which are ignored in the ordinary mean field approximation.
In one and two dimensions we find that the integral on the right-hand side diverges at the lower boundary (infrared divergence).

$$\frac{1}{V}\sum_{\vec{q}} \frac{1}{\gamma_0 - \gamma_{\vec{q}}} \to \int \frac{d^d q}{(2\pi)^d} \frac{1}{\gamma_0 - \gamma_{\vec{q}}} \to \int_0^\Lambda dq \frac{q^{d-1}}{q^2} \to \infty \quad \text{for} \quad d \leq 2 \; . \tag{7.57}$$

Thus $k_B T_c \to 0$. This is a consequence of the spin wave fluctuations which destroy the magnetic moment. This result is also known as the Hohenberg-Mermin-Wagner theorem. It applies to systems with a continuous spin symmetry and short-range interaction. Note that Peierls' domain wall argument fails here, since the domain walls have an infinite width due to the continuous degeneracy of the magnetic ground state, i.e. any direction for the ordered moment has the same energy.

7.2.3 Low-temperature properties

How do the spin wave fluctuations influence the low-temperature behavior? Let us first consider $m(T) = \hbar/2 - \delta m(T)$. We insert this into the self-consistence equation,

$$\begin{aligned} \hbar - \delta m &= \left(\frac{\hbar}{2} - \delta m\right) \frac{2}{V} \sum_{\vec{q}} \left(1 + \sum_{n=1}^{\infty} e^{-\beta\hbar\omega_{\vec{q}} n}\right) \\ &\approx (\hbar - 2\delta m) \left\{1 + \sum_{n=1}^{\infty} \int \frac{d^3 q}{(2\pi)^3} e^{-2Jm\hbar\beta n q^2}\right\} = (\hbar - 2\delta m)\left\{1 + \frac{\zeta(3/2)(k_B T)^{3/2}}{(4\pi J\hbar^2)^{3/2}}\right\} \end{aligned} \tag{7.58}$$

which leads to

$$\delta m(T) \approx \frac{\zeta(3/2)}{(4\pi J\hbar^2)^{3/2}} (k_B T)^{3/2} \; . \tag{7.59}$$

If we compare this with the result of the ordinary mean field approximation, $\delta m \propto \exp(-T_c/T)$ we find that the thermal spin wave fluctuations suppress the magnetic order at $T > 0$ more strongly.
Finally we consider the spin wave contribution to the low-temperature heat capacity. The magnons as bosons have a dispersion $\omega_{\vec{q}} = c_s q^2$ leading to a density of states as

$$D(\omega) \propto \omega^{1/2} \; . \tag{7.60}$$

With this we obtain

$$U \propto \int d\omega \omega^{1/2} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \propto T^{5/2} \quad \Rightarrow \quad C \propto T^{3/2} \tag{7.61}$$

which is also a consequence of low-energy spin wave excitations.

Chapter 8

Renormalization group

While the mean field approximation describes second-order phase transitions in a very handy way, we have seen that it treats fluctuations poorly so that the critical behavior is not adequately reproduced. This is particularly true for the renormalization of the transition point and the critical exponents of quantities which are singular at the phase transition. In this context a powerful method has been developed in the late sixties and seventies which introduce a new concept to describe critical phenomena: *the renormalization group method.* This method is based on a method for the successive decimation of high energy degrees of freedom of the system with the aim to extract the most important information on the low-energy physics from a complex many-body system. In this way the properties of a phase transitions, in particular, its critical regime can be described. There are many variants of the renormalization procedure also beyond the discussion of phase transitions and much development is still going on. Here we will restrict to one special formulation which gives a good insight to the ideas.

8.1 Basic method - Block spin scheme

Close to a second order phase transition fluctuations are large and hard to treat. The renormalization group method has the aim to connect the behavior of a model close to with the behavior of a related model far from the phase transition. The basic idea is to make a change of the length scale at which the system is considered. Close to the critical point the only relevant length scale is the correlation length, the length over which the degrees of freedom effectively interact. This length is diverging, if the critical point approached. The procedure rests on diluting (reducing) the number of degrees of freedom in a proper way so as to shrink effectively the length scale and to "move away" from the critical point.
In order to illustrate the method we consider again the Ising model with the degrees of freedom $s_i = \pm s$ on a regular lattice. The partition function is given by

$$Z(\vec{K}, N) = \sum_{\{s_i\}} e^{\mathcal{H}(\vec{K},\{s_i\},N)} \tag{8.1}$$

where we assume a generalized Hamiltonian of the form

$$\mathcal{H}(\vec{K}, \{s_i\}, N) = NK_0 + K_1 \sum_i s_i + K_2 \sum_{\langle i,j \rangle} s_i s_j + \cdots \tag{8.2}$$

with couplings among many spins, $\vec{K} = (K_0, K_1, K_2, \dots)$. In the standard form of the Ising model we have

$$K_0 = 0 \ , \quad K_1 = H/k_B T \ , \quad K_2 = J/k_B T \ , \quad K_{n>2} = 0 \ . \tag{8.3}$$

The aim is now to reduce the number of degrees of freedom without changing the partition function. This can be done by deriving an appropriate model of the remaining degrees of

freedom. We introduce $b > 1$ which denotes the change of the length scale in the system. In the decimation procedure we reduce the degrees of freedom by factor b^d. In the following we will use the so-called block spin or related formulations which gives an intuitive view of the renormalization group procedure. We separate the spin degrees of freedom into two groups $\{S_b\}$ and $\{s'\}$. The first set will be eliminated while the second set represents the remaining degrees of freedom.

$$Z(\vec{K}, N) = \sum_{\{s'\}} \sum_{\{S_b\}} e^{\mathcal{H}(\vec{K},\{S_b\},\{s'\},N)} = \sum_{\{s'\}} e^{\mathcal{H}(\vec{K}',\{s'\},Nb^{-d})} = Z(\vec{K}', Nb^{-d}) \; . \tag{8.4}$$

Thus we express the Hamiltonian in terms of new coupling constants between the remaining degrees of freedom. Looking at the reduced free energy per spin we find

$$f(\vec{K}) = -\lim_{N\to\infty} \frac{1}{N} \ln\left[Z(\vec{K}, N)\right] = -b^{-d} \lim_{N\to\infty} \frac{1}{Nb^{-d}} \ln\left[Z(\vec{K}', Nb^{-d})\right] = b^{-d} f(\vec{K}') \; . \tag{8.5}$$

The transformation $\vec{K} \to \vec{K}'$ can be repeated in the same way

$$\vec{K}^{(n)} = R\vec{K}^{(n-1)} = R^n \vec{K} \qquad \text{with} \qquad N \to Nb^{-dn} \tag{8.6}$$

where the set of operations $\{R^n\}$ with $n = 0, 1, 2, 3, \ldots$ represents a semigroup, leading to the name *renormalization group*. It is a semigroup only, because it lacks the inversion. There is namely no unique way to undo a decimation step. The renormalization group transformations lead to a "flow" of the coupling constants $\vec{K}$.
The instabilities of the system are determined by so-called unstable *fixed points* where we find

$$R\vec{K}_c = \vec{K}_c \; , \tag{8.7}$$

i.e. the coupling constants do not change under renormalization group transformation. The region of $\vec{K}$ close to the fixed point is most interesting as we can approximate the flow of the coupling constants within a linear approximation,

$$\vec{K} = \vec{K}_c + \delta\vec{K} \qquad \text{and} \qquad R\vec{K} \approx \vec{K}_c + \Lambda\delta\vec{K} \tag{8.8}$$

with Λ being a quadratic matrix of the dimension of $\vec{K}$ which can be infinite in principle. This matrix is generally not Hermitian and its eigenvectors $\vec{e}_i$ (unit length) are not orthogonal. Nevertheless we can express (8.8) as

$$\vec{K} = \vec{K}_c + \sum_{i=0}^{\infty} c_i \vec{e}_i \qquad \text{and} \qquad R\vec{K} = \vec{K}' = \vec{K}_c + \sum_{i=0}^{\infty} c_i b^{y_i} \vec{e}_i \tag{8.9}$$

Thus we find

$$Rc_i = c_i' = c_i b^{y_i} \; . \tag{8.10}$$

The exponents y_i characterize the eigenvectors $\vec{e}_i$. If $y_i > 0$ ($y_i < 0$) then $\vec{e}_i$ is called *relevant* (*irrelevant*). $\vec{e}_i$ with $y_i = 0$ is called *marginal*. Along relevant eigenvectors we move away from the fixed point under successive decimation (unstable fixed point).
Consider the case that only $\vec{e}_1$ is relevant, setting the external field H to zero. The phase transition (critical temperature) corresponds to the temperature T_c where c_1 vanishes (fixed point). Close to the fixed point ($\vec{K}$ close to $\vec{K}_c$ or T close to T_c) we can approximate

$$c_1 = A\left(\frac{T}{T_c} - 1\right) = -A\tau \; , \tag{8.11}$$

and then consider the renormalization group step

$$c_1' = Rc_1 = A\left(\frac{T'}{T_c} - 1\right) = -A\tau' \qquad \Rightarrow \qquad \tau' = b^{y_1}\tau \; . \tag{8.12}$$

Thus the renormalization group step corresponds effectively to a change of the temperature. Let us use this relation first for the length scale. The correlation length is changed in a renormalization group step by

$$\xi \to \xi' = \xi(T)/b = \xi(T') \tag{8.13}$$

The fixed point is characterized by $\xi = \xi/b$ so that only two situations are possible $\xi = \infty$ for the unstable fixed point and $\xi = 0$ for a stable fixed point which can be interpreted as the limit of non-interacting degrees of freedom (no correlations). In case of an unstable fixed point we obtain close to T_c,

$$\frac{|\tau|^{-\nu}}{b} = |\tau'|^{-\nu} \quad \Rightarrow \quad \tau' = b^{1/\nu}\tau \ . \tag{8.14}$$

This leads immediately to

$$\nu = \frac{1}{y_1} \ . \tag{8.15}$$

Therefore the exponent y_1 describing the change of temperature under the renormalization group step is connected directly with the critical exponent, ν of the coherence length.
We now turn to the free energy, still assuming that c_1 is the only component in the renormalization group procedure. Then the singular part of the free energy per spin close to the critical point has the following form:

$$f(\tau) = b^{-d} f(\tau') = b^{-d} f(\tau b^{y_1}) = b^{-dl} f(\tau b^{ly_1}) \ , \tag{8.16}$$

where the last equality means that we consider l renormalization group steps. We now choose l as a real number so that $\tau b^{ly_1} = 1$ and so $b^l = \tau^{-1/y_1}$. Then the free energy takes the form

$$f(\tau) = \tau^{d/y_1} f(1) \tag{8.17}$$

with the critical behavior of the heat capacity $C \propto |\tau|^{-\alpha}$ we find here that

$$2 - \alpha = \frac{d}{y_1} \ . \tag{8.18}$$

Thus, from the exponent y_1 we have obtained ν and α. Equations (8.15) and (8.18) can be combined to the Josephson scaling $\nu d = 2 - \alpha$, which we had seen in Section 5.4.2. Modifications and additional exponents can be obtained by keeping the magnetic field as another coupling constant. For simplicity we ignore this here and turn to the examples.

8.2 One-dimensional Ising model

The one-dimensional Ising model can be solved exactly in a rather simple way. In the absence of a magnetic field the partition function and the reduced free energy are given by

$$Z = [2\cosh(K)]^N \qquad \text{and} \qquad f(K) = \ln[2\cosh(K)] \ , \tag{8.19}$$

respectively, where $K = J/k_B T$.
We define the partition functions as

$$Z = \sum_{\{s\}} e^{NK_0 + K_2 \sum_i s_i s_{i+1}} \ , \tag{8.20}$$

which is convenient to illustrate the way of decimation. Note that $K = K_2$ here. We now reorganize this partition function in order to identify a decimation scheme, where we sum over the spins on the even sides,

$$\begin{aligned} Z &= \sum_{\{s_{odd}\}} \sum_{\{s_{even}\}} e^{NK_0 + K_2 \sum_i (s_{2i-1} + s_{2i+1}) s_{2i}} \\ &= \sum_{\{s_{odd}\}} \prod_i e^{2K_0} \left\{ e^{K_2(s_{2i-1}+s_{2i+1})} + e^{-K_2(s_{2i-1}+s_{2i+1})} \right\} = \sum_{\{s_{odd}\}} \prod_i e^{K_0' + K_2' s_{2i-1} s_{2i+1}} \end{aligned} \tag{8.21}$$

where $s = 1$. The new coupling parameter K' is related through the condition

$$e^{2K_0}\left\{e^{K_2(s_{2i-1}+s_{2i+1})} + e^{-K_2(s_{2i-1}+s_{2i+1})}\right\} = e^{K_0'+K_2' s_{2i-1}s_{2i+1}} \tag{8.22}$$

In order to solve this equation we consider the configurations $(s_{2i-1}, s_{2i+1}) = (+1, +1)$ and $(+1, -1)$ which yields the equations

$$\left.\begin{aligned} e^{2K_0}\left\{e^{2K_2} + e^{-2K_2}\right\} &= e^{K_0'+K_2'} \\ 2e^{2K_0} &= e^{K_0'-K_2'} \end{aligned}\right\} \quad \Rightarrow \quad \left\{\begin{aligned} K_0' &= 2K_0 + \frac{1}{2}\ln\left[4\cosh(2K_2)\right] \\ K_2' &= \frac{1}{2}\ln\left[\cosh(2K_2)\right] \end{aligned}\right. \tag{8.23}$$

Note that this decimation scheme conserves the form of the partition function, i.e. we end up with the same connectivity of spins in the exponent (nearest neighbor coupling). We will see in the next section that this is not generally the case.
There are two fixed points:

$$(K_{0c}, K_{2c}) = (\infty, \infty) \qquad \text{and} \qquad (K_{0c}, K_{2c}) = (-\ln 2, 0)\ . \tag{8.24}$$

For the coupling constant K_2 the first fixed point is unstable (the iterative renormalization leads the coupling constants away from the fixed point) and the second is stable.

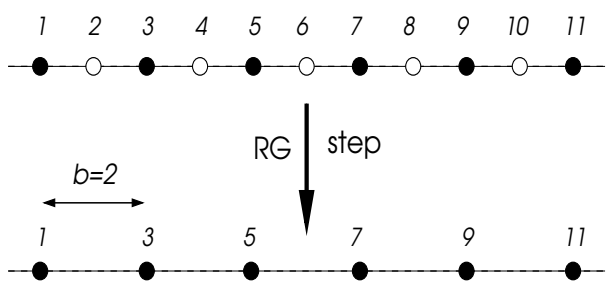

Fig.7.1: Decimation scheme: Every second spin is integrated out to reach a renormalized new system with only half the spins of the previous system.

We do not find a fixed point at a finite value of K_2 which states that no phase transition occurs, as expected in view of Peierls argument. The unstable fixed point corresponds to zero-temperature limit where the spins order in the ground state. The stable fixed point $K_{2c} = 0$ is the limit of non-interacting spins. The renormalization group treatment which had been here performed exactly, shows that there is no phase transition at a finite temperature.

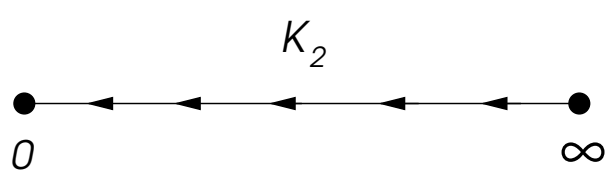

Fig.7.2: Flow of the coupling constant $K_2 = J/k_BT$ of the one-dimensional Ising model under the renormalization group scheme. For any finite coupling and temperature the flow goes towards $K = 0$ the limit of completely decoupled spins.

Therefore we find that starting at any finite value of K_2 leads us through successive application of the decimation procedure towards weaker and weaker coupling K_2. The fixed point of $K_2 = 0$ eventually corresponding to non-interacting spins is the ultimate limit of disordered spins. Through the renormalization group procedure it is possible to generate an effective model which

can be solved perturbatively and obtain the essential physics of the system. We introduce $K_0 = g(K_2)$ and write

$$g(K_2') = \frac{1}{2}\left(\ln 4 + K_2'\right) \ . \tag{8.25}$$

from (8.23). We start with $K_0 = 0$ and write

$$Z_N(K_2) = \sum_{\{s\}} e^{K_2 \sum_i s_i s_{i+1}} = e^{Ng(K_2')} Z_{N/2}(K_2') = e^{Ng(K_2') + Ng(K_2'')/2} Z_{N/4}(K_2'') = \dots \ . \tag{8.26}$$

The reduced free energy

$$f(K_2) = -\frac{1}{N} \ln Z_N(K_2) \tag{8.27}$$

can now be approximated by

$$f^{(n)}(K_2) = -\sum_{n'=1}^{n} \frac{g(K_2^{(n'-1)})}{2^{n'-1}} - \frac{1}{2^n} \ln 2 \ , \tag{8.28}$$

by successively increasing n which leads to $K_2^{(n)} \to 0$. For $K_2 = 0$ we find $f = -\ln 2$. Thus knowing the weak coupling limit allows us to determine the reduced free energy at any parameter K_2 (temperature).

8.3 Two-dimensional Ising model

Also for the two-dimensional Ising model there is an exact solution, due to Onsager, which is, however, considerably more complicated than for the one-dimensional system. The partition function is given by

$$Z = \left[2\cosh(2K)e^I\right]^N \tag{8.29}$$

with

$$I = \int_0^\infty \frac{d\phi}{2\pi} \ln\left\{\frac{1}{2}\left[1 + (1 - \kappa^2 \sin^2\phi)^{1/2}\right]\right\} \tag{8.30}$$

and

$$\kappa = \frac{2\sinh(2K)}{\cosh^2(2K)} \ . \tag{8.31}$$

In this case there is a phase transition at finite temperature given by

$$\sinh(2K_c) = 1 \qquad \Rightarrow \qquad k_B T_c = 2.27J \quad K_c = 0.4407 \ . \tag{8.32}$$

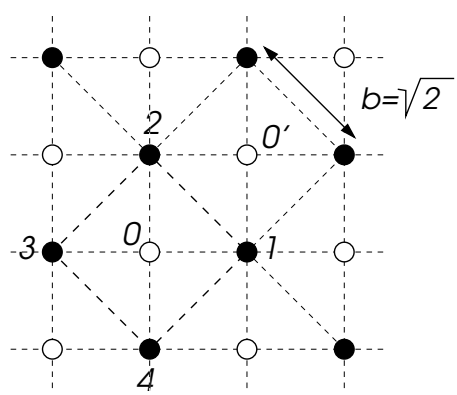

Fig.7.3: Decimation scheme for two-dimensional Ising model: Every second site is integrate yielding an effective coupling among all surrounding spins.

Now we turn to the renormalization group treatment.[1] There are various decimation schemes we could imagine. In analogy to the one-dimensional case we divide the square lattice into two sublattices as shown in Fig. 7.3: The white sites are integrated out. We take the plaquette indicated in the figure. Spins 1, 2, 3, and 4 encircle spin 0. The latter couples through nearest neighbor interaction to the former four spins. Thus, our decimation works as follows

$$\begin{aligned} Z &= \cdots \sum_{s_1,s_2,s_3,s_4} \sum_{s_0} e^{Ks_0(s_1+s_2+s_3+s_4)} \cdots \\ &= \cdots \sum_{s_1,s_2,s_3,s_4} \left[e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)} \right] \cdots \ . \end{aligned} \tag{8.33}$$

We reformulate the partition function for the remaining spin degrees of freedom

$$Z = \cdots \sum_{s_1,s_2,s_3,s_4} e^{K_0'+K_1'(s_1s_2+s_2s_3+s_3s_4+s_4s_1)+K_2'(s_1s_3+s_2s_4)+K_3's_1s_2s_3s_4} \cdots \ . \tag{8.34}$$

Going through the space of spin configurations we find new effective interactions between the four surrounding spins with the relation[2]

$$\begin{aligned} K_0' &= \frac{1}{8} \ln \left\{ \cosh^4(2K) \cosh(4K) \right\} + \ln 2 \\ K_1' &= \frac{1}{8} \ln \left\{ \cosh(4K) \right\} \\ K_2' &= \frac{1}{8} \ln \left\{ \cosh(4K) \right\} \\ K_3' &= \frac{1}{8} \ln \left\{ \cosh(4K) \right\} - \frac{1}{2} \ln \left\{ \cosh(2K) \right\} \end{aligned} \tag{8.38}$$

where K_0' is again connected with the reduced free energy, K_1' and K_2' denote nearest- and next-nearest-neighbor spin-spin interaction, and K_3' gives a four-spin interaction on the plaquette. Note that the neighboring plaquettes contribute to the nearest-neighbor interaction, e.g. summing in Fig. 7.3 over $s_{0'}$ on site $0'$, yields another interaction between s_1 and s_2. Therefore we have to modify the second equation in (8.38) by multiplying by a factor 2,

$$K_1' = \frac{1}{4} \ln \left\{ \cosh(4K) \right\} \ . \tag{8.39}$$

[1] Literature: H.J. Maris and L.P. Kadanoff, Am. J. Phys. 46, 652 (1978).

[2] The renormalization group relations are obtained by looking at different spin configurations for

$$\begin{aligned} & e^{K(s_1+s_2+s_3+s_4)} + e^{-K(s_1+s_2+s_3+s_4)} \\ & \qquad = e^{K_0'+K_1'(s_1s_2+s_2s_3+s_3s_4+s_4s_1)+K_2'(s_1s_3+s_2s_4)+K_3's_1s_2s_3s_4} \ . \end{aligned} \tag{8.35}$$

We use now the configurations

$$(s_1, s_2, s_3, s_4) = (+,+,+,+), (+,+,+,-), (+,-,+,-), (+,+,-,-) \tag{8.36}$$

and obtain the equations,

$$\begin{aligned} e^{4K} + e^{-4K} &= e^{K_0'+4K_1'+2K_2'+K_3'} \ , \\ e^{2K} + e^{-2K} &= e^{K_0'-K_3'} \ , \\ 2 &= e^{K_0'-4K_1'+2K_2'+K_3'} \ , \\ 2 &= e^{K_0'-2K_2'+K_3'} \ , \end{aligned} \tag{8.37}$$

whose solution leads to (8.38).

Unlike in the Ising chain we end up here with a different coupling pattern than we started. More spins are coupled on a wider range. Repeating the decimation procedure would even further enlarge the interaction range and complexity. This is not a problem in principle. However, in order to have a more practical iterative procedure we have to make an approximation. We restrict ourselves to the nearest neighbor interactions which would give a well-defined iterative procedure. But simply ignoring the other couplings which additionally help to align the spins would lead to an oversimplified behavior and would actually give no phase transition. Thus we have to add the other couplings in some way to the nearest-neighbor coupling. It can be shown that the four-spin interaction is small and not important close to the transition point, and we concentrate on K_1' and K_2' only. Let us define the effective nearest-neighbor in a way to give the same ground state energy as both couplings. Each site has four nearest- and four next-nearest neighbors, which yield the energy per site for full spin alignment

$$E_0 = 2NK_1' + 2NK_2' = 2NK' \tag{8.40}$$

Thus we define the new renormalized nearest-neighbor coupling

$$K' = K_1' + K_2' = \frac{3}{8}\ln\{\cosh(4K)\} \tag{8.41}$$

which now can be iterated. We find a stable fixed points of this new equation at $K = 0$ and ∞. There is also an unstable fixed point at

$$K_c = 0.507 \tag{8.42}$$

This unstable fixed point corresponds now to a finite-temperature phase transition at $k_BT_c = 1.97J$, which is lower than the mean field result $k_BT_c = 4J$, but relatively inaccurate compared to the exact result of $2.27J$.

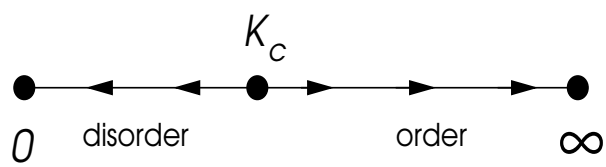

Fig.7.4: Renormalization group flow of coupling constant; The unstable fixed point K_c represents the critical point. On the left hand side, the flow leads to the stable fixed point $K = 0$ corresponding to the uncoupled spins: disorder phase. The right hand side flows to the stable fixed point $K = \infty$, where system is ordered.

It is now interesting to consider the exponents which we had discussed above. Thus we take into account that in our decimation scheme $b = \sqrt{2}$ and calculate

$$\begin{aligned} K' - K_c &= \frac{3}{8}\left[\ln\{\cosh(4K)\} - \ln\{\cosh(4K_c)\}\right] \\ &= \frac{3}{8}(K - K_c)\left.\frac{d}{dK}\ln\{\cosh(4K)\}\right|_{K=K_c} \\ &= (K - K_c)\frac{3}{2}\tanh(4K_c) = 1.45(K - K_c) = b^{y_1}(K - K_c) \end{aligned} \tag{8.43}$$

$$\Rightarrow \qquad b^{y_1} = 2^{y_1/2} = 1.45 \qquad \Rightarrow \qquad y_1 = 2\frac{\ln 1.45}{\ln 2} = 1.07\ .$$

From this result we obtain the critical exponents ν and α:

$$\nu = \frac{1}{y_1} = 0.93 \qquad \text{and} \qquad \alpha = 2 - \frac{d}{y_1} = 0.135\ . \tag{8.44}$$

The exact result is $\nu_{exact} = 1$ (mean field $\nu_{mf} = 1/2$) and $\alpha_{exact} = 0$ meaning that the heat capacity has a logarithmic singularity not describable by an exponent.
The decimation method used here is only one among many which could be imagined and have been used. Unfortunately, for practice reasons approximations had to be made so that the results are only of qualitative value. Nevertheless these results demonstrate that non-trivial properties appear in the critical region close to the second order phase transition.
Other decimations schemes can be used. Decimations in real space are only one type of method, know under the name of block spin method. Alternatively, also decimations schemes in momentum space can be used. Depending on the problem and the purpose different methods are more useful.

Appendix A

2D Ising model: Monte Carlo method and Metropolis algorithm

By Christian Iniotakis

A.1 Monte Carlo integration

In the description of many physical scenarios, one may be confronted with an integration problem, which is not solvable analytically. Thus, the correct result of the integration has to be approximated by evaluating the function at a sufficiently large set of sample points:

$$\int dx\, f(x) \to \sum_{x_i} f(x_i). \tag{A.1}$$

There are several well-established numerical integration methods based on sample points, which are equally spaced, e.g. the midpoint or trapezoidal rules, as well as some more evolved adaptive methods[1]. These methods work fine in lower dimensions. However, if the space of integration is of higher dimension, they are practically not applicable anymore, since the number of sample points grows exponentially with the number of dimension.
In contrast to this, the main idea of Monte Carlo integration is to use sample points, which are generated randomly[2]. For low-dimensional problems, such a method is not useful, if compared to the other methods mentioned above (an example is given in the lecture). Nevertheless, Monte Carlo integration is easy to generalize and is the method of choice for high-dimensional problems.

A.2 Monte Carlo methods in thermodynamic systems

We have already seen, that the the expectation value of a quantity A in the canonical ensemble (where $\beta = 1/k_B T$ is fixed) can be written as

$$\langle A \rangle = \frac{\sum_{S_i} A(S_i) e^{-\beta H(S_i)}}{\sum_{S_i} e^{-\beta H(S_i)}}. \tag{A.2}$$

Here the sums have to be performed over all possible microstates S_i of the system and $H(S_i)$ is the energy of the state S_i. With the partition function

$$Z = \sum_{S_i} e^{-\beta H(S_i)} \tag{A.3}$$

[1] These methods decide, whether and where more additional points should be evaluated.
[2] like in a casino, which gives some hint about the origin of the name.

we may define

$$P(S_i) = \frac{1}{Z} e^{-\beta H(S_i)} \tag{A.4}$$

so that

$$\langle A \rangle = \sum_{S_i} P(S_i) A(S_i). \tag{A.5}$$

The expectation value for A is the sum of the values $A(S_i)$, weighted with the function P. Although this structure looks rather simple, it is generally not possible to evaluate it in a naive way. One concrete problem is the tremendous number[3] of states S_i involved. One might think about using the Monte Carlo method here, generating a random sequence of n sample states $S_{i_0}, S_{i_1}, ..., S_{i_n}$, for which we could evaluate the corresponding $A(S_{i_n})$. However, normally it is not possible to calculate the partition function Z, even with a Monte Carlo technique. Thus we do not know the corresponding weighting factors $P(S_{i_n})$. How can we manage to get the expectation value, then?
Firstly, we notice that the weighting factor P represents the probability distribution of thermodynamic equilibrium, since

$$\sum_{S_i} P(S_i) = 1. \tag{A.6}$$

Thus, a rather elegant solution of the problem would be, to generate a series of sample states for the Monte Carlo method, which contains the states S_i according to their distribution P - instead of a completely random sequence[4]. For these states, we could simply sum up all their corresponding A values to get a good approximation for the expectation value. But still the problem is, how to generate such a series, since we do not know the probability distribution P. What we may access, however, is the relative probability of two states, because the partition function drops out:

$$\frac{P(S_i)}{P(S_j)} = e^{-\beta[H(S_i) - H(S_j)]}. \tag{A.7}$$

It turns out, that an algorithm originally developed by Metropolis et al. solves the problem[5]. It is capable of generating sequences of random states, which fulfill the corresponding probability distribution, based on the knowledge of the relative probabilities only. In the following, we will illustrate the functional principle of the Metropolis algorithm for a very simple example, namely an Ising model consisting of two sites only.

A.3 Example: Metropolis algorithm for the two site Ising model

Consider the two site Ising model, where the configuration space consists of the four states $S_i = \{\uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow, \downarrow\uparrow\}$. Without an applied magnetic field, we have a ground state energy E_G and an excited state energy E_E, and both of them are twofold degenerate. The two states S_1 and S_2 belong to the ground state level, and both S_3 and S_4 to the excited one. In the following, p denotes the probability of the excited state relative to the ground state, given by

$$p = e^{-\beta(E_E - E_G)}. \tag{A.8}$$

Now, take a look at the following algorithm, which produces a sequence of states $S^{(n)}$:

1. Choose a starting state $S^{(0)}$ out of the four S_i.

[3] Note, that we assume a model system with a discrete configuration space here. For a continuous model, the sums should be replaced by integrals over configuration space.

[4] For a non-degenerate system at low temperatures, for example, the ground state should appear much more often in this sequence than any specific state of higher energy (if the sequence is long enough...).

[5] Cf. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

2. Given a state $S^{(n)}$, randomly pick one of the other states and denote it $\tilde{S}$.

3. Generate the next state $S^{(n+1)}$ according to the rule:
   If the energy $H(\tilde{S}) \leq H(S^{(n)})$, set $S^{(n+1)} := \tilde{S}$.
   If the energy $H(\tilde{S}) > H(S^{(n)})$, set $S^{(n+1)} := \tilde{S}$ with probability p,
   and keep $S^{(n+1)} := S^{(n)}$ otherwise.

4. Continue with step 2.

The algorithm works quite simple, but what are its properties? We can answer this question in terms of probability. Let $p_i^{(n)}$ denote the probability, that $S^{(n)} = S_i$. The corresponding probability vector of the nth state lives in the configuration space and is given by

$$\mathbf{p}^{(n)} = (p_1^{(n)}, p_2^{(n)}, p_3^{(n)}, p_4^{(n)})^T. \tag{A.9}$$

One step of the algorithm may be represented by a probability matrix Π in the following way:

$$\mathbf{p}^{(n+1)} = \Pi \mathbf{p}^{(n)}, \tag{A.10}$$

where the matrix elements Π_{ij} are the probabilities $P_{j\to i}$ of the step getting from state S_j to S_i. It is not difficult to find, e.g., $P_{1\to 2} = \frac{1}{3} \cdot 1$, $P_{1\to 3} = P_{1\to 4} = \frac{1}{3} \cdot p$ and $P_{1\to 1} = \frac{2}{3}(1-p)$. Eventually,

$$\Pi = \frac{1}{3} \begin{pmatrix} 2(1-p) & 1 & 1 & 1 \\ 1 & 2(1-p) & 1 & 1 \\ p & p & 0 & 1 \\ p & p & 1 & 0 \end{pmatrix}. \tag{A.11}$$

Note, that Π is diagonalizable. The matrices

$$M = \begin{pmatrix} \frac{1}{p} & 0 & -2 & -1 \\ \frac{1}{p} & 0 & 0 & 1 \\ 1 & -1 & 1 & 0 \\ 1 & 1 & 1 & 0 \end{pmatrix} \tag{A.12}$$

and

$$M^{-1} = \frac{1}{2(1+p)} \begin{pmatrix} p & p & p & p \\ 0 & 0 & -(1+p) & 1+p \\ -p & -p & 1 & 1 \\ -1 & 1+2p & -1 & -1 \end{pmatrix} \tag{A.13}$$

result in

$$M^{-1} \Pi M = \Lambda \tag{A.14}$$

with the diagonal matrix

$$\Lambda = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{3} & 0 & 0 \\ 0 & 0 & \frac{1-2p}{3} & 0 \\ 0 & 0 & 0 & \frac{1-2p}{3} \end{pmatrix}. \tag{A.15}$$

This is quite helpful in finding the actual probability vector after n steps. We have

$$\begin{aligned} \mathbf{p}^{(n)} &= \Pi \mathbf{p}^{(n-1)} \\ &= \Pi^n \mathbf{p}^{(0)} \\ &= M \Lambda^n M^{-1} \mathbf{p}^{(0)}. \end{aligned}$$

The nth power of the diagonal matrix Λ simply is a diagonal matrix with the elements of Λ, but each raised to the power of n. For a large number of iteration steps, $n \to \infty$, only the

top-left entry of Λ^n will survive. The other eigenvalues have a modulus smaller than 1 and vanish accordingly. In this limit, we get

$$\mathbf{p}^{(\infty)} = \frac{1}{2(1+p)} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 \\ p & p & p & p \\ p & p & p & p \end{pmatrix} \mathbf{p}^{(0)} = \frac{1}{2(1+p)} \begin{pmatrix} 1 \\ 1 \\ p \\ p \end{pmatrix}. \tag{A.16}$$

Now, we can list several remarkable properties, which are typical for a Metropolis algorithm in general: Firstly note, that $\mathbf{p}^{(\infty)}$ is independent from the actual starting vector $\mathbf{p}^{(0)}$ due to the normalization condition $\sum_i p_i^{(0)} = 1$. Furthermore, it remains unchanged by Π, since we have

$$\mathbf{p}^{(\infty)} = \Pi \mathbf{p}^{(\infty)}. \tag{A.17}$$

Finally, most important, the elements of $\mathbf{p}^{(\infty)}$ show the correct probability distribution[6]. In the practical use of such a Metropolis algorithm, one has to wait for a sufficiently large number n of first initial steps[7]. After this initial process, the algorithm effectively produces a random sequence of states according to the probability distribution of thermodynamic equilibrium. A sufficiently large number of those states can then be used for the Monte Carlo integration.
The concrete generalization of the sample Metropolis algorithm presented above to an Ising model with a larger amount of sites is straightforward. A typical way is as follows:

1. Choose a starting state $S^{(0)}$.
2. Given a state $S^{(n)}$, keep the spins at all sites, apart from one randomly picked site, where you flip the spin. Denote this new state $\tilde{S}$.
3. Generate the next state $S^{(n+1)}$ according to the rule:
   If $H(\tilde{S}) \leq H(S^{(n)})$, set $S^{(n+1)} := \tilde{S}$.
   If $H(\tilde{S}) > H(S^{(n)})$, set $S^{(n+1)} := \tilde{S}$ with prob. $p = e^{-\beta[H(\tilde{S})-H(S^{(n)})]}$,
   and keep $S^{(n+1)} := S^{(n)}$ otherwise.
4. Continue with step 2.

The basic step 3. remains unchanged. It fulfills the so-called detailed balance property

$$P(S_i) \cdot P_{i \to j} = P(S_j) \cdot P_{j \to i}, \tag{A.18}$$

which is a sufficient condition for P being the stationary probability distribution. Thus, one can be sure to finally get the thermodynamic equilibrium distribution using the Metropolis algorithm. Note, that the algorithm given here differs from the one presented above by a minor point regarding step 2. The new state is not randomly chosen from the huge amount of all possible states, as above. Instead, the new state is generated from the old one by randomly picking a site and flipping its spin, but all the spins at other sites remain unchanged[8]. Alternatively, the local spin flip may be performed not for a randomly chosen site, but for all sites, one after the other, in a sweep. In the lecture, some sample solutions for the $2D$ Ising model, that are based on the Monte Carlo Metropolis method, will be presented. There are even more evolved techniques using cluster updates to overcome the effect of the critical slowing down.

[6] Actually, the Metropolis algorithm implements a Markov chain in configuration space, for which the thermodynamic equilibrium distribution is stationary.

[7] The actual number severely depends on the initial values and the circumstances.

[8] This kind of local updating allows to determine the energy difference and thus the relative probability much faster. An important aspect is to ensure the reachability of any state in a finite number of steps to keep ergodicity.

Appendix B

High-temperature expansion of the 2D Ising model: Finding the phase transition with Padé approximants

By Christian Iniotakis

In this section, we investigate the $2D$ Ising model using a specific approximation method, which allows to determine singular critical points at phase transitions in a rather elegant numerical way. Since we consider only the simplest two-dimensional cases, we may compare the final results with those of exact analytical solutions[1]. We start with the Ising Hamiltonian

$$H = -J \sum_{<i,j>} \sigma_i \sigma_j - h \sum_i \sigma_i. \tag{B.1}$$

Here, we assume a regular lattice of N sites with allowed spin values $\sigma_i = \pm 1$ at site i. The index $< i, j >$ denotes nearest neighbor connections. Due to the constants $J > 0$ and h, it is energetically favorable if a spin is parallel to its next neighbors and to the direction of the magnetic field, respectively. Obviously, the configuration space of this system contains 2^N possible states.

B.1 High-temperature expansion

For a general quantity A, the expectation value is given by

$$\langle A \rangle = \frac{\mathrm{Tr} A \, e^{-\beta H}}{\mathrm{Tr} e^{-\beta H}}, \tag{B.2}$$

where the abbreviation $\beta = 1/k_B T$ has been used. In the following, we concentrate on the average magnetization per spin/site

$$m = \langle \frac{1}{N} \sum_{i=1}^{N} \sigma_i \rangle \tag{B.3}$$

and the resulting zero-field susceptibility

$$\chi_0 = \left. \frac{\partial m}{\partial h} \right|_{h=0}. \tag{B.4}$$

[1] Cf., e.g., L. Onsager, Phys. Rev. **65**, 117 (1944).

The Tr-operator in the expression for the expectation value sums over all 2^N possible states of our system. Furthermore, for the concrete evaluation it is helpful to realize that

$$\mathrm{Tr}\,1 = \mathrm{Tr}\,\sigma_i^{2n}\sigma_j^{2m}...\sigma_k^{2l} = 2^N, \tag{B.5}$$

whereas

$$\mathrm{Tr}\,\sigma_i^{2n+1}\sigma_j^{m}...\sigma_k^{l} = 0. \tag{B.6}$$

In words, as long as we deal with products of even powers of the σ_i only, we get 2^N. However, as soon as at least one of the powers is odd, we get zero.
Exercise 1: Using above relations, show that the reduced zero-field susceptibility

$$\chi = k_B T \chi_0 \tag{B.7}$$

is given by

$$\chi = \frac{1}{N}\frac{\mathrm{Tr}\,\sum_{i,j}\sigma_i\sigma_j e^{-\beta H_0}}{\mathrm{Tr}\,e^{-\beta H_0}} = 1 + \frac{1}{N}\frac{\mathrm{Tr}\,\sum_{i\neq j}\sigma_i\sigma_j e^{-\beta H_0}}{\mathrm{Tr}\,e^{-\beta H_0}} \tag{B.8}$$

with H_0 denoting the zero-field Hamiltonian

$$H_0 = -J\sum_{<i,j>}\sigma_i\sigma_j. \tag{B.9}$$

As a next step, we want to evaluate both the numerator and the denominator of the reduced zero-field susceptibility. For this purpose, we use the identity

$$\begin{aligned} e^{\beta J\sigma_i\sigma_j} &= \sum_{n=0}^{\infty}\frac{(\beta J)^n}{n!}\sigma_i^n\sigma_j^n \\ &= \sum_{n=0}^{\infty}\frac{(\beta J)^{2n}}{(2n)!} + \sigma_i\sigma_j\sum_{n=0}^{\infty}\frac{(\beta J)^{2n+1}}{(2n+1)!} \\ &= \cosh\beta J + \sigma_i\sigma_j\sinh\beta J \\ &= \cosh(\beta J)(1 + w\sigma_i\sigma_j) \end{aligned} \tag{B.10}$$

with the definition

$$w = \tanh\beta J. \tag{B.11}$$

Note, that $w \to 0$ for $T \to \infty$ and $w < 1$ for finite T. Thus, w is an ideal candidate (better than β itself) for a series expansion in a small parameter, starting from the high-temperature regime. Due to

$$e^{-\beta H_0} = e^{\beta J\sum_{<i,j>}\sigma_i\sigma_j} = \prod_{<i,j>} e^{\beta J\sigma_i\sigma_j}, \tag{B.12}$$

Eq. (B.10) can be plugged into the expression for the reduced zero-field susceptibility Eq. (B.8), and we find in orders of w:

$$\begin{aligned} \chi &= 1 + \frac{1}{N}\frac{\mathrm{Tr}\sum_{i\neq j}\sigma_i\sigma_j\prod_{<r,s>}(1 + w\sigma_r\sigma_s)}{\mathrm{Tr}\prod_{<r,s>}(1 + w\sigma_r\sigma_s)} \\ &= 1 + \frac{1}{N}\frac{\mathrm{Tr}\sum_{i\neq j}\sigma_i\sigma_j\left(1 + w\sum_{<r,s>}\sigma_r\sigma_s + w^2\sum_{<r,s>\neq<n,m>}\sigma_r\sigma_s\sigma_n\sigma_m + ...\right)}{\mathrm{Tr}\left(1 + w\sum_{<r,s>}\sigma_r\sigma_s + w^2\sum_{<r,s>\neq<n,m>}\sigma_r\sigma_s\sigma_n\sigma_m + ...\right)}. \end{aligned}$$

n	square lattice, $q = 4$	triangular lattice, $q = 6$	honeycomb lattice, $q = 3$
0	1	1	1
1	4	6	3
2	12	30	6
3	36	138	12
4	100	606	24
5	276	2586	48
6	740	10818	90
7	1972	44574	168
8	5172	181542	318
9	13492	732678	600
10	34876	2 935218	1098
11	89764	11 687202	2004
12	229628	46 296210	3696
13	585508	182 588850	6792
14	1 486308	717 395262	12270
15	3 763460	2809 372302	22140

Table B.1: Coefficients a_n of the high-temperature expansion of the reduced zero-field susceptibility χ in orders of $w = \tanh \beta J$ (cf. Exercise 2). The data for the different lattice types is according to Sykes et al.

Exercise 2: Calculate the lowest orders in the numerator and the denominator. Show, that we end up with

$$\begin{aligned} \chi &= 1 + \frac{1}{N} \frac{2^N N q w + 2^N N q(q-1) w^2 + O(w^3)}{2^N + O(w^3)} \\ &= 1 + q w + q(q-1) w^2 + O(w^3), \end{aligned}$$

where q denotes the number of nearest neighbors in the lattice.
The evaluation of higher coefficients is merely a combinatorial task. In Table B.1, we list the results published by Sykes et al.[2] in 1972.

B.2 Finding the singularity with Padé approximants

The coefficients in Table B.1 grow rapidly for higher orders. In particular, the series

$$\chi = \sum_n a_n w^n \tag{B.13}$$

does not converge for all temperatures T or values of w, respectively. This is not surprising, since we expect a singularity of the form

$$\chi \sim A(w - w_c)^{-\gamma} \tag{B.14}$$

to appear when $w \to w_c^-$ due to the phase transition. The specific values of both w_c and the critical exponent $\gamma > 0$ are unknown so far. And obviously, an "ordinary" series expansion of the Taylor-type is not sufficient to handle such a singularity appropriately. Therefore we employ the method of the so-called Padé approximants[3] in the following, which will allow us to determine the critical values w_c and γ with a high accuracy.

[2] Cf. M.F. Sykes, D.S. Gaunt, P.D. Roberts and J.A. Wyles, J. Phys. A **5**, 624 (1972).
[3] Cf. H. Padé's thesis of the year 1892 as well as G.A. Baker, Phys. Rev. **124**, 768 (1961).

The Padé approximant $[m,n]$ to a given function f is the ratio of a polynomial of degree m divided by a polynomial of degree n

$$[m,n] = \frac{p_0 + p_1 x + p_2 x^2 + ... + p_m x^m}{1 + q_1 x + q_2 x^2 + ... + q_n x^n} \tag{B.15}$$

such that it agrees with f up to order $m+n$:

$$f = [m,n] + O(x^{m+n+1}). \tag{B.16}$$

Note, that the coefficients p_i, q_j of the polynomials are uniquely determined, and with them also is the Padé approximant $[m,n]$. The Padé approximants $[m,0]$ just coincide with the Taylor series expansion for f up to order m and are of no use for our purpose here. However, Padé approximants of higher order in the denominator naturally exhibit poles. This feature makes them good candidates for catching the singularity at the phase transition.
Since the expected singularity is of order γ, whereas the poles of the Padé approximants are restricted to integer orders, we may introduce the following trick: Instead of χ, we use the auxiliary function $\partial_w \ln \chi$, since

$$\begin{aligned} \chi &\sim A(w-w_c)^{-\gamma} \\ \ln \chi &\sim \ln A - \gamma \ln(w-w_c) \\ \partial_w \ln \chi &\sim \frac{-\gamma}{w-w_c}. \end{aligned}$$

Thus we expect the Padé approximants for the function $\partial_w \ln \chi$ to display a singularity at the critical value w_c, representing the physical phase transition. Moreover, the value of the residue corresponding to this singularity should provide us with $-\gamma$. In Table B.2, we list the first coefficients for the auxiliary function $\partial_w \ln \chi$. Results for the concrete numerical evaluation of the Padé approximants will be presented in the lecture. Some samples can be seen in Figs. B.1, B.2 and B.3 for the square, triangular and honeycomb lattice, respectively. We get a very good estimate for the critical exponent compared to its exact value

$$\gamma = 7/4 = 1.75, \tag{B.17}$$

which is independent of the lattice type. Furthermore, the results for the critical values w_c are in excellent agreement with those of analytical solutions given in the brackets:

$$\begin{aligned} w_c^{SQU} &\approx 0.414211 \;\; (\sqrt{2}-1 \approx 0.414214) \\ w_c^{TRI} &\approx 0.267944 \;\; (2-\sqrt{3} \approx 0.267949) \\ w_c^{HON} &\approx 0.577348 \;\; (1/\sqrt{3} \approx 0.577350). \end{aligned}$$

The critical temperature T_c can easily be calculated from w_c. We get

$$\frac{k_B T_c}{J} \approx 2.269 \,/\, 3.641 \,/\, 1.519 \tag{B.18}$$

for the square, triangular and honeycomb lattice, respectively. Note, that the critical temperature roughly scales with the number q of nearest neighbors in the lattice, which are accordingly given by

$$q = 4 \,/\, 6 \,/\, 3. \tag{B.19}$$

This behavior indicates, that a coupling to more neighbors enhances parallel alignment of the spins, allowing the phase transition to occur already at higher temperatures.
Summarizing, employing Padé approximants revealed the phase transitions of the $2D$ Ising model on different lattice types with a high accuracy. The main work within this method lies in calculating sufficiently many coefficients of the power series of the corresponding singular quantity[4]. A generalization to, e.g., the $3D$-case is straightforward.

[4]Note, that the success of this method crucially depends on the concrete type of singularity to deal with.

n	square lattice, $q = 4$	triangular lattice, $q = 6$	honeycomb lattice, $q = 3$
0	4	6	3
1	8	24	3
2	28	90	9
3	48	336	15
4	164	1266	33
5	296	4752	27
6	956	17646	87
7	1760	65760	159
8	5428	245646	297
9	10568	917184	243
10	31068	3422898	795
11	62640	12773952	1503
12	179092	47674386	2499
13	369160	177928824	2355
14	1034828	664051230	7209

Table B.2: Coefficients of the high-temperature expansion of the function $\partial_w \ln \chi$ in orders of $w = \tanh \beta J$. We only give results up to order 14, generated from Table B.1.

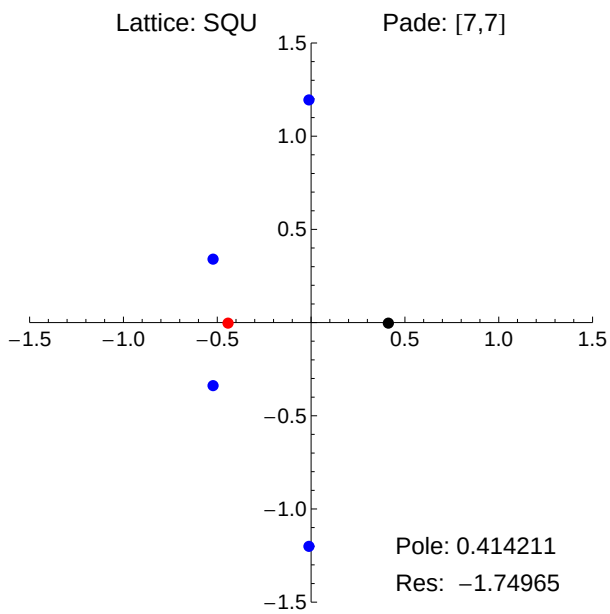

Fig. B.1: Poles of the $[7, 7]$ *Padé approximant for* $\partial_w \ln \chi$ *on the square lattice. The physical pole is at* $w_c \approx 0.414211$ *with residue* -1.7497.

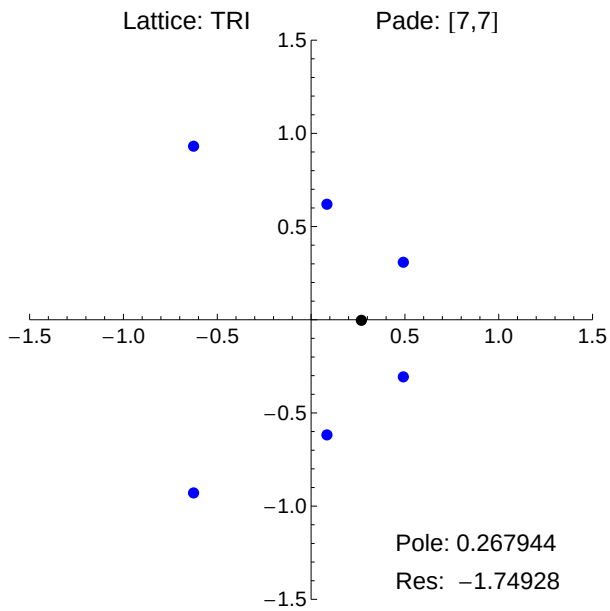

Fig. B.2: Poles of the $[7,7]$ *Padé approximant for* $\partial_w \ln \chi$ *on the triangular lattice. The physical pole is at* $w_c = 0.267944$ *with residue* -1.7493.

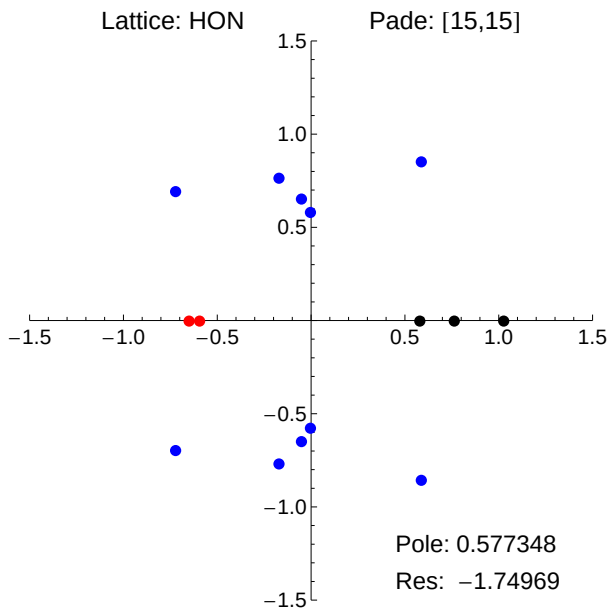

Fig. B.3: Poles of the $[15,15]$ *Padé approximant for* $\partial_w \ln \chi$ *on the honeycomb lattice. The physical pole is at* $w_c = 0.577348$ *with residue* -1.7497.