

Statistical Physics

ETH Zürich – Herbstsemester 2014

Manfred Sigrist, HIT K23.8

Tel.: 3-2584, Email: sigrist@itp.phys.ethz.ch

Webpage: <http://www.itp.phys.ethz.ch/research/condmat/strong/>

Literature:

- *Statistical Mechanics*, K. Huang, John Wiley & Sons (1987).
- *Introduction to Statistical Physics*, K. Huang, Chapman & Hall Books (2010).
- *Equilibrium Statistical Physics*, M. Plischke and B. Bergersen, Prentice-Hall International (1989).
- *Theorie der Wärme*, R. Becker, Springer (1978).
- *Thermodynamik und Statistik*, A. Sommerfeld, Harri Deutsch (1977).
- *Statistische Physik, Vol. V*, L.D. Landau and E.M Lifschitz, Akademie Verlag Berlin (1975).
- *Statistische Mechanik*, F. Schwabl, Springer (2000).
- *Elementary Statistical Physics*, Charles Kittel, John Wiley & Sons (1967).
- *Statistical Mechanics*, R.P. Feynman, Advanced Book Classics, Perseus Books (1998).
- *Statistische Mechanik*, R. Hentschke, Wiley-VCH (2004).
- *Introduction to Statistical Field Theory*, E. Brézin, Cambridge (2010).
- *Statistical Mechanics in a Nutshell*, Luca Peliti, Princeton University Press (2011).
- *Principle of condensed matter physics*, P.M. Chaikin and T.C. Lubensky, Cambridge University Press (1995).
- Many other books and texts mentioned throughout the lecture

Lecture Webpage:

<http://www.itp.phys.ethz.ch/education/hs14/StatPhys>

Contents

1	Kinetic approach to statistical physics	5
1.1	Time evolution and Master equation	5
1.1.1	H -function and information	8
1.1.2	Simulation of a two-state system	9
1.1.3	Equilibrium of a system	11
1.2	Analysis of a closed system	12
1.2.1	H and the equilibrium thermodynamics	12
1.2.2	Master equation	13
1.2.3	Irreversible processes and increase of entropy	14
2	Classical statistical Physics	18
2.1	Gibbsian concept of ensembles	18
2.1.1	Liouville Theorem	19
2.1.2	Equilibrium system	20
2.2	Microcanonical ensemble	20
2.2.1	Entropy	21
2.2.2	Relation to thermodynamics	23
2.2.3	Ideal gas - microcanonical treatment	23
2.3	Canonical ensemble	25
2.3.1	Thermodynamics	26
2.3.2	Equipartition law	27
2.3.3	Ideal gas - canonical treatment	28
2.4	Grand canonical ensemble	28
2.4.1	Relation to thermodynamics	30
2.4.2	Ideal gas - grand canonical treatment	30
2.4.3	Chemical potential in an external field	31
2.5	Fluctuations	31
2.5.1	Energy	31
2.5.2	Particle number	33
2.5.3	Magnetization	34
3	Quantum Statistical Physics	35
3.1	Basis of quantum statistical physics	35
3.2	Density matrix	37
3.3	Ensembles in quantum statistics	38
3.3.1	Microcanonical ensemble	38
3.3.2	Canonical ensemble	39
3.3.3	Grand canonical ensemble	39
3.4	Ideal quantum paramagnet - canonical ensemble	40
3.4.1	Spin 1/2	40
3.4.2	Spin S - classical limit	41
3.5	Ideal quantum gas - grand canonical ensemble	43

3.6	Properties of Fermi gas	46
3.6.1	High-temperature and low-density limit	47
3.6.2	Low-temperature and high-density limit: degenerate Fermi gas	47
3.6.3	Spin-1/2 Fermions in a magnetic field	49
3.7	Bose gas	50
3.7.1	Bosonic atoms	50
3.7.2	High-temperature and low-density limit	50
3.7.3	Low-temperature and high-density limit: Bose-Einstein condensation	51
3.8	Photons and phonons	55
3.8.1	Blackbody radiation - photons	56
3.8.2	Phonons in a solid	58
3.9	Diatomic molecules	60
4	Identical Quantum Particles - Formalism of Second Quantization	64
4.1	Many-body wave functions and particle statistics	64
4.2	Independent, indistinguishable particles	65
4.3	Second Quantization Formalism	66
4.3.1	Creation- and annihilation operators	66
4.3.2	Field operators	68
4.4	Observables in second quantization	69
4.5	Equation of motion	70
4.6	Correlation functions	72
4.6.1	Fermions	72
4.6.2	Bosons	74
4.7	Selected applications	75
4.7.1	Spin susceptibility	75
4.7.2	Bose-Einstein condensate and coherent states	77
4.7.3	Phonons in an elastic medium	81
5	One-dimensional systems of interacting degrees of freedom	84
5.1	Classical spin chain	84
5.1.1	Thermodynamics	84
5.1.2	Correlation function	85
5.1.3	Susceptibility	87
5.2	Interacting lattice gas	88
5.2.1	Transfer matrix method	88
5.2.2	Correlation function	90
5.3	Long-range order versus disorder	92
6	Phase transitions	93
6.1	Ehrenfest classification of phase transitions	93
6.2	Phase transition in the Ising model	95
6.2.1	Mean field approximation	95
6.2.2	Instability of the paramagnetic phase	97
6.2.3	Phase diagram	99
6.3	Gaussian transformation	101
6.3.1	Correlation function and susceptibility	103
6.4	Ginzburg-Landau theory	106
6.4.1	Ginzburg-Landau theory for the Ising model	106
6.4.2	Critical exponents	108
6.4.3	Range of validity of the mean field theory - Ginzburg criterion	109
6.5	Self-consistent field approximation	110
6.5.1	Renormalization of the critical temperature	110

6.5.2	Renormalized critical exponents	112
6.6	Long-range order - Peierls' argument	113
6.6.1	Absence of finite-temperature phase transition in the 1D Ising model . . .	113
6.6.2	Long-range order in the 2D Ising model	114
7	Superfluidity	116
7.1	Quantum liquid Helium	116
7.1.1	Superfluid phase	117
7.1.2	Collective excitations - Bogolyubov theory	119
7.1.3	Gross-Pitaevskii equations	124
7.2	Berezinskii-Kosterlitz-Thouless transition	127
7.2.1	Correlation function	127
7.2.2	Topological excitations and BKT transition	129

Chapter 1

Kinetic approach to statistical physics

Thermodynamics deals with the behavior and relation of quantities of macroscopic systems which are in equilibrium. The concrete time evolution does not enter the discussions in thermodynamics, although systems may change - quasi-statically - between different equilibrium states. A macroscopic system, however, consists of many microscopic entities, many degrees of freedom, such as moving atoms in a gas or magnetic / electric dipoles in magnets or ferroelectrics. Therefore it seems very natural to analyze the time evolution of these entities to get insight into the behavior of macroscopic systems whereby a statistical approach is most adequate, for the simple reason that we cannot track down the temporal behavior of each entity separately.

In this chapter we will discuss a conceptual version of a many-body system to understand how one can view non-equilibrium behavior and how equilibrium is reached and eventually characterized. Entropy will play an essential role to give us the connection to thermodynamics of the equilibrium state. This discussion will also make clear how the immense number of degrees of freedom, N , is essential for the quality of the statistical approach and the emergence of the laws of thermodynamics. The kinetic approach find one important application in kinetic gas theory and Boltzmann's transport theory which will not be covered here (part of the lecture "Theorie der Wärme" in Bachelor of Physics).

1.1 Time evolution and Master equation

We start by considering a model with N units (atoms, ...) which can be in z different micro-states (Fig.1.1):

$$\{s_i^\nu\} \quad \text{with} \quad i = 1, \dots, N; \nu = 1, \dots, z. \quad (1.1)$$

We may define the variable s_i^ν such that if the unit i is in the state ν' then

$$s_i^\nu = \begin{cases} 1 & \nu = \nu', \\ 0 & \nu \neq \nu'. \end{cases} \quad (1.2)$$

Thus \vec{s}_i is a vector with one component (ν') being 1 and the others 0. For the moment, these degrees of freedom are considered to be independent and their z micro-states have the same energy, when we introduce the time evolution of this system. For the purpose of a simple simulation of the time evolution of these units, we introduce discrete, equally spaced time steps t_n with $t_{n+1} - t_n = \Delta t$. During each time step the micro-state of each unit can change from ν to ν' with a probability $p_{\nu\nu'}$ which is connected with the transition rate $\Gamma_{\nu\nu'}$ by

$$p_{\nu\nu'} = \Gamma_{\nu\nu'} \Delta t. \quad (1.3)$$

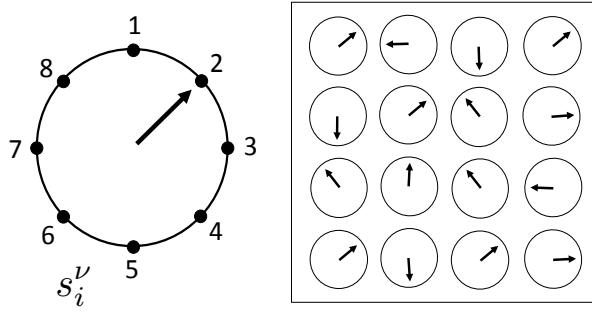


Figure 1.1: A schematic system (box) of N units (circle) with micro-states $\nu = 1, \dots, 8$. Each unit can be in an individual state at a given time.

We require that the reverse processes have equal probability due to time reversal symmetry: $p_{\nu\nu'} = p_{\nu'\nu}$ and, thus, $\Gamma_{\nu\nu'} = \Gamma_{\nu'\nu}$. At a given time, we find N_ν units of the system are in the micro-state ν (Fig.1.2)

$$N_\nu = \sum_{i=1}^N s_i^\nu \quad \text{with} \quad \sum_{\nu=1}^z N_\nu = N. \quad (1.4)$$

Thus, picking at random a unit i we would find it in the micro-state ν with the probability,

$$w_\nu = \frac{N_\nu}{N} \quad \text{with} \quad \sum_{\nu=1}^z w_\nu = 1. \quad (1.5)$$

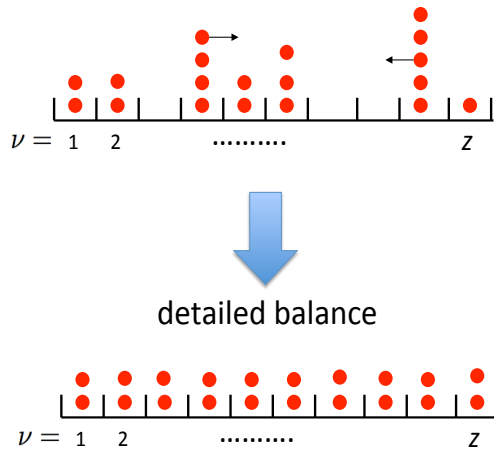


Figure 1.2: Distribution of the units on different micro-states: Evolution towards the fixed point with detailed balance where all micro-states are occupied by the same number of units on average.

Let us now discuss the "budget" of each micro-state ν during the evolution in time: (1) the number N_ν is reduced, because some units in micro-state ν will have a transition to another micro-state ($\nu \rightarrow \nu'$) with the rate $\sum_{\nu'} \Gamma_{\nu\nu'} N_\nu$; (2) the number N_ν increases, since some units in another micro-state undergo a transition to the micro-state ν with the rate $\sum_{\nu'} \Gamma_{\nu'\nu} N_{\nu'}$. Note that these rates are proportional to the number of units in the micro-state which is transformed

into another micro-state, because each unit changes independently with the rate $\Gamma_{\nu\nu'}$. The corresponding budget equation is given by

$$N_\nu(t_{n+1}) = N_\nu(t_n) - \underbrace{\Delta t \sum_{\nu' \neq \nu} \Gamma_{\nu\nu'} N_\nu(t_n)}_{\text{leaving state } \nu} + \underbrace{\Delta t \sum_{\nu' \neq \nu} \Gamma_{\nu'\nu} N_{\nu'}(t_n)}_{\text{entering state } \nu} . \quad (1.6)$$

This set of z iterative equations describes the evolution of the N units in a statistical way, whereby we do not keep track of the state of each individual unit, but only of the number of units in each micro-state. As we will see below (*H*-theorem), starting from an arbitrary initial configuration $\{N_\nu\}$ of the units at $t_1 = 0$, this iteration moves generally towards a fixed point, $N_\nu(t_{n+1}) = N_\nu(t_n)$ which requires that

$$0 = \sum_{\nu' \neq \nu} \Gamma_{\nu\nu'} N_\nu(t_n) - \sum_{\nu' \neq \nu} \Gamma_{\nu'\nu} N_{\nu'}(t_n) . \quad (1.7)$$

There is no time evolution anymore for $N_\nu(t)$, although the units are still changing their states in time. As this equation is true for all ν we find that independently

$$0 = \Gamma_{\nu\nu'} N_\nu(t_n) - \Gamma_{\nu'\nu} N_{\nu'}(t_n) , \quad (1.8)$$

which means that for any pair of micro-states ν and ν' the mutual transitions compensate each other. Equation (1.8) is known as the condition of *detailed balance*.¹ Due to $\Gamma_{\nu\nu'} = \Gamma_{\nu'\nu}$ in our conceptual model, we find the fixed point condition $N_\nu = N_{\nu'} = N/z$, i.e all micro-states are equally occupied.

We now slightly reformulate the iterative equation (1.6) taking the limit of $\Delta t \rightarrow 0$ and dividing it by N :

$$\frac{dw_\nu}{dt} = -w_\nu \sum_{\nu' \neq \nu} \Gamma_{\nu\nu'} + \sum_{\nu' \neq \nu} \Gamma_{\nu'\nu} w_{\nu'} , \quad (1.14)$$

which turns into a differential equation. This is the so-called *master equation* of the system. Also here it is obvious that the detailed balance condition leads to a solution where all probabilities $w_\nu(t)$ are constant in time:

$$w_\nu \Gamma_{\nu\nu'} = w_{\nu'} \Gamma_{\nu'\nu} \quad \Rightarrow \quad \frac{w_\nu}{w_{\nu'}} = \frac{\Gamma_{\nu'\nu}}{\Gamma_{\nu\nu'}} = 1 , w_\nu = \frac{1}{z} . \quad (1.15)$$

¹ We show here that the detailed balance condition follows from rather general arguments even if the condition $\Gamma_{\nu\nu'} = \Gamma_{\nu'\nu}$ is not satisfied. First, we define for the general case

$$N_\nu = \chi_\nu \phi_\nu \quad \text{such that} \quad R_{\nu\nu'} = \Gamma_{\nu\nu'} \chi_\nu = \Gamma_{\nu'\nu} \chi_{\nu'} = R_{\nu'\nu} , \quad (1.9)$$

which leads to the fixed point condition Eq.(1.7),

$$0 = \sum_{\nu'} (R_{\nu\nu'} \phi_\nu - R_{\nu'\nu} \phi_{\nu'}) = \sum_{\nu'} R_{\nu\nu'} (\phi_\nu - \phi_{\nu'}) . \quad (1.10)$$

Note that the condition $\Gamma_{\nu\nu'} = \Gamma_{\nu'\nu}$ would imply $\chi_\nu = \chi_{\nu'}$. Assuming $R_{\nu\nu'} > 0$ for all pairs (ν, ν') (more generally ergodicity is necessary, i.e. the system cannot be decomposed into disconnected subsystems), this equation can only be solved by $\phi_\nu = \phi = \text{const}$ for all ν .

Proof: Assume that

$$\phi_1 = \phi_2 = \dots = \phi_{\nu_1} > \phi_{\nu_1+1} = \phi_{\nu_1+2} = \dots = \phi_{\nu_2} > \phi_{\nu_2+1} = \dots > \dots = \phi_z > 0 \quad (1.11)$$

then for $\nu \leq \nu_1$ we find

$$\sum_{\nu'} R_{\nu\nu'} (\phi_\nu - \phi_{\nu'}) = \sum_{\nu' > \nu_1} R_{\nu\nu'} (\phi_\nu - \phi_{\nu'}) > 0 , \quad (1.12)$$

such that we cannot satisfy Eq.(1.10) and only the solution $\phi_\nu = \phi = \text{const}$ for all ν is possible. Thus, using Eq.(1.9) it follows that

$$R_{\nu\nu'} \phi_\nu - R_{\nu'\nu} \phi_{\nu'} = 0 \quad \Rightarrow \quad \Gamma_{\nu\nu'} N_\nu - \Gamma_{\nu'\nu} N_{\nu'} = 0 , \quad (1.13)$$

and the detailed balance condition is satisfied.

We can define a mean value of a property or quantity "α" associated with each micro-state ν , which we call α_ν :

$$\langle \alpha \rangle = \sum_{\nu} \alpha_{\nu} w_{\nu} . \quad (1.16)$$

Such mean values describe the macro-state of the system. The time evolution of this quantity is easily derived,

$$\begin{aligned} \frac{d}{dt} \langle \alpha \rangle &= \sum_{\nu} \alpha_{\nu} \frac{dw_{\nu}}{dt} = \sum_{\nu} \alpha_{\nu} \left[-w_{\nu} \sum_{\nu' \neq \nu} \Gamma_{\nu\nu'} + \sum_{\nu' \neq \nu} \Gamma_{\nu'\nu} w_{\nu'} \right] \\ &= -\frac{1}{2} \sum_{\nu, \nu'} \{ \alpha_{\nu} - \alpha_{\nu'} \} (w_{\nu} - w_{\nu'}) \Gamma_{\nu\nu'} , \end{aligned} \quad (1.17)$$

where the last equality is obtained by symmetrization using $\Gamma_{\nu\nu'} = \Gamma_{\nu'\nu}$. Obviously the time evolution of $\langle \alpha \rangle$ stops when detailed balance is reached.

1.1.1 *H*-function and information

We introduce the function $H(t)$ which has the following form

$$H(t) = - \sum_{\nu} w_{\nu} \ln w_{\nu} . \quad (1.18)$$

This function can be viewed as a measure for the lack of our knowledge about the microscopic state of our system. Concretely, if at the time t we pick one atom at random, we may ask how well we can predict to find the atom in a given micro-state. Assume that $w_1 = 1$ and $w_{\nu} = 0$ for $\nu = 2, \dots, z$. Then we can be sure to find the micro-state 1. In this case $H(t) = 0$. For generic distributions of probabilities $H(t) > 0$. The larger $H(t)$ the less certain the outcome of our picking experiment is, i.e. the less information is available about the system.

It is interesting to follow the time dependence of $H(t)$,

$$\begin{aligned} \frac{dH(t)}{dt} &= - \sum_{\nu} \frac{dw_{\nu}}{dt} (\ln w_{\nu} + 1) = \sum_{\nu, \nu'} \Gamma_{\nu\nu'} (w_{\nu} - w_{\nu'}) (\ln w_{\nu} + 1) \\ &= \frac{1}{2} \sum_{\nu, \nu'} (\ln w_{\nu} - \ln w_{\nu'}) (w_{\nu} - w_{\nu'}) \Gamma_{\nu\nu'} \geq 0 . \end{aligned} \quad (1.19)$$

Note that $(x - y)(\ln x - \ln y) \geq 0$. This implies that $H(t)$ evolves in a specific direction in time, despite the assumption of time reversal symmetry, which was an essential part in reaching the symmetrized form of Eq.(1.19). The condition $dH/dt = 0$ then requires $w_{\nu} = w_{\nu'}$, corresponding to detailed balance. The inequality (1.19) suggests that detailed balance corresponds to the macroscopic state of the system with maximal possible H and, thus, the maximal uncertainty of knowledge.

Let us consider this idea from a slightly different view point. For given $w_{\nu} = N_{\nu}/N$ in a system of N units, there are

$$\frac{N!}{N_1! N_2! \dots N_z!} = W(N_{\nu}) \quad (1.20)$$

realizations among z^N possible configurations. In the large- N limit we may apply Stirling formula

$$\ln n! \approx n \ln n - n + \frac{1}{2} \ln 2\pi n, \quad (1.21)$$

which then leads to

$$\begin{aligned} \ln W(N_\nu) &\approx N \ln N - N - \sum_\nu [N_\nu \ln N_\nu - N_\nu] \\ &= -N \sum_\nu w_\nu \ln w_\nu = NH(t). \end{aligned} \tag{1.22}$$

where we have ignored terms of the order $\ln N$. Thus, H measures for given set $\{N_\nu\}$ the number of available configurations of the units.

Now we show the maximal H corresponds indeed to the detailed balance condition being then equivalent to the set $\{N_\nu\}$ with the largest possible number of configurations. For this purpose we maximize H as a functional of w_ν through the following extended form of H

$$H' = - \sum_\nu w_\nu \ln w_\nu + \lambda \left\{ \sum_\nu w_\nu - 1 \right\}, \tag{1.23}$$

where we introduced the constraint of normalization of the probability distribution using a Lagrange multiplier. Thus, searching the maximum with respect to w_ν and λ , we get to the equation

$$\frac{dH'}{dw_\nu} = -\ln w_\nu - 1 + \lambda = 0 \quad \text{and} \quad \sum_\nu w_\nu = 1, \tag{1.24}$$

which can only be solved by $w_\nu = e^{\lambda-1} = 1/z$ and constitutes again the condition of detailed balance.

The conclusion of this discussion is that the detailed balance describes the distribution w_ν with the highest probability, i.e. the largest number of different possible realizations yield the same $\{N_1, \dots, N_z\}$. This is indeed the maximal value of $W(N_\nu) = N!/\{(N/z)!\}^z$, the number of realizations. In its time evolution the system, following the master equation, moves towards the fixed point with this property and $H(t)$ grows monotonously until it reaches its maximal value.

1.1.2 Simulation of a two-state system

The master equation (1.14), introduced above, deals with a system of independent units in a statistical way. It corresponds to a rate equation. We would like now to consider a "concrete" model system and analyze how it evolves in time both analytically by solving the master equation and numerically by simulating a system with a not so large number of units. This will be most illustrative in view of the apparent problem we encounter by the fact that our model conserves time reversal symmetry. Nevertheless, there is an apparent preference in the direction of evolution.

We consider a system of N units with two different micro-states ($z = 2$) to perform a computational simulation. We describe the micro-state of unit i by the quantity

$$m_i = \begin{cases} +1 & \nu = 1 \\ -1 & \nu = 2. \end{cases} \tag{1.25}$$

This may be interpreted as a magnetic moment point up (+1) or down (-1). The transition between the two states corresponds simply to a sign change of m_i , which happens with equal probability in both directions (time reversal symmetry). The computational algorithm works in the following way. Within a time step each unit experiences a transition with a probability p ($0 < p < 1$), whereby the probabilistic behavior is realized by a random number generator. This means generate a uniformly distributed random number $R \in [0, 1]$ and then do the following process for all units:

$$m_i(t_{n+1}) = \begin{cases} m_i(t_n) & \text{if } p < R < 1 \\ -m_i(t_n) & \text{if } 0 \leq R \leq p. \end{cases} \tag{1.26}$$

This time series corresponds to a so-called Markov chain which means that the transition at each step is completely independent from previous steps.

After each time step we "measure" the quantities

$$M(t) = \frac{1}{N} \sum_{i=1}^N m_i(t) \quad \text{and} \quad H(t) = - \sum_{\nu=1}^2 w_\nu(t) \ln w_\nu(t) \quad (1.27)$$

where

$$w_1(t) = \frac{1}{2} \{1 + M(t)\} \quad \text{and} \quad w_2(t) = \frac{1}{2} \{1 - M(t)\} . \quad (1.28)$$

Note that $M(t)$ may be interpreted as a average magnetization per unit. The results of the simulations for both quantities are shown in Fig.1.3. In the starting configuration all units have the micro-state $m_i = +1$ (completely polarized). There is only one such configuration, while the fixed point distribution is characterized by $w_1 = w_2 = 1/2$ with a large number of realizations

$$W = \frac{N!}{\{(N/2)!\}^2} \approx 2^N \sqrt{\frac{2}{\pi N}} \quad \text{for large } N , \quad (1.29)$$

following Stirling's formula. This corresponds to $M = 0$. The closer to the fixed point distribution the system is the more realizations are available. We may estimate this by

$$\begin{aligned} W(M) &= \frac{N!}{N_1!N_2!} = \frac{N!}{\{N/2(1+M)\}!\{N/2(1-M)\}!} \\ \Rightarrow \ln W(M) &\approx N \ln 2 - \frac{N}{2} \{(1+M) \ln(1+M) + (1-M) \ln(1-M)\} + \frac{1}{2} \ln \frac{2}{\pi N(1-M^2)} \\ &\approx N \ln 2 + \frac{1}{2} \ln \frac{2}{\pi N} - \frac{M^2 N}{2} \\ \Rightarrow W(M) &\approx 2^N \sqrt{\frac{2}{\pi N}} e^{-M^2 N/2} , \end{aligned} \quad (1.30)$$

where we have used the Stirling formula for large N and the expansion for $M \ll 1$ ($\ln(1+x) = x - \frac{x^2}{2} + \dots$). The number of realizations drop quickly from the maximal value at $M = 0$ with a width $\Delta M = \sqrt{2/N}$. The larger N the larger the fraction of realizations of the system belonging to the macroscopic state with $M \approx 0$.

This explains the overall trend seen in the simulations. The "measured" quantities approach a fixed point, but show fluctuations. These fluctuations shrink with increasing system size N . The relation found from (1.19) is not strictly true, when we consider a specific time series of a finite system. The master equations leading to (1.19) are statistical and consider an averaged situation for very large systems ($N \rightarrow \infty$). The "fixed point" reached after a long time corresponds to the situation that each configuration of micro-states is accessed with the same probability. Macroscopic states deviating from the fixed point occupy less and less of the available configuration space for increasing N .

The master equations of our two-state system are

$$\frac{dw_1}{dt} = \Gamma(w_2 - w_1) \quad \text{and} \quad \frac{dw_2}{dt} = \Gamma(w_1 - w_2) , \quad (1.31)$$

where $\Gamma = \Gamma_{12} = \Gamma_{21}$. Adding and subtracting the two equations leads to

$$\frac{d}{dt}(w_1 + w_2) = 0 \quad \text{and} \quad \frac{d}{dt}(w_1 - w_2) = -2\Gamma(w_1 - w_2) , \quad (1.32)$$

respectively. The first equation states the conservation of the probability $w_1 + w_2 = 1$. The second leads to the exponential approach of $M(t)$ to 0,

$$M(t) = M_0 e^{-2t\Gamma}, \quad (1.33)$$

with $M_0 = M(0) = 1$, from which we also obtain

$$H(t) = -\ln 2 - \frac{1}{2}(1 + e^{-2t\Gamma}) \ln(1 + e^{-2t\Gamma}) - \frac{1}{2}(1 - e^{-2t\Gamma}) \ln(1 - e^{-2t\Gamma}) \approx \ln 2 - e^{-4t\Gamma}. \quad (1.34)$$

where the last approximation holds for times $t \gg 1/4\Gamma$ and shows the relaxation to the unpolarized situation. We see that the relaxation times for M and H differ by a factor two

$$\tau_M = \frac{1}{2\Gamma} \quad \text{and} \quad \tau_H = \frac{1}{4\Gamma} \quad (1.35)$$

which can be observed also roughly by eye in the results of our simulation (Fig.1.3.).

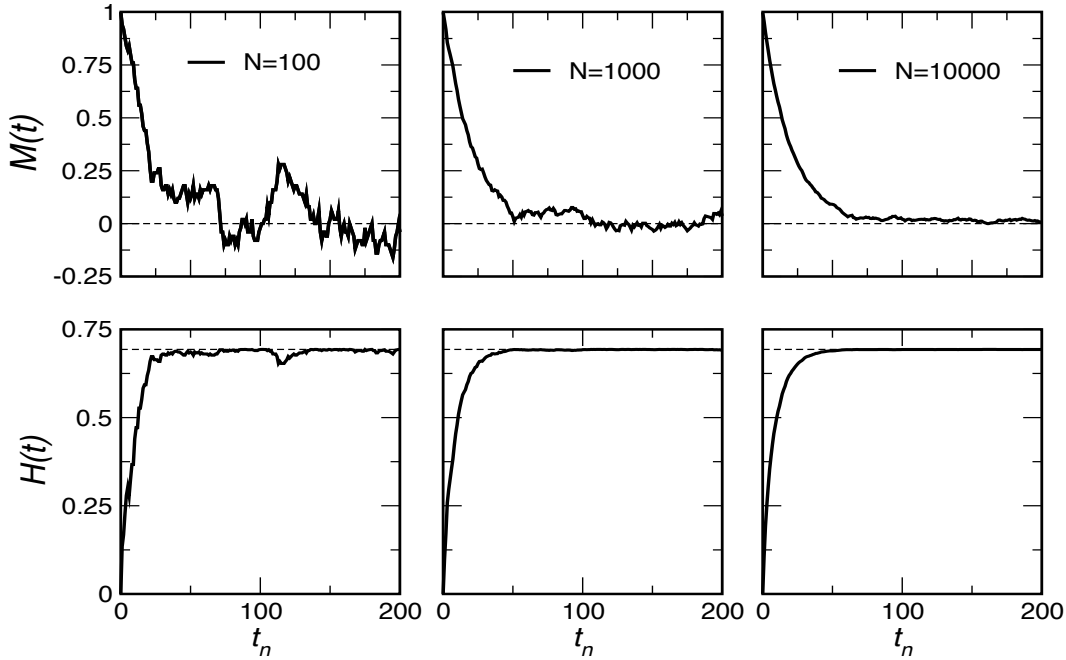


Figure 1.3: Simulation of a two-state system for different numbers of units N : 1^{st} column, $N = 100$; 2^{nd} column, $N = 1000$; 3^{rd} column, $N = 10000$. Note that for sufficiently large t ($\gg \delta/p$), $M(t) \rightarrow 0$ and $H(t) \rightarrow \ln 2$.

1.1.3 Equilibrium of a system

The statistical discussion using the master equation and our simulation of a system with many degrees of freedom shows that the system relaxes towards a fixed point of the probability distribution w_ν , which describes its macroscopic state independent of time. This probability distribution of the micro-states accounts for averaged properties, and allows us to calculate average values of certain physical quantities related to the micro-states. This fixed point is equivalent to the

equilibrium of the system. Deviations from this equilibrium yield non-equilibrium states of the system, which then relax towards the equilibrium, if we allow the system to do so. The equilibrium state is characterized in a statistical sense as the state with the maximal number of realizations in terms of configurations of micro-states of the units. We now aim at getting a connection with macroscopic thermodynamic properties of the system in equilibrium.

1.2 Analysis of a closed system

We turn to a system of N units whose states possess different energies, ϵ_ν . Again we describe the macro-state of the system by means of the probability distribution $w_\nu = N_\nu/N$. The system shall be closed, such that no matter and no energy is exchanged with the environment. Thus, the total energy and the number of units is conserved:

$$\langle \epsilon \rangle = \sum_{\nu=1}^z w_\nu \epsilon_\nu \quad \text{and} \quad 1 = \sum_{\nu=1}^z w_\nu, \quad (1.36)$$

which define the internal energy $U = N\langle \epsilon \rangle = Nu$ unchanged in a closed system, and the normalization of the probability distribution.

1.2.1 H and the equilibrium thermodynamics

As before we define the function $H(t)$, an increasing function of time, saturating at a maximal value, which we consider as the condition for "equilibrium". Time evolution and aspects of non-equilibrium will be addressed later. Rather we search now for the maximum of H with respect to w_ν under the condition of energy conservation. Thus, we introduce again Lagrange multipliers for these constraints

$$H(w_\nu) = - \sum_{\nu} w_\nu \ln w_\nu + \lambda \left\{ \sum_{\nu} w_\nu - 1 \right\} - \frac{1}{\theta} \left\{ \sum_{\nu} w_\nu \epsilon_\nu - \langle \epsilon \rangle \right\} \quad (1.37)$$

and obtain the equation

$$0 = \frac{dH}{dw_\nu} = - \ln w_\nu - 1 + \lambda - \frac{\epsilon_\nu}{\theta}. \quad (1.38)$$

This equation leads to

$$w_\nu = e^{\lambda - 1 - \epsilon_\nu/\theta} \quad \text{with} \quad e^{1-\lambda} = \sum_{\nu} e^{-\epsilon_\nu/\theta} = Z \quad (1.39)$$

which satisfies the normalization condition for w_ν .

We aim now at giving different quantities a thermodynamic meaning. We begin by multiplying Eq.(1.38) by w_ν and sum then over ν . This leads to

$$0 = - \sum_{\nu} \left\{ w_\nu \ln w_\nu + w_\nu(1 - \lambda) + w_\nu \frac{\epsilon_\nu}{\theta} \right\} = H - 1 + \lambda - \frac{\langle \epsilon \rangle}{\theta} \quad (1.40)$$

which we use to replace $1 - \lambda$ in (1.38) and obtain

$$\langle \epsilon \rangle = \theta(\ln w_\nu + H) + \epsilon_\nu. \quad (1.41)$$

The differential reads

$$d\langle \epsilon \rangle = (H + \ln w_\nu)d\theta + \theta \left(dH + \frac{dw_\nu}{w_\nu} \right) + d\epsilon_\nu. \quad (1.42)$$

After multiplying by w_ν and a ν -summation the first term on the right hand side drops out and we obtain

$$d\langle\epsilon\rangle = \theta dH + \sum_{\nu} w_{\nu} d\epsilon_{\nu} . \quad (1.43)$$

Now we view $\langle\epsilon\rangle = u$ as the internal energy per unit and $d\epsilon_{\nu} = \sum_i \frac{\partial\epsilon_{\nu}}{\partial q_i} dq_i$ where q_i is a generalized coordinate, such as a volume, a magnetization etc. Thus $\frac{\partial\epsilon_{\nu}}{\partial q_i} = -F_{i\nu}$ is a generalized force, such as pressure, magnetic field etc. Therefore we write (1.43) as

$$du = \theta dH - \sum_{\nu,i} w_{\nu} F_{i\nu} dq_i = \theta dH - \sum_i \langle F_i \rangle dq_i \quad \Rightarrow \quad dH = \frac{du}{\theta} + \frac{1}{\theta} \sum_i \langle F_i \rangle dq_i . \quad (1.44)$$

This suggests now to make the following identifications:

$$\theta = k_B T \quad \text{and} \quad H = \frac{s}{k_B} , \quad (1.45)$$

where θ represents the temperature T and H the entropy density s . Naturally we identify the relations,

$$\left(\frac{\partial S}{\partial U} \right)_{q_i} = \left(\frac{\partial s}{\partial u} \right)_{q_i} = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial s}{\partial q_i} \right)_u = \langle F_i \rangle . \quad (1.46)$$

In this way we have made a sensible connection to thermodynamics. Below we will use the H -function as equivalent to the entropy.

1.2.2 Master equation

Because the micro-states have different energies, the time evolution as we have discussed by the master equation for completely independent units has to be modified in a way so as to conserve the energy in each time step. This can be guaranteed only by involving two micro-states of different units to be transformed together under the constraint of overall energy conservation. A master equation doing this job has the form

$$\frac{dw_{\nu}}{dt} = \sum_{\nu_1, \nu_2, \nu_3} \{ \Gamma_{\nu\nu_1; \nu_2\nu_3} w_{\nu_2} w_{\nu_3} - \Gamma_{\nu_2\nu_3; \nu\nu_1} w_{\nu} w_{\nu_1} \} . \quad (1.47)$$

For this purpose we assume that there is no correlation between the states of different units. Here $\Gamma_{\nu\nu_1; \nu_2\nu_3}$ denotes the rate for the transition of the pair of states (ν_2, ν_3) to (ν, ν_1) under the condition that $\epsilon_{\nu_2} + \epsilon_{\nu_3} = \epsilon_{\nu} + \epsilon_{\nu_1}$. Time reversal symmetry and the freedom to exchange two states give rise to the following relations:

$$\Gamma_{\nu\nu_1; \nu_2\nu_3} = \Gamma_{\nu_2\nu_3; \nu\nu_1} = \Gamma_{\nu_1\nu; \nu_2\nu_3} = \Gamma_{\nu\nu_1; \nu_3\nu_2} . \quad (1.48)$$

This can be used in order to show that the H -function is only increasing with time,

$$\begin{aligned} \frac{dH}{dt} &= - \sum_{\nu} \frac{dw_{\nu}}{dt} \{ \ln w_{\nu} + 1 \} \\ &= \frac{1}{4} \sum_{\nu, \nu_1, \nu_2, \nu_3} \Gamma_{\nu, \nu_1; \nu_2, \nu_3} (w_{\nu} w_{\nu_1} - w_{\nu_2} w_{\nu_3}) \{ \ln(w_{\nu} w_{\nu_1}) - \ln(w_{\nu_2} w_{\nu_3}) \} \geq 0 . \end{aligned} \quad (1.49)$$

The equilibrium is reached when $dH/dt = 0$ and using (1.39) leads to,

$$w_{\nu} w_{\nu_1} = \frac{e^{-\epsilon_{\nu}/k_B T} e^{-\epsilon_{\nu_1}/k_B T}}{Z^2} = \frac{e^{-\epsilon_{\nu_2}/k_B T} e^{-\epsilon_{\nu_3}/k_B T}}{Z^2} = w_{\nu_2} w_{\nu_3} . \quad (1.50)$$

We now revisit the condition of detailed balance under these new circumstances. On the one hand, we may just set each term in the sum of the right hand side of (1.47) to zero to obtain a detailed balance statement:

$$0 = \Gamma_{\nu\nu_1;\nu_2\nu_3} w_{\nu_2} w_{\nu_3} - \Gamma_{\nu_2\nu_3;\nu\nu_1} w_{\nu} w_{\nu_1} = \Gamma_{\nu\nu_1;\nu_2\nu_3} \{w_{\nu_2} w_{\nu_3} - w_{\nu} w_{\nu_1}\}, \quad (1.51)$$

whereby the second equality is a consequence of time reversal symmetry. On the other hand, we may compress the transition rates in order to reach at a similar form as we had it earlier in (1.8),

$$\Gamma'_{\nu\nu'} w_{\nu} = \Gamma'_{\nu'\nu} w_{\nu'} . \quad (1.52)$$

where we define

$$\Gamma'_{\nu\nu'} = \sum_{\nu_1, \nu_2} \Gamma_{\nu\nu_1;\nu'\nu_2} w_{\nu_1} \quad \text{and} \quad \Gamma'_{\nu'\nu} = \sum_{\nu_1, \nu_2} \Gamma_{\nu\nu_1;\nu'\nu_2} w_{\nu_2} . \quad (1.53)$$

It is important now to notice that time reversal does not invoke $\Gamma'_{\nu\nu'} = \Gamma'_{\nu'\nu}$, but we find that at equilibrium

$$\Gamma'_{\nu'\nu} = \sum_{\nu_1, \nu_2} \Gamma_{\nu\nu_1;\nu'\nu_2} \frac{e^{-\epsilon_{\nu_2}/k_B T}}{Z} = e^{-(\epsilon_{\nu} - \epsilon_{\nu'})/k_B T} \sum_{\nu_1, \nu_2} \Gamma_{\nu\nu_1;\nu'\nu_2} \frac{e^{-\epsilon_{\nu_1}/k_B T}}{Z} = e^{-(\epsilon_{\nu} - \epsilon_{\nu'})/k_B T} \Gamma'_{\nu\nu'} . \quad (1.54)$$

Thus detailed balance implies here different transition rates for the two directions of processes depending on the energy difference between the two micro-states, $\epsilon_{\nu} - \epsilon_{\nu'}$, and the temperature T ,

$$\frac{w_{\nu}}{w_{\nu'}} = \frac{\Gamma'_{\nu'\nu}}{\Gamma'_{\nu\nu'}} = e^{-(\epsilon_{\nu} - \epsilon_{\nu'})/k_B T} . \quad (1.55)$$

The degrees of freedom of each unit fluctuate in the environment (heat reservoir) of all the other units which can interact with it.

1.2.3 Irreversible processes and increase of entropy

Although thermodynamics shows its strength in the description of reversible processes, it provides also important insights into the irreversible changes. An example is the Gay-Lussac experiment. However, the nature of the irreversible process and in particular its time evolution is not part of thermodynamics usually. A process which considers the evolution of a system from a non-equilibrium to its equilibrium state is irreversible generally.

Here we examine briefly some aspects of this evolution by analyzing a closed system consisting of two subsystems (Fig.1.4) , 1 and 2, which are initially independent (inhibited equilibrium) but then at $t = 0$ become very weakly coupled. Both systems shall have the same type of units with their micro-states which they occupy with probabilities $w_{\nu}^{(1)} = N_{\nu}^{(1)}/N_1$ and $w_{\nu}^{(2)} = N_{\nu}^{(2)}/N_2$, respectively (N_i is the number of units in system i). Each subsystem is assumed to be in its equilibrium internally which can be sustained approximatively as long as the coupling between them is weak.

The number of configurations for the combined system is given by the product of the number of configurations of the two subsystems:

$$W = W_1 W_2 \quad \text{with} \quad W_i = \frac{N_i!}{N_1^{(i)}! N_2^{(i)}! \dots N_z^{(i)}!} \quad (1.56)$$

which then leads to the entropy

$$\begin{aligned} S &= k_B \ln W = k_B \ln W_1 + k_B \ln W_2 = S_1 + S_2 \\ &= -N_1 k_B \sum_{\nu} w_{\nu}^{(1)} \ln w_{\nu}^{(1)} - N_2 k_B \sum_{\nu} w_{\nu}^{(2)} \ln w_{\nu}^{(2)} , \end{aligned} \quad (1.57)$$

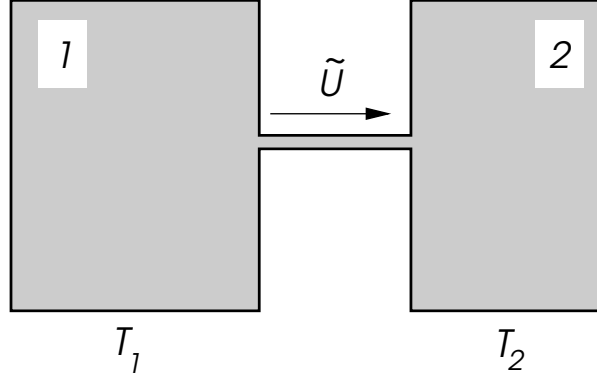


Figure 1.4: A closed system consisting of two weakly coupled subsystems, 1 and 2, with initial temperatures T_1 and T_2 respectively, evolves towards equilibrium through energy transfer from the warmer to the colder subsystem.

using Eq.(1.22) and (1.45). In the complete system the internal energy is conserved, $U = U_1 + U_2$. We define U_{01} and U_{02} as the internal energy of the two subsystems, if they are in equilibrium with each other. The non-equilibrium situation is then parametrized for the energy by the deviation \tilde{U} : $U_1 = U_{01} + \tilde{U}$ and $U_2 = U_{02} - \tilde{U}$. The entropy satisfies at equilibrium

$$S(\tilde{U}) = S_1(U_{01} + \tilde{U}) + S_2(U_{02} - \tilde{U}) \quad (1.58)$$

$$\text{with } 0 = \frac{\partial S}{\partial \tilde{U}} = \frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2} = \frac{1}{T_1} - \frac{1}{T_2} \Rightarrow T_1 = T_2 = T_0,$$

for $\tilde{U} = 0$.² Thus, we find for small \tilde{U} ,

$$\frac{1}{T_1} = \frac{\partial S_1}{\partial U_1} \Big|_{U_1=U_{01}+\tilde{U}} \approx \frac{1}{T_0} + \tilde{U} \frac{\partial^2 S_1}{\partial U_1^2} \Big|_{U_1=U_{01}}, \quad (1.60)$$

$$\frac{1}{T_2} = \frac{\partial S_2}{\partial U_2} \Big|_{U_2=U_{02}-\tilde{U}} \approx \frac{1}{T_0} - \tilde{U} \frac{\partial^2 S_2}{\partial U_2^2} \Big|_{U_2=U_{02}}.$$

With (1.58) we then obtain through expansion in \tilde{U} ,

$$S(\tilde{U}) = S_1(U_{01}) + S_2(U_{02}) + \frac{\tilde{U}^2}{2} \left(\frac{\partial^2 S_1}{\partial U_1^2} \Big|_{U_{01}} + \frac{\partial^2 S_2}{\partial U_2^2} \Big|_{U_{02}} \right) + O(\tilde{U}^3). \quad (1.61)$$

so that the time evolution of the entropy is given by

$$\frac{dS}{dt} = \tilde{U} \frac{d\tilde{U}}{dt} \left(\frac{\partial^2 S_1}{\partial U_1^2} \Big|_{U_{01}} + \frac{\partial^2 S_2}{\partial U_2^2} \Big|_{U_{02}} \right) = \frac{d\tilde{U}}{dt} \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (1.62)$$

where we used Eq.(1.60). Note that the only time dependence appears in \tilde{U} . The derivative $d\tilde{U}/dt$ corresponds to the energy flow from one subsystem to the other. We express $d\tilde{U}/dt$ in terms of the distribution functions of one of the subsystems, say system 1.

$$\frac{d\tilde{U}}{dt} = N_1 \sum_{\nu} \epsilon_{\nu} \frac{dw_{\nu}^{(1)}}{dt} = N_1 \sum_{\nu} \epsilon_{\nu} \frac{\partial w_{\nu}^{(1)}}{\partial T_1} \frac{dT_1}{dt} \approx N_1 \frac{dT_1}{dt} \sum_{\nu} \epsilon_{\nu} \frac{\partial}{\partial T_1} \frac{e^{-\epsilon_{\nu}/k_B T_1}}{Z_1}. \quad (1.63)$$

²Note that the entropy as a thermodynamic potential obeys,

$$S = S(U, q_i) \quad \text{with} \quad dS = \frac{dU}{T} - \sum_i \frac{F_i}{T} dq_i. \quad (1.59)$$

Note that here and in the following

$$w_\nu^{(j)} = \frac{e^{-\epsilon_\nu/k_B T_j}}{Z_j} \quad \text{with} \quad Z_j = \sum_\nu e^{-\epsilon_\nu/k_B T_j} . \quad (1.64)$$

The derivative yields

$$\frac{d\tilde{U}}{dt} \approx N_1 \frac{dT_1}{dt} \left[\sum_\nu \epsilon_\nu^2 w_\nu^{(1)} - \left\{ \sum_\nu \epsilon_\nu w_\nu^{(1)} \right\}^2 \right] \frac{1}{k_B T_1^2} = \frac{N_1}{k_B T_1^2} \frac{dT_1}{dt} \{ \langle \epsilon^2 \rangle_1 - \langle \epsilon \rangle_1^2 \} = C_1 \frac{dT_1}{dt} , \quad (1.65)$$

where C_1 denotes the heat capacity of subsystem 1, since

$$\frac{d\tilde{U}}{dt} = \frac{dT_1}{dt} \frac{\partial \tilde{U}}{\partial T_1} = C_1 \frac{dT_1}{dt} . \quad (1.66)$$

Thus, we have here derived the relation

$$k_B T_1^2 C_1 = N_1 \{ \langle \epsilon^2 \rangle_1 - \langle \epsilon \rangle_1^2 \} , \quad (1.67)$$

which connects the heat capacity with the fluctuations of the energy value. Note that the internal energy of subsystem 1 is not conserved due to the coupling to subsystem 2.

In which direction does the energy flow? Because we know that $dS/dt \geq 0$, from (1.62) follows

$$0 \leq \frac{dS}{dt} = C_1 \frac{dT_1}{dt} \frac{T_2 - T_1}{T_1 T_2} , \quad (1.68)$$

which yields for $T_1 > T_2$ that

$$\frac{dT_1}{dt} < 0 \quad \Rightarrow \quad \frac{d\tilde{U}}{dt} < 0 . \quad (1.69)$$

This means that the energy flow goes from the warmer to the colder subsystem, reducing the temperature of the warmer system and increasing that of the colder subsystem as can be seen by the analogous argument. The flow stops when $T_1 = T_2 = T_0$.

Let us now consider the situation again by means of the master equation. We may approximate the equation of $w_\nu^{(a)}$ by ($a, b = 1, 2$),

$$\frac{dw_{\nu_1}^{(a)}}{dt} \approx \sum_{\nu'_1, \nu_2, \nu'_2} \sum_b \left[\Gamma_{\nu_1, \nu_2; \nu'_1 \nu'_2}^{(ab)} w_{\nu'_1}^{(a)} w_{\nu'_2}^{(b)} - \Gamma_{\nu'_1, \nu'_2; \nu_1 \nu_2}^{(ab)} w_{\nu_1}^{(a)} w_{\nu_2}^{(b)} \right] \quad (1.70)$$

which describes the evolution of the probability distribution transferring in general energy between the two subsystems, as only the overall energy is conserved but not in each subsystem separately,

$$\epsilon_{\nu_1} + \epsilon_{\nu_2} = \epsilon_{\nu'_1} + \epsilon_{\nu'_2} . \quad (1.71)$$

All processes inside each subsystem are considered at equilibrium and give no contribution by the condition of detailed balance. This remains true as long as the subsystems are very large and the coupling between them weak. For symmetry reasons

$$\Gamma_{\nu_1 \nu_2; \nu'_1 \nu'_2}^{(12)} = \Gamma_{\nu'_1 \nu'_2; \nu_1 \nu_2}^{(12)} = \Gamma_{\nu_2 \nu_1; \nu'_1 \nu'_2}^{(12)} = \Gamma_{\nu_1 \nu_2; \nu'_2 \nu'_1}^{(12)} > 0 . \quad (1.72)$$

We use now this equation and estimate $d\tilde{U}/dt$

$$\begin{aligned} \frac{d\tilde{U}}{dt} &= N_1 \sum_{\nu_1, \nu'_1, \nu_2, \nu'_2} \epsilon_{\nu_1} \left[\Gamma_{\nu_1, \nu_2; \nu'_1 \nu'_2}^{(12)} w_{\nu'_1}^{(1)} w_{\nu'_2}^{(2)} - \Gamma_{\nu'_1, \nu'_2; \nu_1 \nu_2}^{(12)} w_{\nu_1}^{(1)} w_{\nu_2}^{(2)} \right] \\ &= \frac{N_1}{2} \sum_{\nu_1, \nu'_1, \nu_2, \nu'_2} (\epsilon_{\nu_1} - \epsilon_{\nu'_1}) \Gamma_{\nu_1 \nu_2; \nu'_1 \nu'_2}^{(12)} \frac{e^{-\epsilon_{\nu'_1}/k_B T_1 - \epsilon_{\nu'_2}/k_B T_2} - e^{-\epsilon_{\nu_1}/k_B T_1 - \epsilon_{\nu_2}/k_B T_2}}{Z_1 Z_2} . \end{aligned} \quad (1.73)$$

Using (1.71) and assuming that T_1 and T_2 are close to each other ($T_1 \approx T_2 \approx T_0$), we obtain may expand in $T_1 - T_2$,

$$\frac{d\tilde{U}}{dt} \approx \frac{N_1}{2Z^2} \sum_{\nu_1, \nu'_1, \nu_2, \nu'_2} \Gamma_{\nu_1 \nu_2; \nu'_1 \nu'_2}^{(12)} e^{-(\epsilon_{\nu_1} + \epsilon_{\nu_2})/k_B T_0} (\epsilon_{\nu_1} - \epsilon_{\nu'_1})^2 \frac{T_2 - T_1}{k_B T_0^2} \approx K(T_2 - T_1) \quad (1.74)$$

with $Z = \sum_{\nu} e^{-\epsilon_{\nu}/k_B T_0} \approx Z_1 \approx Z_2$ and

$$K \approx \frac{N_1}{2Z^2} \sum_{\nu_1, \nu'_1, \nu_2, \nu'_2} \Gamma_{\nu_1 \nu_2; \nu'_1 \nu'_2}^{(12)} e^{-(\epsilon_{\nu_1} + \epsilon_{\nu_2})/k_B T} \frac{(\epsilon_{\nu_1} - \epsilon_{\nu'_1})^2}{k_B T_0^2} > 0. \quad (1.75)$$

The energy flow is proportional to the difference of the temperatures and stops when the two subsystems have the same temperature. It is also here obvious that the spontaneous energy transfer goes from the warmer to the colder reservoir. This corresponds to Fourier's law as $d\tilde{U}/dt$ can be considered as a heat current (energy current) from subsystem 1 to 2, $J_Q = -d\tilde{U}/dt$. This heat transport is an irreversible process leading to an increase of the entropy,

$$\frac{dS}{dt} = \frac{d\tilde{U}}{dt} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \approx K \frac{(T_2 - T_1)^2}{T_0^2} = \frac{J_Q^2}{K T_0^2} \geq 0 \quad (1.76)$$

This irreversible process leads us from the less likely system configuration of an inhibited equilibrium (different temperature in both subsystems) to the most likely of complete equilibrium ($T_1 = T_2 = T_0$) with the entropy

$$S = -N k_B \sum_{\nu} w_{\nu} \ln w_{\nu} \quad \text{with} \quad w_{\nu} = \frac{N_{\nu}}{N} = w_{\nu}^{(1)} = \frac{N_{\nu}^{(1)}}{N_1} = w_{\nu}^{(2)} = \frac{N_{\nu}^{(2)}}{N_2}, \quad (1.77)$$

i.e. the probability distribution is uniform for the whole system with $N = N_1 + N_2$ units.

Chapter 2

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.

2.1 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, \dots, q_{3N} and by the corresponding $3N$ conjugate momenta p_1, \dots, 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.

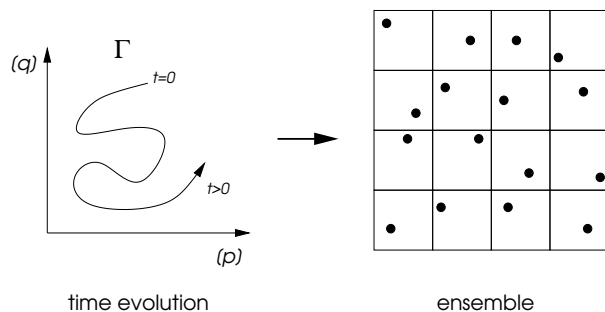


Figure 2.1: Time averages are replaced by averages over an ensemble of systems in different microscopic states, but with the same macroscopic conditions.

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

¹Ergodicity hypothesis: We consider the subspace defined by $\mathcal{H}(p, q) = E$ in Γ . Due to energy conservation a

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 $(p_1, \dots, p_{3N}; q_1, \dots, q_{3N})$). Then

$$\rho(p, q) d^{3N} p d^{3N} q \quad (2.1)$$

gives the number of representative points contained in the small volume $d^{3N} p d^{3N} q$ 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) , $A(p, q)$:

$$\langle A \rangle = \frac{\int dp dq A(p, q) \rho(p, q)}{\int dp dq \rho(p, q)}. \quad (2.2)$$

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

2.1.1 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,

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} \quad \text{and} \quad \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \quad (i = 1, \dots, 3N). \quad (2.3)$$

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

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \quad (2.4)$$

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

$$\frac{D\rho}{Dt} + \rho \vec{\nabla} \cdot \vec{v} = 0. \quad (2.5)$$

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

$$\vec{\nabla} \cdot \vec{v} = \sum_{i=1}^{3N} \left\{ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right\} = \sum_{i=1}^{3N} \underbrace{\left\{ \frac{\partial}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right\}}_{=0} = 0. \quad (2.6)$$

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

$$0 = \frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right\} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial \mathcal{H}}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right\}. \quad (2.7)$$

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 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.

Using Poisson brackets² this equation reads

$$\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\} . \quad (2.9)$$

2.1.2 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

$$0 = \sum_{i=1}^{3N} \left\{ \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right\} = \vec{v} \cdot \vec{\nabla} \rho = \{\mathcal{H}, \rho\} . \quad (2.10)$$

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

$$\langle A \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(p(t), q(t)) dt \quad (2.11)$$

for any starting point $(p(t=0), q(t=0))$ in the space Γ and $(p(t), q(t))$ obeying the equation of motion (2.3). 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

$$\rho(p, q) = \begin{cases} \text{const.} & E \leq \mathcal{H}(p, q) \leq E + \delta E \\ 0 & \text{otherwise} \end{cases} \quad (2.12)$$

where δE is small. The average value of A is then given by (2.2). The validity of this approach is based on the assumption of small mean square fluctuations (standard deviation)

$$\frac{\langle \{A - \langle A \rangle\}^2 \rangle}{\langle A \rangle^2} \ll 1 . \quad (2.13)$$

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

2.2 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

²The Poisson bracket is defined as

$$\{u, v\} = \sum_i \left\{ \frac{\partial u}{\partial q_i} \frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i} \frac{\partial v}{\partial q_i} \right\} = -\{v, u\} . \quad (2.8)$$

energy lies in the range $[E, E + \delta E]$. First we define the phase volume

$$\Phi(E) = \Lambda_N \int_{\mathcal{H}(p,q) \leq E} dpdq, \quad (2.14)$$

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

$$\Lambda_N = \frac{1}{N!h^{3N}} \quad (2.15)$$

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

$$\omega(E) = \Lambda_N \int_{E \leq \mathcal{H}(p,q) \leq E + \delta E} dpdq = \Phi(E + \delta E) - \Phi(E) = \frac{d\Phi(E)}{dE} \delta E. \quad (2.16)$$

Thus we may renormalize the density function $\rho(p, q)$ with the condition,

$$1 = \Lambda_N \int dp dq \rho(p, q) = \frac{\Lambda_N}{\omega(E)} \int_{E \leq \mathcal{H}(p,q) \leq E + \delta E} dp dq \quad (2.17)$$

such that

$$\rho(p, q) = \begin{cases} \frac{1}{\omega(E)} & E \leq \mathcal{H}(p, q) \leq E + \delta E \\ 0 & \text{otherwise} \end{cases}. \quad (2.18)$$

As postulated we choose $\rho(p, q)$ to be a constant in the energy range $[E, E + \delta E]$.

2.2.1 Entropy

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

$$S(E, V, N) = k_B \ln \omega(E). \quad (2.19)$$

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,

$$\mathcal{H}(p, q) = \mathcal{H}_1(p_1, q_1) + \mathcal{H}_2(p_2, q_2), \quad (2.20)$$

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

$$E = E_1 + E_2, \quad N = N_1 + N_2 \quad \text{and} \quad V = V_1 + V_2. \quad (2.21)$$

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,

$$\omega(E) = \sum_{0 \leq E' \leq E} \omega_1(E') \omega_2(E - E'), \quad (2.22)$$

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 obtained by

$$\left. \frac{\partial \omega_1(E') \omega_2(E - E')}{\partial E'} \right|_{E'=E'_0} = 0 \quad (2.25)$$

such that

$$\begin{aligned} 0 &= \left\{ \frac{1}{\omega_1(E')} \frac{\partial \omega_1(E')}{\partial E'} + \frac{1}{\omega_2(E - E')} \frac{\partial \omega_2(E - E')}{\partial E'} \right\}_{E'=E'_0} \\ &= \left. \frac{\partial \ln \omega_1(E_1)}{\partial E_1} \right|_{E_1=E'_0} - \left. \frac{\partial \ln \omega_2(E_2)}{\partial E_2} \right|_{E_2=E-E'_0}. \end{aligned} \quad (2.26)$$

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

$$\left. \frac{\partial S_1(E_1)}{\partial E_1} \right|_{E_1=\bar{E}_1} = \left. \frac{\partial S_2(E_2)}{\partial E_2} \right|_{E_2=\bar{E}_2} \quad (2.27)$$

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

$$\frac{\partial S}{\partial U} = \frac{1}{T} \quad \Rightarrow \quad \frac{1}{T_1} = \frac{1}{T_2}, \quad (2.28)$$

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,

$$\tilde{\omega}(E, V, N) = \omega_1(E_1, V_1, N_1) \omega_2(E_2, V_2, N_2) \quad \text{with} \quad \begin{cases} E = E_1 + E_2 \\ V = V_1 + V_2 \\ N = N_1 + N_2 \end{cases} \quad (2.29)$$

such that the entropy is given by

$$\tilde{S}(E, V, N) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \leq S(E, V, N), \quad (2.30)$$

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.

³Note 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:

$$\omega_1(E'_0) \omega_2(E - E'_0) \leq \omega(E) \leq \frac{E}{\delta E} \omega_1(E'_0) \omega_2(E - E'_0). \quad (2.23)$$

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

$$k_B \ln \omega_1(E'_0) \omega_2(E - E'_0) \leq S(E) \leq k_B \ln \omega_1(E'_0) \omega_2(E - E'_0) + k_B \ln \frac{E}{\delta E}. \quad (2.24)$$

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 (2.22).

2.2.2 Relation to thermodynamics

With (2.19) 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,

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V,N} dE + \left(\frac{\partial S}{\partial V} \right)_{E,N} dV + \left(\frac{\partial S}{\partial N} \right)_{E,V} dN = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN. \quad (2.31)$$

This allows also to calculate the thermodynamic equation of state,

$$p = T \left(\frac{\partial S}{\partial V} \right)_{E,N} \quad (2.32)$$

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

$$\left(\frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{T}, \quad (2.33)$$

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

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{E,V}, \quad (2.34)$$

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

2.2.3 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

$$\mathcal{H}(p, q) = \mathcal{H}(p) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}. \quad (2.35)$$

Hence we obtain the volume

$$\Phi(E) = \Lambda_N \int_{\mathcal{H}(p) \leq E} dpdq = \Lambda_N V^N \int_{\mathcal{H}(p) \leq E} dp. \quad (2.36)$$

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

$$\Phi(E) = \Lambda_N V^N C_{3N} (2mE)^{3N/2} \quad \text{with} \quad C_n = \frac{\pi^{n/2}}{\Gamma(\frac{n}{2} + 1)} \quad (2.39)$$

⁴Volume 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

$$v_{shell} = \mathcal{V}(R) - \mathcal{V}(R - \delta R) = CR^\nu \left[1 - \left(1 - \frac{\delta R}{R} \right)^\nu \right] \quad (2.37)$$

with $\delta R \ll R$, see Fig.2.2 . In the limit ν very large, $\nu \delta R \gg R$, we find

$$v_{shell} \approx \mathcal{V}(R). \quad (2.38)$$

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

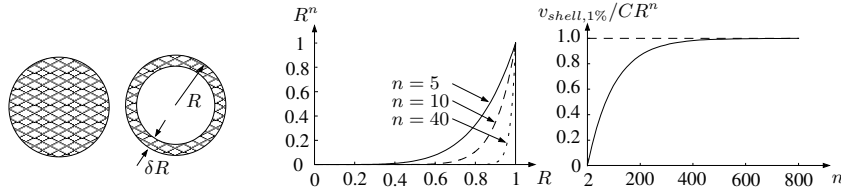


Figure 2.2: The volume of the sphere is located close to the surface in high dimensions, see the central diagram. Thus, the fraction of the volume close to the shell and the total volume converges towards one as $n \rightarrow \infty$ (diagram on the right hand side).

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

$$\omega(E) = \frac{\partial \Phi(E)}{\partial E} \delta E = \Lambda_N C_{3N} V^N \frac{3N}{2} 2m (2mE)^{3N/2-1} \delta E . \quad (2.42)$$

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:

$$S_\omega = k_B \ln \omega(E, V, N) \quad \text{and} \quad S_\Phi = k_B \ln \Phi(E, V, N) \quad (2.43)$$

leading to

$$\begin{aligned} S_\omega &= k_B \ln(\Lambda_N V^N C_{3N}) + k_B \left(\frac{3N}{2} - 1 \right) \ln(2mE) + k_B \ln \left(\frac{3N}{2} 2m \delta E \right) \\ &= k_B \ln(\Lambda_N V^N C_{3N}) + k_B \frac{3N}{2} \ln(2mE) + O(\ln N) = S_\Phi + O(\ln N) . \end{aligned} \quad (2.44)$$

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 ,

$$S(E, V, N) = N k_B \ln \left\{ V \left(\frac{2m\pi E}{h^2} \right)^{3/2} \right\} - \frac{3N}{2} k_B \ln \frac{3N}{2} + \frac{3N}{2} k_B - N k_B \ln N + N k_B \quad (2.45)$$

where we used Stirling's formula

$$\ln n! \approx n \ln n - n + \frac{1}{2} \ln(2\pi n) \quad \text{for } n \rightarrow \infty , \quad (2.46)$$

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

$$S(E, V, N) = N k_B \ln \left\{ \frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right\} + \frac{5}{2} N k_B . \quad (2.47)$$

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

$$U(S, V, N) = E = N \frac{3n^{2/3} h^2}{4\pi m} \exp \left\{ \frac{2S}{3N k_B} - \frac{5}{3} \right\} . \quad (2.48)$$

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

$$I = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_n e^{-(x_1^2 + \cdots + x_n^2)} = \left(\int_{-\infty}^{+\infty} dx e^{-x^2} \right)^n = \pi^{n/2} . \quad (2.40)$$

The same integral in spherical coordinates is given by

$$I = n C_n \int_0^\infty dr r^{n-1} e^{-r^2} = \frac{n}{2} C_n \int_0^\infty dt t^{\frac{n}{2}-1} e^{-t} = \frac{n}{2} C_n \Gamma \left(\frac{n}{2} \right) = C_n \Gamma \left(\frac{n}{2} + 1 \right) \quad (2.41)$$

such that we obtain C_n given in (2.39). Note, $\Gamma(n+1) = n!$ for $n \geq 0$ as an integer.

The thermodynamic quantities are obtained by derivation: the temperature

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} = \frac{2U}{3Nk_B} \quad \Rightarrow \quad U = \frac{3}{2}Nk_B T, \quad (2.49)$$

the pressure

$$p = - \left(\frac{\partial U}{\partial V} \right)_{S,N} = \frac{2U}{3V} = \frac{Nk_B T}{V} \quad \Rightarrow \quad pV = Nk_B T, \quad (2.50)$$

and the chemical potential

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \frac{U}{N} \left(\frac{5}{3} - \frac{2}{3} \frac{S}{Nk_B} \right) = -k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right\}. \quad (2.51)$$

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

2.3 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 (Fig.2.3),

$$\mathcal{H}(p, q) = \mathcal{H}_1(p_1, q_1) + \mathcal{H}_2(p_2, q_2). \quad (2.52)$$

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

$$E \leq E_1 + E_2 \leq E + \delta E. \quad (2.53)$$

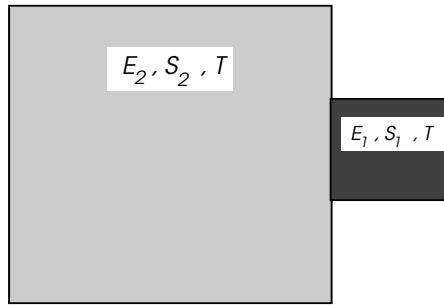


Figure 2.3: The two systems 1 and 2 are coupled thermally. System 2 acts as a huge reservoir fixing the temperature of the system 1 which we want to investigate.

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

$$\omega(E) = \sum_{0 \leq E_1 \leq E} \omega_1(E_1) \omega_2(E - E_1). \quad (2.54)$$

Analogously to our previous discussion in section 2.2.1, 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 (unrenormalized) density function $\rho_1(p_1, q_1)$ of the system 1, by considering the mean value of $A(p, q)$ in system 1,

$$\langle A \rangle_1 = \frac{\int_1 dp_1 dq_1 A(p_1, q_1) \rho_1(p_1, q_1)}{\int_1 dp_1 dq_1 \rho_1(p_1, q_1)} = \frac{\int_1 dp_1 dq_1 A(p_1, q_1) \int_2 dp_2 dq_2 \rho(p, q)}{\int_1 dp_1 dq_1 \int_2 dp_2 dq_2 \rho(p, q)}. \quad (2.55)$$

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 obtain⁶

$$\langle A \rangle_1 = \frac{\int_1 dp_1 dq_1 A(p_1, q_1) \omega_2(E - \mathcal{H}_1(p_1, q_1))}{\int_1 dp_1 dq_1 \omega_2(E - \mathcal{H}_1(p_1, q_1))}. \quad (2.57)$$

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 $\mathcal{H}_1(p_1, q_1)$,

$$\begin{aligned} k_B \ln \omega_2(E - \mathcal{H}_1(p_1, q_1)) &= S_2(E - \mathcal{H}_1(p_1, q_1)) = S_2(E) - \mathcal{H}_1(p_1, q_1) \left. \frac{\partial S_2(\bar{E}_2)}{\partial \bar{E}_2} \right|_{\bar{E}_2=E} + \dots \\ &= S_2(E) - \frac{\mathcal{H}_1(p_1, q_1)}{T} + \dots \end{aligned} \quad (2.58)$$

from which we derive

$$\omega_2(E - \mathcal{H}_1(p_1, q_1)) = e^{S_2(E)/k_B} e^{-\mathcal{H}_1(p_1, q_1)/k_B T}. \quad (2.59)$$

Here T is the temperature of both systems which are in equilibrium.

Within the canonical 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) ,

$$\rho(p, q) = \frac{1}{Z} e^{-\mathcal{H}(p, q)/k_B T}, \quad (2.60)$$

where we introduced the *partition function* Z

$$Z = \Lambda_N \int dp dq e^{-\beta \mathcal{H}(p, q)} \quad \text{with} \quad \beta = \frac{1}{k_B T}, \quad (2.61)$$

which, up to prefactors, corresponds to the volume of the ensemble of system 1, called *canonical ensemble*, again renormalized by Λ_N .⁷

2.3.1 Thermodynamics

The connection to thermodynamics is given by the relation

$$Z = e^{-\beta F(T, V, N)}, \quad (2.62)$$

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,

$$F = U - TS \quad (2.63)$$

with

$$U = \langle \mathcal{H} \rangle \quad \text{and} \quad S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}. \quad (2.64)$$

⁶We use

$$\int_2 dp_2 dq_2 \rho(p, q) \propto \int_{E(p_1, q_1) \leq \mathcal{H}_2(p_2, q_2) \leq E(p_1, q_1) + \delta} dp_2 dq_2 = \omega_2(E(p_1, q_1)) \quad (2.56)$$

where $E(p_1, q_1) = E - \mathcal{H}_1(p_1, q_1)$.

⁷Note 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.

This can be proven using the equation,

$$1 = \Lambda_N \int dp dq e^{\beta(F-\mathcal{H})} , \quad (2.65)$$

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

$$\begin{aligned} 0 &= \Lambda_N \int dp dq e^{\beta(F-\mathcal{H})} \left\{ F + \beta \left(\frac{\partial F}{\partial \beta} \right)_{V,N} - \mathcal{H} \right\} \\ &\Rightarrow F(T, V, N) - U(T, V, N) - T \left(\frac{\partial F}{\partial T} \right)_{V,N} = 0 . \end{aligned} \quad (2.66)$$

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

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} , \quad (2.67)$$

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,

$$U(T, V, N) = \langle \mathcal{H} \rangle = \frac{\Lambda_N}{Z} \int dp dq \mathcal{H} e^{-\beta \mathcal{H}} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z . \quad (2.68)$$

This is the caloric equation of state.

2.3.2 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,

$$\begin{aligned} \left\langle q_\mu \frac{\partial \mathcal{H}}{\partial q_\nu} \right\rangle &= \frac{\Lambda_N}{Z} \int dp dq q_\mu \frac{\partial \mathcal{H}}{\partial q_\nu} e^{-\beta \mathcal{H}} = -\frac{\Lambda_N}{Z\beta} \int dp dq q_\mu \frac{\partial}{\partial q_\nu} e^{-\beta \mathcal{H}} \\ &= -\frac{\Lambda_N}{Z\beta} \underbrace{\int' dp d'q q_\mu e^{-\beta \mathcal{H}}}_{=0} + \frac{\Lambda_N \delta_{\mu\nu}}{Z\beta} \int dp dq e^{-\beta \mathcal{H}} = \delta_{\mu\nu} k_B T , \end{aligned} \quad (2.69)$$

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

$$\left\langle p_\mu \frac{\partial \mathcal{H}}{\partial p_\nu} \right\rangle = \delta_{\mu\nu} k_B T . \quad (2.70)$$

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

$$\mathcal{H}(p, q) = E_{kin}(p) + V(q) \quad \text{with} \quad E_{kin}(\lambda p) = \lambda^2 E_{kin}(p) \quad \text{and} \quad V(\lambda q) = \lambda^\alpha V(q) \quad (2.71)$$

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

$$\langle E_{kin} \rangle = \frac{3N}{2} k_B T \quad \text{and} \quad \langle V \rangle = \frac{3N}{\alpha} k_B T . \quad (2.72)$$

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

2.3.3 Ideal gas - canonical treatment

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

$$\mathcal{H}(p) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}. \quad (2.73)$$

The partition function is given by

$$\begin{aligned} Z &= \Lambda_N \prod_{i=1}^N \int d^3 p_i d^3 q_i e^{-\vec{p}_i^2/2mk_B T} = \Lambda_N \left\{ \int d^3 p d^3 q e^{-\vec{p}^2/2mk_B T} \right\}^N \\ &= \Lambda_N V^N \{2\pi mk_B T\}^{3N/2}. \end{aligned} \quad (2.74)$$

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

$$F(T, V, N) = -k_B T \ln Z = -Nk_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right\} - Nk_B T, \quad (2.75)$$

$$U(T, V, N) = -\frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} k_B T \quad (\text{caloric equation of state}).$$

The entropy is given by

$$S(T, V, N) = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = Nk_B \ln \left\{ \frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right\} + \frac{5N}{2} k_B \quad (2.76)$$

and the pressure by

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T, N} = \frac{Nk_B T}{V} \quad (2.77)$$

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

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} = -k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right\}. \quad (2.78)$$

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.

2.4 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.2.4 . 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

$$N_1 \ll N_2 \quad \text{and} \quad V_1 \ll V_2, \quad (2.79)$$

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

The Hamiltonian can be decomposed into two parts

$$\mathcal{H}(p, q, N) = \mathcal{H}(p_1, q_1, N_1) + \mathcal{H}(p_2, q_2, N_2) \quad (2.80)$$

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

$$Z_N(V, T) = \frac{1}{h^{3N} N!} \int dp dq e^{-\beta \mathcal{H}(p, q, N)}. \quad (2.81)$$

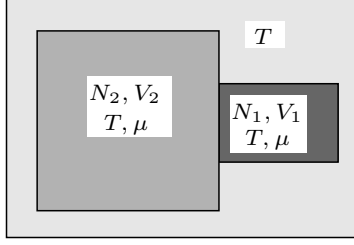


Figure 2.4: The two systems 1 and 2 can exchange matter between each other while the surrounding heat reservoir fixes the temperature of system 1 and 2. System 2 acts as a huge particle reservoir fixing the chemical potential μ of the system 1 which we want to investigate.

The 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 ($N_2 = N - N_1$),

$$\begin{aligned}
Z_N &= \frac{1}{h^{3N} N!} \sum_{N_1=0}^N \frac{N!}{N_1! N_2!} \int dp_1 dp_2 \int_{V_1} dq_1 \int_{V_2} dq_2 e^{-\beta\{\mathcal{H}(p_1, q_1, N_1) + \mathcal{H}(p_2, q_2, N_2)\}} \\
&= \sum_{N_1=0}^N \frac{1}{h^{3N_1} N_1!} \int_{V_1} dp_1 dq_1 e^{-\beta\mathcal{H}(p_1, q_1, N_1)} \frac{1}{h^{3N_2} N_2!} \int_{V_2} dp_2 dq_2 e^{-\beta\mathcal{H}(p_2, q_2, N_2)}.
\end{aligned} \tag{2.82}$$

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) ,

$$\rho(p_1, q_1, N_1) = \frac{e^{-\beta\mathcal{H}(p_1, q_1, N_1)}}{Z_N N_1! h^{3N_2} N_2!} \int_{V_2} dp_2 dq_2 e^{-\beta\mathcal{H}(p_2, q_2, N_2)} \tag{2.83}$$

which is renormalized as

$$\sum_{N_1=0}^N \frac{1}{h^{3N_1}} \int_{V_1} dp_1 dq_1 \rho(p_1, q_1, N_1) = 1. \tag{2.84}$$

We may write

$$\rho(p_1, q_1, N_1) = \frac{Z_{N_2}}{Z_N} \frac{1}{N_1!} e^{-\beta\mathcal{H}(p_1, q_1, N_1)}, \tag{2.85}$$

where we now use the relation

$$\frac{Z_{N_2}(V_2, T)}{Z_N(V, T)} = e^{-\beta\{F(T, V - V_1, N - N_1) - F(T, V, N)\}} \tag{2.86}$$

with

$$F(T, V - V_1, N - N_1) - F(T, V, N) \approx - \left(\frac{\partial F}{\partial V} \right)_{T, N} V_1 - \left(\frac{\partial F}{\partial N} \right)_{T, V} N_1 = -\mu N_1 + p V_1. \tag{2.87}$$

Thus we define

$$z = e^{\beta\mu} \tag{2.88}$$

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

$$\rho(p, q, N) = \frac{z^N}{N!} e^{-\beta\{pV + \mathcal{H}(p, q, N)\}}. \tag{2.89}$$

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

$$\mathcal{Z}(T, V, z) = \sum_{N=0}^{\infty} z^N Z_N(V, T), \quad (2.90)$$

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

2.4.1 Relation to thermodynamics

We use now (2.89) and integrate both sides

$$1 = e^{-\beta pV} \sum_{N=0}^{\infty} \frac{z^N}{N!} \int \frac{dp dq}{h^{3N}} e^{-\beta \mathcal{H}(p,q,N)} = e^{-\beta pV} \mathcal{Z}(T, V, z) \quad (2.91)$$

which leads to

$$\Omega(T, V, \mu) = -pV = -k_B T \ln \mathcal{Z}(T, V, z), \quad (2.92)$$

the grand potential

$$d\Omega = -SdT - pdV - Nd\mu. \quad (2.93)$$

The average value of N is then given by

$$\langle N \rangle = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} = k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} = z \frac{\partial}{\partial z} \ln \mathcal{Z} = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N z^N Z_N. \quad (2.94)$$

It is also convenient to derive again the internal energy

$$U = - \frac{\partial}{\partial \beta} \ln \mathcal{Z} \quad \Rightarrow \quad C_V = \left(\frac{\partial U}{\partial T} \right)_{V,\mu}. \quad (2.95)$$

2.4.2 Ideal gas - grand canonical treatment

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

$$\mathcal{Z}(T, V, z) = \sum_{N=0}^{\infty} z^N Z_N(T, V) = \sum_{N=0}^{\infty} \frac{z^N V^N}{N! h^{3N}} (2\pi m k_B T)^{3N/2} = \exp \left\{ \frac{zV}{h^3} (2\pi m k_B T)^{3/2} \right\}. \quad (2.96)$$

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

$$\langle N \rangle = z \frac{\partial}{\partial z} \frac{zV}{h^3} (2\pi m k_B T)^{3/2} = \frac{zV}{h^3} (2\pi m k_B T)^{3/2} \quad \Rightarrow \quad \mathcal{Z} = e^{\langle N \rangle}. \quad (2.97)$$

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

$$P_N = e^{-\langle N \rangle} \frac{\langle N \rangle^N}{N!} \approx \frac{1}{\sqrt{2\pi \langle N \rangle}} e^{-(N - \langle N \rangle)^2 / 2 \langle N \rangle} \quad (2.98)$$

which is strongly peaked at $N = \langle N \rangle \gg 1$.⁸ The fluctuations are given by

$$\langle N^2 \rangle - \langle N \rangle^2 = z \frac{\partial \langle N \rangle}{\partial z} = \langle N \rangle \quad \Rightarrow \quad \kappa_T = \frac{v}{k_B T} = \frac{1}{p}. \quad (2.99)$$

⁸Note 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 $T \rightarrow 0$, if $\mu < 0$ and energy has to be paid to add a particle.

The grand potential is given by

$$\Omega(T, V, \mu) = -k_B T e^{\beta\mu} \frac{V}{h^3} (2\pi m k_B T)^{3/2} = -k_B T \langle N \rangle = -pV. \quad (2.100)$$

The chemical potential is obtained by solving Eq.(2.97) for μ

$$\mu = -k_B T \ln \left(\frac{V(2\pi m k_B T)^{3/2}}{\langle N \rangle h^3} \right). \quad (2.101)$$

2.4.3 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 $\phi(\tilde{h}) = mg\tilde{h}$, where \tilde{h} and g denote the altitude and the earth acceleration of gravity, respectively. We introduce a reference chemical potential μ_0 as a constant. Then we write for the chemical potential,

$$\mu = \mu_0 + mg\tilde{h} - k_B T \ln \left\{ \frac{(2\pi m k_B T)^{3/2}}{nh^3} \right\} \quad (2.102)$$

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 $n = n_0$,

$$\mu(T) = \mu_0 + k_B T \ln \left\{ \frac{(2\pi m k_B T)^{3/2}}{n_0 h^3} \right\} \Rightarrow mg\tilde{h} = k_B T \ln \left(\frac{n_0}{n} \right). \quad (2.103)$$

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

$$n(\tilde{h}) = n_0 e^{-\beta mg\tilde{h}}, \quad (2.104)$$

and with the (local) equation of state we find

$$p(\tilde{h}) = n(\tilde{h}) k_B T = p_0 e^{-\beta mg\tilde{h}}. \quad (2.105)$$

This is the famous barometer formula.

2.5 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.

2.5.1 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:

$$\Lambda_N \int dp dq [U - \mathcal{H}] e^{\beta(F - \mathcal{H})} = 0. \quad (2.106)$$

	Microcanonical ensemble	Canonical ensemble	Grand canonical ensemble
density (unrenormalized)	$\rho(p, q) = \delta(E - \mathcal{H}(p, q))$	$\rho(p, q) = e^{-\beta\mathcal{H}(p, q)}$	$\rho(p, q) = e^{-\beta(\mathcal{H}(p, q) - \mu N)}$ $= z^N e^{-\beta\mathcal{H}(p, q)}$
partition function	$Z_{m'can} = \Lambda_N \int dpdq \rho(p, q)$ $= \omega(E)$	$Z_N = \Lambda_N \int dpdq \rho(p, q)$ $= \Lambda_N \int dpdq e^{-\beta\mathcal{H}(p, q)}$	$\mathcal{Z} = \sum_{N=0}^{\infty} \Lambda_N \int dpdq \rho(p, q, N)$ $= \sum_{N=0}^{\infty} z^N Z_N$
average value	$\langle A \rangle = \frac{\Lambda_N}{\omega(E)} \int dpdq \rho(p, q) A(p, q)$	$\langle A \rangle = \frac{\Lambda_N}{Z_N} \int dpdq \rho(p, q) A(p, q)$	$\langle A \rangle = \sum_{N=0}^{\infty} \frac{\Lambda_N}{\mathcal{Z}} \int dpdq \rho(p, q, N) A(p, q, N)$
thermodyn. potential	$S(E, V, N) = k_B \log \omega(E, V, N)$	$F(T, V, N) = -k_B T \log Z_N(T, V)$	$\Omega(T, V, \mu) = -k_B T \log \mathcal{Z}(T, V, \mu)$

Figure 2.5: Synopsis of the three ensembles for a gas.

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

$$0 = \frac{\partial U}{\partial \beta} + \Lambda_N \int dp dq (U - \mathcal{H}) \left[F - T \frac{\partial F}{\partial T} - \mathcal{H} \right] e^{\beta(F - \mathcal{H})} = \frac{\partial U}{\partial \beta} + \langle (U - \mathcal{H})^2 \rangle. \quad (2.107)$$

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

$$\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \langle (U - \mathcal{H})^2 \rangle = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T} = k_B T^2 C_V. \quad (2.108)$$

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

$$\frac{\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2}{\langle \mathcal{H} \rangle^2} \propto \frac{1}{N} \quad (2.109)$$

which is a sign of the equivalence of microcanonical and canonical ensembles. In the thermodynamic limit $N \rightarrow \infty$, 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

$$\begin{aligned} Z &= e^{-\beta F_{can}(T)} = \Lambda_N \int dp dq e^{-\beta\mathcal{H}(p, q)} = \int_0^{\infty} dE \omega(E) e^{-\beta E} \\ &= \int_0^{\infty} dE e^{-\beta E + \ln \omega(E)} = \int_0^{\infty} dE e^{\beta(T S_{m'can}(E) - E)} \end{aligned} \quad (2.110)$$

where the entropy $S(E) = S_{m'can}(E)$ is defined according to the microcanonical ensemble. The maximum of the integrand at $E = E_0$ is defined by the condition, see Fig.2.6,

$$T \left. \frac{\partial S}{\partial E} \right|_{E=E_0} = 1 \quad \text{and} \quad \left. \frac{\partial^2 S}{\partial E^2} \right|_{E=E_0} < 0. \quad (2.111)$$

Note that

$$\left. \frac{\partial^2 S}{\partial E^2} \right|_{E=E_0} = \left. \frac{\partial}{\partial E} \frac{1}{T} \right|_{E=E_0} = -\frac{1}{T^2} \left. \frac{\partial T}{\partial E} \right|_{E=E_0} = -\frac{1}{T^2 C_V} < 0. \quad (2.112)$$

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

$$TS(E) - E = TS(E_0) - E_0 - \frac{1}{2TC_V}(E - E_0)^2 + \dots \quad (2.113)$$

such that with $U = E_0$,

$$\begin{aligned} Z &\approx e^{\beta(TS-U)} \int_0^\infty dE e^{-(E-U)^2/2k_B T^2 C_V} = e^{\beta(TS-U)} \sqrt{2\pi k_B T^2 C_V} \\ \Rightarrow F_{\text{can}} &\approx U - TS_{\text{m'can}} - \frac{1}{2} k_B T \ln \{2\pi k_B T^2 C_V\} = U - TS_{\text{m'can}} + O(\ln N). \end{aligned} \quad (2.114)$$

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

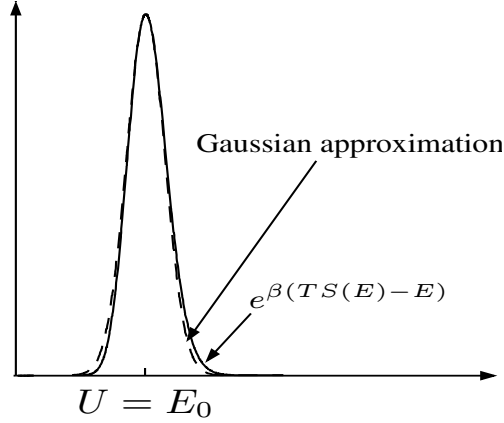


Figure 2.6: Saddle point approximation of the partition function: integrand in Eq.(2.110) and the approximation in Eq.(2.114). Solid line is the full integrand and dashed line its Gaussian approximation.

2.5.2 Particle number

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

$$\langle N^2 \rangle - \langle N \rangle^2 = z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln \mathcal{Z} = z \frac{\partial}{\partial z} \frac{1}{\mathcal{Z}} \sum_N N z^N Z_N = \frac{1}{\mathcal{Z}} \sum_N N^2 z^N Z_N - \left\{ \frac{1}{\mathcal{Z}} \sum_N N z^N Z_N \right\}^2 \quad (2.115)$$

from which we derive

$$\langle N^2 \rangle - \langle N \rangle^2 = -k_B T \frac{\partial^2}{\partial \mu^2} \Omega(T, V, \mu) = k_B T \frac{\partial \langle N \rangle}{\partial \mu}. \quad (2.116)$$

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

$$SdT - Vdp + Nd\mu = 0 \quad (2.117)$$

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

$$d\mu = v dp - \frac{S}{N} dT \quad \Rightarrow \quad \left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial p}{\partial v} \right)_T. \quad (2.118)$$

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

$$\begin{aligned} \left(\frac{\partial}{\partial v}\right)_{V,T} &= \left(\frac{\partial N}{\partial v}\right)_{V,T} \left(\frac{\partial}{\partial N}\right)_{V,T} = -\frac{N^2}{V} \left(\frac{\partial}{\partial N}\right)_{V,T}, \\ \left(\frac{\partial}{\partial v}\right)_{N,T} &= \left(\frac{\partial V}{\partial v}\right)_{N,T} \left(\frac{\partial}{\partial V}\right)_{N,T} = N \left(\frac{\partial}{\partial V}\right)_{N,T}. \end{aligned} \quad (2.119)$$

From (2.118) then conclude

$$-\frac{N^2}{V} \left(\frac{\partial \mu}{\partial N}\right)_{V,T} = V \left(\frac{\partial p}{\partial V}\right)_{N,T} \Rightarrow \frac{1}{N} \left(\frac{\partial N}{\partial \mu}\right)_{V,T} = -\frac{1}{vV} \left(\frac{\partial V}{\partial p}\right)_{N,T} = \frac{\kappa_T}{v}. \quad (2.120)$$

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

$$\kappa_T = \frac{v}{\langle N \rangle k_B T} \{ \langle N^2 \rangle - \langle N \rangle^2 \}. \quad (2.121)$$

2.5.3 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

$$\vec{M} = \sum_{i=1}^N \vec{m}_i. \quad (2.122)$$

The average value of the magnetization is

$$\langle M_z \rangle = N \langle m_{1,z} \rangle = \int \prod_{i=1}^N d\Omega_i M_z e^{\beta[F - \mathcal{H}(\vec{m}_1, \dots, \vec{m}_N; \vec{H})]} = - \left(\frac{\partial F}{\partial H_z} \right)_{T,N}. \quad (2.123)$$

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

$$\mathcal{H}(\vec{m}_1, \dots, \vec{m}_N; \vec{H}) = \mathcal{H}_0(\vec{m}_1, \dots, \vec{m}_N) - \vec{H} \cdot \vec{M}. \quad (2.124)$$

Now we discuss the equation,

$$0 = \int d\Omega_1 \cdots d\Omega_N (\langle M_z \rangle - M_z) e^{\beta(F - \mathcal{H})}, \quad (2.125)$$

taking the derivative with respect to the field H_z leads to

$$\begin{aligned} 0 &= \frac{\partial \langle M_z \rangle}{\partial H} - \beta \int d\Omega_1 \cdots d\Omega_N (\langle M_z \rangle - M_z) \frac{\partial}{\partial H_z} (F - \mathcal{H}) e^{\beta(F - \mathcal{H})} \\ &= \chi_{zz} - \beta \int d\Omega_1 \cdots d\Omega_N (\langle M_z \rangle - M_z)^2 e^{\beta(F - \mathcal{H})} = \chi_{zz} - \beta \langle (\langle M_z \rangle - M_z)^2 \rangle. \end{aligned} \quad (2.126)$$

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

$$\chi_{zz} = \frac{1}{k_B T} \{ \langle M_z^2 \rangle - \langle M_z \rangle^2 \}. \quad (2.127)$$

Chapter 3

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.

3.1 Basis of quantum statistical physics

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

$$|\Psi\rangle = \sum_n c_n |\psi_n\rangle \quad (3.1)$$

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:

$$\mathcal{H}|\psi_n\rangle = \varepsilon_n |\psi_n\rangle \quad \text{with} \quad \langle\psi_n|\psi_{n'}\rangle = \delta_{nn'} \quad \text{and} \quad 1 = \sum_n |\psi_n\rangle\langle\psi_n|. \quad (3.2)$$

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

$$1 = \langle\Psi|\Psi\rangle = \sum_{n,n'} c_n^* c_{n'} \langle\psi_n|\psi_{n'}\rangle = \sum_n |c_n|^2. \quad (3.3)$$

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 \hat{A} , and their expectation value is

$$\langle\Psi|\hat{A}|\Psi\rangle = \sum_{n,n'} c_n^* c_{n'} \langle\psi_n|\hat{A}|\psi_{n'}\rangle. \quad (3.4)$$

This expectation value is generally time dependent through the wavefunction $c_n = c_n(t) = c_n(0)e^{-i\varepsilon_n t/\hbar}$.

Using the viewpoint of time evolution of the system, let us now consider the measurement of a macroscopic observable. This 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.),

$$\langle\hat{A}\rangle = \overline{\langle\Psi|\hat{A}|\Psi\rangle} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \sum_{n,n'} c_n^*(t) c_{n'}(t) \langle\psi_n|\hat{A}|\psi_{n'}\rangle = \sum_{n,n'} \overline{c_n^* c_{n'}} \langle\psi_n|\hat{A}|\psi_{n'}\rangle. \quad (3.5)$$

As the dynamics (time evolution) follows from the Hamiltonian of the systems, $|\Psi\rangle$ is a state of fixed energy, $E_\Psi = \sum_n |c_n(t)|^2 \varepsilon_n$. Like in the classical case we may represent the average value $\langle \hat{A} \rangle$ also by an average over an ensemble of equivalent systems,

$$\langle \hat{A} \rangle = \sum_{n,n'} \rho_{nn'} \langle \psi_n | \hat{A} | \psi_{n'} \rangle \quad (3.6)$$

with $\rho_{nn'} = c_n^* c_{n'}$. The time dependence of c_n yields

$$\overline{c_n^* c_{n'}} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt c_n^*(0) c_{n'}(0) e^{i(\varepsilon_n - \varepsilon_{n'})t/\hbar} = |c_n|^2 \delta_{nn'} \quad (3.7)$$

such that all terms invoking coherent interference ($c_n^* c_{n'}$ with $n \neq n'$) vanish such that

$$\langle \hat{A} \rangle = \sum_n |c_n|^2 \langle \psi_n | \hat{A} | \psi_n \rangle \quad (3.8)$$

where we note that $|c_n|^2$ is time independent. The same result in the ensemble picture requires that

$$\rho_{nn'} = |c_n|^2 \delta_{nn'} \quad (3.9)$$

implying that there is no interference between different member systems of a given ensemble.

Postulates of quantum statistical physics

The quantum statistical physics is based on two key postulates:

- Equal probability:

$$\overline{c_n^* c_n} = \begin{cases} r, & E \leq \varepsilon_n \leq E + \delta E, \\ 0, & \text{otherwise,} \end{cases} \quad (3.10)$$

where r is a real constant.

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

$$\overline{c_n^* c_{n'}} = 0, \quad (3.11)$$

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 we consider a system as described effectively by a wavefunction b_n ,

$$|\Psi\rangle_{\text{eff}} = \sum_n b_n |\psi_n\rangle \quad (3.12)$$

(unrenormalized state) with

$$|b_n|^2 = \begin{cases} 1 & E \leq \varepsilon_n \leq E + \delta E \\ 0 & \text{otherwise} \end{cases} \quad (3.13)$$

and b_n have a random phase. Then average values can be considered as the expectation value

$$\langle \hat{A} \rangle = \frac{\sum_n |b_n|^2 \langle \psi_n | \hat{A} | \psi_n \rangle}{\sum_n |b_n|^2} \quad (3.14)$$

whereby each eigenstate of the Hamiltonian with energy in the given energy interval $[E, E + \delta E]$ appears in the state $|\Psi\rangle_{\text{eff}}$ with the same probability.

3.2 Density matrix

Mixed states or incoherent superpositions of states are conveniently described by density matrices $\hat{\rho}$.¹

We define first the density matrix as an operator through its matrix elements

$$\langle \psi_n | \hat{\rho} | \psi_{n'} \rangle = \rho_{nn'} = |c_n|^2 \delta_{nn'} . \quad (3.20)$$

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

$$\hat{\rho} = \sum_n |c_n|^2 |\psi_n\rangle \langle \psi_n| . \quad (3.21)$$

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

$$\langle \hat{A} \rangle = \frac{\sum_n \langle \psi_n | \hat{A} \hat{\rho} | \psi_n \rangle}{\sum_n \langle \psi_n | \hat{\rho} | \psi_n \rangle} = \frac{tr(\hat{A} \hat{\rho})}{tr \hat{\rho}} . \quad (3.22)$$

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

$$tr(A') = tr(UAU^{-1}) = tr(AU^{-1}U) = tr(A) . \quad (3.23)$$

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,

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = [\mathcal{H}, \hat{\rho}] = 0 . \quad (3.24)$$

It is obvious that the density matrix defined in (3.21) commutes with \mathcal{H} . Compare this with Liouville's theorem of classical mechanics.

¹We distinguish pure and mixed states. A pure state given as superposition, for instance, energy eigenstates (Eq.(3.1))

$$|\Psi\rangle = \sum_n c_n |\psi_n\rangle \quad (3.15)$$

leads to the density matrix of a pure state, if we assume phase coherence of the wavefunction c_n :

$$\hat{\rho}_{\text{pure}} = |\Psi\rangle \langle \Psi| = \sum_{n,n'} c_n^* c_{n'} |\psi_n\rangle \langle \psi_{n'}| \quad (3.16)$$

whereby the mixed terms $c_n^* c_{n'}$ with $n \neq n'$ are interference terms. For mixed states we assume that there is no phase coherence in the wavefunctions such that all mixed terms disappear. Such a state represented by density matrix has the form

$$\hat{\rho}_{\text{mixed}} = \sum_n |c_n|^2 |\psi_n\rangle \langle \psi_n| . \quad (3.17)$$

Note that

$$tr(\hat{\rho}_{\text{pure}}) = tr(\hat{\rho}_{\text{mixed}}) = 1 \quad \Rightarrow \quad \begin{cases} tr(\hat{\rho}_{\text{pure}}^2) = 1 , \\ tr(\hat{\rho}_{\text{mixed}}^2) \leq 1 . \end{cases} \quad (3.18)$$

Average (expectation) values are calculated in both cases the same way:

$$\langle \hat{A} \rangle = tr(\hat{\rho} \hat{A}) = \begin{cases} \sum_{n,n'} c_n^* c_{n'} \langle \psi_n | \hat{A} | \psi_{n'} \rangle & \text{pure} , \\ \sum_n |c_n|^2 \langle \psi_n | \hat{A} | \psi_n \rangle & \text{mixed} . \end{cases} \quad (3.19)$$

	Classical Statistical Physics	Quantum Statistical Physics
observable	phase space function $A(p, q)$	Hermitian operator \hat{A}
density	density function $\rho(p, q)$	density matrix $\hat{\rho}$
sum / integral	phase space integral $\Lambda_N \int dp dq \dots$	trace over Hilbertspace $tr(\dots)$
renormalized density	$\Lambda_N \int dp dq \rho(p, q) = 1$	$tr(\hat{\rho}) = 1$
statistical average	$\langle A \rangle = \Lambda_N \int dp dq \rho(p, q) A(p, q)$	$\langle \hat{A} \rangle = tr(\hat{\rho} \hat{A})$
Liouville's theorem	$\frac{\partial \rho}{\partial t} = \{\mathcal{H}, \rho\}$ (Poisson bracket)	$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}, \hat{\rho}]$ (commutator)
stationary ensembles	$\{\mathcal{H}, \rho\} = 0$	$[\mathcal{H}, \hat{\rho}] = 0$

3.3 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.

3.3.1 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 $\rho_{nn'} = \delta_{nn'} |b_n|^2$. 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,

$$|b_n|^2 = \begin{cases} 1 & E \leq \epsilon_n \leq E + \delta E \\ 0 & \text{otherwise} . \end{cases} \quad (3.25)$$

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

$$\hat{\rho} = \sum_{E \leq \epsilon_n \leq E + \delta E} |\psi_n\rangle \langle \psi_n| \quad \text{with} \quad tr \hat{\rho} = \sum_n \rho_{nn} = \omega(E) . \quad (3.26)$$

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

$$S(E, V) = k_B \ln \omega(E) . \quad (3.27)$$

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:

$$\Phi(E) = \sum_{\epsilon_n \leq E} 1 \quad \Rightarrow \quad \omega(E) = \sum_{E \leq \epsilon_n \leq E + \delta E} 1 = \frac{d\Phi(E)}{dE} \delta E . \quad (3.28)$$

3.3.2 Canonical ensemble

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

$$\rho(p, q) = e^{-\beta \mathcal{H}(p, q)} \quad \rightarrow \quad \rho_{nn'} = \delta_{nn'} e^{-\beta \epsilon_n} , \quad (3.29)$$

and we define the partition function as

$$Z = \sum_n e^{-\beta \epsilon_n} = \text{tr} \hat{\rho} = e^{-\beta F(T, V, N)} \quad (3.30)$$

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

$$\hat{\rho} = \sum_n |\psi_n\rangle e^{-\beta \epsilon_n} \langle \psi_n| = e^{-\beta \mathcal{H}} \underbrace{\sum_n |\psi_n\rangle \langle \psi_n|}_{=1} = e^{-\beta \mathcal{H}} . \quad (3.31)$$

Thus the partition function can also be expressed as

$$Z = \text{tr} e^{-\beta \mathcal{H}} \quad (3.32)$$

and average values of observables are given by

$$\langle \hat{A} \rangle = \frac{\text{tr}(\hat{A} e^{-\beta \mathcal{H}})}{\text{tr} e^{-\beta \mathcal{H}}} = \frac{1}{Z} \text{tr}(\hat{A} e^{-\beta \mathcal{H}}) . \quad (3.33)$$

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

$$F(T, V, N) = -k_B T \ln Z . \quad (3.34)$$

3.3.3 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,

$$\hat{\rho} = e^{-\beta(\mathcal{H} - \mu \hat{N})} \quad (3.35)$$

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

$$\mathcal{Z} = \text{tr} e^{-\beta(\mathcal{H} - \mu \hat{N})} = \sum_N z^N Z_N \quad (3.36)$$

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

$$\Omega(T, V, \mu) = -k_B T \ln \mathcal{Z} . \quad (3.37)$$

3.4 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.

3.4.1 Spin 1/2

We consider N quantum spin 1/2 moments ($S = \hbar/2$) where for each spin the Hilbert space contains two states, $|s, s_z\rangle = \{|1/2, \pm 1/2\rangle\}$ 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,

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i = -\frac{\mu_B g}{\hbar} \sum_{i=1}^N \vec{H} \cdot \hat{S}_i = -\frac{g\mu_B}{2} \sum_{i=1}^N \vec{H} \cdot \hat{\sigma}_i \quad (3.38)$$

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

$$\hat{\sigma}^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \hat{\sigma}^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (3.39)$$

and $\hat{\sigma}^0$ is the 2×2 unit matrix. The following property for Pauli matrices,

$$(\vec{a} \cdot \hat{\sigma})(\vec{b} \cdot \hat{\sigma}) = \vec{a} \cdot \vec{b} \hat{\sigma}^0 + i(\vec{a} \times \vec{b}) \cdot \hat{\sigma} \quad (3.40)$$

yield the simple relation,

$$(\vec{a} \cdot \hat{\sigma})^{2n} = |\vec{a}|^{2n} \hat{\sigma}^0 \quad \text{and} \quad (\vec{a} \cdot \hat{\sigma})^{2n+1} = |\vec{a}|^{2n} \vec{a} \cdot \hat{\sigma} \quad (3.41)$$

and $tr \hat{\sigma} = 0$ and $tr \hat{\sigma}^0 = 2$ in order to determine the partition function²,

$$\begin{aligned} Z &= tr \left\{ e^{-\beta \mathcal{H}} \right\} = tr \left\{ e^{\beta \mu_B \sum_i \vec{H} \cdot \hat{\sigma}_i} \right\} = \left(tr \left\{ e^{\beta \mu_B \vec{H} \cdot \hat{\sigma}} \right\} \right)^N \\ &= \left(tr \left\{ \hat{\sigma}^0 \cosh(\beta \mu_B H) + \vec{H} \cdot \hat{\sigma} \sinh(\beta \mu_B H) \right\} \right)^N = (2 \cosh(\beta \mu_B H))^N, \end{aligned} \quad (3.45)$$

²For independent spin degrees of freedom we use the product state

$$|\Psi_{s_1, s_2, \dots, s_N}\rangle = |s_{1z}\rangle \otimes |s_{2z}\rangle \otimes \dots \otimes |s_{Nz}\rangle \quad (3.42)$$

with the short notation $|\frac{1}{2}, s_{iz}\rangle = |s_{iz}\rangle$. If the Hamiltonian can be written in terms of independent degrees of freedom, $\mathcal{H}(s_1, s_2, \dots, s_N) = \sum_{i=1}^N \mathcal{H}_i(s_i)$ (all \mathcal{H}_i are identical), then the partition function can be split into a product form

$$Z_N = tr_{|\Psi\rangle} \left(e^{-\beta \mathcal{H}} \right) = tr_{|\Psi\rangle} \left(\prod_{i=1}^N e^{-\beta \mathcal{H}_i} \right) = \prod_{i=1}^N \left(tr_{|s_i\rangle} e^{-\beta \mathcal{H}_i} \right) = \left(tr_{|s_1\rangle} \{ e^{-\beta \mathcal{H}_1} \} \right)^N = Z_1^N. \quad (3.43)$$

Next we calculate the average value $\langle \hat{S}_{1z} \rangle$ of one single spins

$$\langle \hat{S}_{1z} \rangle = \frac{tr_{|\Psi\rangle} (\hat{S}_{1z} e^{-\beta \mathcal{H}})}{tr_{|\Psi\rangle} (e^{-\beta \mathcal{H}})} = \frac{tr_{|\Psi\rangle} \left(\{ \prod_{i \neq 1} e^{-\beta \mathcal{H}_i} \} \hat{S}_{1z} e^{-\beta \mathcal{H}_1} \right)}{tr_{|\Psi\rangle} \left(\{ \prod_{i \neq 1} e^{-\beta \mathcal{H}_i} \} e^{-\beta \mathcal{H}_1} \right)} = \frac{Z_1^{N-1} tr_{|s_1\rangle} (\hat{S}_{1z} e^{-\beta \mathcal{H}_1})}{Z_1^N} = \frac{tr_{|s_1\rangle} \hat{S}_{1z} e^{-\beta \mathcal{H}_1}}{Z_1} \quad (3.44)$$

where $H = |\vec{H}|$ and $\hat{H} = \vec{H}/H$.³ We obtain the free energy

$$F = -Nk_B T \ln[2 \cosh(\beta\mu_B H)] = \begin{cases} -N\mu_B H & k_B T \ll \mu_B H \\ -Nk_B T \ln 2 & k_B T \gg \mu_B H \end{cases} \quad (3.47)$$

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

$$S(T) = -\frac{\partial F}{\partial T} = Nk_B \ln[2 \cosh(\beta\mu_B H)] - Nk_B \beta\mu_B H \tanh(\beta\mu_B H) \quad (3.48)$$

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

$$\begin{aligned} M_n &= \mu_B \sum_{i=1}^N \langle \hat{n} \cdot \hat{\sigma}_i \rangle = \mu_B N \langle \hat{n} \cdot \hat{\sigma}_1 \rangle \\ &= N \frac{\text{tr} \left\{ \mu_B \hat{n} \cdot \hat{\sigma} \left[\hat{\sigma}^0 \cosh(\beta\mu_B H) + \hat{H} \cdot \hat{\sigma} \sinh(\beta\mu_B H) \right] \right\}}{2 \cosh(\beta\mu_B H)} = N \hat{n} \cdot \hat{H} \mu_B \tanh(\beta\mu_B H) \end{aligned} \quad (3.49)$$

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 ,

$$\begin{aligned} \chi_{zz} &= \mu_B^2 \beta N \{ \langle \hat{\sigma}^{z2} \rangle - \langle \hat{\sigma}^z \rangle^2 \} = \mu_B^2 \beta N \{ \langle \hat{\sigma}^0 \rangle - \langle \hat{\sigma}^z \rangle^2 \} \\ &= \frac{\mu_B^2 N}{k_B T} \{ 1 - \tanh^2(\beta\mu_B H) \} = \frac{\mu_B^2 N}{k_B T} \frac{1}{\cosh^2(\beta\mu_B H)}. \end{aligned} \quad (3.50)$$

This yields a high-temperature behavior ($k_B T \gg \mu_B H$)

$$\chi_{zz}(T) = \frac{\mu_B^2 N}{k_B T} \quad (3.51)$$

corresponding to a Curie-behavior.

3.4.2 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 $\{|s, s_z\rangle\} = \{|s, -s\rangle, |s, -s + 1\rangle, \dots, |s, s - 1\rangle, |s, s\rangle\}$ with $\hat{S}^2 |s, s_z\rangle = \hbar^2 s(s + 1) |s, s_z\rangle$ 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,

$$\mathcal{H} = -\frac{g\mu_B}{\hbar} \sum_{i=1}^N \hat{S}_i \cdot \vec{H} = -\frac{g\mu_B}{\hbar} \sum_{i=1}^N \hat{S}_i^z H, \quad (3.52)$$

³Evaluation of exponential function: Expansion in a Taylor-series,

$$\begin{aligned} e^{\beta\mu_B \vec{H} \cdot \hat{\sigma}} &= \sum_{n=0}^{\infty} \frac{(\beta\mu_B)^n}{n!} (\vec{H} \cdot \hat{\sigma})^n = \sum_{\tilde{n}=0}^{\infty} \left[\frac{(\beta\mu_B)^{2\tilde{n}}}{(2\tilde{n})!} H^{2\tilde{n}} \hat{\sigma}_0 + \frac{(\beta\mu_B)^{2\tilde{n}+1}}{(2\tilde{n}+1)!} H^{2\tilde{n}+1} (\hat{H} \cdot \hat{\sigma}) \right] \\ &= \hat{\sigma}^0 \cosh(\beta\mu_B H) + \hat{H} \cdot \hat{\sigma} \sinh(\beta\mu_B H). \end{aligned} \quad (3.46)$$

where we used the relations (3.41).

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,

$$\begin{aligned} Z &= \text{tr} \left\{ e^{-\beta \mathcal{H}} \right\} = \text{tr} \left\{ \prod_{i=1}^N e^{\beta g \mu_B H \hat{S}_i^z / \hbar} \right\} = \left(\sum_{s_z=-s}^s \langle s, s_z | e^{\beta g \mu_B H \hat{S}_i^z / \hbar} | s, s_z \rangle \right)^N = \left(\sum_{s_z=-s}^s e^{\beta g \mu_B H s_z} \right)^N \\ &= \left(e^{-\beta g \mu_B H s} \sum_{n=0}^{2s} e^{\beta g \mu_B H n} \right)^N = \left(e^{-\beta g \mu_B H s} \frac{e^{\beta g \mu_B H (2s+1)} - 1}{e^{\beta g \mu_B H} - 1} \right)^N = \left(\frac{\sinh(\beta \mu_B H (2s+1))}{\sinh(\beta \mu_B H)} \right)^N. \end{aligned} \quad (3.53)$$

We obtain the free energy

$$F = -N k_B T \ln \left\{ \frac{\sinh(\beta \mu_B H (2s+1))}{\sinh(\beta \mu_B H)} \right\} \quad (3.54)$$

and the internal energy

$$U = -N \mu_B H \left\{ (2s+1) \coth(\beta \mu_B H (2s+1)) - \coth(\beta \mu_B H) \right\} = -N \mu_B H 2s B_s(\beta \mu_B H) \quad (3.55)$$

where $B_s(x)$ is the "Brillouin function".

$$B_s(x) = \frac{2s+1}{2s} \coth[(2s+1)x] - \frac{1}{2s} \coth(x) = \begin{cases} \frac{2}{3}(s+1)x + \dots & x \ll (2s+1)^{-1}, \\ 1 - \frac{1}{s}e^{-x} + \dots & x \gg (2s+1)^{-1}. \end{cases} \quad (3.56)$$

In Fig.3.1 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,

$$M_z = g \mu_B \sum_{i=1}^N \langle \hat{S}_i^z \rangle = N \mu_B 2s B_s(\beta \mu_B H), \quad (3.57)$$

which also identifies the internal energy as $U = -M_z H$. The other components vanish, $M_x = M_y = 0$.

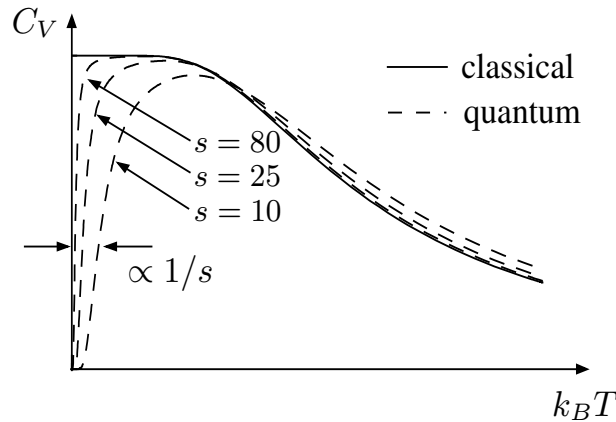


Figure 3.1: As the spin s increases, the "quantum" heat capacity approaches the classical heat capacity.

The limit of $s \gg 1$ leads us to the classical limit⁴. Let us examine this by simultaneously fixing $2s\mu_B = m$ to be finite. The free energy and entropy take the limit for $k_B T \gg mH$,

$$F = -Nk_B T \ln 2s \quad \text{and} \quad S = Nk_B \ln 2s \quad (3.62)$$

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) $2sk_B T \gg mH \gg k_B T$: we find

$$F = -NmH + Nk_B T \ln(\beta mH/s) \quad \text{and} \quad S = Nk_B \ln 2s - Nk_B \ln(2\beta mH) + Nk_B \quad (3.63)$$

which corresponds essentially to the low-temperature classical regime.

(2) $mH \gg 2sk_B T$: we obtain

$$F = -NmH \left(1 - \frac{1}{2s}\right) + O\left(Te^{-2\beta mH/s}\right) \quad \text{and} \quad S \rightarrow 0 \quad (3.64)$$

which corresponds to the quantum result. This quantum range shrinks for increasing s , see Fig.3.1 .

3.5 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 (anti-symmetric) 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

$$\psi_{\vec{p}}(\vec{r}) = \langle \vec{r} | \psi_{\vec{p}} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{p}\cdot\vec{r}/\hbar} \quad \text{with} \quad \epsilon_{\vec{p}} = \frac{\vec{p}^2}{2m} . \quad (3.65)$$

⁴*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,

$$Z = \int \prod_{i=1}^N \left\{ \frac{d\Omega_i}{4\pi} e^{\beta \vec{m}_i \cdot \vec{H}} \right\} = \left(\int \frac{d\Omega}{4\pi} e^{\beta mH \cos \theta} \right)^N = \left(\frac{\sinh(\beta mH)}{\beta mH} \right)^N . \quad (3.58)$$

The free energy is given by

$$F - F_0 = -Nk_B T \{ \ln(\sinh(\beta mH)) - \ln(\beta mH) \} = \begin{cases} -NmH + Nk_B T \ln(2\beta mH) & k_B T \ll mH \\ -\frac{Nk_B T}{3!} \left(\frac{mH}{k_B T} \right)^2 & k_B T \gg mH \end{cases} \quad (3.59)$$

and the entropy in the limiting cases,

$$S - S_0 = - \left(\frac{\partial F}{\partial T} \right)_{H,N} = \begin{cases} -Nk_B \ln(2\beta mH) + Nk_B & k_B T \ll mH \\ -\frac{N}{3} \left(\frac{mH}{k_B T} \right)^3 & k_B T \gg mH \end{cases} \quad (3.60)$$

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

$$S_0 = Nk_B \ln(2s + 1) \approx Nk_B \ln(2s) \quad \text{and} \quad F_0 = -Nk_B T \ln(2s + 1) \approx Nk_B T \ln(2s) . \quad (3.61)$$

corresponding to the count of states in the quantum system: $(2s + 1)^N$.

Introducing periodic boundary conditions we quantize the momentum quantum number. For this purpose we assume a cubic system with edge length L and $V = L^3$. The wavefunction satisfies the boundary conditions

$$\psi_{\vec{p}}(\vec{r} + (L, 0, 0)) = \psi_{\vec{p}}(\vec{r} + (0, L, 0)) = \psi_{\vec{p}}(\vec{r} + (0, 0, L)) = \psi_{\vec{p}}(\vec{r}) \quad (3.66)$$

which is satisfied, if

$$\vec{p} = \frac{2\pi\hbar}{L}(n_x, n_y, n_z) = \frac{h}{L}(n_x, n_y, n_z) \quad \text{with} \quad n_x, n_y, n_z \in \mathbb{Z}. \quad (3.67)$$

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

$$\mathcal{Z} = \sum_{\{n_{\vec{p}}\}} g_{\{n_{\vec{p}}\}} e^{-\beta(E - \mu N)_{\{n_{\vec{p}}\}}}, \quad (3.68)$$

with

$$E = \sum_{\vec{p}} \epsilon_{\vec{p}} n_{\vec{p}} \quad \text{and} \quad N = \sum_{\vec{p}} n_{\vec{p}}. \quad (3.69)$$

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.⁵ The factor $g_{\{n_{\vec{p}}\}}$ is given by

$$g_{\{n_{\vec{p}}\}} = \begin{cases} 1 & \text{indistinguishable particles (Fermions and Bosons)}, \\ \prod_{\vec{p}} \frac{1}{n_{\vec{p}}!} & \text{classical particles (Boltzmann)}. \end{cases} \quad (3.71)$$

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 $n_{\vec{p}} = 0, 1, 2, \dots$. Thus, calculating the partition function we obtain for Fermions/Bosons,

$$\begin{aligned} \mathcal{Z} &= \sum_{n_{\vec{p}_1}, n_{\vec{p}_2}, \dots} \left[\left\{ z e^{-\beta \epsilon_{\vec{p}_1}} \right\}^{n_{\vec{p}_1}} \left\{ z e^{-\beta \epsilon_{\vec{p}_2}} \right\}^{n_{\vec{p}_2}} \dots \right] \\ &= \prod_{\vec{p}} \sum_{n_{\vec{p}}} \left(z e^{-\beta \epsilon_{\vec{p}}} \right)^{n_{\vec{p}}} = \begin{cases} \prod_{\vec{p}} \left(1 + z e^{-\beta \epsilon_{\vec{p}}} \right) & \text{Fermions} \\ \prod_{\vec{p}} \frac{1}{1 - z e^{-\beta \epsilon_{\vec{p}}}} & \text{Bosons} \end{cases} \end{aligned} \quad (3.72)$$

with $z = e^{\beta\mu}$ as the fugacity.⁶

⁵Note that sums over \vec{p} are discrete sums over \vec{n} due to Eq.(3.67), but for large L can be approximated well by integrals

$$\sum_{\vec{p}} = \sum_{\vec{n}} \approx \int d^3 n = \frac{L^3}{(2\pi\hbar)^3} \int d^3 p = \frac{V}{h^3} \int d^3 p. \quad (3.70)$$

⁶ *Classical particles:* The partition function is given by

$$\mathcal{Z} = \sum_{n_{\vec{p}_1}, n_{\vec{p}_2}, \dots} \left[\frac{1}{n_{\vec{p}_1}!} \left\{ z e^{-\beta \epsilon_{\vec{p}_1}} \right\}^{n_{\vec{p}_1}} \frac{1}{n_{\vec{p}_2}!} \left\{ z e^{-\beta \epsilon_{\vec{p}_2}} \right\}^{n_{\vec{p}_2}} \dots \right] = \sum_{N=0}^{\infty} z^N \frac{1}{N!} \left\{ \sum_{\vec{p}} e^{-\beta \epsilon_{\vec{p}}} \right\}^N = \sum_{N=0}^{\infty} z^N Z_N^{(class)}, \quad (3.73)$$

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

From the partition function we arrive at the equation of state

$$\frac{pV}{k_B T} = -\beta\Omega(T, V, \mu) = \begin{cases} \sum_{\vec{p}} \ln(1 + ze^{-\beta\epsilon_{\vec{p}}}) & \text{Fermions,} \\ -\sum_{\vec{p}} \ln(1 - ze^{-\beta\epsilon_{\vec{p}}}) & \text{Bosons,} \end{cases} \quad (3.74)$$

and the particle number

$$N = z \frac{\partial}{\partial z} \ln \mathcal{Z} = \begin{cases} \sum_{\vec{p}} \frac{1}{e^{\beta\epsilon_{\vec{p}}} z^{-1} + 1} & \text{Fermions,} \\ \sum_{\vec{p}} \frac{1}{e^{\beta\epsilon_{\vec{p}}} z^{-1} - 1} & \text{Bosons.} \end{cases} \quad (3.75)$$

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

$$\begin{aligned} \langle n_{\vec{p}} \rangle &= \frac{1}{\mathcal{Z}} \left\{ \prod_{\vec{p}' \neq \vec{p}} \sum_{n_{\vec{p}'}} (ze^{-\beta\epsilon_{\vec{p}'}})^{n_{\vec{p}'}} \right\} \sum_{n_{\vec{p}}} n_{\vec{p}} (ze^{-\beta\epsilon_{\vec{p}}})^{n_{\vec{p}}} \\ &= \frac{\sum_{n_{\vec{p}}} n_{\vec{p}} (ze^{-\beta\epsilon_{\vec{p}}})^{n_{\vec{p}}}}{\sum_{n_{\vec{p}}} (ze^{-\beta\epsilon_{\vec{p}}})^{n_{\vec{p}}}} = -k_B T \frac{\partial}{\partial \epsilon_{\vec{p}}} \ln \mathcal{Z} = \begin{cases} \frac{1}{z^{-1} e^{\beta\epsilon_{\vec{p}}} + 1} & \text{Fermions,} \\ \frac{1}{z^{-1} e^{\beta\epsilon_{\vec{p}}} - 1} & \text{Bosons.} \end{cases} \end{aligned} \quad (3.76)$$

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

Eventually we compare the grand potential and the internal energy. Using (3.74) we obtain

$$\begin{aligned} \Omega &= \mp k_B T \sum_{\vec{p}} \ln(1 \pm ze^{-\beta\epsilon_{\vec{p}}}) = \mp k_B T \int d\epsilon g(\epsilon) \ln(1 \pm ze^{-\beta\epsilon}) \\ &= \mp V k_B T \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\epsilon \epsilon^{1/2} \ln(1 \pm ze^{-\beta\epsilon}) \\ &= -\frac{2}{3} V \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{z^{-1} e^{\beta\epsilon} \pm 1}, \end{aligned} \quad (3.77)$$

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

$$g(\epsilon) = \sum_{\vec{p}} \delta(\epsilon - \epsilon_{\vec{p}}) = V \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}, \quad (3.78)$$

for the energy integration. Now we consider the internal energy

$$U = \sum_{\vec{p}} \langle n_{\vec{p}} \rangle \epsilon_{\vec{p}} = \int_0^\infty d\epsilon g(\epsilon) \frac{\epsilon}{z^{-1} e^{\beta\epsilon} \pm 1} = V \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{z^{-1} e^{\beta\epsilon} \pm 1}. \quad (3.79)$$

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

$$U = \frac{3}{2} pV. \quad (3.80)$$

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 .

3.6 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

$$\begin{aligned} \frac{p}{k_B T} &= \frac{4\pi}{h^3} (2s + 1) \int_0^\infty dp p^2 \ln \left(1 + z e^{-\beta \epsilon_{\vec{p}}} \right), \\ \frac{1}{v} = \frac{N}{V} = n &= \frac{4\pi}{h^3} (2s + 1) \int_0^\infty dp p^2 \frac{1}{z^{-1} e^{\beta \epsilon_{\vec{p}}} + 1}, \end{aligned} \quad (3.81)$$

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

$$\begin{aligned} \frac{p}{k_B T} &= \frac{2s + 1}{\lambda^3} f_{5/2}(z) \\ n = \frac{1}{v} &= \frac{2s + 1}{\lambda^3} f_{3/2}(z) \end{aligned} \quad (3.82)$$

where $\lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. These functions are defined as⁷

$$\begin{aligned} f_{5/2}(z) &= \frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 \ln(1 + z e^{-x^2}) = - \sum_{l=1}^{\infty} (-1)^l \frac{z^l}{l^{5/2}} \\ f_{3/2}(z) &= z \frac{\partial}{\partial z} f_{5/2}(z) = - \sum_{l=1}^{\infty} (-1)^l \frac{z^l}{l^{3/2}}. \end{aligned} \quad (3.84)$$

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 find⁸

$$\begin{aligned} f_{5/2}(z) &\approx \frac{8}{15\sqrt{\pi}} (\ln z)^{5/2} \left[1 + \frac{5\pi^2}{8(\ln z)^2} + \dots \right] \\ f_{3/2}(z) &= \frac{4}{3\sqrt{\pi}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8(\ln z)^2} + \dots \right]. \end{aligned} \quad (3.88)$$

⁷Expansion of $f_{5/2}(z)$:

$$\frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 \ln(1 + z e^{-x^2}) = - \frac{4}{\sqrt{\pi}} \int_0^\infty dx \sum_{l=1}^{\infty} x^2 (-1)^l \frac{z^l e^{-lx^2}}{l} = - \sum_{l=1}^{\infty} (-1)^l \frac{z^l}{l^{5/2}}. \quad (3.83)$$

⁸Derivation of the large- z -expansion: Use $\nu = \mu/k_B T = \ln z$ and rewrite

$$f_{5/2}(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty dy y^{1/2} \ln(1 + e^{\nu-y}) = \frac{8}{15\sqrt{\pi}} \int_{-\nu}^\infty dy' (y' + \nu)^{5/2} \frac{e^{y'}}{(1 + e^{y'})^2}, \quad (3.85)$$

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

$$\begin{aligned} f_{5/2}(z) &= \frac{8}{15\sqrt{\pi}} \int_{-\infty}^{+\infty} dy' \left[\nu^{5/2} + \frac{5}{2} \nu^{3/2} y' + \frac{15}{8} \nu^{1/2} y'^2 + \dots \right] \frac{e^{y'}}{(1 + e^{y'})^2} \\ &= \frac{8}{15\sqrt{\pi}} \left[I_0 \nu^{5/2} + \frac{5}{2} I_1 \nu^{3/2} + \frac{15}{8} I_2 \nu^{1/2} + \dots \right] \end{aligned} \quad (3.86)$$

where

$$I_n = \int_{-\infty}^{+\infty} dy \frac{y^n e^y}{(1 + e^y)^2} \quad \Rightarrow \quad I_0 = 1, I_1 = 0, I_2 = \frac{\pi^2}{3}, \dots \quad (3.87)$$

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

3.6.1 High-temperature and low-density limit

Low density (high temperature) implies $\lambda^3 n \ll 1$ and $z = e^{\beta\mu} \ll 1$. We can use now (3.82)

$$\lambda^3 n = (2s+1) \left\{ z - \frac{z^2}{2^{3/2}} + \dots \right\} \quad \Rightarrow \quad z = \frac{\lambda^3 n}{2s+1} + \frac{(\lambda^3 n)^2}{2^{3/2}(2s+1)^2} + \dots \quad (3.89)$$

This allows us to replace z in the equation of state ⁹,

$$\frac{p}{k_B T} \approx \frac{2s+1}{\lambda^3} \left\{ z - \frac{z^2}{2^{5/2}} \right\} \approx \frac{N}{V} \left\{ 1 + \frac{\lambda^3 n}{2^{5/2}(2s+1)} \right\} \quad (3.91)$$

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,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{V}{N k_B T} \frac{1}{1 + \frac{\lambda^3 n}{2^{5/2}(2s+1)}} \quad (3.92)$$

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

$$\langle n_{\vec{p}} \rangle = \frac{1}{z^{-1} e^{\beta\epsilon_{\vec{p}}} + 1} \approx z e^{-\beta\epsilon_{\vec{p}}} \approx \frac{\lambda^3 n}{2s+1} e^{-\beta\epsilon_{\vec{p}}} = \frac{1}{2s+1} \frac{nh^3}{(2\pi m k_B T)^{3/2}} e^{-\beta\epsilon_{\vec{p}}} \quad (3.93)$$

corresponding to the Maxwell-Boltzmann distribution per spin. With the general relation (3.80) we obtain immediately the internal energy and the heat capacity

$$U \approx \frac{3}{2} N k_B T \left\{ 1 + \frac{\lambda^3 n}{2^{5/2}(2s+1)} \right\} \quad \text{and} \quad C_V = \frac{3}{2} N k_B \left\{ 1 - \frac{N \lambda^3}{2^{7/2}(2s+1)V} \right\} \quad (3.94)$$

including the first quantum corrections.

3.6.2 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

$$\langle n_{\vec{p}} \rangle = \Theta(\mu - \epsilon_{\vec{p}}) = \begin{cases} 1, & \epsilon_{\vec{p}} < \mu, \\ 0, & \epsilon_{\vec{p}} > \mu. \end{cases} \quad (3.95)$$

The Fermions occupy states within a sphere in momentum space, the Fermi sphere (Fig.3.2). The particle density n is

$$n = \frac{N}{V} = \frac{2s+1}{h^3} \int d^3 p \langle n_{\vec{p}} \rangle = \frac{2s+1}{h^3} \frac{4\pi}{3} p_F^3 = \frac{(2s+1)k_F^3}{6\pi^2} \quad (3.96)$$

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

$$U_0 = \frac{2s+1}{h^3} V \int d^3 p \epsilon_{\vec{p}} \langle n_{\vec{p}} \rangle = \frac{2s+1}{h^3} 4\pi V \int_0^{p_F} dp p^2 \frac{p^2}{2m} = \frac{2s+1}{h^3} \frac{4\pi V}{5} p_F^3 \frac{p_F^2}{2m} = \frac{3}{5} N \epsilon_F \quad (3.97)$$

⁹Note that the lowest order expansion reproduces the chemical potential of the classical ideal gas, as given in Eq.(2.51) and (2.78):

$$z = e^{\beta\mu} \approx \frac{N}{V} \lambda^3 \quad \Rightarrow \quad \mu = -k_B T \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} \quad (3.90)$$

where ϵ_F denotes the Fermi energy. The zero-point pressure is obtained through (3.74),

$$p_0 = \frac{2 U_0}{3 V} = \frac{2 N}{5 V} \epsilon_F . \quad (3.98)$$

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.

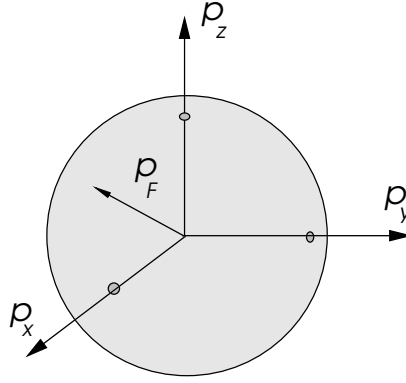


Figure 3.2: Fermi sphere of occupied single particle states. Fermi radius p_F .

Next we turn to finite temperatures for which the occupation number broadens the step at p_F . We use now (3.88, 3.96) to obtain the relation

$$\left(\frac{\epsilon_F}{k_B T} \right)^{3/2} = \frac{3 \sqrt{\pi} \lambda^3 N}{4 2s + 1 V} = \left(\frac{\mu}{k_B T} \right)^{3/2} + \frac{\pi^2}{8} \left(\frac{\mu}{k_B T} \right)^{-1/2} + \dots , \quad (3.99)$$

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

$$\mu(T) = \epsilon_F \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + \dots \right) , \quad (3.100)$$

and analogously we obtain for the pressure,

$$p(T) = p_0 \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + \dots \right) . \quad (3.101)$$

Again we derive the internal energy from the relation (3.74)

$$U = \frac{3}{2} p V = U_0 \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + \dots \right) , \quad (3.102)$$

which also leads to the heat capacity for fixed N

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{5\pi^2}{6} U_0 \frac{k_B^2 T}{\epsilon_F^2} + \dots = \frac{\pi^2}{2} k_B^2 \frac{N}{\epsilon_F} T + \dots , \quad (3.103)$$

see Fig.3.3. This is the famous linear temperature dependence of the heat capacity, which can be well observed for electrons in simple metals: $C_V = \gamma T + \dots$ with γ as the Sommerfeld coefficient. Obviously now the third law of thermodynamics is satisfied, $C_N \xrightarrow{T \rightarrow 0} 0$. Also the entropy goes to zero linearly in T .

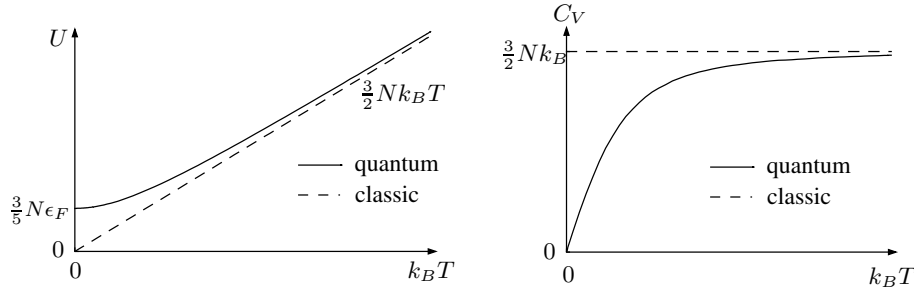


Figure 3.3: The internal energy U and the heat capacity C_V in the quantum situation compared with the classical situation.

3.6.3 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,

$$\mathcal{H}_Z = -\frac{g\mu_B}{\hbar} \sum_{i=1}^N s_i^z H \quad (3.104)$$

with $g = 2$ as gyromagnetic ratio and μ_B the Bohr magneton. The energy difference between spins parallel and antiparallel to the applied field can be absorbed into a spin-dependent fugacity,¹⁰

$$z_{\pm} = e^{\beta\mu \pm \beta\mu_B H} , \quad (3.108)$$

such that the density of Fermions is given by

$$n = \frac{N}{V} = \frac{1}{v} = \frac{1}{\lambda^3} \{f_{3/2}(z_+) + f_{3/2}(z_-)\} = n_+ + n_- \quad (3.109)$$

and the magnetization

$$m = \frac{M}{V} = \mu_B(n_+ - n_-) = \frac{\mu_B}{\lambda^3} \{f_{3/2}(z_+) - f_{3/2}(z_-)\} . \quad (3.110)$$

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

$$\chi = \left. \frac{\partial m}{\partial H} \right|_{H=0} = \frac{\mu_B^2}{\lambda^3 k_B T} 2z \left. \frac{\partial f_{3/2}(z)}{\partial z} \right|_{H=0} = \frac{2\mu_B^2}{\lambda^3 k_B T} f_{1/2}(z) \quad (3.111)$$

¹⁰We calculate the grand canonical partition function

$$\mathcal{Z} = \prod_{\vec{p}} \left\{ \sum_{n_{\vec{p}}} \left(z e^{-\beta\epsilon_{\vec{p}} + \beta\mu_B H} \right)^{n_{\vec{p}}} \right\} \left\{ \sum_{n_{\vec{p}}} \left(z e^{-\beta\epsilon_{\vec{p}} - \beta\mu_B H} \right)^{n_{\vec{p}}} \right\} = \prod_{\vec{p}} \prod_{\sigma=+,-} \sum_{n_{\vec{p}}} \left(z_{\sigma} e^{-\beta\epsilon_{\vec{p}}} \right)^{n_{\vec{p}}} \quad (3.105)$$

where z_{σ} is defined as in Eq.(3.108). The grand canonical potential is given by

$$\Omega = -k_B T \ln \mathcal{Z} = -\frac{k_B T}{\lambda^3} \{f_{5/2}(z_+) + f_{5/2}(z_-)\} \quad (3.106)$$

from which we determine the magnetization

$$\begin{aligned} m &= -\frac{1}{V} \frac{\partial \Omega}{\partial H} = \frac{k_B T}{\lambda^3} \sum_{\sigma} \frac{\partial}{\partial H} f_{5/2}(z_{\sigma}) = \frac{k_B T}{\lambda^3} \sum_{\sigma} \frac{\partial z_{\sigma}}{\partial H} \frac{\partial}{\partial z} f_{5/2}(z) \Big|_{z=z_{\sigma}} \\ &= \frac{\mu_B}{\lambda^3} \sum_{\sigma} \sigma z_{\sigma} \frac{\partial}{\partial z} f_{5/2}(z) \Big|_{z=z_{\sigma}} = \frac{\mu_B}{\lambda^3} \sum_{\sigma} \sigma f_{3/2}(z_{\sigma}) \end{aligned} \quad (3.107)$$

corresponding to Eq.(3.110).

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

High-temperature limit: We replace $z \ll 1$ in Eq.(3.111) using Eq.(3.89) with $n = 1/v$ and find

$$\chi = \frac{\mu_B^2 n}{k_B T} \left\{ 1 - \frac{\lambda^3 n}{2^{5/2}} \right\}. \quad (3.112)$$

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,

$$\chi = \frac{\mu_B^2}{\lambda^3 k_B T} \frac{4}{\sqrt{\pi}} (\ln z)^{1/2} = \frac{\mu_B^2}{\lambda^3 k_B T} \frac{4}{\sqrt{\pi}} \left(\frac{\epsilon_F}{k_B T} \right)^{1/2} = \mu_B^2 \frac{3n}{2\epsilon_F}. \quad (3.113)$$

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

3.7 Bose gas

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

3.7.1 Bosonic atoms

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

$$\frac{p}{k_B T} = \frac{1}{\lambda^3} g_{5/2}(z) = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}} \quad (3.114)$$

$$\frac{1}{v} = \frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}.$$

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

$$g_{3/2}(1) = \sum_l \frac{1}{l^{3/2}} = \zeta(3/2) \approx 2.612 \quad \text{and} \quad g_{5/2}(1) = \sum_l \frac{1}{l^{5/2}} = \zeta(5/2) \approx 1.342 \quad (3.115)$$

where $\zeta(x)$ is Riemann's ζ -function (see Fig.3.4).

3.7.2 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

$$p(T) = \frac{N}{V} k_B T \left\{ 1 - \frac{N}{2^{5/2}} \frac{\lambda^3}{V} + \dots \right\}. \quad (3.116)$$

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

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,N} = \frac{V}{N k_B T} \frac{1}{1 - \frac{\lambda^3 N}{2^{3/2} V}}. \quad (3.117)$$

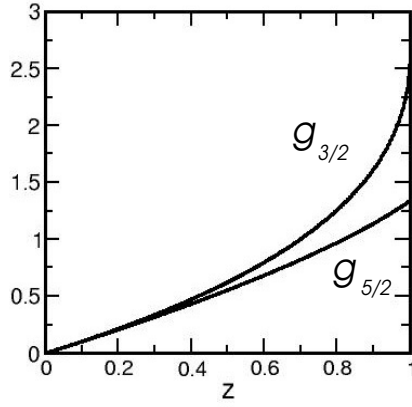


Figure 3.4: Functions $g_{3/2}(z)$ and $g_{5/2}(z)$.

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

$$2^{3/2} = \frac{N}{V} \lambda^3, \quad (3.118)$$

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

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

Let us now consider Eq. (3.114) 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 (3.114). Therefore μ approaches the singular point at 0 ($z = 1$). The critical point is determined by

$$g_{3/2}(1) = \zeta(3/2) = \frac{N}{V} \lambda^3 \quad \Rightarrow \quad \begin{cases} T_c = \frac{h^2}{2\pi k_B m [\zeta(3/2) V/N]^{2/3}}, \\ V_c = \frac{N}{\zeta(3/2)} \frac{h^3}{(2\pi m k_B T)^{3/2}}. \end{cases} \quad (3.119)$$

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 (3.118) 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 (3.114) and (3.119) arises in the step

$$N = \sum_{\vec{p}} \frac{1}{e^{\beta(\epsilon_{\vec{p}} - \mu)} - 1} \rightarrow \frac{V}{h^3} \int d^3p \frac{1}{e^{\beta(\epsilon_{\vec{p}} - \mu)} - 1}. \quad (3.120)$$

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

$$\rho(p) = \frac{p^2}{e^{\beta(\epsilon_{\vec{p}} - \mu)} - 1} \quad \Rightarrow \quad \rho(0) = 0. \quad (3.121)$$

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.3.5). Thus, the correct density is

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) + n_0(T) = n_n(T) + n_0(T) \quad (3.122)$$

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 (3.122) we find the temperature dependence of n_0 (see Fig.3.5),

$$n_0(T) = \frac{N}{V} \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right]. \quad (3.123)$$

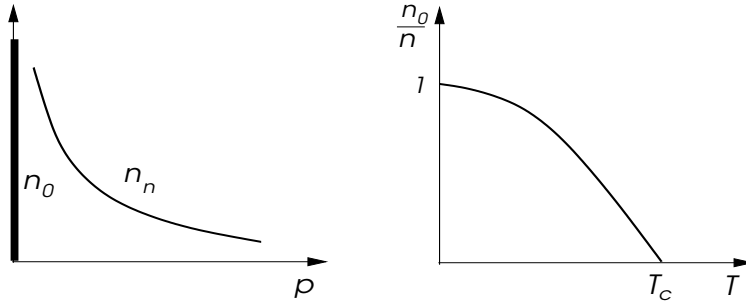


Figure 3.5: Occupation: Left panel: A macroscopic fraction of particle occupy the momentum $p = 0$ -state for $T < T_c$. Right panel: Temperature dependence of the condensate fraction.

Next we also determine the equation of state,

$$p = \begin{cases} \frac{k_B T}{\lambda^3} g_{5/2}(z), & V > V_c \\ \frac{k_B T}{\lambda^3} g_{5/2}(1), & V < V_c \end{cases}. \quad (3.124)$$

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

$$\frac{\partial V}{\partial z} = -N \lambda^3 \frac{g'_{3/2}(z)}{g_{3/2}(z)^2}, \quad (3.125)$$

and consider

$$\frac{\partial p}{\partial V} = \frac{k_B T}{\lambda^3} g'_{5/2}(z) \frac{\partial z}{\partial V} \quad \Rightarrow \quad \kappa_T = \frac{N \lambda^6}{V k_B T g_{3/2}(z)^2} \frac{g'_{3/2}(z)}{g'_{5/2}(z)}, \quad (3.126)$$

where we use the notation $g'_n(z) = dg_n(z)/dz$. As anticipated earlier the compressibility diverges at the transition $V \rightarrow V_c$ (or $T \rightarrow T_c$), since the derivative $g'_{3/2}(z) \rightarrow \infty$ for $z \rightarrow 1$. In the condensed phase the pressure is independent of V as is obvious from (3.124). 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

$$S(T, V, \mu) = - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu} = \left(\frac{\partial pV}{\partial T} \right)_{V, \mu} = \begin{cases} Nk_B \left(\frac{5v}{2\lambda^3} g_{5/2}(z) - \ln z \right), & T > T_c, \\ Nk_B \frac{5}{2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_c} \right)^{3/2}, & T < T_c, \end{cases} \quad (3.127)$$

where we used (3.114).¹¹ For the heat capacity at fixed particle number N we find from the internal energy $U = \frac{3}{2}pV$,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V, N} = \begin{cases} Nk_B \left(\frac{15v}{4\lambda^3} g_{5/2}(z) - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \right), & T > T_c, \\ Nk_B \frac{15}{4} \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_c} \right)^{3/2}, & T < T_c. \end{cases} \quad (3.131)$$

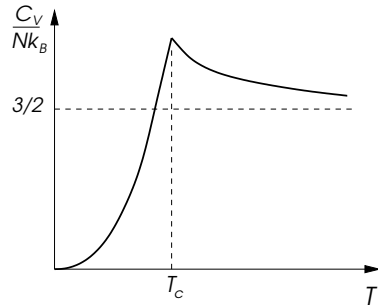


Figure 3.6: Heat capacity: C_V has a cusp at the transition and vanishes as $T^{3/2}$ towards zero-temperature. In the high-temperature limit C_v approaches $3Nk_B/2$ which corresponds to the equipartition law of a mono-atomic gas.

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

$$\frac{S}{N} = s \left(\frac{T}{T_c} \right)^{3/2} = \frac{n_n(T)}{n} s \quad \text{with} \quad s = \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \quad (3.132)$$

¹¹Calculation of the temperature derivatives: (1) Fixed chemical potential:

$$\begin{aligned} \frac{\partial}{\partial T} \frac{V k_B T}{\lambda^3} g_{5/2}(z) &= \frac{5V k_B}{\lambda^3} g_{5/2}(z) + \underbrace{\frac{V k_B T}{\lambda^3} \frac{g_{3/2}(z)}{z} \frac{\partial z}{\partial T}}_{= -k_B \frac{V}{\lambda^3} g_{3/2}(z) \beta \mu = -Nk_B \ln z} \\ &= -k_B \frac{V}{\lambda^3} g_{3/2}(z) \beta \mu = -Nk_B \ln z \end{aligned} \quad (3.128)$$

where we used $\frac{\partial}{\partial z} g_{5/2} = g_{3/2}/z$.

(2) Fixed particle number: we use

$$g_{3/2}(z) = \frac{N}{V} \lambda^3 \quad \Rightarrow \quad \frac{dg_{3/2}}{dT} = \frac{g_{1/2}(z)}{z} \frac{dz}{dT} = -\frac{3}{2} \frac{N \lambda^3}{V T} \quad (3.129)$$

which leads to the relation

$$\frac{dg_{5/2}}{dT} = \frac{g_{3/2}(z)}{z} \frac{dz}{dT} = -\frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)} \frac{N \lambda^3}{V}. \quad (3.130)$$

This leads to the expression for the heat capacity.

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 $T = T_c$.

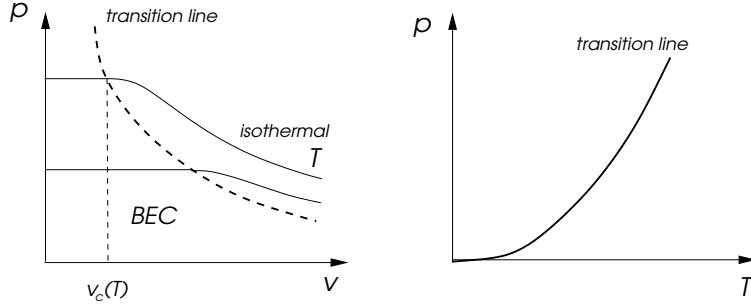


Figure 3.7: Phase diagrams; left panel: p - v -diagram; the isothermal lines reach the transition line with zero-slope, i.e. the compressibility diverges. Right panel: p - T -diagram; the condensed phase corresponds to the transition line, there is no accessible space above the transition line.

We consider now the phase diagram of various state variable.

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

$$p_0 v^{5/3} = \frac{h^2}{2\pi m} \frac{g_{5/2}(1)}{[g_{3/2}(1)]^{5/3}}, \quad (3.133)$$

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

$$p_0 = \frac{k_B T}{\lambda^3} g_{5/2}(1) \propto T^{5/2} \quad (3.134)$$

which is the vapor pressure (constant for $T < T_c$) (see Fig.3.7). We use this line to determine the latent heat l per particle via the Clausius-Clapeyron relation,

$$\frac{dp_0}{dT} = \frac{l}{T \Delta v} \quad \text{with} \quad l = T \Delta s. \quad (3.135)$$

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

$$l = T v_c \frac{dp_0}{dT} = T v_c \frac{5}{2} \frac{k_B g_{5/2}(1)}{\lambda^3} = T \frac{5}{2} k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \quad (3.136)$$

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 (3.132).

Examples of the Bose-Einstein condensates is the quantum fluid ^4He which shows a condensation below $T_\lambda \approx 2.18\text{K}$ into a superfluid phase. We will discuss this in more detail in Chapt. 7. 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.3.8).

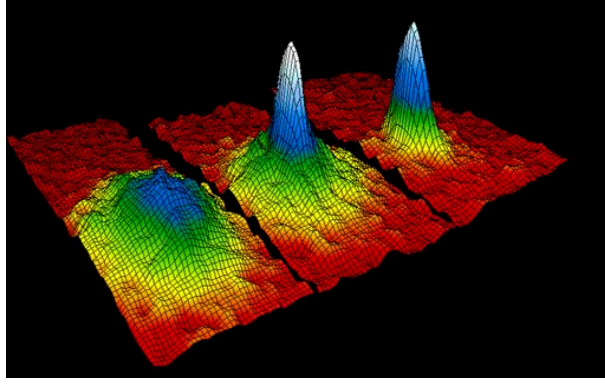


Figure 3.8: Velocity distribution of Rb-atoms: Left panel: $T > T_c$; middle panel: $T \sim T_c$; right panel $T \ll T_c$. A peak at the center develops corresponding to the fraction of particles with "zero-velocity" and at the same time the fraction of particles with finite velocity shrinks. (Source: http://www.nist.gov/public_affairs/gallery/bosein.htm)

3.8 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

$$\epsilon_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad \text{with} \quad n = 0, 1, 2, \dots \quad (3.137)$$

and the eigenstates $|n\rangle$.¹² 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

$$Z = \text{tr} e^{-\beta\mathcal{H}} = \sum_{n=0}^{\infty} \langle n | e^{-\beta\mathcal{H}} | n \rangle = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \quad (3.141)$$

The internal energy is obtained through

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \quad (3.142)$$

¹²Harmonic oscillator with the Hamiltonian

$$\mathcal{H} = \frac{\hat{P}^2}{2} + \frac{\omega^2}{2}\hat{Q}^2 = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \quad (3.138)$$

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

$$\left. \begin{aligned} \hat{Q} &= \sqrt{\frac{\hbar}{2\omega}} (a + a^\dagger) \\ \hat{P} &= -i\omega \sqrt{\frac{\hbar}{2\omega}} (a - a^\dagger) \end{aligned} \right\} \Rightarrow [a, a^\dagger] = 1 \quad \Leftrightarrow \quad [\hat{Q}, \hat{P}] = i\hbar \quad (3.139)$$

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

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad \text{and} \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \quad (3.140)$$

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.

The heat capacity is

$$C = \frac{dU}{dT} = k_B \left(\frac{\hbar\omega}{2k_B T} \right)^2 \frac{1}{\sinh^2(\beta\hbar\omega/2)}, \quad (3.143)$$

with the limiting properties

$$C = \begin{cases} k_B & k_B T \gg \hbar\omega \\ k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 e^{-\beta\hbar\omega} & k_B T \ll \hbar\omega. \end{cases} \quad (3.144)$$

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

$$\langle n \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} n e^{-\beta\epsilon_n} = \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (3.145)$$

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

3.8.1 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

$$\left(\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \vec{\nabla}^2 \right) \vec{A} = 0 \quad (3.146)$$

and the electric and magnetic field are then

$$\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} \quad \text{and} \quad \vec{B} = \vec{\nabla} \times \vec{A}, \quad (3.147)$$

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

$$\vec{A}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}, \lambda} \left\{ A_{\vec{k}\lambda} \vec{e}_{\vec{k}\lambda} e^{i\vec{k}\cdot\vec{r} - i\omega t} + A_{\vec{k}\lambda}^* \vec{e}_{\vec{k}\lambda}^* e^{-i\vec{k}\cdot\vec{r} + i\omega t} \right\} \quad \text{with} \quad \begin{cases} \omega = \omega_{\vec{k}} = c|\vec{k}|, \\ \vec{e}_{\vec{k}\lambda} \cdot \vec{k} = 0, \end{cases} \quad (3.148)$$

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,

$$\vec{k} = \frac{2\pi}{L} (n_x, n_y, n_z) \quad \text{with} \quad n_i = 0, \pm 1, \pm 2, \dots \quad (3.149)$$

Each of the parameter set (\vec{k}, λ) denotes a mode representing an independent harmonic oscillator. These oscillators can be quantized again in the standard way.¹³ 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.

¹³Canonical quantization of the radiation field: Introduce the variables

$$Q_{\vec{k}\lambda} = \frac{1}{\sqrt{4\pi c}} (A_{\vec{k}\lambda} + A_{\vec{k}\lambda}^*) \quad \text{and} \quad P_{\vec{k}\lambda} = \frac{i\omega_{\vec{k}}}{\sqrt{4\pi c}} (A_{\vec{k}\lambda} - A_{\vec{k}\lambda}^*) \quad (3.150)$$

which leads to the following expression for the Hamiltonian

$$\mathcal{H} = \int d^3r \frac{\vec{E}^2 + \vec{B}^2}{8\pi} = \sum_{\vec{k}, \lambda} \frac{\omega_{\vec{k}}^2}{2\pi c^2} |A_{\vec{k}\lambda}|^2 = \frac{1}{2} \sum_{\vec{k}, \lambda} (P_{\vec{k}\lambda}^2 + \omega_{\vec{k}}^2 Q_{\vec{k}\lambda}^2). \quad (3.151)$$

The partition function is then derived from that of a harmonic oscillator

$$Z = \prod_{\vec{k}, \lambda} \frac{e^{-\beta \hbar \omega_{\vec{k}}/2}}{1 - e^{-\beta \hbar \omega_{\vec{k}}}} = \prod_{\vec{k}} \left(\frac{e^{-\beta \hbar \omega_{\vec{k}}/2}}{1 - e^{-\beta \hbar \omega_{\vec{k}}}} \right)^2 \quad (3.153)$$

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

$$U(T) = -\frac{\partial \ln Z}{\partial \beta} = 2 \sum_{\vec{k}} \frac{\hbar \omega_{\vec{k}}}{e^{\beta \hbar \omega_{\vec{k}}} - 1} = \int d\omega D(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} = V \int d\omega u(\omega, T) \quad (3.154)$$

where we have neglected the zero point motion term (irrelevant constant). The density of modes in (3.154) is denoted as

$$D(\omega) = \sum_{\vec{k}, \lambda} \delta(\omega - \omega_{\vec{k}}) = \frac{2V}{(2\pi)^3} 4\pi \int dk k^2 \delta(\omega - ck) = V \frac{\omega^2}{\pi^2 c^3} \quad (3.155)$$

which leads to the spectral energy density

$$u(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}, \quad (3.156)$$

which is the famous Planck formula (Fig.3.9). There are two limits

$$u(\omega, T) \approx \begin{cases} k_B T \frac{\omega^2}{\pi^2 c^3} & \hbar \omega \ll k_B T \quad \text{Rayleigh-Jeans-law} \\ \frac{\hbar \omega^3}{\pi^2 c^3} e^{-\beta \hbar \omega} & \hbar \omega \gg k_B T \quad \text{Wien's law} \end{cases} \quad (3.157)$$

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

$$\hbar \omega_0 = 2.82 k_B T. \quad (3.158)$$

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

$$\frac{U}{V} = \int d\omega u(\omega, T) = \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3} \propto T^4. \quad (3.159)$$

The energy current density of a blackbody is defined as

$$\frac{U}{V} c = \frac{\text{energy}}{\text{area} \cdot \text{time}}. \quad (3.160)$$

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

$$P_{em} = \frac{U}{V} c \frac{1}{4\pi} \int' d\Omega_{\vec{k}} \frac{\vec{k} \cdot \vec{n}}{|\vec{k}|} = \frac{U}{V} c \frac{1}{4\pi} \int' d\Omega_{\vec{k}} \cos \theta = \frac{U c}{4V} = \frac{\pi^2}{60} \frac{(k_B T)^4}{\hbar^3 c^2} = \sigma T^4 \quad (3.161)$$

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 $\cos \theta > 0$.

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

$$\mathcal{H} = \sum_{\vec{k}, \lambda} \hbar \omega_{\vec{k}} \left(a_{\vec{k}\lambda}^\dagger a_{\vec{k}\lambda} + \frac{1}{2} \right) = \sum_{\vec{k}, \lambda} \hbar \omega_{\vec{k}} \left(n_{\vec{k}\lambda} + \frac{1}{2} \right) \quad (3.152)$$

where $A_{\vec{k}\lambda} \rightarrow a_{\vec{k}\lambda}$ annihilates and $A_{\vec{k}\lambda}^* \rightarrow a_{\vec{k}\lambda}^\dagger$ creates a photon in the mode (\vec{k}, λ) .

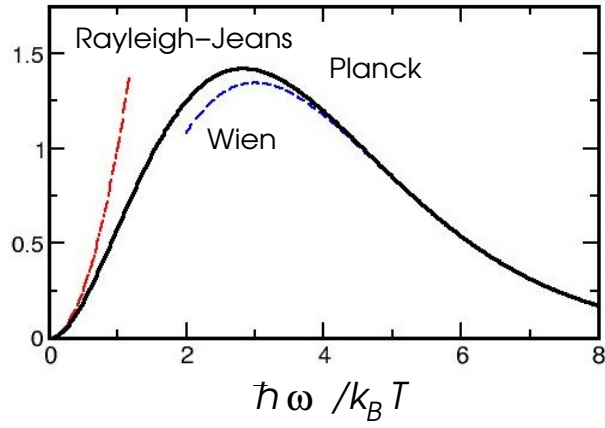


Figure 3.9: Spectral density of black body radiation.

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.

3.8.2 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:

$$\frac{1}{c_l^2} \frac{\partial^2 \vec{u}}{\partial t^2} - \vec{\nabla}(\vec{\nabla} \cdot \vec{u}) = 0 \quad \text{longitudinal sound mode ,} \quad (3.162)$$

$$\frac{1}{c_t^2} \frac{\partial^2 \vec{u}}{\partial t^2} - \vec{\nabla}^2 \vec{u} = 0 \quad \text{transversal sound mode .}$$

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:

$$\omega_{\vec{k}}^{(l)} = c_l |\vec{k}| \quad \text{and} \quad \omega_{\vec{k}}^{(t)} = c_t |\vec{k}| . \quad (3.163)$$

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

$$D(\omega) = \frac{V\omega^2}{2\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) . \quad (3.164)$$

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

$$3N_A = \sum_{|\vec{k}| \leq k_D} 3 = \frac{3V}{(2\pi)^3} 4\pi \int_0^{k_D} dk k^2 = \frac{Vk_D^3}{2\pi^2} \Rightarrow k_D = \left(\frac{6\pi^2 N_A}{V} \right)^{1/3} \quad (3.165)$$

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

$$\frac{3}{c_{eff}^3} = \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right). \quad (3.166)$$

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

$$\frac{U(T)}{V} = \int_0^{\omega_D} d\omega u(\omega, T). \quad (3.167)$$

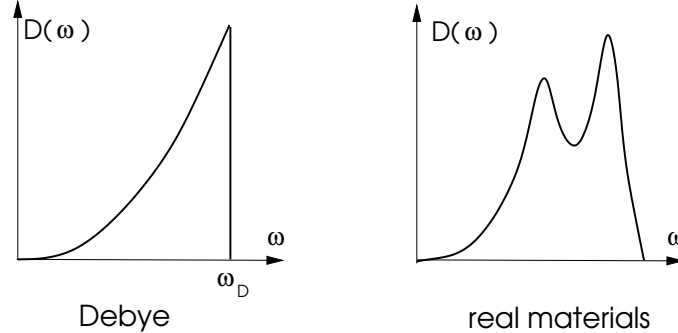


Figure 3.10: Density of states of phonons. Left panel: Debye model; right panel: more realistic spectrum. Note that the low frequency part in both cases follows an ω^2 law and leads to the T^3 -behavior of the heat capacity at low temperature. This is a consequence of the linear dispersion which is almost independent of the lattice structure and coupling.

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

$$U(T) = V \frac{(k_B T)^4}{(2\pi\hbar)^3} \frac{3}{c_{eff}^3} 4\pi \underbrace{\int_0^\infty dx \frac{x^3}{e^x - 1}}_{= \pi^4/15} = V \frac{\pi^2 (k_B T)^4}{10\hbar^3 c_{eff}^3} = \frac{3\pi^4 k_B T}{5} \left(\frac{T}{\theta_D} \right)^3 N_A \quad (3.168)$$

and correspondingly the low-temperature heat capacity is

$$C_V = \frac{12\pi^4}{5} N_A k_B \left(\frac{T}{\theta_D} \right)^3, \quad (3.169)$$

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

$$\frac{1}{e^{\beta\hbar\omega} - 1} \approx \frac{1}{\beta\hbar\omega} - \frac{1}{2} + \frac{\beta\hbar\omega}{12}. \quad (3.170)$$

This yields for the internal energy

$$\begin{aligned} U(T) &= \frac{3V}{2\pi^2 c_{eff}^3} \int_0^{\omega_D} d\omega \left(\omega^2 k_B T - \frac{\hbar\omega^3}{2} + \frac{\hbar^2\omega^4}{12k_B T} \right) + \dots \\ &= 3N_A k_B T \left\{ 1 - \frac{3}{8} \frac{\hbar\omega_D}{k_B T} + \frac{1}{20} \left(\frac{\hbar\omega_D}{k_B T} \right)^2 \right\} + \dots \end{aligned} \quad (3.171)$$

and leads to the heat capacity

$$C_V = 3N_A k_B \left\{ 1 - \frac{1}{20} \frac{\theta_D^2}{T^2} \right\} + \dots \quad (3.172)$$

In the high-temperature limit the heat capacity approaches the value of the equipartition law for $3N_A$ harmonic oscillators (Fig.3.11).

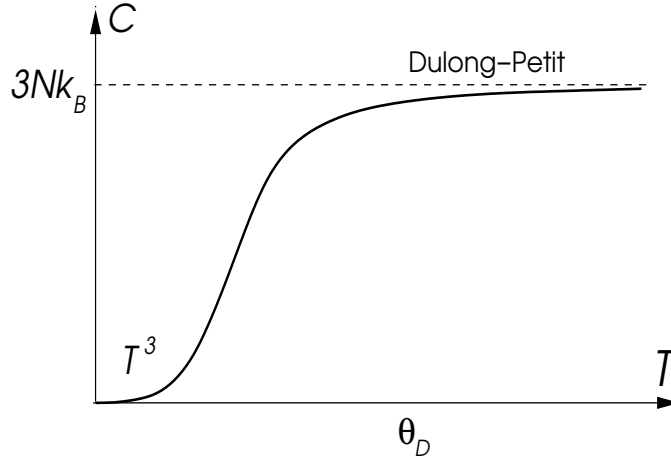


Figure 3.11: Heat capacity: Low-temperature behavior follows a T^3 -law. At high-temperature the universal Dulong-Petit law recovers, which is a classical result of the equipartition law for particles in a harmonic potential.

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

3.9 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,

$$v(r) = 4\epsilon \left[\left(\frac{\tilde{r}}{r} \right)^{12} - \left(\frac{\tilde{r}}{r} \right)^6 \right] \quad (3.173)$$

with ϵ as the potential depth and $r_0 = 2^{1/6}\tilde{r}$ as the minimal point, see Fig.3.12 . Quantum 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} ,

$$\mathcal{H} = \frac{\vec{p}^2}{2m^*} + v(r) = \frac{\vec{p}^2}{2m^*} + A(r - r_0)^2 - \epsilon \approx \frac{p_r^2}{2m^*} + \frac{\vec{L}^2}{2m^*r_0^2} + A(r - r_0)^2 - \epsilon \quad (3.174)$$

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

$$E_n^{vib} = \hbar\omega \left(n + \frac{1}{2} \right) \quad \text{and} \quad E_l^{rot} = \frac{\hbar^2 l(l+1)}{2m^*r_0^2} \quad (3.175)$$

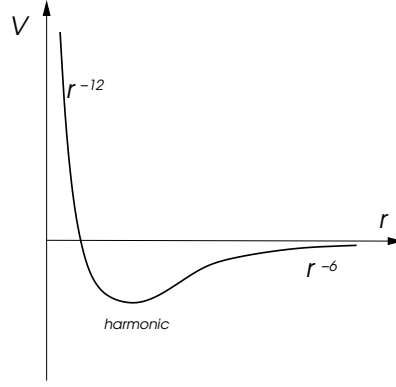


Figure 3.12: Lenard-Jones potential.

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),

$$Z_{trans} = \prod_{\vec{p}} \frac{1}{1 - ze^{-\beta \vec{p}^2/4m}}. \quad (3.176)$$

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

$$Z_{vib} = \left(\frac{e^{-\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega}} \right)^{N/2} \quad (3.177)$$

and

$$Z_{rot} = \left(\sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)/I_{rot}} \right)^{N/2} \quad (3.178)$$

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

$$\begin{aligned} Z_{rot} &\approx \left(\int_0^{\infty} dl (2l+1) e^{-\beta l(l+1)/I_{rot}} \right)^{N/2} = \left(-I_{rot} k_B T \int_0^{\infty} dl \frac{d}{dl} e^{-\beta l(l+1)/I_{rot}} \right)^{N/2} \\ &= (I_{rot} k_B T)^{N/2} = \left(2 \frac{T}{\theta_{rot}} \right)^{N/2}. \end{aligned} \quad (3.179)$$

We may expand further in β/I_{rot} ¹⁴ and find

$$Z_{rot} \approx \left(2 \frac{T}{\theta_{rot}} + \frac{1}{3} + \frac{\theta_{rot}}{30T} + \dots \right)^{N/2}. \quad (3.181)$$

¹⁴We use the Euler-MacLaurin sum,

$$\sum_{l=0}^{\infty} f(l) = \int_0^{\infty} df(l) + \frac{1}{2}f(0) + \sum_{k=1}^{\infty} \frac{(-1)^k B_k}{(2k)!} f^{(2k-1)}(0) + R_{\infty}, \quad (3.180)$$

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

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

$$Z_{rot} \approx \left(1 + 3e^{-\beta 2/I_{rot}} + \dots\right)^{N/2}. \quad (3.182)$$

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.3.13,

$$\frac{2C(T)}{N} = \begin{cases} \frac{3}{2}k_B + 3k_B \left(\frac{\theta_{rot}}{T}\right)^2 e^{-\theta_{rot}/T} & T_c \ll T \ll \theta_{rot} \\ \frac{3}{2}k_B + k_B + \frac{k_B}{180} \left(\frac{\theta_{rot}}{T}\right)^2 + k_B \left(\frac{\theta_{vib}}{2T}\right)^2 e^{-\theta_{vib}/T} & \theta_{rot} \ll T \ll \theta_{vib} \\ \frac{3}{2}k_B + k_B + k_B & \theta_{vib} \ll T \ll T_{dis} \\ 3k_B & T_{dis} \ll T. \end{cases} \quad (3.183)$$

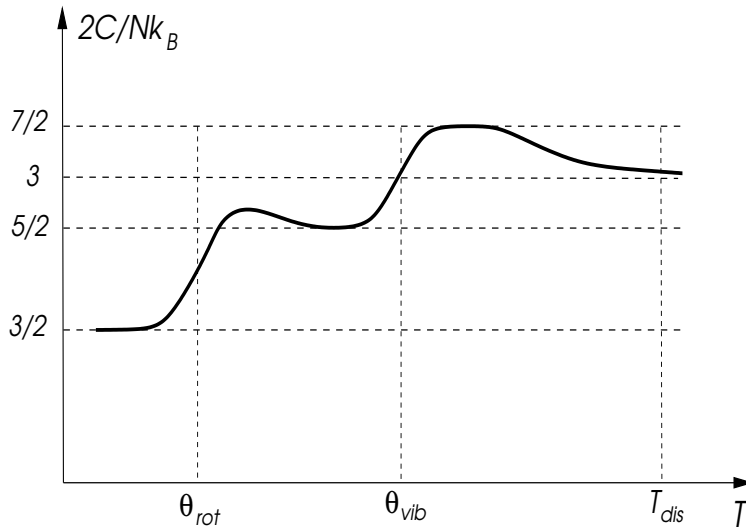


Figure 3.13: Schematic behavior of heat capacity of a diatomic molecule.

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 loses 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 $\theta_{rot} \sim 85K$.¹⁵ There is no Bose-Einstein condensation for H_2 , because it solidifies at $14K$.

¹⁵ 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. $l = 0, 2, 4, \dots$ (called "para-hydrogen"), while for the spin triplet configuration odd parity is required, i.e. $l = 1, 3, 5, \dots$ (called "ortho-hydrogen"). As a consequence in the partition function (3.178) 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

$$\frac{2C}{N} \approx \frac{3}{2}k_B + 9k_B \left(\frac{\theta_{rot}}{T}\right)^2 e^{-\theta_{rot}/T} \quad (3.184)$$

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

Chapter 4

Identical Quantum Particles - Formalism of Second Quantization

This chapter gives an introduction to 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.

4.1 Many-body wave functions and particle statistics

The Hamiltonian describing the dynamics of a systems of many identical quantum particles must be invariant under exchange (permutation) of particle degrees of freedom (coordinate, momentum, spin etc). The identical quantum 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,

$$\psi(\vec{r}_1, s_1; \vec{r}_2, s_2; \dots; \vec{r}_N, s_N) \quad (4.1)$$

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 $\psi(1, \dots, N)$. Analogously we define many-body operators,

$$\hat{A}(1, \dots, N) = A(\hat{r}_1, \hat{p}_1, \hat{S}_1; \dots; \hat{r}_N, \hat{p}_N, \hat{S}_N) \quad (4.2)$$

with \hat{r}_j, \hat{p}_j and \hat{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 particles i and j ($1 \leq i, j \leq N$),

$$\begin{aligned} \hat{P}_{ij}\psi(1, \dots, i, \dots, j, \dots, N) &= \psi(1, \dots, j, \dots, i, \dots, N), \\ \hat{P}_{ij}\hat{A}(1, \dots, i, \dots, j, \dots, N) &= \hat{A}(1, \dots, j, \dots, i, \dots, N). \end{aligned} \quad (4.3)$$

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

$$[\mathcal{H}, \hat{P}_{ij}] = 0 \quad (4.4)$$

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

$$\mathcal{H}|\psi\rangle = E|\psi\rangle \quad \Rightarrow \quad \mathcal{H}\hat{P}_{ij}|\psi\rangle = \hat{P}_{ij}\mathcal{H}|\psi\rangle = E\hat{P}_{ij}|\psi\rangle, \quad (4.5)$$

where we define the wave function as

$$\psi(1, \dots, N) = \langle 1, \dots, N | \psi \rangle. \quad (4.6)$$

We distinguish now between Fermions and Bosons through their behavior under transpositions \hat{P}_{ij} ,

$$\psi(1, \dots, i, \dots, j, \dots, N) = \begin{cases} +\psi(1, \dots, j, \dots, i, \dots, N) & \text{Bosons,} \\ -\psi(1, \dots, j, \dots, i, \dots, N) & \text{Fermions.} \end{cases} \quad (4.7)$$

This means that bosonic wave functions are completely symmetric under exchange of particles, while fermionic wave functions are completely antisymmetric¹. 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

$$\psi(1, \dots, i, \dots, i, \dots, N) = -\psi(1, \dots, i, \dots, i, \dots, N) = 0, \quad (4.8)$$

which implies the Pauli exclusion principle.

4.2 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

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i \quad \text{with} \quad \mathcal{H}_i = \frac{\hat{p}_i^2}{2m} + V(\hat{r}_i). \quad (4.9)$$

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

$$\mathcal{H}_i \psi_\nu(\vec{r}_i, s_i) = \epsilon_\nu \psi_\nu(\vec{r}_i, s_i). \quad (4.10)$$

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

$$\sum_s \int d^3r |\psi_\nu(\vec{r}, s)|^2 = 1. \quad (4.11)$$

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

For Bosons we write

$$\langle \vec{r}_1, s_1; \dots, \vec{r}_N, s_N | \Psi_B \rangle = \Psi_B(1, \dots, N) = \sum_{\hat{P} \in S_N} \hat{P} \psi_{\nu_1}(\vec{r}_1, s_1) \cdots \psi_{\nu_N}(\vec{r}_N, s_N) \quad (4.12)$$

and for Fermions

$$\langle \vec{r}_1, s_1; \dots, \vec{r}_N, s_N | \Psi_F \rangle = \Psi_F(1, \dots, N) = \sum_{\hat{P} \in S_N} \text{sgn}(\hat{P}) \hat{P} \psi_{\nu_1}(\vec{r}_1, s_1) \cdots \psi_{\nu_N}(\vec{r}_N, s_N) \quad (4.13)$$

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. ⁴He 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. ³He 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 $\text{sgn}(\hat{P})$ 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*,

$$\Psi_F(1, \dots, N) = \text{Det} \begin{bmatrix} \psi_{\mu_1}(1) & \cdots & \psi_{\mu_1}(N) \\ \vdots & & \vdots \\ \psi_{\mu_N}(1) & \cdots & \psi_{\mu_N}(N) \end{bmatrix}. \quad (4.14)$$

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

$$\begin{aligned} \langle \Psi_B | \Psi_B \rangle &= N! n_{\nu_1}! \cdots n_{\nu_N}!, \\ \langle \Psi_F | \Psi_F \rangle &= N!, \end{aligned} \quad (4.15)$$

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.

4.3 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 ,

$$\mathcal{F} = \bigoplus_{n=0}^{\infty} \mathcal{Q}_n. \quad (4.16)$$

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 representations*,

$$|n_{\nu_1}, n_{\nu_2}, \dots\rangle \quad (4.17)$$

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

4.3.1 Creation- and annihilation operators

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

$$\hat{a}_\nu : \mathcal{Q}_n \rightarrow \mathcal{Q}_{n-1} \quad \text{and} \quad \hat{a}_\nu^\dagger : \mathcal{Q}_n \rightarrow \mathcal{Q}_{n+1}. \quad (4.18)$$

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

Bosons: Let us first consider Bosons which, for simplicity, do not possess a spin. The two operators have the following property,

$$\hat{a}_\nu |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots\rangle = \sqrt{n_\nu} |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu - 1, \dots\rangle, \quad (4.19)$$

$$\hat{a}_\nu^\dagger |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots\rangle = \sqrt{n_\nu + 1} |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu + 1, \dots\rangle,$$

and

$$\langle n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots | \hat{a}_\nu^\dagger = \sqrt{n_\nu} \langle n_{\nu_1}, n_{\nu_2}, \dots, n_\nu - 1, \dots |, \quad (4.20)$$

$$\langle n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots | \hat{a}_\nu = \sqrt{n_\nu + 1} \langle n_{\nu_1}, n_{\nu_2}, \dots, n_\nu + 1, \dots |.$$

It is obvious that

$$\hat{a}_\nu |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu = 0, \dots\rangle = 0 \quad \text{and} \quad \langle n_{\nu_1}, n_{\nu_2}, \dots, n_\nu = 0, \dots | \hat{a}_\nu^\dagger = 0. \quad (4.21)$$

The operators satisfy the following commutation relations,

$$[\hat{a}_\nu, \hat{a}_{\nu'}^\dagger] = \delta_{\nu\nu'} \quad \text{and} \quad [\hat{a}_\nu, \hat{a}_{\nu'}] = [\hat{a}_\nu^\dagger, \hat{a}_{\nu'}^\dagger] = 0. \quad (4.22)$$

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,

$$|n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots\rangle = \frac{\dots (\hat{a}_\nu^\dagger)^{n_\nu} \dots (\hat{a}_{\nu_2}^\dagger)^{n_{\nu_2}} (\hat{a}_{\nu_1}^\dagger)^{n_{\nu_1}}}{\sqrt{n_{\nu_1}! n_{\nu_2}! \dots}} |0\rangle. \quad (4.23)$$

The number operator is defined as

$$\hat{n}_\nu = \hat{a}_\nu^\dagger \hat{a}_\nu \quad \text{with} \quad \hat{n}_\nu |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots\rangle = n_\nu |n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots\rangle \quad (4.24)$$

and the total number of particles is obtained through the operator

$$\hat{N} = \sum_i \hat{n}_{\nu_i}. \quad (4.25)$$

Knowing the spectrum of the Hamiltonian of independent particles as given in Eq.(4.10) we may express the Hamiltonian as

$$\mathcal{H} = \sum_\nu \epsilon_\nu \hat{a}_\nu^\dagger \hat{a}_\nu = \sum_\nu \epsilon_\nu \hat{n}_\nu. \quad (4.26)$$

Fermions: 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}_ν^\dagger and \hat{a}_ν which obey anti-commutation rules,

$$\{\hat{a}_\nu, \hat{a}_{\nu'}^\dagger\} = \delta_{\nu\nu'} \quad \text{and} \quad \{\hat{a}_\nu, \hat{a}_{\nu'}\} = \{\hat{a}_\nu^\dagger, \hat{a}_{\nu'}^\dagger\} = 0, \quad (4.27)$$

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

$$\hat{a}_\nu^\dagger \hat{a}_\nu^\dagger = 0 \quad \text{and} \quad \hat{a}_\nu \hat{a}_\nu = 0 \quad (4.28)$$

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

$$\hat{a}_\nu^\dagger |\dots, n_\nu = 1, \dots\rangle = \hat{a}_\nu^\dagger \hat{a}_\nu^\dagger |\dots, n_\nu = 0, \dots\rangle = 0. \quad (4.29)$$

A general state may be written as

$$|n_{\nu_1}, n_{\nu_2}, \dots, n_\nu, \dots\rangle = \dots (\hat{a}_\nu^\dagger)^{n_\nu} \dots (\hat{a}_{\nu_2}^\dagger)^{n_{\nu_2}} (\hat{a}_{\nu_1}^\dagger)^{n_{\nu_1}} |0\rangle \quad (4.30)$$

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,

$$|n_1, n_2, n_3, n_4\rangle = |1, 1, 1, 1\rangle = \hat{a}_4^\dagger \hat{a}_3^\dagger \hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle. \quad (4.31)$$

Removing now one particle yields

$$\begin{aligned} \hat{a}_2 |1, 1, 1, 1\rangle &= \hat{a}_2 [\hat{a}_4^\dagger \hat{a}_3^\dagger \hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle] = \hat{a}_4^\dagger \hat{a}_3^\dagger \hat{a}_2 \hat{a}_2^\dagger \hat{a}_1^\dagger |0\rangle = \hat{a}_4^\dagger \hat{a}_3^\dagger (1 - \hat{a}_2^\dagger \hat{a}_2) \hat{a}_1^\dagger |0\rangle \\ &= \hat{a}_4^\dagger \hat{a}_3^\dagger \hat{a}_1^\dagger |0\rangle = |1, 0, 1, 1\rangle \end{aligned} \quad (4.32)$$

and now analogously

$$\begin{aligned}\hat{a}_3|1, 1, 1, 1\rangle &= \hat{a}_3[\hat{a}_4^\dagger\hat{a}_3^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger]|0\rangle = -\hat{a}_4^\dagger\hat{a}_3\hat{a}_3^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger|0\rangle = -\hat{a}_4^\dagger(1 - \hat{a}_3^\dagger\hat{a}_3)\hat{a}_2^\dagger\hat{a}_1^\dagger|0\rangle \\ &= -\hat{a}_4^\dagger\hat{a}_2^\dagger\hat{a}_1^\dagger|0\rangle = -|1, 1, 0, 1\rangle.\end{aligned}\quad (4.33)$$

Obviously, the order of the operators is important and should not be ignored when dealing with Fermions.

4.3.2 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,

$$\psi_{\vec{k}} = \frac{1}{\sqrt{V}}e^{i\vec{k}\cdot\vec{r}} \quad \text{with} \quad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \quad (4.34)$$

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

$$\hat{\Psi}_s(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \hat{a}_{\vec{k}s} \quad \text{and} \quad \hat{\Psi}_s^\dagger(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} \hat{a}_{\vec{k}s}^\dagger \quad (4.35)$$

and the inverse,

$$\hat{a}_{\vec{k}}^\dagger = \int d^3r \frac{e^{i\vec{k}\cdot\vec{r}}}{\sqrt{V}} \hat{\Psi}^\dagger(\vec{r}) \quad \text{und} \quad \hat{a}_{\vec{k}} = \int d^3r \frac{e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{V}} \hat{\Psi}(\vec{r}) \quad (4.36)$$

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

$$\hat{\Psi}_s(\vec{r})^\dagger|0\rangle = |\vec{r}, s\rangle \quad \text{and} \quad \phi_s(\vec{r}) = \langle \vec{r}, s | \phi \rangle = \langle 0 | \hat{\Psi}_s(\vec{r}) | \phi \rangle. \quad (4.37)$$

Moreover we have the condition

$$\hat{\Psi}_s(\vec{r})|0\rangle = 0 \quad \text{and} \quad \langle 0 | \hat{\Psi}_s^\dagger(\vec{r}) = 0. \quad (4.38)$$

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

$$\hat{\Psi}_s(\vec{r})\hat{\Psi}_{s'}^\dagger(\vec{r}') \mp \hat{\Psi}_{s'}^\dagger(\vec{r}')\hat{\Psi}_s(\vec{r}) = \frac{1}{V} \sum_{\vec{k}, \vec{k}'} e^{i\vec{k}\cdot\vec{r} - i\vec{k}'\cdot\vec{r}'} \underbrace{(\hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \mp \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}s})}_{= \delta_{\vec{k}\vec{k}',} \delta_{ss'}} = \delta(\vec{r} - \vec{r}') \delta_{ss'} \quad (4.39)$$

and analogously

$$\hat{\Psi}_s(\vec{r})\hat{\Psi}_{s'}(\vec{r}') \mp \hat{\Psi}_{s'}(\vec{r}')\hat{\Psi}_s(\vec{r}) = 0 \quad \text{and} \quad \hat{\Psi}_s^\dagger(\vec{r})\hat{\Psi}_{s'}^\dagger(\vec{r}') \mp \hat{\Psi}_{s'}^\dagger(\vec{r}')\hat{\Psi}_s^\dagger(\vec{r}) = 0 \quad (4.40)$$

for Bosons (-) and Fermions (+). Taking these relations it becomes also clear that

$$\begin{aligned}\langle \vec{r}', s' | \vec{r}, s \rangle &= \langle 0 | \hat{\Psi}_{s'}(\vec{r}') \hat{\Psi}_s(\vec{r})^\dagger | 0 \rangle \\ &= \langle 0 | \delta(\vec{r} - \vec{r}') \delta_{ss'} | 0 \rangle \mp \underbrace{\langle 0 | \hat{\Psi}_s(\vec{r})^\dagger \hat{\Psi}_{s'}(\vec{r}') | 0 \rangle}_{=0} = \delta(\vec{r} - \vec{r}') \delta_{ss'}.\end{aligned}\quad (4.41)$$

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

$$\hat{\Psi}_s^\dagger(\vec{r})|\vec{r}_1, s_1; \dots; \vec{r}_N, s_N\rangle = \sqrt{N+1}|\vec{r}_1, s_1; \dots; \vec{r}_N, s_N; \vec{r}, s\rangle, \quad (4.42)$$

such that

$$|\vec{r}_1, s_1; \vec{r}_2, s_2; \dots; \vec{r}_N, s_N\rangle = \frac{1}{\sqrt{N!}} \widehat{\Psi}_{s_N}^\dagger(\vec{r}_N) \cdots \widehat{\Psi}_{s_1}^\dagger(\vec{r}_1) |0\rangle. \quad (4.43)$$

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

$$|\vec{r}_1, s_1; \vec{r}_2, s_2; \dots; \vec{r}_N, s_N\rangle = \pm |\vec{r}_2, s_2; \vec{r}_1, s_1; \dots; \vec{r}_N, s_N\rangle \quad (4.44)$$

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.(4.12, 4.13),

$$\Phi(1, \dots, N) = \langle \vec{r}_1, s_1; \dots, \vec{r}_N, s_N | n_{\vec{k}_1, s_1}, n_{\vec{k}_2, s_2}, \dots \rangle. \quad (4.45)$$

Note that $N = \sum_{\vec{k}, s} n_{\vec{k}, s}$. Taking care of the symmetry / antisymmetry of the many-body wave function we recover the renormalization behavior in Eqs.(4.42, 4.43).

4.4 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

$$\widehat{\rho}(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \widehat{r}_i). \quad (4.46)$$

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

$$\begin{aligned} \langle \phi' | \widehat{\rho}(\vec{r}) | \phi \rangle &= \int d^3 r_1 \cdots d^3 r_N \langle \phi' | \vec{r}_1, \dots, \vec{r}_N \rangle \langle \vec{r}_1, \dots, \vec{r}_N | \sum_i \delta(\vec{r} - \widehat{r}_i) | \phi \rangle \\ &= \int d^3 r_1 \cdots d^3 r_N \sum_i \delta(\vec{r} - \vec{r}_i) \langle \phi' | \vec{r}_1, \dots, \vec{r}_N \rangle \langle \vec{r}_1, \dots, \vec{r}_N | \phi \rangle \\ &= N \int d^3 r_1 \cdots d^3 r_{N-1} \langle \phi' | \vec{r}_1, \dots, \vec{r}_{N-1}, \vec{r} \rangle \langle \vec{r}_1, \dots, \vec{r}_{N-1}, \vec{r} | \phi \rangle, \end{aligned} \quad (4.47)$$

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

$$\widehat{\rho}(\vec{r}) = \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r}), \quad (4.48)$$

which leads to

$$\begin{aligned} \langle \phi' | \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r}) | \phi \rangle &= \int d^3 r_1 \cdots d^3 r_{N-1} \langle \phi' | \widehat{\Psi}^\dagger(\vec{r}) | \vec{r}_1, \dots, \vec{r}_{N-1} \rangle \langle \vec{r}_1, \dots, \vec{r}_{N-1} | \widehat{\Psi}(\vec{r}) | \phi \rangle \\ &= N \int d^3 r_1 \cdots d^3 r_{N-1} \langle \phi' | \vec{r}_1, \dots, \vec{r}_{N-1}, \vec{r} \rangle \langle \vec{r}_1, \dots, \vec{r}_{N-1}, \vec{r} | \phi \rangle \end{aligned} \quad (4.49)$$

which is obviously identical to Eq.(4.47).

According to Eq.(4.26) the kinetic energy can be expressed as

$$\mathcal{H}_{kin} = \sum_{\vec{k}} \frac{\hbar^2 \vec{k}^2}{2m} \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} = \sum_{\vec{k}} \frac{\hbar^2 \vec{k}^2}{2m} \hat{n}_{\vec{k}} \quad (4.50)$$

which, using Eq.(7.19), may also be expressed in field operator language as

$$\begin{aligned}\mathcal{H}_{kin} &= \frac{1}{2mV} \sum_{\vec{k}} \int d^3r d^3r' \left(\hbar \vec{\nabla} e^{i\vec{k}\cdot\vec{r}} \right) \left(\hbar \vec{\nabla}' e^{-i\vec{k}\cdot\vec{r}'} \right) \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r}') \\ &= \frac{\hbar^2}{2m} \int d^3r (\vec{\nabla} \hat{\Psi}^\dagger(\vec{r})) \cdot (\vec{\nabla} \hat{\Psi}(\vec{r})).\end{aligned}\tag{4.51}$$

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,

$$\hat{H}_{pot} = \int d^3r U(\vec{r}) \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r}) = \int d^3r U(\vec{r}) \hat{\rho}(\vec{r}).\tag{4.52}$$

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

$$\hat{\vec{J}}(\vec{r}) = \frac{\hbar}{2mi} \left(\hat{\Psi}^\dagger(\vec{r}) (\vec{\nabla} \hat{\Psi}(\vec{r})) - (\vec{\nabla} \hat{\Psi}^\dagger(\vec{r})) \hat{\Psi}(\vec{r}) \right)\tag{4.53}$$

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

$$\hat{\vec{S}}(\vec{r}) = \frac{\hbar}{2} \sum_{ss'} \hat{\Psi}_s^\dagger(\vec{r}) \vec{\sigma}_{ss'} \hat{\Psi}_{s'}(\vec{r}),\tag{4.54}$$

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

$$\hat{\rho}_{\vec{q}} = \int d^3r e^{-i\vec{q}\cdot\vec{r}} \hat{\rho}(\vec{r}) = \sum_{\vec{k},s} \hat{a}_{\vec{k},s}^\dagger \hat{a}_{\vec{k}+\vec{q},s}\tag{4.55}$$

$$\hat{\vec{S}}_{\vec{q}} = \frac{\hbar}{2} \sum_{\vec{k},s,s'} \hat{a}_{\vec{k},s}^\dagger \vec{\sigma}_{ss'} \hat{a}_{\vec{k}+\vec{q},s'}\tag{4.56}$$

$$\hat{\vec{J}}_{\vec{q}} = \frac{\hbar}{m} \sum_{\vec{k},s} \left(\vec{k} + \frac{\vec{q}}{2} \right) \hat{a}_{\vec{k},s}^\dagger \hat{a}_{\vec{k}+\vec{q},s}.\tag{4.57}$$

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

$$\hat{H}_{int} = \frac{1}{2} \sum_{s,s'} \int d^3r d^3r' \hat{\Psi}_s^\dagger(\vec{r}) \hat{\Psi}_{s'}^\dagger(\vec{r}') V(\vec{r} - \vec{r}') \hat{\Psi}_{s'}(\vec{r}') \hat{\Psi}_s(\vec{r}) = \frac{1}{2V} \sum_{\vec{k},\vec{k}',\vec{q}} \sum_{s,s'} V_{\vec{q}} \hat{a}_{\vec{k}+\vec{q},s}^\dagger \hat{a}_{\vec{k}'-\vec{q},s'}^\dagger \hat{a}_{\vec{k}',s'} \hat{a}_{\vec{k},s},\tag{4.58}$$

where the factor 1/2 corrects for double counting and

$$V(\vec{r}) = \frac{1}{V} \sum_{\vec{q}} V_{\vec{q}} e^{i\vec{q}\cdot\vec{r}}.\tag{4.59}$$

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 $\hbar\vec{q}$.

4.5 Equation of motion

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

$$\mathcal{H} = \sum_{\vec{k}} \epsilon_{\vec{k}} \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}\tag{4.60}$$

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

$$\hat{a}_{\vec{k}}(t) = e^{i\mathcal{H}t/\hbar} \hat{a}_{\vec{k}} e^{-i\mathcal{H}t/\hbar}. \quad (4.61)$$

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

$$\begin{aligned} i\hbar \frac{d}{dt} \hat{a}_{\vec{k}} &= -[\mathcal{H}, \hat{a}_{\vec{k}}] = -\sum_{\vec{k}'} \epsilon_{\vec{k}'} [\hat{a}_{\vec{k}'}^\dagger, \hat{a}_{\vec{k}'}, \hat{a}_{\vec{k}}] \\ &= -\sum_{\vec{k}'} \epsilon_{\vec{k}'} \begin{cases} \hat{a}_{\vec{k}'}^\dagger \underbrace{[\hat{a}_{\vec{k}'}, \hat{a}_{\vec{k}}]}_{=0} + \underbrace{[\hat{a}_{\vec{k}'}^\dagger, \hat{a}_{\vec{k}}]}_{=-\delta_{\vec{k}, \vec{k}'}} \hat{a}_{\vec{k}'}, & \text{for Bosons} \\ \hat{a}_{\vec{k}'}^\dagger \underbrace{\{\hat{a}_{\vec{k}'}, \hat{a}_{\vec{k}}\}}_{=0} - \underbrace{\{\hat{a}_{\vec{k}'}^\dagger, \hat{a}_{\vec{k}}\}}_{=\delta_{\vec{k}, \vec{k}'}} \hat{a}_{\vec{k}'}, & \text{for Fermions} \end{cases} \\ &= \sum_{\vec{k}'} \epsilon_{\vec{k}'} \hat{a}_{\vec{k}'} \delta_{\vec{k}, \vec{k}'} = \epsilon_{\vec{k}} \hat{a}_{\vec{k}}, \end{aligned} \quad (4.62)$$

and analogously

$$i\hbar \frac{d}{dt} \hat{a}_{\vec{k}}^\dagger = -[\mathcal{H}, \hat{a}_{\vec{k}}^\dagger] = -\epsilon_{\vec{k}} \hat{a}_{\vec{k}}^\dagger. \quad (4.63)$$

A further important relation in the context of statistical physics is

$$e^{-\beta\mathcal{H}} \hat{a}_{\vec{k}}^\dagger e^{\beta\mathcal{H}} = e^{-\beta\epsilon_{\vec{k}}} \hat{a}_{\vec{k}}^\dagger. \quad (4.64)$$

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

$$e^{\beta\mu\hat{N}} \hat{a}_{\vec{k}}^\dagger e^{-\beta\mu\hat{N}} = e^{\beta\mu} \hat{a}_{\vec{k}}^\dagger. \quad (4.65)$$

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

$$\begin{aligned} e^{-\beta\mathcal{H}} \hat{a}_{\vec{k}}^\dagger e^{\beta\mathcal{H}} |\Phi\rangle &= e^{\beta E} e^{-\beta\mathcal{H}} \hat{a}_{\vec{k}}^\dagger |\Phi\rangle = \sqrt{n_{\vec{k}} + 1} e^{\beta E} e^{-\beta\mathcal{H}} |n_{\vec{k}_1}, \dots, n_{\vec{k}} + 1, \dots\rangle \\ &= \sqrt{n_{\vec{k}} + 1} e^{\beta(E-E')} |n_{\vec{k}_1}, \dots, n_{\vec{k}} + 1, \dots\rangle = e^{\beta(E-E')} \hat{a}_{\vec{k}}^\dagger |\Phi\rangle \end{aligned} \quad (4.66)$$

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 $\hat{a}_{\vec{k}}^\dagger$ 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.(4.65).

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

$$\langle \hat{n}_{\vec{k}} \rangle = \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle = \frac{\text{tr}\{e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}\}}{\text{tr}e^{-\beta\mathcal{H}'}} , \quad (4.67)$$

where we use the Hamiltonian $\mathcal{H}' = \mathcal{H} - \mu\hat{N}$. We can rearrange the numerator of (4.67) using Eqs.(4.64) and (4.65),

$$\begin{aligned} \text{tr}\{e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}\} &= \text{tr}\{e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}}^\dagger e^{\beta\mathcal{H}'} e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}}\} = e^{-\beta(\epsilon_{\vec{k}} - \mu)} \text{tr}\{\hat{a}_{\vec{k}}^\dagger e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}}\} \\ &= e^{-\beta(\epsilon_{\vec{k}} - \mu)} \text{tr}\{e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}} \hat{a}_{\vec{k}}^\dagger\} = e^{-\beta(\epsilon_{\vec{k}} - \mu)} \text{tr}\{e^{-\beta\mathcal{H}'} [1 \pm \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}]\}, \end{aligned} \quad (4.68)$$

where '+' and '-' stand for Bosons and Fermions, respectively. Inserting this into Eq.(4.67) we find,

$$\langle \hat{n}_{\vec{k}} \rangle = e^{-\beta(\epsilon_{\vec{k}} - \mu)} (1 \pm \langle \hat{n}_{\vec{k}} \rangle) \quad \Rightarrow \quad \langle \hat{n}_{\vec{k}} \rangle = \begin{cases} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1} & \text{Bosons} \\ \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} + 1} & \text{Fermions} \end{cases} \quad (4.69)$$

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

4.6 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.

4.6.1 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.3.6.2. 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,

$$|\Phi_0\rangle = \prod_{\vec{k}}^{|k| \leq k_F} \prod_{s=\uparrow, \downarrow} \hat{a}_{\vec{k}s}^\dagger |0\rangle \quad (4.70)$$

and $n_{\vec{k}} = \langle \Phi_0 | \hat{n}_{\vec{k}} | \Phi_0 \rangle = \Theta(k_F - |\vec{k}|)$ is a step function with $\hat{n}_{\vec{k}} = \sum_s \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s}$.

First we formulate the *one-particle correlation function* in real space using field operators,²

$$\frac{n}{2} g_s(\vec{r} - \vec{r}') = \langle \hat{\Psi}_s^\dagger(\vec{r}) \hat{\Psi}_s(\vec{r}') \rangle \quad (4.72)$$

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,

$$\begin{aligned} \frac{n}{2} g_s(\vec{r} - \vec{r}') &= \frac{1}{V} \sum_{\vec{k}, \vec{k}'} e^{-i\vec{k} \cdot \vec{r} + i\vec{k}' \cdot \vec{r}'} \underbrace{\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}'s} \rangle}_{= \langle \hat{n}_{\vec{k}s} \rangle \delta_{\vec{k}, \vec{k}'}} \quad . \end{aligned} \quad (4.73)$$

At $T = 0$ we obtain

$$\begin{aligned} \frac{n}{2} g_s(\vec{r} - \vec{r}') &= \int_{|\vec{k}| \leq k_F} \frac{d^3 k}{(2\pi)^3} e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} = \frac{1}{(2\pi)^2} \int_0^{k_F} dk k^2 \int_{-1}^{+1} d \cos \theta e^{ik|\vec{r} - \vec{r}'| \cos \theta} \\ &= \frac{1}{2\pi^2 |\vec{r} - \vec{r}'|} \int_0^{k_F} dk k \sin(k|\vec{r} - \vec{r}'|) = \frac{3n}{2} \frac{\sin x - x \cos x}{x^3} \Big|_{x=k_F |\vec{r} - \vec{r}'|} \quad . \end{aligned} \quad (4.74)$$

Note the limits: $g_s(\vec{r} \rightarrow 0) = 1$ and $g_s(\vec{r} \rightarrow \infty) = 0$ where $g_s(\vec{r} - \vec{r}')$ corresponds to the overlap of the two states

$$\sqrt{\frac{2}{n}} \hat{\Psi}_s(\vec{r}) |\Phi_0\rangle \quad \text{and} \quad \sqrt{\frac{2}{n}} \hat{\Psi}_s(\vec{r}') |\Phi_0\rangle \quad . \quad (4.75)$$

²The correlation function at zero-temperature is given by the expectation value for the ground state,

$$\frac{n}{2} g_s(\vec{r} - \vec{r}') = \langle \Phi_0 | \hat{\Psi}_s^\dagger(\vec{r}) \hat{\Psi}_s(\vec{r}') | \Phi_0 \rangle \quad , \quad (4.71)$$

which is just the zero-temperature limit of Eq.(4.72).

Analogous results can be calculated for finite temperatures (here $T \gg T_F$), where for the "classical" limit an analytical result can be found based on the Maxwell-Boltzmann distribution:

$$\langle \hat{n}_{\vec{k}s} \rangle = \frac{n}{2} \frac{(2\pi)^3}{(\sqrt{\pi}A)^3} e^{-k^2/A^2} \quad \text{with} \quad A^2 = \frac{2mk_B T}{\hbar^2} = \frac{4\pi}{\lambda^2}, \quad (4.76)$$

leading to

$$\frac{n}{2} g_s(\vec{r} - \vec{r}') = \frac{n}{2\pi^{3/2} A^3} \int d^3k e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')} e^{-k^2/A^2} = \frac{n}{2} e^{-A^2(\vec{r}-\vec{r}')^2/4} = \frac{n}{2} e^{-\pi(\vec{r}-\vec{r}')^2/\lambda^2} \quad (4.77)$$

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

$$\left(\frac{n}{2}\right)^2 g_{ss'}(\vec{r} - \vec{r}') = \langle \hat{\Psi}_s^\dagger(\vec{r}) \hat{\Psi}_{s'}^\dagger(\vec{r}') \hat{\Psi}_{s'}(\vec{r}') \hat{\Psi}_s(\vec{r}) \rangle \quad (4.78)$$

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,

$$\left(\frac{n}{2}\right)^2 g_{ss'}(\vec{r} - \vec{r}') = \frac{1}{V^2} \sum_{\vec{k}, \vec{k}', \vec{q}, \vec{q}'} e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} e^{-i(\vec{q}-\vec{q}')\cdot\vec{r}'} \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s'}^\dagger \hat{a}_{\vec{q}'s'} \hat{a}_{\vec{k}'s} \rangle. \quad (4.79)$$

In order to evaluate the mean value $\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s'}^\dagger \hat{a}_{\vec{q}'s'} \hat{a}_{\vec{k}'s} \rangle$ we use the same technique as presented in Sect.4.5.³

From this it follows straightforwardly for $s = s'$,

$$\left(\frac{n}{2}\right)^2 g_{ss}(\vec{r} - \vec{r}') = \frac{1}{V^2} \sum_{\vec{k}, \vec{q}} \left(1 - e^{-i(\vec{k}-\vec{q})\cdot(\vec{r}-\vec{r}')}\right) \langle \hat{n}_{\vec{k}s} \rangle \langle \hat{n}_{\vec{q}s} \rangle = \left(\frac{n}{2}\right)^2 [1 - g_s(\vec{r} - \vec{r}')^2], \quad (4.84)$$

and we can write,

$$g_{ss}(\vec{r} - \vec{r}') = \begin{cases} 1 - \frac{9(\sin x - x \cos x)^2}{x^6} \Big|_{x=k_F|\vec{r}-\vec{r}'|} & T = 0, \\ 1 - e^{-2\pi(\vec{r}-\vec{r}')^2/\lambda^2} & T \gg T_F. \end{cases} \quad (4.85)$$

³Evaluation of $\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s'}^\dagger \hat{a}_{\vec{q}'s'} \hat{a}_{\vec{k}'s} \rangle$: We separate the task into two cases: (1) $s = s'$ and (2) $s \neq s'$.

(1) $s = s'$:

$$\begin{aligned} \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}'s} \rangle &= \frac{1}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}'s} \right] = \frac{1}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}s}^\dagger e^{\beta\mathcal{H}'} e^{-\beta\mathcal{H}'} \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}'s} \right] \\ &= \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}'s} \hat{a}_{\vec{k}s}^\dagger \right] = \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} (\delta_{\vec{k},\vec{k}'} - \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}'s}) \right] \\ &= \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \right] \delta_{\vec{k},\vec{k}'} - \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}'s} \right] \\ &= e^{-\beta(\epsilon_{\vec{k}}-\mu)} \langle \hat{n}_{\vec{q},s} \rangle \delta_{\vec{q},\vec{q}'} \delta_{\vec{k},\vec{k}'} - \frac{e^{-\beta(\epsilon_{\vec{k}}-\mu)}}{Z} \text{tr} \left[e^{-\beta\mathcal{H}'} \hat{a}_{\vec{q}s}^\dagger (\delta_{\vec{q}',\vec{k}} - \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}'s}) \hat{a}_{\vec{k}'s} \right] \\ &= e^{-\beta(\epsilon_{\vec{k}}-\mu)} \langle \hat{n}_{\vec{q},s} \rangle (\delta_{\vec{q},\vec{q}'} \delta_{\vec{k},\vec{k}'} - \delta_{\vec{q}',\vec{k}} \delta_{\vec{q},\vec{k}'}) + e^{-\beta(\epsilon_{\vec{k}}-\mu)} \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}'s} \rangle. \end{aligned} \quad (4.80)$$

From this we find

$$\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s}^\dagger \hat{a}_{\vec{q}'s} \hat{a}_{\vec{k}'s} \rangle = \frac{1}{e^{\beta(\epsilon_{\vec{k}}-\mu)} + 1} \langle \hat{n}_{\vec{q},s} \rangle (\delta_{\vec{q},\vec{q}'} \delta_{\vec{k},\vec{k}'} - \delta_{\vec{q}',\vec{k}} \delta_{\vec{q},\vec{k}'}) = \langle \hat{n}_{\vec{k},s} \rangle \langle \hat{n}_{\vec{q},s} \rangle (\delta_{\vec{q},\vec{q}'} \delta_{\vec{k},\vec{k}'} - \delta_{\vec{q}',\vec{k}} \delta_{\vec{q},\vec{k}'}). \quad (4.81)$$

(2) $s \neq s'$:

$$\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s'}^\dagger \hat{a}_{\vec{q}'s'} \hat{a}_{\vec{k}'s} \rangle = e^{-\beta(\epsilon_{\vec{k}}-\mu)} \left\{ \langle \hat{n}_{\vec{q},s} \rangle \delta_{\vec{q},\vec{q}'} \delta_{\vec{k},\vec{k}'} + \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s'}^\dagger \hat{a}_{\vec{q}'s'} \hat{a}_{\vec{k}'s} \rangle \right\} \quad (4.82)$$

analogous to case (1), such that

$$\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{q}s'}^\dagger \hat{a}_{\vec{q}'s'} \hat{a}_{\vec{k}'s} \rangle = \langle \hat{n}_{\vec{k},s} \rangle \langle \hat{n}_{\vec{q},s} \rangle \delta_{\vec{q},\vec{q}'} \delta_{\vec{k},\vec{k}'} . \quad (4.83)$$

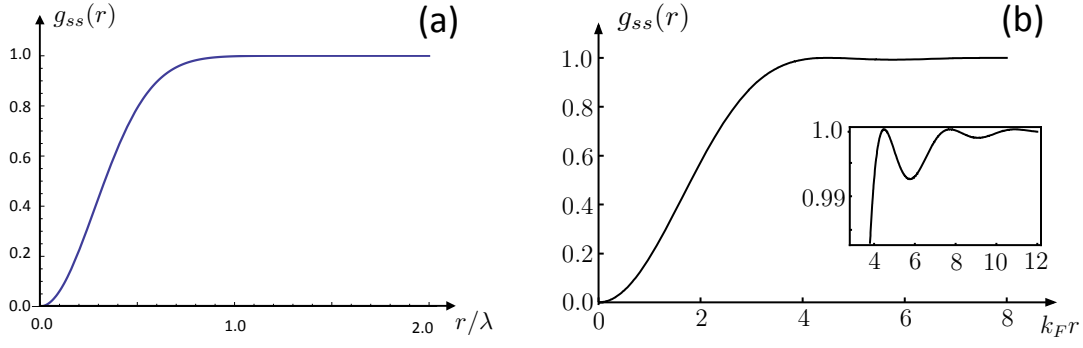


Figure 4.1: The equal-spin pair correlation function for Fermions: (a) $T \gg T_F$ and (b) $T = 0$.

Fig.4.1 shows the equal-spin correlation function which goes to zero for $\vec{r} \rightarrow 0$, since Fermions avoid each other. This dip in the correlation is called exchange hole and has a radius of order λ (thermal wave length) for $T \gg T_F$ and k_F^{-1} in the groundstate. Note that in the latter case the correlation function shows a weak oscillator with wavevector k_F .

The case of $s \neq s'$ leads to $g_{ss'}(\vec{r}) = 1$, i.e. there is no correlation between $s = 1/2$ -Fermions of opposite spin. The probability to find another Fermion around the position of a Fermion at \vec{r} corresponds to

$$g(\vec{r}) = \frac{1}{2}[g_{\uparrow\uparrow}(\vec{r}) + g_{\downarrow\downarrow}(\vec{r})]. \quad (4.86)$$

The density depletion around such a Fermion is then,

$$\begin{aligned} n \int d^3r (g(\vec{r}) - 1) &= -\frac{n}{2} \int d^3r \{g_s(\vec{r})\}^2 = -\frac{2}{n} \int d^3r \frac{1}{V^2} \sum_{\vec{k}, \vec{k}'} \langle \hat{n}_{\vec{k}s} \rangle \langle \hat{n}_{\vec{k}'s} \rangle e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} \\ &= -\frac{2}{nV} \sum_{\vec{k}} \langle \hat{n}_{\vec{k}s} \rangle^2 = \begin{cases} -1 & T = 0, \\ -\frac{\lambda^3 n}{2^{5/2}} & T \gg T_F. \end{cases} \end{aligned} \quad (4.87)$$

which means that the exchange hole expels one Fermion such that each Fermion "defends" a given volume against other Fermions of the same spin for $T = 0$, while the exchange hole shrinks like λn^3 for $T \gg T_F$.

4.6.2 Bosons

Analogous to the Fermions we consider first the single-particle correlation function for $s = 0$ Bosons,

$$g_1(\vec{r} - \vec{r}') = \langle \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r}') \rangle = \frac{1}{V} \sum_{\vec{k}, \vec{k}'} e^{-i\vec{k} \cdot \vec{r} + i\vec{k}' \cdot \vec{r}'} \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}'} \rangle = \frac{1}{V} \sum_{\vec{k}} \langle \hat{n}_{\vec{k}} \rangle e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')}, \quad (4.88)$$

which in the limit $\vec{r}' \rightarrow \vec{r}$ approaches the constant density n and vanishes at very large distances. For $T = 0$ we consider the groundstate, the Bose-Einstein condensate, $\langle \hat{n}_{\vec{k}} \rangle = N \delta_{\vec{k}, 0}$ and for $T \gg T_c$ we use the classical distribution (Eq.(4.76)) where T_c is the critical temperature for Bose-Einstein condensation.

$$g_1(\vec{r} - \vec{r}') = \begin{cases} n & T = 0, \\ n e^{-\pi(\vec{r} - \vec{r}')/\lambda^2} & T \gg T_c. \end{cases} \quad (4.89)$$

The pair correlation functions reads,

$$\begin{aligned}
g_2(\vec{r} - \vec{r}') &= \langle \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}^\dagger(\vec{r}') \hat{\Psi}(\vec{r}') \hat{\Psi}(\vec{r}) \rangle \\
&= \frac{1}{V^2} \sum_{\vec{k}, \vec{k}', \vec{q}, \vec{q}'} e^{-i(\vec{k}-\vec{k}') \cdot \vec{r} - i(\vec{q}-\vec{q}') \cdot \vec{r}'} \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{q}}^\dagger \hat{a}_{\vec{q}'} \hat{a}_{\vec{k}'} \rangle, \tag{4.90}
\end{aligned}$$

Analogous to the Fermions we evaluate⁴

$$\langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{q}}^\dagger \hat{a}_{\vec{q}'} \hat{a}_{\vec{k}'} \rangle = (1 - \delta_{\vec{k}\vec{q}}) \left\{ \delta_{\vec{k}\vec{k}'} \delta_{\vec{q}\vec{q}'} + \delta_{\vec{k}\vec{q}'} \delta_{\vec{q}\vec{k}'} \right\} \langle \hat{n}_{\vec{k}} \rangle \langle \hat{n}_{\vec{q}} \rangle + \delta_{\vec{k}\vec{q}} \delta_{\vec{k}\vec{k}'} \delta_{\vec{q}\vec{q}'} (\langle \hat{n}_{\vec{k}}^2 \rangle - \langle \hat{n}_{\vec{k}} \rangle) \tag{4.92}$$

This leads to

$$\begin{aligned}
g_2(\vec{r} - \vec{r}') &= \frac{1}{V^2} \left[\sum_{\vec{k}, \vec{q}} (1 - \delta_{\vec{k}\vec{q}}) \left(1 + e^{-i(\vec{k}-\vec{q}) \cdot (\vec{r}-\vec{r}')} \right) \langle \hat{n}_{\vec{k}} \rangle \langle \hat{n}_{\vec{q}} \rangle + \sum_{\vec{k}} (\langle \hat{n}_{\vec{k}}^2 \rangle - \langle \hat{n}_{\vec{k}} \rangle) \right] \\
&= \frac{1}{V^2} \left[\sum_{\vec{k}, \vec{q}} \langle \hat{n}_{\vec{k}} \rangle \langle \hat{n}_{\vec{q}} \rangle + \sum_{\vec{k}} \left\{ \langle \hat{n}_{\vec{k}}^2 \rangle - \langle \hat{n}_{\vec{k}} \rangle^2 - \langle \hat{n}_{\vec{k}} \rangle (\langle \hat{n}_{\vec{k}} \rangle + 1) \right\} + \left| \sum_{\vec{k}} e^{-i\vec{k} \cdot (\vec{r}-\vec{r}')} \langle \hat{n}_{\vec{k}} \rangle \right|^2 \right] \\
&= n^2 + g_1(\vec{r} - \vec{r}')^2 + \frac{1}{V^2} \sum_{\vec{k}} \left\{ \langle \hat{n}_{\vec{k}}^2 \rangle - \langle \hat{n}_{\vec{k}} \rangle^2 - \langle \hat{n}_{\vec{k}} \rangle (\langle \hat{n}_{\vec{k}} \rangle + 1) \right\} \tag{4.93}
\end{aligned}$$

For $T = 0$ with $\langle \hat{n}_{\vec{k}} \rangle = N \delta_{\vec{k},0}$ ($\langle \hat{n}_{\vec{k}}^2 \rangle = N^2 \delta_{\vec{k},0}$) we obtain

$$g_2(\vec{r} - \vec{r}') = 2n^2 - \frac{1}{V^2} N(N+1) = \frac{N(N-1)}{V^2}, \tag{4.94}$$

so no correlation is observed. The probability to pick the first particle is $n = N/V$ and a second one $(N-1)/V$ ($\approx n$ for large N). For the high-temperature limit, $T \gg T_c$, the correlation function is given

$$g_2(\vec{r} - \vec{r}') = n^2 + g_1(\vec{r} - \vec{r}')^2 = n^2 \left(1 + e^{-2\pi(\vec{r}-\vec{r}')^2/\lambda^2} \right). \tag{4.95}$$

The probability of finding two Bosons at the same position is twice as large as for long distances, see Fig. 4.2 . Thus, in contrast to Fermions (Fig.4.1), Bosons like to cluster together.

The radius of bunching of the Bosons in the limit $T \gg T_c$ is of order λ and shrinks with increasing T (classical limit).

4.7 Selected applications

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

4.7.1 Spin susceptibility

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

$$\chi = \frac{1}{Vk_B T} \left\{ \langle \hat{M}_z^2 \rangle - \langle \hat{M}_z \rangle^2 \right\}, \tag{4.96}$$

⁴Special case of $\langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{q}}^\dagger \hat{a}_{\vec{q}'} \hat{a}_{\vec{k}'} \rangle$ for $\delta_{\vec{k}\vec{q}} \delta_{\vec{k}\vec{k}'} \delta_{\vec{q}\vec{q}'}$:

$$\langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \hat{a}_{\vec{k}} \rangle = \langle \hat{a}_{\vec{k}}^\dagger \{ \hat{a}_{\vec{k}} \hat{a}_{\vec{k}}^\dagger - 1 \} \hat{a}_{\vec{k}} \rangle = \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle - \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle = \langle \hat{n}_{\vec{k}}^2 \rangle - \langle \hat{n}_{\vec{k}} \rangle \tag{4.91}$$

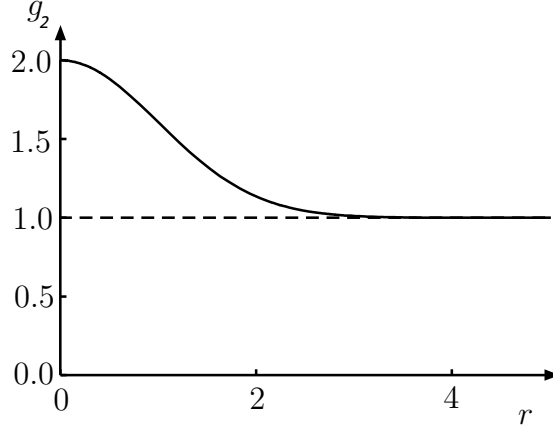


Figure 4.2: The pair correlation function for Bosons. $g_2(r)$ is given in units of n^{-2} and r in units of $\lambda/\sqrt{2\pi}$.

where

$$\hat{M}_z = \frac{g\mu_B}{\hbar} \int d^3r \hat{S}_z(\vec{r}) = \mu_B \sum_{\vec{k}} \sum_{ss'} \hat{a}_{\vec{k}s}^\dagger \sigma_{ss'}^z \hat{a}_{\vec{k}s'} = \mu_B \sum_{\vec{k},s} s \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \quad (4.97)$$

using Sect.4.4. Moreover, $g = 2$ and $s = \pm 1$. First we calculate the magnetization in zero magnetic field,

$$\langle \hat{M}_z \rangle = \mu_B \sum_{\vec{k},s} s \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \rangle = \mu_B \sum_{\vec{k},s} s n_{\vec{k}} = 0. \quad (4.98)$$

Now we turn to

$$\langle \hat{M}_z^2 \rangle = \mu_B^2 \sum_{\vec{k},s} \sum_{\vec{k}',s'} ss' \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \rangle, \quad (4.99)$$

which we determine like in Sect.4.6.1,

$$\begin{aligned} \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \rangle &= \frac{1}{Z} \text{tr} \left\{ e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \right\} = \frac{e^{-\beta(\epsilon_{\vec{k}} - \mu)}}{Z} \text{tr} \left\{ e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \hat{a}_{\vec{k}s}^\dagger \right\} \\ &= \frac{e^{-\beta(\epsilon_{\vec{k}} - \mu)}}{Z} \left[\text{tr} \left\{ e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \right\} \delta_{\vec{k}\vec{k}'} \delta_{ss'} + \text{tr} \left\{ e^{-\beta\mathcal{H}'} \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \right\} \right] \\ &= e^{-\beta(\epsilon_{\vec{k}} - \mu)} \left\{ \left(1 - \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \rangle \right) \delta_{\vec{k}\vec{k}'} \delta_{ss'} + \langle \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \rangle \right\} - e^{-\beta(\epsilon_{\vec{k}} - \mu)} \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \rangle \end{aligned} \quad (4.100)$$

which leads straightforwardly to

$$\langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \rangle = \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \rangle \left(1 - \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \rangle \right) \delta_{\vec{k}\vec{k}'} \delta_{ss'} + \langle \hat{a}_{\vec{k}s}^\dagger \hat{a}_{\vec{k}s} \rangle \langle \hat{a}_{\vec{k}'s'}^\dagger \hat{a}_{\vec{k}'s'} \rangle. \quad (4.101)$$

We now insert this result into Eq.(4.99) and obtain

$$\langle \hat{M}_z^2 \rangle = 2\mu_B^2 \sum_{\vec{k}} \langle \hat{n}_{\vec{k}s} \rangle (1 - \langle \hat{n}_{\vec{k}s} \rangle) = 2\mu_B^2 \sum_{\vec{k}} \frac{1}{4 \cosh^2(\beta(\epsilon_{\vec{k}} - \mu)/2)}, \quad (4.102)$$

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

$$\langle \hat{M}_z^2 \rangle \approx \mu_B^2 V \int_{-\infty}^{+\infty} d\epsilon N(\epsilon_F) \frac{1}{4 \cosh^2(\beta\epsilon/2)} = V \mu_B^2 k_B T N(\epsilon_F), \quad (4.103)$$

where the density of states is defined as

$$N(\epsilon) = \frac{1}{V} \sum_{\vec{k}, s} \delta(\epsilon - \epsilon_{\vec{k}}). \quad (4.104)$$

Then the spin susceptibility is given as the Pauli susceptibility,

$$\chi = \mu_B^2 N(\epsilon_F) = \mu_B^2 \frac{3n}{2\epsilon_F}, \quad (4.105)$$

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 $N(\epsilon_F)k_B T$ Fermions can be spin polarised (thermal softening of the Fermi sea). Thus, the factor $(k_B T)^{-1}$ is compensated by the shrinking density of polarisable spins as temperature decreases.⁵

4.7.2 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 in more detail than in Sect.4.6.2,

$$g(\vec{r} - \vec{r}') = \langle \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r}') \rangle = \frac{1}{V} \sum_{\vec{k}, \vec{k}'} \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}'} \rangle e^{i(\vec{k}' \cdot \vec{r}' - \vec{k} \cdot \vec{r})} = \frac{1}{V} \sum_{\vec{k}} \langle \hat{n}_{\vec{k}} \rangle e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')}, \quad (4.109)$$

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

$$g(\vec{R}) = \frac{1}{V} \sum_{\vec{k}} \frac{e^{-i\vec{k} \cdot \vec{R}}}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1}, \quad (4.110)$$

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

$$g(\vec{R}) = \frac{1}{V} \sum_{\vec{k}} \frac{1 - i\vec{k} \cdot \vec{R} - (\vec{k} \cdot \vec{R})^2 / 2 + \dots}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1} = n - \frac{\vec{R}^2}{6} \langle \vec{k}^2 \rangle + \dots, \quad (4.111)$$

where $n = N/V$ is the particle density⁶ and

$$\langle \vec{k}^2 \rangle = \frac{2mU}{\hbar^2 V} = \begin{cases} 6\pi n \lambda^{-2} & T \gg T_c \\ 3.08\pi n \lambda^{-2} (T/T_c)^{3/2} & T < T_c \end{cases} \quad (4.113)$$

⁵ *Classical limit:* The classical limit can be discussed using the Maxwell-Boltzmann distribution function,

$$n_{\vec{k}s} = \frac{n\lambda^3}{2} e^{-k^2 \lambda^2 / 4\pi}, \quad (4.106)$$

with λ as the thermal wavelength. Inserting into Eq.(4.102) we obtain

$$\langle \hat{M}_z^2 \rangle = 2\mu_B^2 V \int \frac{d^3 k}{(2\pi)^3} n_{\vec{k}s} (1 - n_{\vec{k}s}) = 2\mu_B^2 V \int \frac{d^3 k}{(2\pi)^3} \left\{ \frac{n\lambda^3}{2} e^{-k^2 \lambda^2 / 4\pi} - \frac{n^2 \lambda^6}{4} e^{-k^2 \lambda^2 / 2\pi} \right\} = \mu_B^2 V n \left(1 - \frac{\lambda^3 n}{2^{5/2}} \right), \quad (4.107)$$

which using Eq.(4.96) leads to the susceptibility found earlier in Eq.(3.112).

$$\chi = \frac{\mu_B^2 n}{k_B T} \left(1 - \frac{\lambda^3 n}{2^{5/2}} \right) \quad (4.108)$$

The factor $1 - n_{\vec{k}s}$ in Eq.(4.102) introduces the quantum correction in the second term.

⁶ Average for an isotropic momentum distribution function $\langle \hat{n}_{\vec{k}} \rangle$:

$$\langle (\vec{R} \cdot \vec{k})^2 \rangle = \sum_{j=x,y,z} R_j^2 \langle k_j^2 \rangle = \frac{\langle \vec{k}^2 \rangle}{3} (R_x^2 + R_y^2 + R_z^2) = \frac{\langle \vec{k}^2 \rangle}{3} \vec{R}^2, \quad (4.112)$$

because $\langle k_x^2 \rangle = \langle k_y^2 \rangle = \langle k_z^2 \rangle = \langle \vec{k}^2 \rangle / 3$ and $\langle k_x k_y \rangle = \langle k_y k_z \rangle = \langle k_z k_x \rangle = 0$.

where U is the internal energy of the Bose gas. The correlation falls off quadratically for finite, but small \vec{R} ($|\vec{R}| \ll \lambda$). Note that the in the $T \rightarrow 0$ limit the correlation function does not drop in agreement with Eq.(4.89). For the long-distance limit we note that only the small wave vectors contribute to the k -sum so that we may expand the integrand in the following way ($\beta(\epsilon_{\vec{k}} - \mu) \ll 1$),

$$g(\vec{R}) \approx \int \frac{d^3k}{(2\pi)^3} \frac{e^{-i\vec{k}\cdot\vec{R}}}{\beta(\epsilon_{\vec{k}} - \mu)} = \frac{2mk_B T}{\hbar^2} \int \frac{d^3k}{(2\pi)^3} \frac{e^{-i\vec{k}\cdot\vec{R}}}{k^2 + k_0^2} \quad (4.114)$$

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

$$g(\vec{R}) \approx \frac{mk_B T}{(2\pi)^4 \hbar^2} \frac{e^{-k_0|\vec{R}|}}{|\vec{R}|} = \frac{e^{-k_0|\vec{R}|}}{(2\pi)^3 \lambda^2 |\vec{R}|}. \quad (4.115)$$

The single-particle correlation function decays exponentially for large distances (Fig.4.3). This behavior is valid for $T > T_c$ where $\mu < 0$.

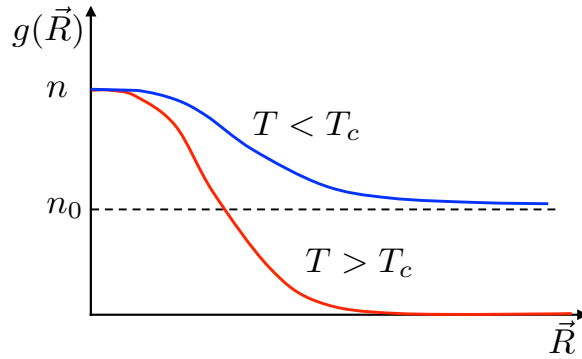


Figure 4.3: Schematic behavior of the single-particle correlation function in the normal ($T > T_c$) and the Bose-Einstein condensed phase ($T < T_c$). n is the overall particle density and n_0 the density of condensed particles.

For $T < T_c$ the chemical potential lies at the lowest single-particle state, i.e. $\mu = 0$ for free Bosons, such that $k_0 = 0$. The short-distance behavior is still described by Eq.(4.111). For the long-distance behavior we conclude from Eq.(4.115) 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

$$\langle \hat{n}_{\vec{k}} \rangle = n_0 \delta(\vec{k}) + \frac{1}{(2\pi)^3} \frac{1}{e^{\beta(\epsilon_{\vec{k}} - \mu)} - 1}, \quad (4.116)$$

such that for $|\vec{R}| \rightarrow \infty$,

$$g(\vec{R}) = n_0 + \frac{1}{(2\pi)^3 \lambda^2 |\vec{R}|}. \quad (4.117)$$

The correlation function approaches a finite value on long distances in the presence of a Bose-Einstein condensate (Fig.4.3).

Bogolyubov approximation:

We consider this now from the view point of the field operator for free Bosons,

$$\hat{\Psi}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \hat{a}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} = \frac{\hat{a}_0}{\sqrt{V}} + \frac{1}{\sqrt{V}} \sum_{\vec{k} \neq 0} \hat{a}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}. \quad (4.118)$$

The correlation function in Eq.(4.117) suggests the following approximation: $\hat{a}_0 \rightarrow a_0 = \sqrt{N_0}$. For a Bose-Einstein condensate we may replace the operator \hat{a}_0 simply by a complex number, such that

$$\widehat{\Psi}(\vec{r}) \rightarrow \widehat{\Psi}(\vec{r}) = \psi_0(\vec{r}) + \delta\widehat{\Psi}(\vec{r}) , \quad (4.119)$$

with $\psi_0(\vec{r}) = \sqrt{n_0}e^{i\phi}$, where ϕ is an arbitrary phase and $n_0 = N_0/V$. 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}_ν of a Bosonic state of energy ϵ_ν . Let us call this state $|\Psi_\alpha\rangle$ with the property,

$$\hat{a}_\nu|\Psi_\alpha\rangle = \alpha|\Psi_\alpha\rangle , \quad (4.120)$$

where α is a complex number. Such a state is given by

$$|\Psi_\alpha\rangle = e^{-|\alpha|^2/2} \sum_{N_\nu} \frac{\alpha^{N_\nu}}{\sqrt{N_\nu!}} |N_\nu\rangle ; , \quad (4.121)$$

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

$$\langle\hat{n}_\nu\rangle = \langle\Psi_\alpha|\hat{a}_\nu^\dagger\hat{a}_\nu|\Psi_\alpha\rangle = \langle\Psi_\alpha|\alpha^*\alpha|\Psi_\alpha\rangle = \alpha^*\alpha = |\alpha|^2 \quad (4.122)$$

and the variance is

$$\langle\hat{n}_\nu^2\rangle - \langle\hat{n}_\nu\rangle^2 = \langle\hat{a}_\nu^\dagger\hat{a}_\nu\hat{a}_\nu^\dagger\hat{a}_\nu\rangle - |\alpha|^4 = \langle\hat{a}_\nu^\dagger\hat{a}_\nu\rangle + \langle\hat{a}_\nu^\dagger\hat{a}_\nu^\dagger\hat{a}_\nu\hat{a}_\nu\rangle - |\alpha|^4 = |\alpha|^2 + |\alpha|^4 - |\alpha|^4 = |\alpha|^2 \quad (4.123)$$

such that

$$\frac{\langle\hat{n}_\nu^2\rangle - \langle\hat{n}_\nu\rangle^2}{\langle\hat{n}_\nu\rangle^2} = \frac{1}{|\alpha|^2} = \frac{1}{\langle\hat{n}_\nu\rangle} . \quad (4.124)$$

Taking now the $\vec{k} = 0$ state as coherent we identify

$$\hat{a}_0|\Psi\rangle = \alpha_0|\Psi\rangle = \sqrt{N_0}e^{i\phi}|\Psi\rangle . \quad (4.125)$$

In this spirit we find that the mean value is

$$\langle\widehat{\Psi}(\vec{r})\rangle = \psi_0(\vec{r}) , \quad (4.126)$$

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 particles ($N_0 \gg 1$), 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 (see also Chapter 6), the *condensate wavefunction* of Eq.(4.126),

$$\psi_0(\vec{r}) = |\psi_0(\vec{r})|e^{i\phi(\vec{r})} = \sqrt{n_0}e^{i\phi} . \quad (4.127)$$

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.(4.127)) and a state with

fixed phase has no definite particle number.⁷ First we consider the wave function of the coherent state in the number representation,

$$\Psi_N = \langle N | \Psi_\alpha \rangle = e^{-|\alpha|^2/2} \frac{\alpha^N}{\sqrt{N!}} \quad (4.132)$$

with $\alpha = \sqrt{N_0} e^{i\phi_0}$. Thus, the probability for the particle number N is given by

$$P_N = |\Psi_N|^2 = e^{N_0} \frac{N_0^N}{N!} \approx \frac{1}{\sqrt{2\pi N_0}} e^{-(N-N_0)^2/2N_0} \quad (4.133)$$

for large N_0 . On the other hand, projecting into the phase representation,

$$\begin{aligned} \Psi_\phi &= \langle \phi | \Psi_\alpha \rangle = \sum_{N=0}^{\infty} \langle \phi | N \rangle \langle N | \Psi_\alpha \rangle = \frac{e^{-|\alpha|^2/2}}{\sqrt{2\pi}} \sum_{N=0}^{\infty} \frac{\alpha^N e^{-i\phi N}}{\sqrt{N!}} \\ &\approx \frac{1}{\sqrt{2\pi}} \int_0^\infty dN \frac{e^{-(N-N_0)^2/4N_0}}{(2\pi N_0)^{1/4}} e^{-iN(\phi-\phi_0)} = \left(\frac{N_0}{2\pi}\right)^{1/4} e^{-(\phi-\phi_0)^2 N_0/4} \end{aligned} \quad (4.134)$$

such that

$$P_\phi = |\langle \phi | \Psi_\alpha \rangle|^2 \approx \sqrt{\frac{N_0}{2\pi}} e^{-(\phi-\phi_0)^2 N_0/2}. \quad (4.135)$$

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,

$$\left. \begin{aligned} \Delta\phi^2 &= \langle \Psi_\alpha | (\hat{\phi} - \phi_0)^2 | \Psi_\alpha \rangle = \frac{1}{N_0} \\ \Delta N^2 &= \langle \Psi_\alpha | (\hat{N} - N_0)^2 | \Psi_\alpha \rangle = N_0 \end{aligned} \right\} \Rightarrow \Delta N \Delta\phi = 1, \quad (4.136)$$

compatible with a commutation relation of the form $[\hat{N}, \hat{\phi}] = i$.

⁷*Phase and number operator eigenstates:* They define the number operator and the phase operator and their corresponding eigenstates.

$$\hat{N}|N\rangle = N|N\rangle \quad \text{and} \quad e^{i\hat{\phi}}|\phi\rangle = e^{i\phi}|\phi\rangle \quad (4.128)$$

where the two states are connected by the Fourier transform

$$|\phi\rangle = \frac{1}{\sqrt{2\pi}} \sum_{N=0}^{\infty} e^{iN\phi} |N\rangle \quad \text{with} \quad \langle N|\phi\rangle = \frac{e^{iN\phi}}{\sqrt{2\pi}} \quad (4.129)$$

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 a finite Hilbert space $\{|N\rangle\}$ assuming that $0 \leq N \leq L-1 \gg 1$. Then we can restrict ourselves to a discrete set of phases $\phi = \phi_k = 2\pi k/L$ with $k = 0, \dots, L-1$ (analog to wave vectors in a finite system with periodic boundary conditions). Now it is easy to see that

$$\langle \phi_k | \phi_{k'} \rangle = \delta_{k,k'}. \quad (4.130)$$

Keeping this in mind we take the limit $L \rightarrow \infty$.

Based on this above operators can be represented as

$$\hat{N} = \sum_{N=0}^{\infty} N |N\rangle \langle N| \quad \text{and} \quad e^{i\hat{\phi}} = \sum_{N=0}^{\infty} |N\rangle \langle N+1|; \quad (4.131)$$

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.

4.7.3 Phonons in an elastic medium

We consider here vibrations of an elastic media using a simplified model of longitudinal waves only. As in Sect.3.8.2 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

$$E_{\text{kin}} = \frac{\rho_m}{2} \int d^3r \left(\frac{\partial \vec{u}(\vec{r}, t)}{\partial t} \right)^2 \quad \text{and} \quad E_{\text{el}} = \frac{\lambda_e}{2} \int d^3r (\vec{\nabla} \cdot \vec{u}(\vec{r}, t))^2, \quad (4.137)$$

where ρ_m is the mass density of the medium and λ_e denotes the elastic modulus. Note that we use a simplified elastic term which involves density fluctuations only, corresponding to $\vec{\nabla} \cdot \vec{u}$, and ignores the contributions of shear distortion. This two energies are now combined to the Lagrange functional $L[\vec{u}] = E_{\text{kin}} - E_{\text{el}}$, whose variation with respect to $\vec{u}(\vec{r}, t)$ yields the wave equation,

$$\frac{1}{c_l^2} \frac{\partial^2}{\partial t^2} \vec{u} - \vec{\nabla}(\vec{\nabla} \cdot \vec{u}) = 0, \quad (4.138)$$

for longitudinal waves with the sound velocity $c_l = \sqrt{\lambda_e/\rho_m}$ (Eq.(3.162)). The general solution can be represented as a superposition of plane waves,

$$\vec{u}(\vec{r}, t) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \vec{e}_{\vec{k}} \left(q_{\vec{k}}(t) e^{i\vec{k} \cdot \vec{r}} + q_{\vec{k}}^*(t) e^{-i\vec{k} \cdot \vec{r}} \right), \quad (4.139)$$

with polarization vector $\vec{e}_{\vec{k}} = \vec{k}/|\vec{k}|$ and the amplitudes $q_{\vec{k}}(t)$ satisfy the equation,

$$\frac{d^2}{dt^2} q_{\vec{k}} + \omega_{\vec{k}}^2 q_{\vec{k}} = 0, \quad (4.140)$$

with the frequency $\omega_{\vec{k}} = c_l |\vec{k}| = c_l k$. We may rewrite the energy, $E = E_{\text{kin}} + E_{\text{el}}$, in terms of $q_{\vec{k}}$,

$$E = \sum_{\vec{k}} \rho_m \omega_{\vec{k}}^2 \left[q_{\vec{k}}(t) q_{\vec{k}}^*(t) + q_{\vec{k}}^*(t) q_{\vec{k}}(t) \right]. \quad (4.141)$$

which we express in a symmetrized form, for future convenience. Now we introduce new variables

$$Q_{\vec{k}} = \sqrt{\rho_m} (q_{\vec{k}} + q_{\vec{k}}^*) \quad \text{and} \quad P_{\vec{k}} = \frac{d}{dt} Q_{\vec{k}} = -i\omega_{\vec{k}} \sqrt{\rho_m} (q_{\vec{k}} - q_{\vec{k}}^*), \quad (4.142)$$

leading to the energy

$$E = \frac{1}{2} \sum_{\vec{k}} \left(P_{\vec{k}}^2 + \omega_{\vec{k}}^2 Q_{\vec{k}}^2 \right). \quad (4.143)$$

This corresponds to a set of independent harmonic oscillators labelled by the wave vectors \vec{k} , as we have seen in Sect.3.8. We now turn to the step of canonical quantization replacing the variables $(P_{\vec{k}}, Q_{\vec{k}}) \rightarrow (\hat{P}_{\vec{k}}, \hat{Q}_{\vec{k}})$ which satisfy the standard commutation relation,

$$[\hat{Q}_{\vec{k}}, \hat{P}_{\vec{k}'}] = i\hbar \delta_{\vec{k}, \vec{k}'}. \quad (4.144)$$

This can be reexpressed in terms of lowering and raising operators,

$$\hat{b}_{\vec{k}} = \frac{1}{\sqrt{2\hbar\omega_{\vec{k}}}} \left(\omega_{\vec{k}} \hat{Q}_{\vec{k}} + i\hat{P}_{\vec{k}} \right), \quad \hat{b}_{\vec{k}}^\dagger = \frac{1}{\sqrt{2\hbar\omega_{\vec{k}}}} \left(\omega_{\vec{k}} \hat{Q}_{\vec{k}} - i\hat{P}_{\vec{k}} \right), \quad (4.145)$$

which obey the following commutation relations due to Eq.(4.144),

$$[\hat{b}_{\vec{k}}, \hat{b}_{\vec{k}'}^\dagger] = \delta_{\vec{k}, \vec{k}'}, \quad [\hat{b}_{\vec{k}}, \hat{b}_{\vec{k}'}] = [\hat{b}_{\vec{k}}^\dagger, \hat{b}_{\vec{k}'}^\dagger] = 0. \quad (4.146)$$

Therefore $\hat{b}_{\vec{k}}^\dagger$ 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

$$\mathcal{H} = \sum_{\vec{k}} \hbar\omega_{\vec{k}} \left(\hat{b}_{\vec{k}}^\dagger \hat{b}_{\vec{k}} + \frac{1}{2} \right) = \sum_{\vec{k}} \hbar\omega_{\vec{k}} \left(\hat{n}_{\vec{k}} + \frac{1}{2} \right) \quad (4.147)$$

whose eigenstates are given in the occupation number representation, $|n_{\vec{k}_1}, n_{\vec{k}_2}, \dots\rangle$. We can now also introduce the corresponding field operator using Eq.(4.139),

$$\hat{u}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \vec{e}_{\vec{k}} \sqrt{\frac{\hbar}{2\rho_m\omega_{\vec{k}}}} \left[\hat{b}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \hat{b}_{\vec{k}}^\dagger e^{-i\vec{k}\cdot\vec{r}} \right] \quad (4.148)$$

which is not an eigen operator for the occupation number states. Actually the thermal mean value of the field vanishes $\langle \hat{u}(\vec{r}) \rangle = 0$.

Correlation function:

The correlation function is given by

$$\begin{aligned} g(\vec{r} - \vec{r}') &= \langle \hat{u}(\vec{r}) \cdot \hat{u}(\vec{r}') \rangle - \langle \hat{u}(\vec{r}) \rangle \cdot \langle \hat{u}(\vec{r}') \rangle = \langle \vec{u}(\vec{r}) \cdot \vec{u}(\vec{r}') \rangle \\ &= \frac{1}{V} \sum_{\vec{k}, \vec{k}'} \frac{\hbar \vec{e}_{\vec{k}} \cdot \vec{e}_{\vec{k}'}}{2\rho_m \sqrt{\omega_{\vec{k}} \omega_{\vec{k}'}}} \left\langle \left[\hat{b}_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \hat{b}_{\vec{k}}^\dagger e^{-i\vec{k}\cdot\vec{r}} \right] \left[\hat{b}_{\vec{k}'} e^{i\vec{k}'\cdot\vec{r}'} + \hat{b}_{\vec{k}'}^\dagger e^{-i\vec{k}'\cdot\vec{r}'} \right] \right\rangle. \end{aligned} \quad (4.149)$$

Note that

$$\langle \hat{b}_{\vec{k}}^\dagger \hat{b}_{\vec{k}'} \rangle = \langle \hat{n}_{\vec{k}} \rangle \delta_{\vec{k}, \vec{k}'}, \quad \langle \hat{b}_{\vec{k}} \hat{b}_{\vec{k}'}^\dagger \rangle = \{1 + \langle \hat{n}_{\vec{k}} \rangle\} \delta_{\vec{k}, \vec{k}'}, \quad \langle \hat{b}_{\vec{k}}^\dagger \hat{b}_{\vec{k}'}^\dagger \rangle = \langle \hat{b}_{\vec{k}} \hat{b}_{\vec{k}'} \rangle = 0, \quad (4.150)$$

such that

$$g(\vec{r} - \vec{r}') = \frac{\hbar}{2\rho_m V} \sum_{\vec{k}} \frac{1}{\omega_{\vec{k}}} \left\{ (1 + \langle \hat{n}_{\vec{k}} \rangle) e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} + \langle \hat{n}_{\vec{k}} \rangle e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')} \right\} \quad (4.151)$$

Melting:

Instead of calculating the correlation function $\vec{r} \neq \vec{r}'$ we now analyze the local (onsite) fluctuation, i.e $\vec{r} = \vec{r}'$,

$$\langle \vec{u}(\vec{r})^2 \rangle = \frac{\hbar}{2\rho_m V} \sum_{\vec{k}} \frac{1}{\omega_{\vec{k}}} \{ (1 + 2\langle \hat{n}_{\vec{k}} \rangle) \} = \frac{\hbar}{2\rho_m V} \sum_{\vec{k}} \frac{1}{\omega_{\vec{k}}} \coth \left(\frac{\beta \hbar \omega_{\vec{k}}}{2} \right). \quad (4.152)$$

With $\omega_{\vec{k}} = c_l k$ and the fact the number of degrees of freedom are limited, as described in Sect.3.8.2 ($k \leq k_D$), we find

$$\langle \vec{u}(\vec{r})^2 \rangle = \frac{\hbar}{(2\pi)^2 \rho_m c_l} \int_0^{k_D} dk k \coth \left(\frac{\beta \hbar c_l k}{2} \right) = \begin{cases} \frac{k_D k_B T}{2\pi^2 \lambda_e} & T \gg \Theta_D, \\ \frac{k_D k_B \Theta_D}{8\pi^2 \lambda_e} & T \ll \Theta_D, \end{cases} \quad (4.153)$$

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 the

condition that the lattice is stable for $\langle \vec{u}^2 \rangle < L_m^2 a^2$. Thus we obtain a melting temperature T_m with

$$L_m^2 = \frac{\langle \vec{u}^2 \rangle}{a^2} = \frac{k_B T_m}{2\pi\lambda_e a^3} \quad \Rightarrow \quad k_B T_m = 2\pi\lambda_e a^3 L_m^2 = 2\pi\rho_m a^3 c_l^2 L_m^2 = 2\pi M_i c_l^2 L_m^2, \quad (4.154)$$

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 T_m .

At sufficiently low temperature we can also observe *quantum melting* which occurs due to quantum fluctuations, the zero-point motion of the atoms in a lattice. We consider $T \ll \Theta_D$ and fix the temperature,

$$L_m^2 = \frac{k_B \Theta_D}{8\pi a^3 \lambda_e} = \frac{\hbar}{8a^4 \rho_m a^4 c_l} \quad \Rightarrow \quad c_{lm} = \frac{\hbar}{8\rho_m a^4 L_m^2} \quad (4.155)$$

which defines a critical value for the sound velocity, c_{lm} , which here is temperature independent. For $c_l > c_{lm}$ the fluctuations are small enough that lattice stable, because it stiff enough, while for $c_l < c_{lm}$ the lattice is "soft" such that the zero-point motion destroys the lattice. We will see in Chapt.7 that the ${}^4\text{He}$ shows such a quantum melting transition at very low temperature under pressure (pressure increases elastic constant and sound velocity), where the solid phase is stable at high pressure and turns into a liquid under decreasing the pressure.

Lower dimensions:

We consider the elastic medium at lower dimensions. For two dimensions, we rewrite Eq.(4.153),

$$\langle \vec{u}(\vec{r})^2 \rangle = \frac{\hbar}{4\pi c_l \rho_m} \int_0^{k_D} dk \coth\left(\frac{\beta \hbar c_l k}{2}\right) \quad (4.156)$$

and find that for all temperatures $T > 0$ the integral diverges at lower integral boundary ("infrared divergence"). Only at $T = 0$ we find

$$\langle \vec{u}(\vec{r})^2 \rangle = \frac{\hbar k_D}{4\pi c_l \rho_m} = \frac{k_B \Theta_D}{4\pi c_l^2 \rho_m} = \frac{k_B \Theta_D}{4\pi \lambda_e} \quad (4.157)$$

finite. Thus in two dimension the lattice forming an elastic medium is only stable at zero temperature. But still we can have quantum melting, if the lattice becomes sufficiently soft.

In one dimension Eq.(4.153) turns into

$$\langle \vec{u}(\vec{r})^2 \rangle = \frac{\hbar}{2\pi c_l \rho_m} \int_0^{k_D} dk \frac{1}{k} \coth\left(\frac{\beta \hbar c_l k}{2}\right), \quad (4.158)$$

which (infrared) diverges at all temperatures including $T = 0$. Quantum and thermal fluctuations are strong enough in one dimension to destabilize any lattice.

Chapter 5

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.

5.1 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:

$$\mathcal{H}(\vec{s}_i) = J \sum_{i=1}^N \vec{s}_i \cdot \vec{s}_{i+1} \quad (5.1)$$

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).

5.1.1 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

$$Z = \int \frac{d\Omega_1}{4\pi} \dots \frac{d\Omega_{N+1}}{4\pi} e^{-\beta J \sum_i \vec{s}_i \cdot \vec{s}_{i+1}}, \quad (5.2)$$

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

¹We follow here M.E. Fisher, American Journal of Physics **32**, 343 (1964).

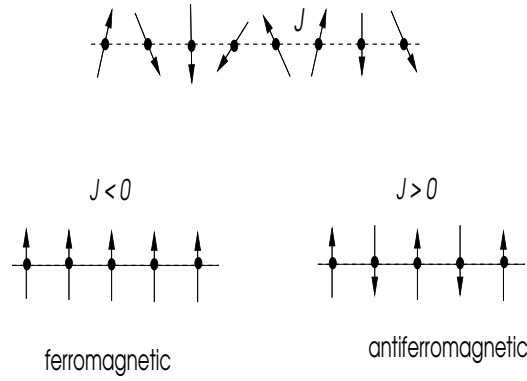


Figure 5.1: Spin chain: Coupling J between spins of arbitrary orientation. $J < 0$: ferromagnetic alignment preferred; $J > 0$: antiferromagnetic alignment preferred.

we may write

$$\begin{aligned}
 Z &= \prod_{i=1}^N \left\{ \int e^{-\beta J \vec{s}_i \cdot \vec{s}_{i+1}} \frac{d\Omega_i}{4\pi} \right\} \int \frac{d\Omega_{N+1}}{4\pi} = \prod_{i=1}^N \left\{ \int e^{-\beta J S^2 \cos \theta_i} \frac{d\Omega_i}{4\pi} \right\} \int \frac{d\Omega_{N+1}}{4\pi} \\
 &= \left\{ \frac{1}{2} \int_{-1}^{+1} dx e^{-\beta J S^2 x} \right\}^N = \left\{ \frac{\sinh(\beta J S^2)}{\beta J S^2} \right\}^N
 \end{aligned} \tag{5.3}$$

which looks similar to the expression obtained for the classical ideal paramagnet (see Sect.3.4.2). 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,

$$\begin{aligned}
 F(T, N) &= N k_B T \ln(\beta J S^2) - N k_B T \ln \{ \sinh(\beta J S^2) \} , \\
 U(T, N) &= N k_B T - N J S^2 \coth(\beta J S^2) .
 \end{aligned} \tag{5.4}$$

In the low-temperature limit, $\beta J S^2 \gg 1$, the internal energy approaches the ground state energy, $U \rightarrow -N|J|S^2$, 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 ,

$$C = N k_B \left\{ 1 - \left(\frac{\beta J S^2}{\sinh(\beta J S^2)} \right)^2 \right\} \tag{5.5}$$

with a similar form as for the ideal paramagnet. Note, that $C \rightarrow N k_B$ in the zero-temperature limit and, consequently, the third law of thermodynamic is not satisfied (see Fig.5.2).

5.1.2 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

$$\begin{aligned}
 \Gamma_l &= \langle \vec{s}_i \cdot \vec{s}_{i+l} \rangle = \langle s_i^x s_{i+l}^x \rangle + \langle s_i^y s_{i+l}^y \rangle + \langle s_i^z s_{i+l}^z \rangle = 3 \langle s_i^z s_{i+l}^z \rangle \\
 &= \frac{3}{Z(4\pi)^{N+1}} \int d\Omega_1 \cdots d\Omega_{N+1} S^2 \cos \Theta_i \cos \Theta_{i+l} e^{-\beta J S^2 \sum_i \cos \theta_i} .
 \end{aligned} \tag{5.6}$$

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

$$\begin{aligned} \Gamma_l &= 3S^2 \left(\frac{\beta JS^2}{\sinh(\beta JS^2)} \right)^{l+1} \int \frac{d\Omega_i}{4\pi} \cos \Theta_i e^{-\beta JS^2 \cos \theta_i} \\ &\quad \times \int \frac{d\Omega_{i+1}}{4\pi} e^{-\beta JS^2 \cos \theta_{i+1}} \dots \int d\Omega_{i+l} \cos \Theta_{i+l} \end{aligned} \quad (5.7)$$

Taking again the direction of spin \vec{s}_{i+1} as the reference for the spin \vec{s}_i we find the relation²

$$\cos \Theta_i = \cos \Theta_{i+1} \cos \theta_i + \sin \Theta_{i+1} \sin \theta_i \cos \phi_i . \quad (5.10)$$

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

$$\begin{aligned} \Gamma_l &= 3S^2 \left(\frac{\beta JS^2}{\sinh(\beta JS^2)} \right)^{l+1} \int \frac{d\Omega_i}{4\pi} \cos \theta_i e^{-\beta JS^2 \cos \theta_i} \\ &\quad \times \int \frac{d\Omega_{i+1}}{4\pi} \cos \Theta_{i+1} e^{-\beta JS^2 \cos \theta_{i+1}} \dots \int \frac{d\Omega_{i+l}}{4\pi} \cos \Theta_{i+l} \\ &= \Gamma_{l-1} \frac{\beta JS^2}{\sinh(\beta JS^2)} \int \frac{d\Omega_i}{4\pi} \cos \theta_i e^{-\beta JS^2 \cos \theta_i} = \Gamma_{l-1} u(\beta JS^2) \end{aligned} \quad (5.11)$$

with

$$u(x) = \frac{1}{x} - \coth x \approx \begin{cases} \frac{1}{x} - \text{sign}(x) & x \gg 1 , \\ \frac{x}{3} & x \ll 1 . \end{cases} \quad (5.12)$$

If we take into account that $\Gamma_{l=0} = S^2$ we find

$$\Gamma_l = S^2 [u(\beta JS^2)]^l = S^2 e^{-l/\xi} (-\text{sign}(J))^l \quad \text{with} \quad \xi^{-1} = -\ln\{|u(\beta JS^2)|\} . \quad (5.13)$$

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 :

$$\xi(T) = \begin{cases} [\ln(3k_B T/|J|S^2)]^{-1} & k_B T \gg |J|S^2 \\ \frac{|J|S^2}{k_B T} & k_B T \ll |J|S^2 \end{cases} \quad (5.14)$$

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 $u \rightarrow 1$ such that

$$\Gamma_l(T = 0) = S^2 (-\text{sign} J)^l \quad (5.15)$$

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 $\Gamma_l \rightarrow 0$ for $l \rightarrow \infty$.

²Consider \vec{s}_1 and \vec{s}_2 and take $\hat{y}' \perp \hat{z}, \vec{s}_2$ with $|\hat{y}'| = |\hat{z}| = 1$:

$$\vec{s}_1 = \vec{s}_2 \cos \theta_1 + (\hat{y}' \times \vec{s}_2) \sin \theta_1 \cos \phi_1 + \hat{y}' S \sin \theta_1 \sin \phi_1 \quad (5.8)$$

and multiply by \hat{z} :

$$\underbrace{\hat{z} \cdot \vec{s}_1}_{=S \cos \Theta_1} = \cos \theta_1 \underbrace{\hat{z} \cdot \vec{s}_2}_{=S \cos \Theta_2} + \hat{y}' \cdot \underbrace{(\vec{s}_2 \times \hat{z})}_{=\hat{y}' S \sin \Theta_2} \sin \theta_1 \cos \phi_1 . \quad (5.9)$$

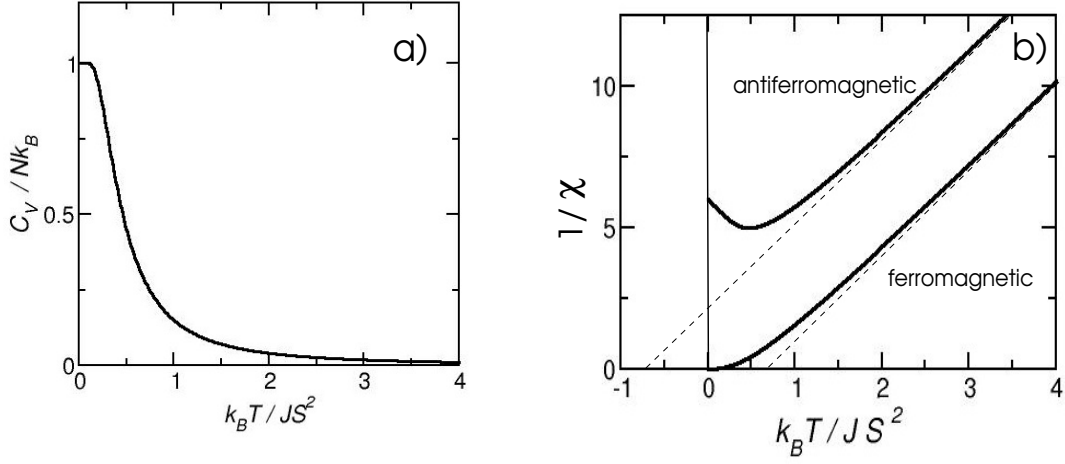


Figure 5.2: Thermodynamic properties of spin chain: a) heat capacity: saturates at low temperature to Nk_B like the potential energy of a two-dimensional harmonic oscillator; b) Susceptibility plotted inversely: ferromagnetic case show divergence at $T = 0$ and antiferromagnetic case approaches non-monotonically 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.

5.1.3 Susceptibility

Finally we want to study the susceptibility by assuming a coupling to the magnetic field of the form

$$\mathcal{H}' = \mathcal{H} - g \sum_{i=1}^{N+1} \vec{s}_i \cdot \vec{H}. \quad (5.16)$$

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 (2.127) 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

$$\chi_{zz} = \frac{1}{Nk_B T} \{ \langle m_z^2 \rangle - \langle m_z \rangle^2 \} = \frac{g^2}{Nk_B T} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \{ \langle s_i^z s_j^z \rangle - \langle s_i^z \rangle \langle s_j^z \rangle \}. \quad (5.17)$$

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

$$\begin{aligned} \chi_{zz} &= \frac{g^2}{3Nk_B T} \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} \Gamma_{|i-j|} \approx \frac{g^2}{3Nk_B T} \sum_{i=1}^N \left(\Gamma_{l=0} + 2S^2 \sum_{l=1}^{\infty} u^l \right) \\ &= \frac{g^2}{3k_B T} S^2 \left(1 + \frac{2u}{1-u} \right) = \frac{g^2 S^2}{3k_B T} \frac{1 + u(\beta JS^2)}{1 - u(\beta JS^2)}. \end{aligned} \quad (5.18)$$

Here we use that for large systems ($N \rightarrow \infty$) the corrections due to boundary contributions is negligible. This susceptibility at high temperature ($k_B T \gg |J|S^2$) follows the Curie behavior

$$\chi_{zz} = \frac{g^2 S^2}{3k_B T} \quad (5.19)$$

irrespective of the sign of J . For the antiferromagnetic coupling χ_{zz} goes through a maximum at $k_B T_{max} \approx 0.238JS^2$ to a finite zero-temperature value. On the other hand, in the ferromagnetic case χ_{zz} diverges at low temperatures

$$\chi_{zz} = \frac{g^2 S^2}{3} \frac{2|J|S^2}{(k_B T)^2}, \quad (5.20)$$

more strongly than the Curie $1/T$ behavior.

Let us now also look at the first lowest order correction in the high-temperature limit,

$$\frac{1}{\chi_{zz}} \approx \frac{3k_B T}{g^2 S^2} \left(1 + \frac{2JS^2}{3k_B T} \right) = \frac{3k_B}{g^2 S^2} (T - \Theta_W) \quad \Rightarrow \quad \chi_{zz} = \frac{C}{T - \Theta_W} \quad (5.21)$$

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. 5.2).

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.5.3). As our discussion in this section shows, there is no ordering at any finite temperature.

5.2 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. We introduce nearest-neighbor interaction and neglect the kinetic energy. Then the Hamiltonian can be formulated as

$$\mathcal{H} = V \sum_{i=1}^L n_i n_{i+1} - \mu \sum_{i=1}^L \left(n_i - \frac{1}{2} \right) \quad (5.22)$$

where the lattice has L sites and we assume periodic boundary conditions such that $i = L + 1 \rightarrow i = 1$. The coupling strength V for the interaction can be attractive ($V < 0$) or repulsive ($V > 0$). The chemical potential is introduced and leave the particle number free, i.e. we work with the 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.

5.2.1 Transfer matrix method

Let us immediately determine the partition function,

$$\mathcal{Z} = \sum_{\{n_i\}} e^{-\beta \mathcal{H}}. \quad (5.23)$$

We introduce the 2×2 -matrix (transfer matrix) for the bonds $(i, i + 1)$,

$$P_{n_i, n_{i+1}} = e^{-\beta[Vn_i n_{i+1} - \mu(n_i + n_{i+1} - 1)/2]} \\ \Rightarrow \quad \hat{P} = \begin{pmatrix} P_{00} & P_{01} \\ P_{10} & P_{11} \end{pmatrix} = \begin{pmatrix} e^{-\beta\mu/2} & 1 \\ 1 & e^{-\beta V + \beta\mu/2} \end{pmatrix}. \quad (5.24)$$

³In 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

$$\begin{aligned}\mathcal{Z}_2 &= \sum_{n_1, n_2} e^{-\beta \mathcal{H}(n_1, n_2)} = \sum_{n_1, n_2} P_{n_1, n_2} P_{n_2, n_1} = \text{tr}\{\hat{P}^2\} \\ &= P_{00}P_{00} + P_{01}P_{10} + P_{10}P_{01} + P_{11}P_{11} = e^{-\beta\mu} + 1 + 1 + e^{-2\beta V + \beta\mu}\end{aligned}\quad (5.25)$$

This allows us to rewrite the sum in the partition function as

$$\mathcal{Z} = \sum_{n_1=0,1} \sum_{n_2=0,1} \cdots \sum_{n_L=0,1} P_{n_1, n_2} P_{n_2, n_3} \cdots P_{n_{L-1}, n_L} P_{n_L, n_1} = \text{tr}\{\hat{P}^L\} = \sum_{n_1=0,1} P_{n_1, n_1}^L, \quad (5.26)$$

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,

$$\lambda_{\pm} = e^{-\beta V/2} \cosh\left(\beta \frac{V-\mu}{2}\right) \pm \sqrt{e^{-\beta V} \sinh^2\left(\beta \frac{V-\mu}{2}\right) + 1} \quad (5.27)$$

and

$$\mathcal{Z} = \lambda_+^L + \lambda_-^L \approx \lambda_+^L \quad \text{for } L \gg 1. \quad (5.28)$$

Then the grand canonical potential and internal energy are given by

$$\Omega(T, \mu) = -k_B T \ln \lambda_+^L = -L k_B T \ln \left[e^{-\beta V/2} \cosh\left(\beta \frac{V-\mu}{2}\right) + \sqrt{e^{-\beta V} \sinh^2\left(\beta \frac{V-\mu}{2}\right) + 1} \right]. \quad (5.29)$$

The particle number of the system can then be calculated easily,

$$N = L \langle n_i \rangle = \frac{L}{2} - \left(\frac{\partial \Omega}{\partial \mu} \right)_T \quad (5.30)$$

and the results are given in Figs.5.3 and 5.4 where $N(\mu)$ is plotted for different temperatures. The two cases show distinct behaviors which is connected with the ground state properties. For attractive interaction N changes in a single step, while for repulsive interactions two steps appear with an intermediate plateau at $N = L/2$.

The zero-temperature limit yields,

$$\Omega(T, \mu) = -\frac{L}{2} \begin{cases} V - |\mu - V| & V < |\mu - V| \\ 0 & V > |\mu - V| \end{cases} \quad (5.31)$$

which leads to

$$N = \frac{L}{2} \begin{cases} 1 + \text{sign}(\mu - V) & V < |\mu - V| \\ 1 & V > |\mu - V| \end{cases} \quad (5.32)$$

The condition $V > |\mu - V|$ is never satisfied for $V < 0$, while it is valid in the range $0 < \mu < 2V$ for $V > 0$. Thus, the case $V < 0$ has two (Fig.5.3) and the case $V > 0$ has three regimes (Fig.5.4), indicating that the two cases are different. Indeed there are two ground states for $V < 0$ correspond to a completely filled or empty lattice, the latter being favored by the attractive interaction. On the other hand, the repulsive interaction $V > 0$ favors an intermediate state where only every second lattice site is occupied.

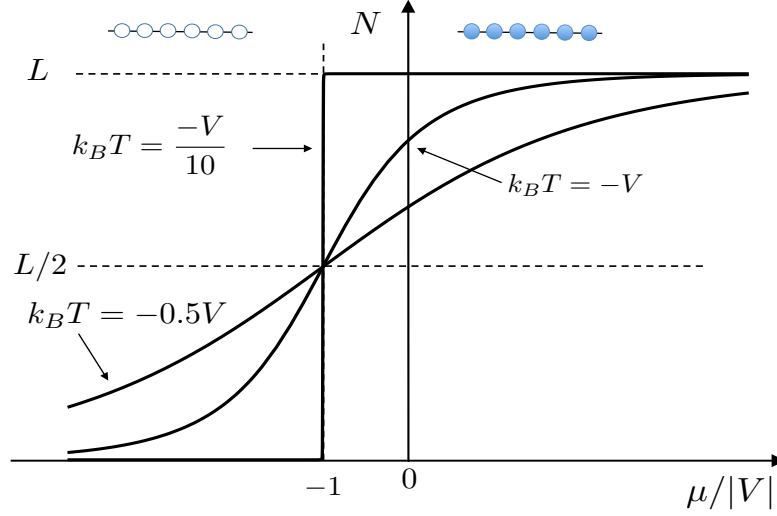


Figure 5.3: Particle number as a function of the chemical potential for $V < 0$ (attractive interaction) for three different temperatures. The ground state corresponds to a completely empty (full) lattice for $\mu < -|V|$ ($\mu > -|V|$).

5.2.2 Correlation function

The transfer matrix method is also very convenient to obtain the correlation function,

$$\Gamma_l = \langle n_i n_{i+l} \rangle - \langle n_i \rangle \langle n_{i+l} \rangle. \quad (5.33)$$

We consider first the average particle density,

$$\begin{aligned} \langle n_i \rangle &= \frac{1}{\mathcal{Z}} \sum_{n_1, \dots, n_L} P_{n_1, n_2} P_{n_2, n_3} \cdots P_{n_{i-1}, n_i} n_i P_{n_i, n_{i+1}} \cdots P_{n_L, n_1} \\ &= \frac{1}{\mathcal{Z}} \text{tr} \left\{ \hat{P}^{i-1} \hat{w} \hat{P}^{L-i} \right\} = \frac{1}{\mathcal{Z}} \text{tr} \left\{ \hat{w} \hat{P}^L \right\} \end{aligned} \quad (5.34)$$

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

$$\hat{U} \hat{P} \hat{U}^{-1} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} = \hat{P}' \quad \text{and} \quad \hat{U} \hat{w} \hat{U}^{-1} = \begin{pmatrix} w'_{00} & w'_{01} \\ w'_{10} & w'_{11} \end{pmatrix} = \hat{w}'. \quad (5.35)$$

This leads to

$$\langle n_i \rangle = \frac{1}{\mathcal{Z}} \text{tr} \left\{ \hat{w}' \hat{P}' \right\} = \frac{w'_{00} \lambda_+^L + w'_{11} \lambda_-^L}{\lambda_+^L + \lambda_-^L} \rightarrow w'_{00}. \quad (5.36)$$

In the same way we treat now

$$\begin{aligned} \langle n_i n_{i+l} \rangle &= \frac{1}{\mathcal{Z}} \text{tr} \left\{ \hat{P}^{i-1} \hat{w} \hat{P}^l \hat{w} \hat{P}^{L-i+l-1} \right\} = \frac{1}{\mathcal{Z}} \text{tr} \left\{ \hat{w} \hat{P}^l \hat{w} \hat{P}^{L-l} \right\} = \frac{1}{\mathcal{Z}} \text{tr} \left\{ \hat{w}' (\hat{P}')^l \hat{w}' (\hat{P}')^{L-l} \right\} \\ &= \frac{w'^2_{00} \lambda_+^L + w'_{01} w'_{10} (\lambda_+^l \lambda_-^{L-l} + \lambda_-^l \lambda_+^{L-l}) + w'^2_{11} \lambda_-^L}{\lambda_+^L + \lambda_-^L} \rightarrow w'^2_{00} + w'_{01} w'_{10} \left(\frac{\lambda_-}{\lambda_+} \right)^l. \end{aligned} \quad (5.37)$$

The correlation function is given by

$$\Gamma_l = w'_{01} w'_{10} \left(\frac{\lambda_-}{\lambda_+} \right)^l = n^2 e^{-l/\xi} [\text{sign}(\lambda_-/\lambda_+)]^l \quad (5.38)$$

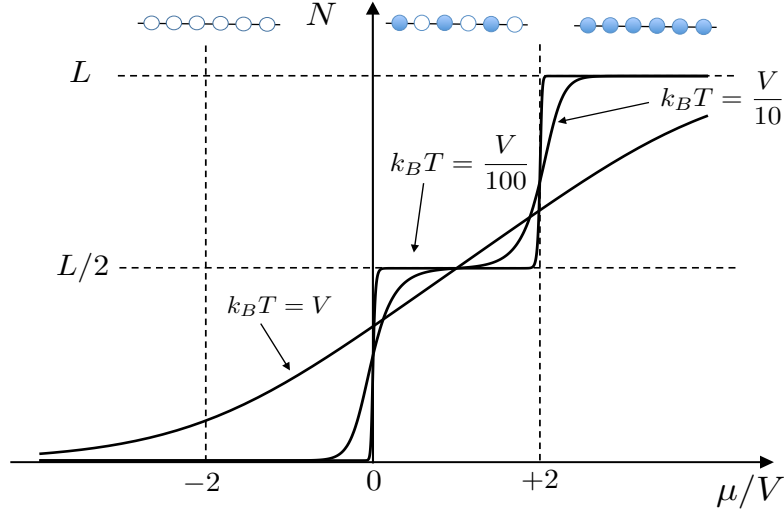


Figure 5.4: Particle number as a function of the chemical potential for $V > 0$ (repulsive interaction) for three different temperatures. The ground state corresponds to a completely empty (full) lattice for $\mu < 0$ ($\mu > 2|V|$) and to a state with every second site only filled for $0 < \mu < 2|V|$.

where we identify $\Gamma_{l=0}$ with n^2 and the correlation length

$$\xi = \frac{1}{\ln|\lambda_+/\lambda_-|}. \quad (5.39)$$

Now let us interpret the correlation function by writing

$$n_i = \langle n_i \rangle + \delta n_i \quad (5.40)$$

where by definition, $\langle n_i \rangle = \langle \langle n_i \rangle + \delta n_i \rangle = \langle n_i \rangle + \langle \delta n_i \rangle$ yields $\langle \delta n_i \rangle = 0$. Thus, the correlation function (5.33) reads also

$$\Gamma_l = \langle \delta n_i \delta n_{i+l} \rangle \quad (5.41)$$

and describes the correlation from the deviation from the average value.

For $V < 0$ the correlation function decays monotonically with the same sign, because the particles rather occupy neighboring sites to benefit from the attractive interaction. If there is a particle on site i we then find, $\delta n_{i+l} > 0$.

In contrast, for $V > 0$ the correlation function shows alternating sign due to the trend to form a particle density modulation, i.e. the particles prefer to occupy only every second lattice site only in order to avoid the energy cost of the repulsive nearest-neighbor interaction. Thus, if there is a particle on site i the neighboring site is more likely unoccupied, i.e. $\delta n_{i\pm 1} < 0$ while the next-nearest neighbors are again more likely occupied with $\delta n_{i\pm 2} > 0$ and so on.

In the special case $\mu = V > 0$ (intermediate range in Fig.5.4) we obtain

$$\Gamma_l = \frac{1}{2}(-\tanh(\beta V/4))^l \quad \text{and} \quad \xi = \frac{1}{\ln|\coth(\beta V/4)|}. \quad (5.42)$$

In the zero-temperature limit ξ diverges, but is finite for any $T > 0$. At $T = 0$ the state is a perfectly alternating particle arrangement with degeneracy 2, as the particles may occupy either all even- or all odd-numbered sites only.

It is important that both the thermodynamics as well as the correlation functions are determined through the eigenvalues of the transfer matrix \hat{P} .

5.3 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,

$$\tilde{\Gamma}_l = \langle \vec{s}_i \cdot \vec{s}_{i+l} \rangle - \langle \vec{s}_i \rangle \cdot \langle \vec{s}_{i+l} \rangle = \langle \delta \vec{s}_i \cdot \delta \vec{s}_{i+l} \rangle \xrightarrow{l \rightarrow \infty} 0 \quad (5.43)$$

which is true for a spin system with or without order ($\delta \vec{s}_i = \vec{s}_i - \langle \vec{s}_i \rangle$). By rewriting

$$\lim_{l \rightarrow \infty} \langle \vec{s}_i \cdot \vec{s}_{i+l} \rangle = \langle \vec{s}_i \rangle \cdot \langle \vec{s}_{i+l} \rangle, \quad (5.44)$$

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

$$\langle \vec{s}_i \rangle = \begin{cases} \hat{z}S & J < 0 \\ \hat{z}(-1)^i S & J > 0 \end{cases} \quad (5.45)$$

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.(5.44) is then finite.⁴ Also the lattice gas in one dimension does not show long-range order except at $T = 0$.

Interestingly, in the case of quantum systems quantum phase fluctuations 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, $\hat{S}_{\text{tot}} = \sum_{i=1}^{N+1} \hat{s}_i$ and \hat{S}_{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),

$$|\Psi_{\text{FM}}\rangle = |\uparrow\uparrow\uparrow \dots\rangle \quad \Rightarrow \quad \hat{S}_{\text{tot}}^z |\Psi_{\text{FM}}\rangle = (N + 1)\hbar s |\Psi_{\text{FM}}\rangle. \quad (5.48)$$

In case of the antiferromagnetic chain the (classical) state with alternating spins $|\Psi_{\text{cAF}}\rangle = |\uparrow\downarrow\uparrow\downarrow \dots\rangle$, is not an eigenstate of the quantum Heisenberg Hamiltonian and consequently not the ground state of the quantum antiferromagnetic chain. Our discussions of the melting transition in Sect. 4.7.3 have shed some light on the role of thermal and quantum fluctuation in this context, and indicate that dimensionality of a system is crucial for the stability of ordered phases.

⁴Previously we encountered long-range order in a Bose-Einstein condensate looking at the correlation function in Eqs.(4.109) and (4.117). Extending the correlation function to

$$\tilde{g}(\vec{R}) = \langle \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r} + \vec{R}) \rangle - \langle \hat{\Psi}^\dagger(\vec{r}) \rangle \langle \hat{\Psi}(\vec{r} + \vec{R}) \rangle, \quad (5.46)$$

we find that always $\lim_{\vec{R} \rightarrow \infty} \tilde{g}(\vec{R}) = 0$, since with the Bogolyubov approximation,

$$\lim_{\vec{R} \rightarrow \infty} \langle \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r} + \vec{R}) \rangle = \lim_{\vec{R} \rightarrow \infty} \langle \hat{\Psi}^\dagger(\vec{r}) \rangle \langle \hat{\Psi}(\vec{r} + \vec{R}) \rangle = \lim_{\vec{R} \rightarrow \infty} \psi_0^*(\vec{r}) \psi_0(\vec{r} + \vec{R}) = n_0 \quad (5.47)$$

for $T < T_c$ and a constant phase ϕ of $\psi_0(\vec{r})$.

Chapter 6

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 a 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 $F(T, V, N, \dots)$ and the Gibbs free energy $G(T, p, N, \dots)$,

$$F = U - TS \quad \text{and} \quad G = H - TS. \quad (6.1)$$

These potentials show anomalies (singularities) at the phase transition.

In this chapter we will consider the Ising model as one of the simplest models to describe phase transitions from a statistical physics point of view. Based on this model we will introduce various ways and concepts of addressing phase transitions.

6.1 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 n^{th} order, if the following properties hold:

$$\left. \left(\frac{\partial^m G}{\partial T^m} \right)_p \right|_{T=T_{c+}} = \left. \left(\frac{\partial^m G}{\partial T^m} \right)_p \right|_{T=T_{c-}} \quad \text{and} \quad \left. \left(\frac{\partial^m G}{\partial p^m} \right)_{T=T_{c+}} = \left. \left(\frac{\partial^m G}{\partial p^m} \right)_{T=T_{c-}} \quad (6.2)$$

for $m \leq n - 1$, and

$$\left. \left(\frac{\partial^n G}{\partial T^n} \right)_p \right|_{T=T_{c+}} \neq \left. \left(\frac{\partial^n G}{\partial T^n} \right)_p \right|_{T=T_{c-}} \quad \text{and} \quad \left. \left(\frac{\partial^n G}{\partial p^n} \right)_{T=T_{c+}} \neq \left. \left(\frac{\partial^n G}{\partial p^n} \right)_{T=T_{c-}} \quad (6.3)$$

The same definition is used for the free energy. In practice this classification is rarely used beyond $n = 2$.

$n = 1$: A discontinuity is found in the entropy and in the volume:

$$S = - \left(\frac{\partial G}{\partial T} \right)_p \quad \text{and} \quad V = \left(\frac{\partial G}{\partial p} \right)_T \quad (6.4)$$

The discontinuity of the entropy experimentally corresponds to 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.

$n = 2$: 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:

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p, \kappa_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2} \right)_T, \alpha = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial p} \right) \quad (6.5)$$

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 as 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:

$$dG_l = dG_g \quad \Rightarrow \quad -S_l dT + V_l dp = -S_g dT + V_g dp. \quad (6.6)$$

This allows us to get from the vapor pressure curve ($p(T)$ at the phase boundary in the p - T -plane) the relation

$$\frac{dp}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T \Delta V} \quad (6.7)$$

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 :

$$S_A(T, p) = S_B(T, p) \quad \text{and} \quad V_A(T, p) = V_B(T, p), \quad (6.8)$$

which yields the relations through the equality of their differentials,

$$dS_A = \left(\frac{\partial S_A}{\partial T} \right)_p dT + \left(\frac{\partial S_A}{\partial p} \right)_T dp = \left(\frac{\partial S_B}{\partial T} \right)_p dT + \left(\frac{\partial S_B}{\partial p} \right)_T dp = dS_B, \quad (6.9)$$

$$dV_A = \left(\frac{\partial V_A}{\partial T} \right)_p dT + \left(\frac{\partial V_A}{\partial p} \right)_T dp = \left(\frac{\partial V_B}{\partial T} \right)_p dT + \left(\frac{\partial V_B}{\partial p} \right)_T dp = dV_B.$$

We now use the Maxwell relation

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p = -V\alpha \quad (6.10)$$

and obtain

$$\frac{dp}{dT} = - \frac{\left(\frac{\partial S_B}{\partial T} \right)_p - \left(\frac{\partial S_A}{\partial T} \right)_p}{\left(\frac{\partial S_B}{\partial p} \right)_T - \left(\frac{\partial S_A}{\partial p} \right)_T} = \frac{\Delta C_p}{TV \Delta \alpha} \quad (6.11)$$

and analogously

$$\frac{dp}{dT} = - \frac{\left(\frac{\partial V_B}{\partial T} \right)_p - \left(\frac{\partial V_A}{\partial T} \right)_p}{\left(\frac{\partial V_B}{\partial p} \right)_T - \left(\frac{\partial V_A}{\partial p} \right)_T} = \frac{\Delta \alpha}{\Delta \kappa_T}. \quad (6.12)$$

Various other relations exist and are of experimental importance.

6.2 Phase transition in the Ising model

To discuss a concrete system we introduce here 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 5). We write the model Hamiltonian as

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j - \sum_i s_i H. \quad (6.13)$$

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 and the Ising model may also be considered as an extreme limit of anisotropic spin-spin interaction, where only one component of the spins couples to neighboring spins.

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.

6.2.1 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 (quadratic lattice) case. For three dimensions only numerical simulations or approximative calculations are possible. One rather frequently used approximative method to study the phase transition and the magnetically ordered phase is the so-called mean field approximation. In the lattice model we can consider each spin s_i as being coupled to a reservoir consisting 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, as we will show below.

Let us now tackle the problem in a more systematic way. We rewrite the spin for each site

$$s_i = \langle s_i \rangle + (s_i - \langle s_i \rangle) = m + (s_i - m) = m + \delta s_i \quad (6.14)$$

and insert it into the Hamiltonian, where we approximate $\langle s_i \rangle = m$ uniformly.

$$\begin{aligned} \mathcal{H} &= -J \sum_{\langle i,j \rangle} \{m + (s_i - m)\} \{m + (s_j - m)\} - \sum_i s_i H \\ &= -J \sum_{\langle i,j \rangle} \{m^2 + m(s_i - m) + m(s_j - m) + \delta s_i \delta s_j\} - \sum_i s_i H \\ &= -J \sum_i \left(z m s_i - \frac{z}{2} m^2 \right) - \sum_i s_i H - J \sum_{\langle i,j \rangle} \delta s_i \delta s_j. \end{aligned} \quad (6.15)$$

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,

$$E_{ij} = \frac{\langle \delta s_i \delta s_j \rangle}{\langle s_i \rangle \langle s_j \rangle} = \frac{\langle \delta s_i \delta s_j \rangle}{m^2} \ll 1, \quad (6.16)$$

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 will be important in the context of the *critical phenomena*. We now write the mean field Hamiltonian

$$\mathcal{H}_{mf} = - \sum_i s_i h_{\text{eff}} + NJ \frac{z}{2} m^2 \quad \text{with} \quad h_{\text{eff}} = Jzm + H, \quad (6.17)$$

which has the form of an ideal paramagnet in a magnetic field h_{eff} . It is easy to calculate the partition function and the free energy as a function of the parameter m ,

$$\begin{aligned} Z_N(T, m, H) &= \prod_i \sum_{s_i = \pm s} e^{-\beta Jzm^2/2 + \beta h_{\text{eff}} s_i} = \left\{ \sum_{\bar{s} = \pm s} e^{-\beta Jzm^2/2 + \beta h_{\text{eff}} \bar{s}} \right\}^N \\ &= e^{-\beta Jzm^2 N/2} \{2 \cosh(\beta s h_{\text{eff}})\}^N \end{aligned} \quad (6.18)$$

and

$$F(T, H, m) = -k_B T \ln Z_N = NJ \frac{z}{2} m^2 - Nk_B T \ln \{2 \cosh(\beta s h_{\text{eff}})\}. \quad (6.19)$$

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,

$$0 = \frac{\partial F}{\partial m} = NJzm - NJzs \tanh(\beta s h_{\text{eff}}). \quad (6.20)$$

This equation is equivalent to the self-consistence equation for the mean value of s_i :

$$m = \langle s_i \rangle = \frac{e^{-\beta Jzm^2 N/2}}{Z_N} \sum_{\{s_j\}} s_i e^{\sum_{i'=1}^N s_{i'} h_{\text{eff}}} = \frac{\sum_{s_i = \pm s} s_i e^{\beta s_i h_{\text{eff}}}}{\sum_{s_i = \pm s} e^{\beta s_i h_{\text{eff}}}} = s \tanh(\beta s h_{\text{eff}}) = -\frac{1}{N} \left(\frac{\partial F}{\partial H} \right)_{T, m} \quad (6.21)$$

This is a non-linear equation whose solution determines m and eventually through the free energy all thermodynamic properties. In zero magnetic field this equation is given as

$$m = s \tanh \left(\frac{Jzsm}{k_B T} \right) \quad (6.22)$$

which yields Fig.6.1 for a graphical solution. ¹

¹*Variational approach:* Consider the Ising model (6.13) 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

$$\omega(M) = \frac{N!}{\left[\frac{1}{2}(N+M)\right]! \left[\frac{1}{2}(N-M)\right]!} \quad (6.23)$$

configurations corresponding to a given M . We may now determine the free energy as $F = U - TS = \langle H \rangle_M - k_B T \ln \omega(M)$ in the following way:

$$U = \langle H \rangle_M = -J \sum_{\langle i, j \rangle} \langle s_i s_j \rangle = -\frac{JNzs^2}{2} (w_+ w_+ + w_- w_- - w_+ w_- - w_- w_+) = -\frac{JNzs^2}{2} \tilde{m}^2 \quad (6.24)$$

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. $w_+ w_+ + w_- w_- - w_+ w_- - w_- w_+$ ($w_+ w_- + w_- w_+$) 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,

$$TS = k_B T \ln \omega(M) \approx Nk_B T \left[\ln 2 - \frac{1}{2}(1 + \tilde{m}) \ln(1 + \tilde{m}) - \frac{1}{2}(1 - \tilde{m}) \ln(1 - \tilde{m}) \right]. \quad (6.25)$$

Thus, we have expressed the free energy by a variational phase represented by independent spins whose variational

6.2.2 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

$$\chi(T) = N \left. \frac{d\langle s_i \rangle}{dH} \right|_{H=0} = - \left. \frac{d^2 F}{dH^2} \right|_{H=0} = - \left. \frac{d}{dH} \left\{ \frac{\partial F}{\partial H} + \frac{\partial F}{\partial m} \frac{\partial m}{\partial H} \right\} \right|_{H=0} = - \left. \frac{d}{dH} \frac{\partial F}{\partial H} \right|_{H=0} \quad (6.27)$$

where we used the equilibrium condition (6.20). Thus we obtain

$$\begin{aligned} \chi(T) &= N \left. \frac{dm}{dH} \right|_{H=0} = N s \left. \frac{d}{dH} \tanh [\beta(Jzs m(H) + sH)] \right|_{H=0} \\ &= \frac{Ns}{k_B T} \left\{ Jzs \left. \frac{dm}{dH} \right|_{H=0} + s \right\} = \frac{s}{k_B T} Jzs \chi(T) + \frac{Ns^2}{k_B T} . \end{aligned} \quad (6.28)$$

where we used that for a paramagnet $m(H=0) = 0$. This leads to the susceptibility

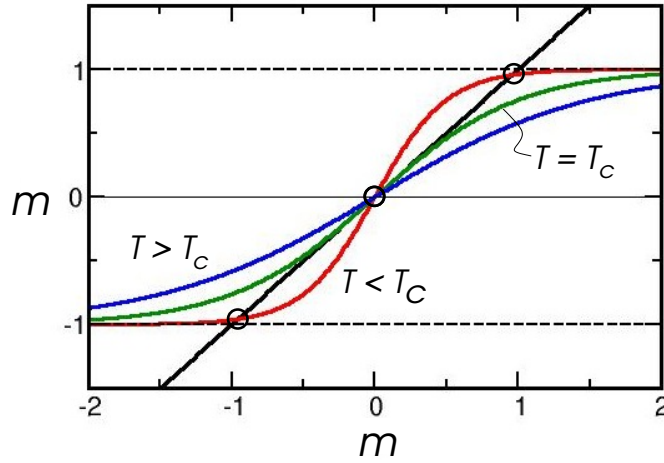


Figure 6.1: Graphical solution of the self-consistency equation (6.22). The crossing points of the straight line and the step-like function gives the solution. There is only one solution at $m = 0$ for $T \geq T_c$ and three solutions for $T < T_c$.

$$\chi(T) = \frac{Ns^2}{k_B T - Jzs^2} \quad (6.29)$$

which is modified compared to that of the ideal paramagnet. If $k_B T \rightarrow Jzs^2$ from above $\chi(T)$ is singular. We define this as the critical temperature

$$T_c = \frac{Jzs^2}{k_B} . \quad (6.30)$$

parameter is the mean moment $m = \langle s \rangle = s(w_+ - w_-) = s\tilde{m}$. We minimize F with respect to \tilde{m} ,

$$0 = \frac{\partial F}{\partial \tilde{m}} = -Jzs^2 N \tilde{m} + \frac{Nk_B T}{2} \ln \left(\frac{1 + \tilde{m}}{1 - \tilde{m}} \right) \Rightarrow \tilde{m} = \tanh \left(\frac{Jzs^2 \tilde{m}}{k_B T} \right) \quad (6.26)$$

which corresponds to Eq.(6.22) 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.

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 (6.22) in the absence of a magnetic field. Looking at Fig. 6.1 we find that indeed the critical temperature T_c plays an important role in separating two types of solutions of Eq.(6.22). 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. From Fig.6.1 we see that the critical temperature can be derived from Eq.(6.22) by requiring that the slope of both sides at $m = 0$ is identical. Thus taking the derivative we find

$$1 = \frac{Jzs^2}{k_B T} \cosh^{-2} \left(\frac{Jzsm}{k_B T} \right) \Big|_{m=0} = \frac{Jzs^2}{k_B T} \quad \Rightarrow \quad T_c = \frac{Jzs^2}{k_B} \quad (6.31)$$

which agrees with Eq.(6.30).

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.

$$F(T, H, m) \approx NJz \left[\frac{m^2}{2} - \frac{k_B T}{Jz} \left\{ \frac{(\beta sh_{\text{eff}})^2}{2} - \frac{(\beta sh_{\text{eff}})^4}{12} \right\} \right] - Nk_B T \ln 2 \quad (6.32)$$

For $H = 0$ we obtain

$$\begin{aligned} F(T, H = 0, m) &\approx F_0(T) + NJz \left[\left(1 - \frac{T_c}{T} \right) \frac{m^2}{2} + \frac{1}{12s^2} \left(\frac{T_c}{T} \right)^3 m^4 \right] \\ &\approx F_0(T) + NJz \left[\left(\frac{T}{T_c} - 1 \right) \frac{m^2}{2} + \frac{m^4}{12s^2} \right] \end{aligned} \quad (6.33)$$

where for the last step we took into account that our expansion is only valid for $T \approx T_c$. Moreover, $F_0 = -Nk_B T \ln 2$. This form of the free energy expansion is the famous Landau theory of a continuous phase transition (for more details see later in Sect.6.4).

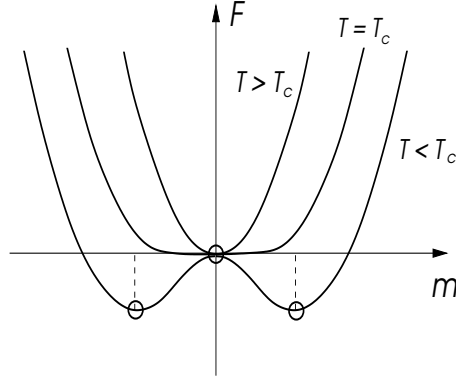


Figure 6.2: Landau free energy: $T > T_c$: 2^{nd} -order term is positive and minimum of F at $m = 0$; $T = T_c$, 2^{nd} vanishes and free energy minimum at $m = 0$ becomes very shallow; $T < T_c$: 2^{nd} -order term is negative and minimum of F is at finite value of m , bounded by the 4^{th} -order 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 (2^{nd} -order) changes sign and a finite value of m minimizes F (see Fig. 6.2). The minimization leads to

$$m(T) = \begin{cases} \pm s\sqrt{3\tau} & T < T_c \\ 0 & T \geq T_c \end{cases} \quad (6.34)$$

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

$$F(T) = F_0(T) - \frac{3Nk_B T_c \tau^2}{4} \Theta(\tau) \quad \text{and} \quad S(T) = -\frac{\partial F(T)}{\partial T} = Nk_B \ln 2 - \frac{3Nk_B \tau}{2} \Theta(\tau), \quad (6.35)$$

and eventually we obtain for the heat capacity,

$$\frac{C}{T} = \frac{\partial S}{\partial T} = \frac{3Nk_B}{2T_c} \Theta(\tau) + C_0 \quad (6.36)$$

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.

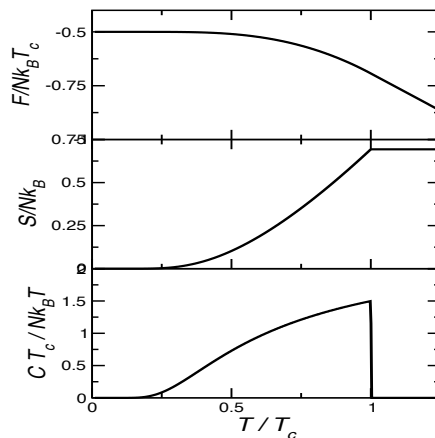


Figure 6.3: Thermodynamic quantities within mean field theory. Free energy, entropy and heat capacity.

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 behavior for the whole temperature range as shown in Fig. 6.3. 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.

6.2.3 Phase diagram

So far we have concentrated on the situation without magnetic field. In this case the phase transition leads to one of two degenerate ordered phases, $m = +|m|$ or $m = -|m|$. An applied magnetic field lifts this degeneracy by introducing a bias for one of the two states, favoring the order with m parallel to the field. In a finite field the transition turns into a crossover, since there is already a driven 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. 6.4).

Next we turn to the behavior of the magnetization m as a function of the magnetic field and temperature (illustrated in Fig. 6.5 and 6.6). 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.

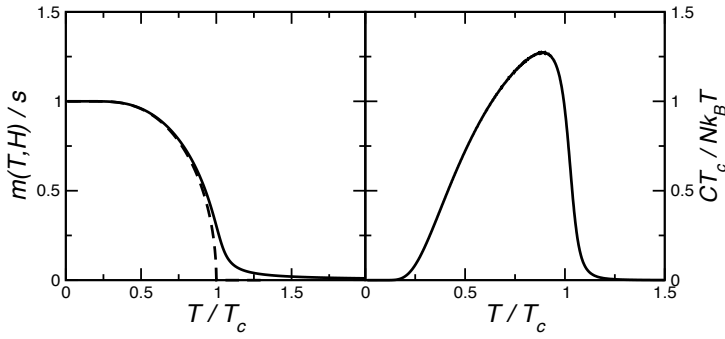


Figure 6.4: Ising system in a finite magnetic field: (left panel) Magnetization as a function of temperature in a fixed magnetic field (solid line) and in zero field (dashed line); (right panel) heat capacity for a fixed magnetic field. In a magnetic field no sharp transition exists.

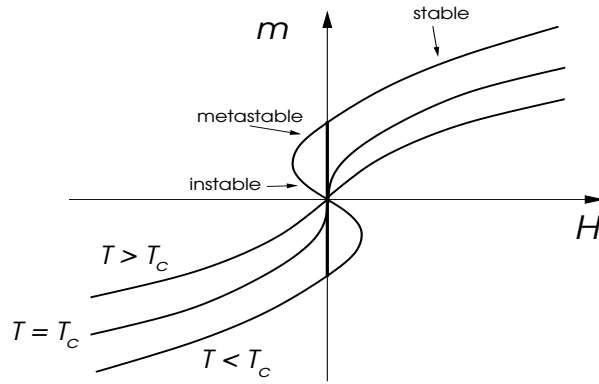


Figure 6.5: Magnetization as a function of magnetic field for different temperatures.

For all temperatures $T > T_c$, the magnetization $m(H)$ is a single-valued function in Fig. 6.5. 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.² 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

²*Metastable and unstable states:* We consider the uniform free energy of the magnetization m including the Zeeman coupling to the external field H , $F'(m, H) = F(m) - mH$. The (local) minimum of the free energy is determined by

$$\frac{\partial F'}{\partial m} = \frac{\partial F}{\partial m} - H = 0 \quad \text{and} \quad \frac{\partial^2 F'}{\partial m^2} = \frac{\partial^2 F}{\partial m^2} > 0. \quad (6.37)$$

while a local maximum has a negative second derivative. Considering the derivative with respect to H at the extrema defined by Eq.(6.37), for $m = m(H)$,

$$\frac{d}{dH} \frac{\partial F'}{\partial m} \Big|_{m=m(H)} = \frac{\partial^2 F}{\partial m^2} \frac{dm}{dH} \Big|_{m=m(H)} - 1 = 0. \quad (6.38)$$

Therefore,

$$\chi = \frac{dm}{dH} = \begin{cases} \left(\frac{\partial^2 F}{\partial m^2}\right)^{-1} > 0 & \text{stable / metastable} \\ \left(\frac{\partial^2 F}{\partial m^2}\right)^{-1} < 0 & \text{unstable.} \end{cases} \quad (6.39)$$

encounter a level-crossing of the free energy for the two states at $H = 0$ and the 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).³

This is visualized in a three-dimensional graph in m , H and T (Fig. 6.6). The shaded region appearing for $T < T_c$ is the region where the two degenerate phases coexist. As m is changed in this region, the fraction of the two degenerate finite magnetization phases is changed continuously following a Maxwell construction.

$$m(q) = q|m(H = 0, T)| + (1 - q)\{-|m(H = 0, T)|\} = (2q - 1)|m(H = 0, T)| \quad (6.40)$$

where q can change continuously with $0 \leq q \leq 1$. This may be viewed as domains of the two states changing in size.

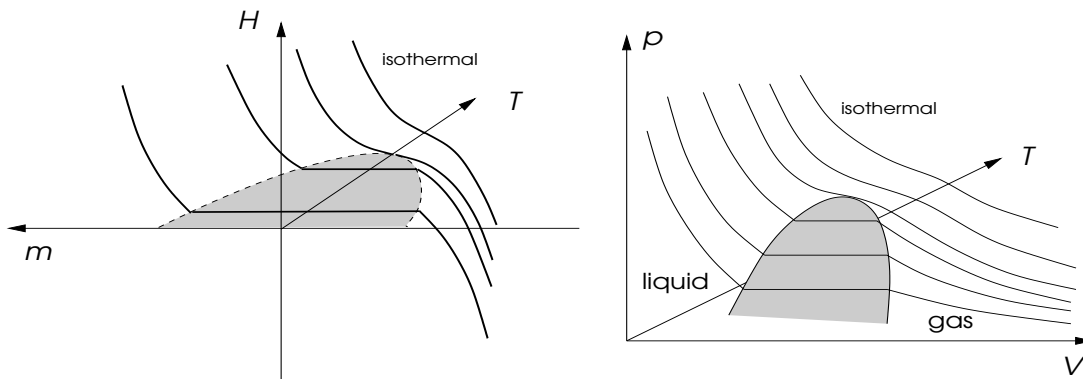


Figure 6.6: Left panel: phase diagram of ferromagnetic Ising model in (H, m, T) ; right panel: phase diagram of the liquid-gas transition in (p, V, T) . In both cases the shaded region represents a coexistence region.

In the H - T -plane this shaded region is simply a line for the first order transition of a discontinuously changing magnetization.

6.3 Gaussian transformation

We analyze the mean field approximation in a different formulation, using the Gaussian transformation. The partition function of the Ising model can be rewritten by introducing a continuous

³Note 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.

auxiliary field ϕ_i :

$$\begin{aligned}
Z &= \sum_{\{s_i\}} e^{-\frac{\beta}{2} \sum_{i,j} J_{ij} s_i s_j + \beta \sum_i s_i H_i} \\
&= \frac{1}{(2\pi k_B T)^{N/2} \sqrt{\det J}} \int_{-\infty}^{+\infty} \left(\prod_{i'} d\phi_{i'} \right) e^{\frac{\beta}{2} \sum_{i,j} (J^{-1})_{ij} (\phi_i - H_i) (\phi_j - H_j)} \prod_i \sum_{s_i = \pm s} e^{\beta \phi_i s_i} \\
&= \frac{1}{(2\pi k_B T)^{N/2} \sqrt{\det J}} \int_{-\infty}^{+\infty} \left(\prod_{i'} d\phi_{i'} \right) e^{\frac{\beta}{2} \sum_{i,j} (J^{-1})_{ij} (\phi_i - H_i) (\phi_j - H_j) + \sum_i \ln[2 \cosh(\beta s \phi_i)]}
\end{aligned} \tag{6.41}$$

where we use the $N \times N$ -matrix

$$J_{ij} = \begin{cases} -J & (i, j) \text{ nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \tag{6.42}$$

and $(J^{-1})_{ij}$ is the inverse of J_{ij} . We assume the magnetic field to be site dependent, which will be convenient later. We used the identity

$$\begin{aligned}
\int_{-\infty}^{+\infty} d\phi e^{-\frac{\phi^2}{2a} + s\phi} &= e^{\frac{a}{2}s^2} \int_{-\infty}^{+\infty} d\phi e^{-\frac{1}{2a}(\phi - sa)^2} = \sqrt{2\pi a} e^{\frac{a}{2}s^2} \\
\Rightarrow \int_{-\infty}^{+\infty} \left(\prod_i d\phi_i \right) e^{-\frac{1}{2} \sum_{i,j} \phi_i (A^{-1})_{ij} \phi_j + \sum_i \phi_i s_i} &= (2\pi)^{N/2} \sqrt{\det A} e^{\frac{1}{2} \sum_{ij} s_i A_{ij} s_j}
\end{aligned} \tag{6.43}$$

with A being a positive definite $N \times N$ -matrix. This exact rewriting of the partition function is called Gaussian transformation (also known as Hubbard-Stratonovich transformation).⁴ 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

$$Z = C \int_{-\infty}^{+\infty} \left(\prod_{i'} d\phi_{i'} \right) e^{-\beta S(\phi_i, H_i)} = e^{-\beta F} \tag{6.44}$$

with $C = 1/(2\pi k_B T)^{N/2} \sqrt{\det J}$ and

$$S(\phi_i, H_i) = -\frac{1}{2} \sum_{i,j} (J^{-1})_{ij} (\phi_i - H_i) (\phi_j - H_j) - \frac{1}{\beta} \sum_i \ln[2 \cosh(\beta s \phi_i)]. \tag{6.45}$$

The evaluation of these integrals in Eq.(6.44) is, however, as difficult as it was to determine the partition function for the original formulation with Ising spins. One approximation is based on the proposal that the integral is dominated by the maximum of the integrand. The type of evaluation is known as saddle point approximation (sometimes also called method of steepest descent). Thus, one replaces the auxiliary field by the value $\bar{\phi}_i$ which dominates the integral for the partition function.⁵ This method is similar to discussions we had earlier when we tested the equivalence of different ensembles, although statistically less reliable as we will see later. It relies on the assumption that the fluctuations of the field ϕ_i around $\bar{\phi}_i$ are small - something

⁴Reference: "Field Theory, the Renormalization Group, and Critical Phenomena", Daniel J. Amit, World Scientific.

⁵Method of steepest descent: We consider the integral

$$I = \int_a^b e^{Ng(x)} dx \tag{6.46}$$

which has to be tested. Therefore we look for the minimum of S now and approximate Z then by

$$Z \approx C e^{-\beta S(\bar{\phi}_i, H_i)} \quad \text{with} \quad 0 = \left. \frac{\partial S}{\partial \phi_i} \right|_{\phi_i = \bar{\phi}_i} = - \sum_j (J^{-1})_{ij} (\bar{\phi}_j - H_j) - s \tanh(\beta s \bar{\phi}_i) \quad (6.49)$$

which leads to the saddle-point equation

$$\bar{\phi}_i = H_i - s \sum_j J_{ij} \tanh(\beta s \bar{\phi}_j) \quad (6.50)$$

For $H_i = 0$ the saddle point is given by the uniform solution $\bar{\phi}_i = \bar{\phi}$, satisfying

$$\bar{\phi} = -s \sum_j J_{ij} \tanh(\beta s \bar{\phi}) = J z s \tanh(\beta s \bar{\phi}) . \quad (6.51)$$

This yields the same critical temperature for the onset of a finite solution for $\bar{\phi}$ as the mean field solution, following the same scheme of discussion as above. The relation to m of the mean field approximation is given by the condition

$$\langle s_i \rangle = k_B T \frac{\partial \ln Z}{\partial H_i} = - \frac{dS(\bar{\phi}_i, H_i)}{dH_i} = - \frac{\partial S}{\partial H_i} = - \sum_j (J^{-1})_{ij} (\bar{\phi}_j - H_j) = s \tanh(\beta s \bar{\phi}_i) \quad (6.52)$$

such that

$$m = s \tanh(\beta s \bar{\phi}) \quad \Rightarrow \quad \bar{\phi} = J z m . \quad (6.53)$$

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.

6.3.1 Correlation function and susceptibility

We consider first the correlation function

$$\Gamma_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle = (k_B T)^2 \frac{\partial^2 \ln Z}{\partial H_i \partial H_j} \approx -k_B T \frac{d^2 S(\bar{\phi}_i, H_i)}{dH_i dH_j} . \quad (6.54)$$

With (6.52) we obtain

$$\beta \Gamma_{ij} = \frac{d}{dH_j} s \tanh(\beta s \bar{\phi}_i) = \beta s^2 \cosh^{-2}(\beta s \bar{\phi}) \frac{d\bar{\phi}_i}{dH_j} \quad (6.55)$$

which if inverted yields

$$\Gamma_{ij}^{-1} = \frac{1}{s^2} \cosh^2(\beta s \bar{\phi}) \frac{dH_j}{d\bar{\phi}_i} = \frac{1}{s^2} \cosh^2(\beta s \bar{\phi}) \left\{ \delta_{ij} + \frac{\beta s^2 J_{ij}}{\cosh^2(\beta s \bar{\phi})} \right\} \quad (6.56)$$

and $N \gg 1$ and $g(x)$ a function with a unique maximum at $x = \bar{x}$ in the interval $[a, b]$, i.e.

$$g(x) = g(\bar{x}) + g'(\bar{x})(x - \bar{x}) + \frac{1}{2} g''(\bar{x})(x - \bar{x})^2 + \dots . \quad (6.47)$$

For the maximum, the conditions $g'(\bar{x}) = 0$ and $g''(\bar{x}) < 0$ holds. We approximate the integral

$$I \approx e^{Ng(\bar{x})} \int_a^b dx e^{-\frac{1}{2} N |g''(\bar{x})| (x - \bar{x})^2} \approx e^{Ng(\bar{x})} \int_{-\infty}^{+\infty} dx e^{-\frac{1}{2} N |g''(\bar{x})| (x - \bar{x})^2} = \left(\frac{2\pi}{N |g''(\bar{x})|} \right)^{1/2} e^{Ng(\bar{x})} \quad (6.48)$$

which is exact in the limit $N \rightarrow \infty$. Considering $\ln I$ we find that $\ln I \approx Ng(\bar{x}) + O(\ln N)$.

where we use (6.50)

$$H_j = \bar{\phi}_j + s \sum_{j'} J_{jj'} \tanh(\beta s \bar{\phi}_{j'}) \quad \Rightarrow \quad \frac{dH_j}{d\bar{\phi}_i} = \delta_{ij} + \frac{\beta s^2 J_{ij}}{\cosh^2(\beta s \bar{\phi})}. \quad (6.57)$$

The following Fourier-transformations lead to a simple form for (6.56),⁶

$$J_{ij} = \frac{1}{N} \sum_{\vec{q}} J(\vec{q}) e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}, \quad \Gamma_{ij} = \frac{1}{N} \sum_{\vec{q}} \Gamma(\vec{q}) e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}, \quad \delta_{ij} = \frac{1}{N} \sum_{\vec{q}} e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \quad (6.62)$$

with

$$\Gamma(\vec{q}) = \frac{k_B T \Gamma_0}{1 + \Gamma_0 J(\vec{q})} \quad \text{with} \quad \Gamma_0 = \frac{\beta s^2}{\cosh^2(\beta s \bar{\phi})} = \beta s^2 \{1 - \tanh^2(\beta s \bar{\phi})\} = \beta (s^2 - m^2), \quad (6.63)$$

using (6.53). On a d -dimensional hypercubic lattice with only nearest-neighbor coupling, we obtain for the Fourier transformed coupling strength,

$$J(\vec{q}) = \frac{1}{N} \sum_{i,j} J_{ij} e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} = -2J \sum_{\alpha=1}^d \cos q_\alpha a \quad (6.64)$$

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

$$J(\vec{q}) \approx -Jz + Jq^2 a^2 \quad (6.65)$$

$$\Rightarrow \quad \Gamma(\vec{q}) \approx \frac{k_B T}{\frac{k_B T}{s^2 - m^2} - Jz + Jq^2 a^2} \approx \frac{k_B T s^2}{k_B (T - T_c) + J s^2 q^2 a^2 + k_B T m^2 / s^2}$$

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,

$$\Gamma(\vec{q}) = \frac{A}{1 + \xi^2 q^2} \quad (6.66)$$

where ξ is the correlation length, as introduced in (5.13).

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.

$$\chi = \beta \sum_{i,j} \{ \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle \} = \beta \sum_{i,j} \Gamma_{ij} = N \beta \Gamma(\vec{q} = 0) = \frac{N s^2}{k_B (T - T_c) + k_B T m^2 / s^2} \quad (6.67)$$

⁶For 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

$$a_i = \sum_j \Gamma_{ij}^{-1} b_j \quad \Rightarrow \quad \sum_j \Gamma_{ij} a_j = b_i. \quad (6.58)$$

We perform now the Fourier transform of the second equation,

$$\frac{1}{N} \sum_i \sum_j \Gamma_{ij} a_j e^{-i\vec{q} \cdot \vec{r}_i} = \frac{1}{N} \sum_i \sum_j \Gamma_{ij} a_j e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} e^{-i\vec{q} \cdot \vec{r}_j} = \Gamma(\vec{q}) a(\vec{q}) = \frac{1}{N} \sum_i b_i e^{-i\vec{q} \cdot \vec{r}_i} = b(\vec{q}). \quad (6.59)$$

On the other hand, we find

$$\frac{1}{N} \sum_i \sum_j \Gamma_{ij}^{-1} b_j e^{-i\vec{q} \cdot \vec{r}_i} = \frac{1}{N} \sum_i \sum_j \Gamma_{ij}^{-1} b_j e^{-i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} e^{-i\vec{q} \cdot \vec{r}_j} = \Gamma^{-1}(\vec{q}) b(\vec{q}) = \frac{1}{N} \sum_i a_i e^{-i\vec{q} \cdot \vec{r}_i} = a(\vec{q}), \quad (6.60)$$

leading to the relation

$$\Gamma^{-1}(\vec{q}) = \frac{1}{\Gamma(\vec{q})}, \quad (6.61)$$

which is a convenient way to handle the inverted matrix Γ_{ij}^{-1} .

We use now the earlier mean field result for $m^2 = 3s^2\tau$ in (6.34) and obtain for the regime very close to T_c the behavior,

$$\chi(T) = \begin{cases} \frac{Ns^2}{k_B(T - T_c)} & T > T_c, \\ \frac{Ns^2}{2k_B|T - T_c|} & T < T_c, \end{cases} \quad (6.68)$$

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 $r \rightarrow \infty$. 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 large \vec{q} such that in $\Gamma(\vec{q})$ only small \vec{q} are important.

For simplicity we consider only the three-dimensional case,

$$\begin{aligned} \Gamma_{\vec{r}} &= \int \frac{d^3q}{(2\pi)^3} \Gamma(\vec{q}) e^{i\vec{q}\cdot\vec{r}} \approx \frac{A}{4\pi^2} \int_0^\infty dq q^2 \int d\theta \sin\theta \frac{e^{iqr \cos\theta}}{1 + \xi^2 q^2} = \frac{A}{4\pi^2 i r} \int_0^\infty dq q \frac{e^{iqr} - e^{-iqr}}{1 + \xi^2 q^2} \\ &= \frac{A}{4\pi^2 i r} \int_{-\infty}^{+\infty} dq q \frac{e^{iqr}}{1 + \xi^2 q^2} = \frac{A}{4\pi} \frac{e^{-r/\xi}}{r \xi^2} = \frac{k_B T}{4\pi J} \frac{e^{-r/\xi}}{r} \end{aligned} \quad (6.69)$$

where we used residue calculation for the last integral and introduced the parametrization,

$$A = \frac{s^2}{1 - T_c/T} = \frac{k_B T \xi^2}{J a^2} \quad \text{and} \quad \xi^2 = \frac{J s^2 a^2}{k_B (T - T_c)}. \quad (6.70)$$

The general form of the correlation function for other dimensions d is

$$\Gamma_{\vec{r}} \propto \frac{e^{-r/\xi}}{r^{(d-1)/2}} \quad (6.71)$$

if $T > T_c$.⁷ In all cases there is a correlation length which diverges as we approach $T \rightarrow T_{c+}$. At T_c we find

$$\Gamma_{\vec{r}} = \frac{k_B T}{J a^2} \int \frac{d^d q}{(2\pi)^d} \frac{e^{i\vec{q}\cdot\vec{r}}}{q^2} \propto \begin{cases} \ln r & d = 2 \\ r^{2-d} & d \neq 2 \end{cases} \quad (6.75)$$

This suggests that for $T \rightarrow T_{c+}$ the correlation function should rather behave as

$$\Gamma_{\vec{r}} \propto \begin{cases} \ln r e^{-r/\xi} & d = 2 \\ \frac{e^{-r/\xi}}{r^{d-2}} & d \neq 2 \end{cases} \quad (6.76)$$

⁷Note that the correlation function in \vec{q} -space

$$\Gamma(\vec{q}) = \frac{A}{1 + \xi^2 \vec{q}^2} \quad \Leftrightarrow \quad (1 + \xi^2 \vec{q}) \Gamma(\vec{q}) = A \quad (6.72)$$

is the Fourier transform of the differential equation

$$A \delta(\vec{r}) = \{1 - \xi^2 \vec{\nabla}^2\} \Gamma_{\vec{r}} = \left\{ 1 - \frac{\xi^2}{r^{d-1}} \frac{\partial}{\partial r} r^{d-1} \frac{\partial}{\partial r} \right\} \Gamma_{\vec{r}}. \quad (6.73)$$

With the ansatz $\Gamma_{\vec{r}} = r^b e^{-r/\xi}$ we obtain easily, $b = (1 - d)/2$ as given in (6.71). At the transition point we have $\xi^{-1} = 0$ such that the differential equation has then the form,

$$\vec{\nabla}^2 \Gamma_{\vec{r}} = \tilde{A} \delta(\vec{r}) \quad \Rightarrow \quad \Gamma_{\vec{r}} \propto \begin{cases} r & d = 1 \\ \ln r & d = 2 \\ r^{2-d} & d \geq 3 \end{cases}, \quad (6.74)$$

as given in (6.75).

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

$$\lim_{r \rightarrow \infty} \Gamma_{\vec{r}} = 0 \quad (6.77)$$

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

$$\lim_{|\vec{r}_i - \vec{r}_j| \rightarrow \infty} \langle s_i s_j \rangle = \langle s_i \rangle \langle s_j \rangle = \begin{cases} 0 & T > T_c, \\ m^2 & T < T_c. \end{cases} \quad (6.78)$$

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.

6.4 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 can be extended to a highly convenient method which allows us to discuss phase transition more generally, in particular, those of second order. Landau's concept of the disorder-to-order transition 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* whereby the system chooses one among several degenerate states. The number of choices corresponds to the order of \mathcal{G}/\mathcal{G}' , i.e. order of \mathcal{G} divided by order of \mathcal{G}' . 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.

6.4.1 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} ,

$$\hat{K}m = -m. \quad (6.79)$$

The two states with positive and negative m are degenerate. The relevant symmetry group above the phase transition is

$$\mathcal{G} = G \times \mathcal{K} \quad (6.80)$$

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 independent of the crystal lattice rotations such that G remains untouched through the transition so that the corresponding subgroup is

$$\mathcal{G}' = G \subset \mathcal{G} \quad (6.81)$$

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

$$\begin{aligned} F[m; H, T] &= F_0(H, T) + \int d^d r \left\{ \frac{A}{2} m(\vec{r})^2 + \frac{B}{4} m(\vec{r})^4 - H(\vec{r})m(\vec{r}) + \frac{\kappa}{2} [\vec{\nabla} m(\vec{r})]^2 \right\} \\ &= F_0(H, T) + \int d^d r f(m, \vec{\nabla} m; H, T) \end{aligned} \quad (6.82)$$

where we choose the coefficients according to the expansion done in (6.33) as

$$A = \frac{Jz}{a^d} \left(\frac{T}{T_c} - 1 \right) = -\frac{Jz}{a^d} \tau \quad \text{and} \quad B = \frac{Jz}{3s^2 a^d}. \quad (6.83)$$

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

$$m(\vec{r}) = \frac{1}{N_b} \sum_{i \in \Lambda_b(\vec{r})} \langle s_i \rangle \quad \text{with} \quad N_b = \frac{a^d}{L_b^d} \quad (6.84)$$

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

$$0 = \frac{\delta F}{\delta m} \quad \Rightarrow \quad 0 = \frac{\partial f}{\partial m} - \vec{\nabla} \cdot \frac{\partial f}{\partial \vec{\nabla} m} = -\kappa \vec{\nabla}^2 m + Am + Bm^3 - H \quad (6.85)$$

Let us compare this equation with the saddle-point equation (6.50,6.51) assuming $H = 0$. It is sufficient to keep only the terms of first order in m . We then take the equations (6.50,6.53) and expand the self-consistence equation to linear order

$$\begin{aligned} \bar{\phi}_i &= \bar{\phi}(\vec{r}_i) = -s \sum_j J_{ij} \tanh(\beta s \bar{\phi}(\vec{r}_j)) \approx -\beta s^2 \sum_j J_{ij} \bar{\phi}(\vec{r}_j) = \beta s^2 \sum_{\{\vec{a}\}_{n.n.}} J \bar{\phi}(\vec{r}_i + \vec{a}) \\ &= \beta s^2 J \left[z \bar{\phi}(\vec{r}_i) + \sum_{\{\vec{a}\}_{n.n.}} \vec{a} \cdot \vec{\nabla} \bar{\phi}(\vec{r}_i) + \frac{1}{2} \sum_{\{\vec{a}\}_{n.n.}} \sum_{\mu, \nu = x, y, \dots} a_\mu a_\nu \frac{\partial^2}{\partial r_\mu \partial r_\nu} \bar{\phi}(\vec{r}_i) \right]. \end{aligned} \quad (6.86)$$

The sum $\sum_{\{\vec{a}\}_{n.n.}}$ runs over nearest-neighbor sites. Note that the second term in the bracket [...] vanishes due to symmetry. Now using the coarse graining procedure we may replace $\bar{\phi}(\vec{r}_i) = Jz m(\vec{r})$ and obtain

$$0 = Jz \left(\frac{T}{T_c} - 1 \right) m(\vec{r}) - Ja^2 \vec{\nabla}^2 m(\vec{r}), \quad (6.87)$$

and the comparison of coefficients leads to

$$\kappa = Ja^{2-d}. \quad (6.88)$$

We may rewrite the equation (6.87) as

$$0 = m - \xi^2 \vec{\nabla}^2 m \quad \text{with} \quad \xi^2 = \frac{a^2 k_B T_c}{z k_B (T - T_c)} = \frac{Js^2 a^2}{k_B (T - T_c)} \quad (6.89)$$

where we introduced the length ξ which is exactly equal to the correlation length for $T > T_c$ in (6.70).

6.4.2 Critical exponents

Close to the phase transition at T_c various quantities have a specific temperature or field dependence which follows powerlaws in $\tau = 1 - T/T_c$ or H with characteristic exponents, 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

$$C(T) \propto |\tau|^{-\alpha} \quad \text{and} \quad \chi(T) \propto |\tau|^{-\gamma} \quad (6.90)$$

for both $\tau > 0$ and $\tau < 0$. Also the correlation length displays a powerlaw

$$\xi(T) \propto |\tau|^{-\nu} . \quad (6.91)$$

For $\tau > 0$ (ordered phase) the magnetization grows as

$$m(T) \propto |\tau|^\beta . \quad (6.92)$$

At $T = T_c$ ($\tau = 0$) the magnetization has the field dependence

$$m \propto H^{1/\delta} \quad (6.93)$$

and the correlation function has a powerlaw dependence on the distance r

$$\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2+\eta}} . \quad (6.94)$$

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 (6.94) we assume that we can write $\Gamma_{\vec{r}}$ as

$$\Gamma_{\vec{r}} \propto \frac{1}{r^{d-2+\eta}} g(r/\xi) . \quad (6.95)$$

According to our previous discussion the susceptibility is given by the integral of $\Gamma_{\vec{r}}$ over space

$$\chi \propto \int d^d r \Gamma_{\vec{r}} \propto \int d^d r \frac{1}{r^{d-2+\eta}} g(r/\xi) \propto \xi^{2-\eta} \int d^d y \frac{1}{y^{d-2+\eta}} g(y) \propto |\tau|^{-\nu(2-\eta)} \propto |\tau|^{-\gamma} \quad (6.96)$$

which leads to $\gamma = \nu(2 - \eta)$.

Let us now determine the exponents within mean field theory. The only one we have not found so far is δ . Using the Ginzburg-Landau equations for $\tau = 0$ leads to

$$Bm^3 = H \quad \Rightarrow \quad \delta = 3 \quad (6.97)$$

Thus the list of exponents is

$$\alpha = 0, \quad \beta = \frac{1}{2}, \quad \gamma = 1, \quad \delta = 3, \quad \nu = \frac{1}{2}, \quad \eta = 0 \quad (6.98)$$

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.

6.4.3 Range of validity of the mean field theory - Ginzburg criterion

In Eq. (6.16) 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 concretely 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 natural "system size". The natural length scale for fluctuations 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

$$E_{ij} = \frac{\langle (s_i - \langle s_i \rangle)(s_j - \langle s_j \rangle) \rangle}{\langle s_i \rangle \langle s_j \rangle} \quad (6.99)$$

we estimate denominator and numerator in the same volume V_ξ in the following way,

$$E_{GL} = \frac{\sum_{j \in \Lambda_\xi} \Gamma_{0j}}{\sum_{j \in \Lambda_\xi} \langle s_0 \rangle \langle s_j \rangle}, \quad (6.100)$$

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 the fluctuation-dissipation theorem relating the correlation function and the susceptibility and obtain,

$$\int_{V_\xi} d^d r \Gamma_{\vec{r}} = f k_B T \frac{\chi(T)}{N}. \quad (6.101)$$

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 $\Gamma_{\vec{r}}$,

$$\int_0^\xi dr \frac{r^{d-1}}{r^{d-2}} g(r/\xi) = f \int_0^\infty dr \frac{r^{d-1}}{r^{d-2}} g(r/\xi) \quad \Rightarrow \quad \xi^2 \int_0^1 dx x g(x) = f \xi^2 \int_0^\infty dx x g(x), \quad (6.102)$$

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

$$\sum_{j \in V_\xi} \langle s_0 \rangle \langle s_j \rangle = m(T)^2 N_\xi \quad (6.103)$$

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

$$f k_B T_c \frac{\chi(T)}{N} \ll \left(\frac{\xi}{a} \right)^d m(T)^2 \quad \Rightarrow \quad \frac{f s^2}{2\tau} \ll 3s^2 \tau \left(\frac{\xi_0}{a} \right)^d \tau^{-d/2} \quad (6.104)$$

with ξ_0 as the correlation length at zero-temperature. Since we are testing the mean field theory we have used here the mean field exponents of Eq.(6.98). From these we obtain the range of validity

$$\tau^{\frac{4-d}{2}} \gg \frac{f}{6} \left(\frac{a}{\xi_0} \right)^d \quad (6.105)$$

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

$$\Delta T = T_c - T \sim T_c \left\{ \frac{f}{6} \left(\frac{a}{\xi_0} \right)^d \right\}^{\frac{2}{4-d}} \quad (6.106)$$

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.

6.5 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.(6.44)

$$Z = C \int_{-\infty}^{+\infty} \left(\prod_i d\phi_i \right) e^{-\beta S(\phi_i, H_i)}. \quad (6.107)$$

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 $\langle \phi_i \rangle = 0$.

6.5.1 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,

$$\begin{aligned} S(\phi) &\approx S_0 - \frac{1}{2} \left\{ \sum_{i,j} (J^{-1})_{ij} \phi_i \phi_j + k_B T \sum_{i,j} \left\langle \frac{\partial^2 \ln[2 \cosh(\beta s \phi_i)]}{\partial \phi_i \partial \phi_j} \right\rangle \phi_i \phi_j \right\} \\ &= S_0 - \frac{1}{2} \sum_{i,j} \left\{ (J^{-1})_{ij} + \beta s^2 \delta_{ij} \left\langle \frac{1}{\cosh^2(\beta s \phi_i)} \right\rangle \right\} \phi_i \phi_j \\ &\approx S_0 - \frac{1}{2} \sum_{i,j} \left\{ (J^{-1})_{ij} + \beta s^2 \delta_{ij} (1 - \beta^2 s^2 \langle \phi_i^2 \rangle) \right\} \phi_i \phi_j. \end{aligned} \quad (6.108)$$

We take $\langle \phi_i^2 \rangle = \langle \phi^2 \rangle$ independent of position. Now we turn to Fourier space,

$$\phi_i = \frac{1}{N} \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q} \cdot \vec{r}_i} \quad \text{with} \quad \phi_{\vec{q}}^* = \phi_{-\vec{q}}, \quad (6.109)$$

and we obtain

$$\begin{aligned} S(\phi) &= S_0 - \frac{1}{2N} \sum_{\vec{q}} \left\{ \frac{1}{J(\vec{q})} + \beta s^2 (1 - \beta^2 s^2 \langle \phi^2 \rangle) \right\} \phi_{\vec{q}} \phi_{-\vec{q}} \\ &\approx S_0 + \frac{1}{2JzN} \sum_{\vec{q}} \left\{ \frac{q^2 a^2}{z} + 1 - Jz s^2 \beta + Jz s^4 \beta^3 \langle \phi^2 \rangle \right\} \phi_{\vec{q}} \phi_{-\vec{q}} \\ &= S_0 + \frac{a^d}{2J^2 z^2 N} \sum_{\vec{q}} \left\{ \kappa q^2 + A + 3Jz B s^6 \beta^3 \langle \phi^2 \rangle \right\} \phi_{\vec{q}} \phi_{-\vec{q}} \end{aligned} \quad (6.110)$$

A slightly more compact form is reached by taking the relation $\phi_{\vec{q}} = Jzm_{\vec{q}}$ following Eq.(6.53) and $k_B T_c = Jzs^2$ such that

$$S = S_0 + \frac{a^d}{2N} \sum_{\vec{q}} \{ \kappa q^2 + A + 3B \langle m^2 \rangle \} m_{\vec{q}} m_{-\vec{q}} = S_0 + \frac{1}{2} \sum_{\vec{q}} G^{-1}(\vec{q}) m_{\vec{q}} m_{-\vec{q}} \quad (6.111)$$

taking the coefficients from the above Ginzburg-Landau formulation. Now we may rewrite the partition function in this approximation as

$$\begin{aligned} Z' &= Z_0 \prod'_{\vec{q}} \int dm_{\vec{q}} dm_{-\vec{q}} \exp \{ -\beta G^{-1}(\vec{q}) m_{\vec{q}} m_{-\vec{q}} / 2 \} \\ &= Z_0 \prod'_{\vec{q}} \int dm'_{\vec{q}} dm''_{\vec{q}} \exp \left\{ -\beta G^{-1}(\vec{q}) (m'^2_{\vec{q}} + m''^2_{-\vec{q}}) / 2 \right\} \end{aligned} \quad (6.112)$$

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

$$\begin{aligned} \langle m^2 \rangle &= \frac{1}{L^d} \int d^d r \langle m(\vec{r})^2 \rangle = \frac{1}{N^2} \sum_{\vec{q}} \langle m_{\vec{q}} m_{-\vec{q}} \rangle \\ &= \frac{1}{N^2} \sum_{\vec{q}} \langle m'^2_{\vec{q}} + m''^2_{\vec{q}} \rangle = \frac{k_B T}{N^2} \sum_{\vec{q}} G(\vec{q}) = \frac{1}{L^d} \sum_{\vec{q}} \frac{k_B T}{A + 3B \langle m^2 \rangle + \kappa q^2} \end{aligned} \quad (6.113)$$

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 (6.65).

On the other hand, we can determine the susceptibility using the fluctuations,

$$\begin{aligned} \chi(T) &= \beta \frac{1}{L^d} \int d^d r d^d r' \{ \langle m(\vec{r}) m(\vec{r}') \rangle - \langle m(\vec{r}) \rangle \langle m(\vec{r}') \rangle \} \\ &= \beta \langle m^2_{\vec{q}=0} \rangle = G(\vec{q}=0) = \frac{1}{A + 3B \langle m^2 \rangle} . \end{aligned} \quad (6.114)$$

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

$$\chi^{-1} = [A + 3B \langle m^2 \rangle] = A + \frac{3B k_B T}{L^d} \sum_{\vec{q}} \frac{1}{\chi^{-1} + \kappa q^2} , \quad (6.115)$$

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 $L^{-d} \sum_{\vec{q}} \rightarrow \int d^d q / (2\pi)^d$ and setting $\chi^{-1} = 0$ we reach at equation

$$A_c = Jz a^{-d} \left(\frac{T_c^*}{T_c} - 1 \right) = - \frac{Jz a^{-d} C_d k_B T_c^*}{s^2 (2\pi)^d} \int_0^\Lambda dq \frac{q^{d-1}}{\kappa q^2} \quad (6.116)$$

where $C_d = \int d\Omega$ is the surface area of a unit-sphere in d dimensions as defined in Eq.(2.39). Thus the renormalized transition temperature is

$$T_c^* = \frac{T_c}{1 + \frac{C_d z (\Lambda a)^{d-2}}{(2\pi)^d d - 2}} < T_c . \quad (6.117)$$

Therefore the transition temperature is reduced by the fluctuations. The dimension $d = d_L = 2$ appears as a lower critical dimension. For dimension $d \leq d_L$ 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.⁸

The renormalization of T_c in Eq.(6.117) contains the fluctuation-induced correction term,

$$\frac{C_d z (2\pi)^d (\Lambda a)^{d-2}}{d-2} \approx \frac{2d\pi^{d/2}}{(2\pi)^d \Gamma(1+d/2)(d-2)} \xrightarrow{d \gg 1} \frac{1}{2^d \pi^{d/2} (d/2)!} \xrightarrow{d \rightarrow \infty} 0 \quad (6.118)$$

such that $T_c^* \rightarrow T_c$ for infinity dimensions. This means that fluctuations do not affect the mean field solution at all in infinite dimension. Each site is coupled to a reservoir of infinite neighbours, making fluctuation negligible.⁹

6.5.2 Renormalized critical exponents

Now we turn to the behavior of the susceptibility at the new critical temperature. For this purpose we rewrite (6.115) with the help of (6.116) and obtain for $T \rightarrow T_{c+}^*$

$$\begin{aligned} \chi^{-1} &= (A - A_c) + \frac{3BC_d}{(2\pi)^d} \int_0^\Lambda dq q^{d-1} \left[\frac{k_B T}{\chi^{-1} + \kappa q^2} - \frac{k_B T_c^*}{\kappa q^2} \right] \\ &\approx (A - A_c) - \frac{3BC_d k_B T_c^*}{(2\pi)^d \kappa} \int_0^\Lambda dq \frac{q^{d-3}}{1 + \chi \kappa q^2} \\ &= (A - A_c) - \frac{3BC_d k_B T_c^*}{(2\pi)^d \kappa} \{\kappa \chi\}^{(2-d)/2} \int_0^{\Lambda \sqrt{\kappa \chi}} dx \frac{x^{d-3}}{1 + x^2}. \end{aligned} \quad (6.119)$$

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

$$\begin{aligned} \chi^{-1} &\approx (A - A_c) - \frac{3BC_d k_B T_c^*}{(2\pi)^d \kappa} \{\kappa \chi\}^{(2-d)/2} \frac{\{\Lambda(\kappa \chi)^{1/2}\}^{d-4}}{d-4} \\ &= (A - A_c) - \frac{3BC_d k_B T_c^*}{(2\pi)^d \kappa^2} \frac{\Lambda^{d-4}}{d-4} \chi^{-1} = \frac{k_B}{a^d s^2} (T - T_c^*) - \frac{C_d z^2}{2(2\pi)^d} \frac{T_c^*}{T_c} \frac{(\Lambda a)^{d-4}}{d-4} \chi^{-1} \end{aligned} \quad (6.120)$$

$$\Rightarrow \chi(T) = \frac{a^d s^2}{k_B (T - T_c^*)} \left\{ 1 + \frac{C_d z^2}{2(2\pi)^d} \frac{T_c^*}{T_c} \frac{(\Lambda a)^{d-4}}{d-4} \right\}^{-1} \propto |T - T_c^*|^{-1}.$$

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. Obviously for $d \rightarrow \infty$ we recover the mean field result as exact with the same arguments as in the last section.

Next we consider $d < d_c = 4$. In this case the integral over x in (6.119) converges and the upper bound does not enter in the limit $T \rightarrow T_c^*$. The integral only depends on d and is given by $K_d = \Gamma[(d-2)/2] \Gamma[(4-d)/2]$. Therefore, we obtain

$$\chi^{-1} = (A - A_c) - \frac{3BC_d k_B T_c^*}{(2\pi)^d \kappa^{d/2}} K_d \chi^{(2-d)/2}. \quad (6.121)$$

⁸Actually for the Ising model this approach overestimates the effect of fluctuations. As we will show in Sect.6.6.2 there is long-range order at finite temperatures for $d = 2$. However, we have seen in Sect.4.7.3 that long-range order of a solid (crystalline lattice) is destroyed at any finite temperature for $d = 1$ and 2. The same is true for quantum spin systems (Heisenberg model).

⁹Note that for practical reason one assumes that the coupling scales so that $Jz = \text{const}$ in order to obtain a non-divergent mean field T_c .

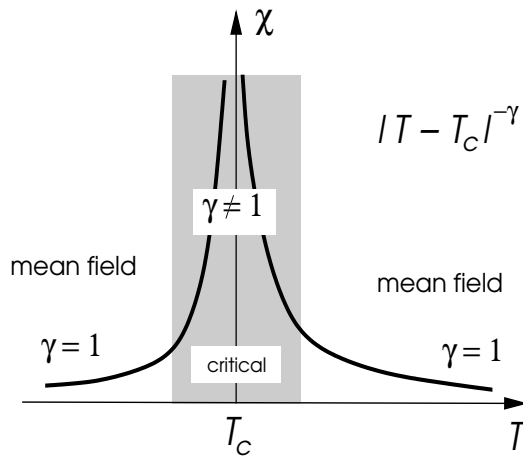


Figure 6.7: Critical region.

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

$$\chi(T) \propto |T - T_c^*|^{-\gamma} \quad \text{with} \quad \gamma = \frac{2}{d-2}. \quad (6.122)$$

Away from T_c^* the second case holds and we return back to the usual mean field behavior,

$$\chi(T) \propto |T - T_c^*|^{-1}. \quad (6.123)$$

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

$$\nu = \frac{\gamma}{2}. \quad (6.124)$$

6.6 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.

6.6.1 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

$$\Delta F = 2Js^2 - k_B T \ln(N - 1). \quad (6.125)$$

Taking now the thermodynamic limit $N \rightarrow \infty$ would yield for any finite temperature a negative ΔF such that the ordered phase (without domain wall) would be unfavorable.

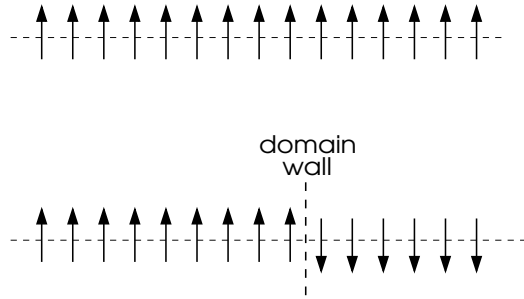


Figure 6.8: Domain wall as the lowest excitation.

In the one-dimensional Ising chain long-range order exists only at zero temperature analogously to the classical spin chain discussed earlier.

6.6.2 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 $N \rightarrow \infty$. 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

$$E(L) = 2Js^2L. \quad (6.126)$$

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

$$\langle s_j \rangle = s(P_+ - P_-) \quad (6.127)$$

where in the case of long range order $\langle s_j \rangle > 0$ due to the boundary condition. Moreover the correlation function satisfies for $|i - j| \rightarrow \infty$,

$$\langle s_i s_j \rangle \rightarrow \langle s_i \rangle \langle s_j \rangle = s^2(P_+ - P_-)^2 \quad (6.128)$$

which is finite for the long-range ordered system, if $P_+ \neq P_-$. Thus our proof has to address this point.

We consider the system at low temperature such that the correlation length is long and different states are most effectively described by configurations of domain walls which are rather dilute. The partition function is then given by

$$Z = \sum_{c \in \Gamma} e^{-KL_c} \quad K = 2\beta J s^2 \quad (6.129)$$

where Γ is the set of configurations and L_c is the total length of all domain walls of configuration c . If the spin $s_j = +s$ ($-s$) then there is an even (odd) number of domain walls encircling the site j . Thus the probability that the spin $s_j = \pm s$ is given by

$$P_{\pm} = \frac{1}{Z} \sum_{c \in \Gamma_j^{\pm}} e^{-KL_c} \quad (6.130)$$

Now we consider P_- whose sum over c includes one innermost domain wall encircling site j . Thus we may rewrite

$$P_- = \frac{1}{Z} \sum_L g(L) e^{-KL} \sum_{c \in \Gamma_j^+} e^{-KLc} = \sum_L g(L) e^{-KL} P_+ \quad (6.131)$$

where $g(L)$ is the number of shapes of the innermost domain wall of length L . Note that Γ_j^+ contains all configurations of domain walls including an even number of walls encircling j and all others not encircling j .

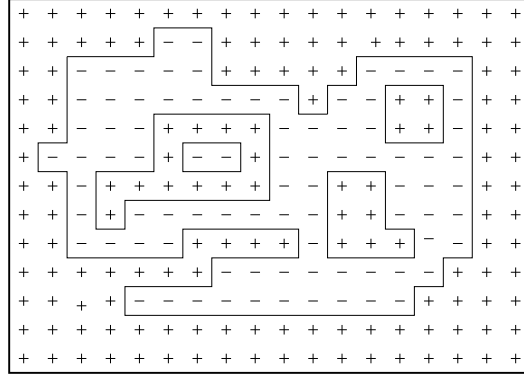


Figure 6.9: Domain wall configurations.

We now try to find an upper bound for $g(L)$. 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 $g(L)$,

$$g(L) < 4 \times 3^{L-1} \times \frac{1}{L} \times \frac{1}{2} \times \left(\frac{L}{4}\right)^2 = \frac{L^2}{24L} e^{L \ln 3}, \quad (6.132)$$

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

$$P_- < \sum_{L \geq 4} \frac{L^2}{24L} e^{L(\ln 3 - K)} P_+ < \sum_{L=4,6,8,\dots} \frac{L^2}{96} e^{L(\ln 3 - K)} \quad (6.133)$$

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

$$P_+ - P_- > 0 \quad \Rightarrow \quad \lim_{|i-j| \rightarrow \infty} \langle s_i s_j \rangle = \text{const.} \quad (6.134)$$

which means that we have long-range order at a finite temperature.

Chapter 7

Superfluidity

Only the noble 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 ^4He (^3He). Note that the nucleus of ^4He consists of two protons and two neutrons, resulting in a Boson, while ^3He has only one neutron and forms a fermionic atom. Only under pressure eventually solidification occurs (Fig. 7.1). 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.7.1, we recognize a profound difference for the superfluid phase between ^4He (left panel) and ^3He (right panel). The bosonic atoms undergo a Bose-Einstein condensation to become a superfluid below $T_\lambda \approx 2.18\text{K}$ 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 ^4He .

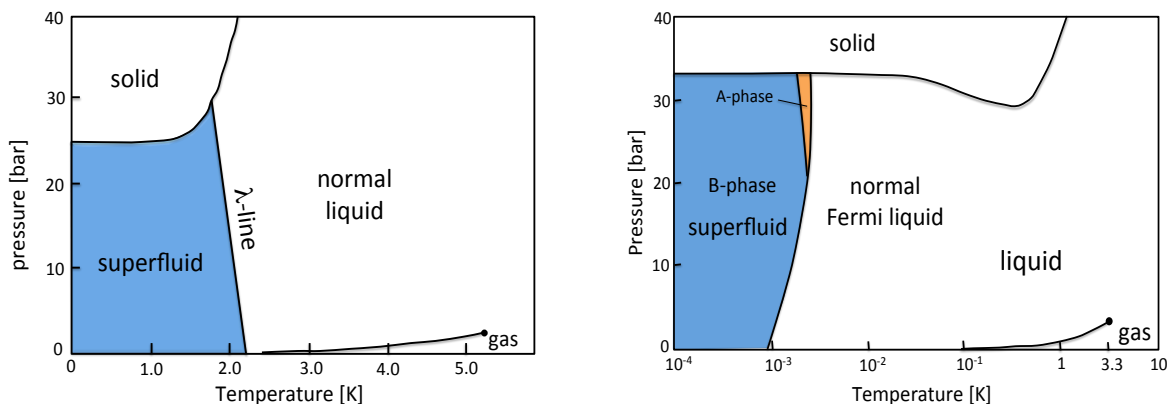


Figure 7.1: Phase diagrams of Helium. Left panel: bosonic ^4He . Right panel: fermionic ^3He . Note the logarithmic temperature scale in the right panel. While ^4He has one superfluid phase, there are two, the A- and B-phase, for ^3He .

7.1 Quantum liquid Helium

We consider now the quantum liquid ^4He .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

¹The quantum liquid ^3He 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 by²

$$V(r) = Ae^{-r/r_1} - B\left(\frac{r_2}{r}\right)^6 \quad (7.1)$$

with $A = 489\text{eV}$, $B = 9.3 \times 10^{-5}\text{eV}$, $r_1 = 0.22 \text{ \AA}$ and $r_2 = 4.64 \text{ \AA}$. 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 $r_0 \approx 3\text{\AA}$ 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 $d \approx 4.4\text{\AA}$. 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,

$$\frac{\Delta r}{d} \leq L_m \quad \text{with} \quad L_m \approx 0.1, \quad (7.2)$$

such that for the solid the atom would have to be confined with a range of linear size $\Delta r \approx 0.5\text{\AA}$. Taking Heisenberg's uncertainty principle, $\Delta r \times \Delta p \approx \hbar$ we obtain for the zero-point energy,

$$\Delta E = \frac{\Delta p^2}{2m} \approx \frac{1}{2m} \left(\frac{\hbar}{\Delta r}\right)^2 \approx 8.6 \times 10^{-4}\text{eV}, \quad (7.3)$$

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 ($T < 5\text{K}$). We encounter "quantum melting" at very low temperatures, when we lower the pressure isothermally through the critical pressure $p_c \sim 25\text{bar}$ (see also in Sect. 4.7.3). Classical thermally driven melting is observed for isobar increase of temperature from the solid phase with the pressure clearly above 25 bar.

7.1.1 Superfluid phase

Around $T_\lambda \approx 2.17\text{K}$ 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.7.2). There is an obvious similarity with the specific heat of Bosons as shown in Fig.3.6, 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 ^4He . 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,

$$\begin{aligned} K : \quad & \vec{P} & E \\ K' : \quad & \vec{P}' = \vec{P} - M\vec{v} & E' = E - \vec{P} \cdot \vec{v} + \frac{M}{2}\vec{v}^2 \end{aligned} \quad (7.4)$$

²Reference: J.C. Slater and J.G. Kirkwood, Phys. Rev. 37, 682 (1931).

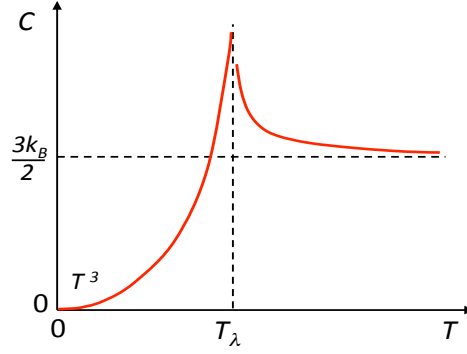


Figure 7.2: Specific heat at the superfluid transition T_λ .

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 tube, K' , is given by

$$\Delta E' = \epsilon(\vec{p}) + \vec{p} \cdot \vec{v}. \quad (7.5)$$

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

$$\Delta E' = \frac{\vec{p}^2}{2m} + \vec{p} \cdot \vec{v} = \frac{p^2}{2m} - vp < 0 \quad \Rightarrow \quad p < 2mv. \quad (7.6)$$

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,

$$\epsilon(\vec{p}) = c_s |\vec{p}| = c_s p, \quad (7.7)$$

corresponding to a sound-like excitation. Inserting this in Eq.(7.6) 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. 7.3. 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

$$\epsilon(p) = \begin{cases} c_s p & p \ll p_0 \\ \Delta + \frac{(p - p_0)^2}{2m^*} & p \approx p_0 \end{cases} \quad (7.8)$$

where for ^4He the parameters are

$$c_s = 240 \text{ ms}^{-1}, \quad \frac{p_0}{\hbar} = 1.9 \text{ \AA}^{-1}, \quad \frac{\Delta}{k_B} = 8.7 \text{ K}, \quad m^* = 0.16 m_{\text{He}}. \quad (7.9)$$

The critical velocity is now given by the lowest possible excitation within Eq.(7.5), corresponding to the dashed line in Fig.7.3,

$$v_c \approx \frac{\epsilon(p_0)}{p_0} = \frac{\Delta}{p_0} = 60 \text{ ms}^{-1}. \quad (7.10)$$

Note that the roton minimum is a precursor of solid He. Under pressure Δ shrinks and eventually

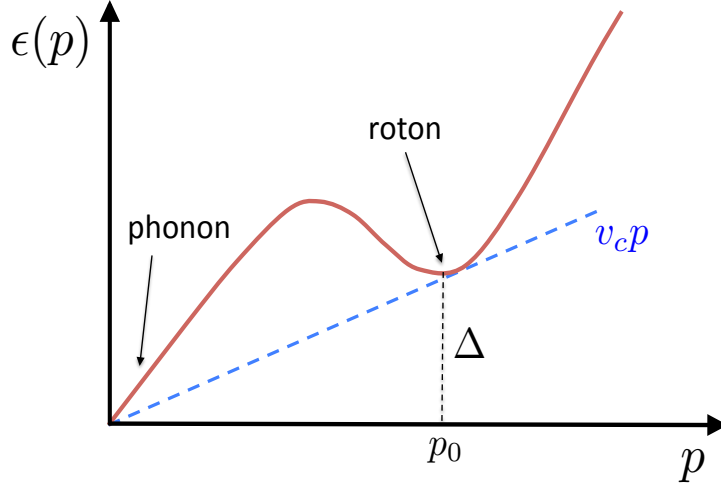


Figure 7.3: Spectrum of a real superfluid with a linear sound-like behavior at low energy and a local minimum around p_0 , the rotons. The dashed line ($v_c p$) indicates the maximal velocity of the superfluid to sustain frictionless flow, i.e. flow without generating elementary excitations which would 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.

7.1.2 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,

$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{int}} \quad (7.11)$$

with

$$\mathcal{H}_{\text{kin}} = \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu) \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \quad (7.12)$$

$$\mathcal{H}_{\text{int}} = \frac{1}{2} \int d^3 r d^3 r' \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}^\dagger(\vec{r}') V(\vec{r} - \vec{r}') \hat{\Psi}(\vec{r}') \hat{\Psi}(\vec{r})$$

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.(4.35), using the relation,

$$\hat{\Psi}(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} \hat{a}_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \quad (7.13)$$

and obtain,

$$\mathcal{H}_{\text{int}} = \frac{U}{2V} \sum_{\vec{k}, \vec{k}', \vec{q}} \hat{a}_{\vec{k}+\vec{q}}^\dagger \hat{a}_{\vec{k}'-\vec{q}}^\dagger \hat{a}_{\vec{k}} \hat{a}_{\vec{k}'} \quad (7.14)$$

Now we turn to the Bogolyubov approximation introduced in Sect. 4.7.2, by identifying the \hat{a}_0^\dagger 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:

$\vec{k}, \vec{k}', \vec{q}$	$\hat{a}_{\vec{k}+\vec{q}}^\dagger \hat{a}_{\vec{k}'}^\dagger \hat{a}_{-\vec{q}} \hat{a}_{\vec{k}} \hat{a}_{\vec{k}'}$	$\vec{k}, \vec{k}', \vec{q}$	$\hat{a}_{\vec{k}+\vec{q}}^\dagger \hat{a}_{\vec{k}'}^\dagger \hat{a}_{-\vec{q}} \hat{a}_{\vec{k}} \hat{a}_{\vec{k}'}$
$\vec{k} = \vec{k}' = \vec{q} = 0$	N_0^2	$\vec{k} = \vec{k}' = 0, \vec{q} \neq 0$	$N_0 \hat{a}_{\vec{q}}^\dagger \hat{a}_{-\vec{q}}^\dagger$
$\vec{q} = -\vec{k} \neq 0, \vec{k}' = 0$	$N_0 \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}$	$\vec{q} = \vec{k}' \neq 0, \vec{k} = 0$	$N_0 \hat{a}_{\vec{k}'}^\dagger \hat{a}_{\vec{k}'}$
$\vec{k} = -\vec{k}' = -\vec{q} \neq 0$	$N_0 \hat{a}_{\vec{k}} \hat{a}_{-\vec{k}}$	$\vec{q} = \vec{k} = 0, \vec{k}' \neq 0$	$N_0 \hat{a}_{\vec{k}'}^\dagger \hat{a}_{\vec{k}'}$
$\vec{q} = \vec{k}' = 0, \vec{k} \neq 0$	$N_0 \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}}$		

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,

$$\begin{aligned} \mathcal{H}' = & -\mu N_0 + \frac{UN_0^2}{2V} + \sum_{\vec{k} \neq 0} \left\{ \epsilon_{\vec{k}} - \mu + \frac{UN_0}{V} \right\} \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \\ & + \frac{UN_0}{2V} \sum_{\vec{k} \neq 0} \left\{ \hat{a}_{\vec{k}}^\dagger \hat{a}_{-\vec{k}}^\dagger + \hat{a}_{-\vec{k}} \hat{a}_{\vec{k}} + \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} + \hat{a}_{-\vec{k}}^\dagger \hat{a}_{-\vec{k}} \right\}. \end{aligned} \quad (7.15)$$

The requirement that the total particle number remains constant on average at lowest temperature leads to $\mu = Un_0$ (derivation is somewhat tedious and omitted here),

$$\mathcal{H}' = -N_0 \frac{Un_0}{2} + \frac{1}{2} \sum_{\vec{k} \neq 0} \left[\{ \epsilon_{\vec{k}} + Un_0 \} (\hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} + \hat{a}_{-\vec{k}}^\dagger \hat{a}_{-\vec{k}}) + Un_0 (\hat{a}_{\vec{k}}^\dagger \hat{a}_{-\vec{k}}^\dagger + \hat{a}_{-\vec{k}} \hat{a}_{\vec{k}}) \right]. \quad (7.16)$$

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 $\hat{a}_{\vec{k}}^\dagger \hat{a}_{-\vec{k}}^\dagger$ 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

$$\mathcal{H}' = \frac{1}{2} \sum_{\vec{k} \neq 0} E_{\vec{k}} (\hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{\vec{k}} + \hat{\gamma}_{-\vec{k}}^\dagger \hat{\gamma}_{-\vec{k}}) + E_0 - \mu N_0. \quad (7.17)$$

where the operators $\hat{\gamma}_{\vec{k}}^\dagger$ ($\hat{\gamma}_{\vec{k}}$) create (annihilate) independent *Bogolyubov quasiparticles*. The following *Bogolyubov transformation* allows us to reach this form,³

$$\hat{a}_{\vec{k}} = \hat{\gamma}_{\vec{k}} u_{\vec{k}} - \hat{\gamma}_{-\vec{k}}^\dagger v_{\vec{k}} \quad \text{and} \quad \hat{a}_{-\vec{k}} = \hat{\gamma}_{-\vec{k}} u_{\vec{k}} - \hat{\gamma}_{\vec{k}}^\dagger v_{\vec{k}}, \quad (7.23)$$

³*Bogolyubov transformation:* We insert the transformation (7.23) into the second term of the Hamiltonian (7.16) and obtain for a fixed \vec{k} ,

$$\begin{aligned} & (\epsilon_{\vec{k}} + Un_0) \left\{ (\hat{\gamma}_{\vec{k}}^\dagger u_{\vec{k}} - \hat{\gamma}_{-\vec{k}}^\dagger v_{\vec{k}}) (\hat{\gamma}_{\vec{k}} u_{\vec{k}} - \hat{\gamma}_{-\vec{k}}^\dagger v_{\vec{k}}) + (\hat{\gamma}_{-\vec{k}}^\dagger u_{\vec{k}} - \hat{\gamma}_{\vec{k}}^\dagger v_{\vec{k}}) (\hat{\gamma}_{-\vec{k}} u_{\vec{k}} - \hat{\gamma}_{\vec{k}}^\dagger v_{\vec{k}}) \right\} \\ & + Un_0 \left\{ (\hat{\gamma}_{\vec{k}}^\dagger u_{\vec{k}} - \hat{\gamma}_{-\vec{k}}^\dagger v_{\vec{k}}) (\hat{\gamma}_{-\vec{k}}^\dagger u_{\vec{k}} - \hat{\gamma}_{\vec{k}}^\dagger v_{\vec{k}}) + (\hat{\gamma}_{-\vec{k}}^\dagger u_{\vec{k}} - \hat{\gamma}_{\vec{k}}^\dagger v_{\vec{k}}) (\hat{\gamma}_{\vec{k}} u_{\vec{k}} - \hat{\gamma}_{-\vec{k}}^\dagger v_{\vec{k}}) \right\} \end{aligned} \quad (7.18)$$

where the new operators satisfy the relation,

$$[\hat{\gamma}_{\vec{k}}, \hat{\gamma}_{\vec{k}}^\dagger] = [\hat{\gamma}_{-\vec{k}}, \hat{\gamma}_{-\vec{k}}^\dagger] = 1 \quad \Rightarrow \quad [\hat{a}_{\vec{k}}, \hat{a}_{\vec{k}}^\dagger] = u_{\vec{k}}^2 - v_{\vec{k}}^2 = 1. \quad (7.24)$$

The diagonalization leads to

$$E_{\vec{k}} = \sqrt{\epsilon_{\vec{k}}^2 + 2Un_0\epsilon_{\vec{k}}} \quad \text{and} \quad E_0 = \frac{1}{2} \sum_{\vec{k} \neq 0} [E_{\vec{k}} - \epsilon_{\vec{k}} - Un_0] - N_0 \frac{Un_0}{2} \quad (7.25)$$

and the transformation coefficients,

$$\left. \begin{aligned} u_{\vec{k}} &= \frac{1}{\sqrt{1 - \chi_{\vec{k}}^2}} \\ v_{\vec{k}} &= \frac{\chi_{\vec{k}}}{\sqrt{1 - \chi_{\vec{k}}^2}} \end{aligned} \right\} \Rightarrow \begin{cases} \chi_{\vec{k}} &= 1 + \frac{\epsilon_{\vec{k}}}{Un_0} - \sqrt{\left(1 + \frac{\epsilon_{\vec{k}}}{Un_0}\right)^2 - 1} \\ &= 1 + \frac{\epsilon_{\vec{k}}}{Un_0} - \frac{E_{\vec{k}}}{Un_0}. \end{cases} \quad (7.26)$$

The spectrum of the elementary excitations is linear in the small momentum limit, $\vec{k} \rightarrow 0$,

$$E_{\vec{k}} \approx c_s p = \sqrt{\frac{Un_0}{m}} \hbar k, \quad (7.27)$$

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 $\epsilon_{\vec{k}}$,

$$E_{\vec{k}} \approx \epsilon_{\vec{k}} + Un_0 \quad (7.28)$$

with a shift of Un_0 (see Fig.7.4). 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,

$$v_c = c_s = \sqrt{\frac{Un_0}{m}} \quad (7.29)$$

which is higher than the real v_c discussed above. The constant E_0 is the ground state energy.

where we assume that $u_{\vec{k}}$ and $v_{\vec{k}}$ are real. We now separate the terms to compare with Eq.(7.17),

$$\begin{aligned} &(\hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{\vec{k}} + \hat{\gamma}_{-\vec{k}}^\dagger \hat{\gamma}_{-\vec{k}})[(\epsilon_{\vec{k}} + Un_0)(u_{\vec{k}}^2 + v_{\vec{k}}^2) - 2Un_0 u_{\vec{k}} v_{\vec{k}}] + 2(\epsilon_{\vec{k}} + Un_0)v_{\vec{k}}^2 - 2Un_0 u_{\vec{k}} v_{\vec{k}} \\ &+ (\hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{-\vec{k}}^\dagger + \hat{\gamma}_{-\vec{k}} \hat{\gamma}_{\vec{k}})[Un_0(u_{\vec{k}}^2 + v_{\vec{k}}^2) - 2(\epsilon_{\vec{k}} + Un_0)u_{\vec{k}} v_{\vec{k}}]. \end{aligned} \quad (7.19)$$

With the condition that $u_{\vec{k}}^2 - v_{\vec{k}}^2 = 1$ from Eq.(7.24) we parametrize $u_{\vec{k}} = \cosh \theta_{\vec{k}}$ and $v_{\vec{k}} = \sinh \theta_{\vec{k}}$. In order to get the terms in the second line of Eq.(7.19) to vanish we find then

$$0 = Un_0 \cosh 2\theta_{\vec{k}} - (\epsilon_{\vec{k}} + Un_0) \sinh 2\theta_{\vec{k}} \quad \Rightarrow \quad \tanh 2\theta_{\vec{k}} = \frac{Un_0}{\epsilon_{\vec{k}} + Un_0} \quad (7.20)$$

which leads after using some identities of hyperbolic functions to $u_{\vec{k}}$ and $v_{\vec{k}}$ in Eq.(7.26). Moreover by comparison with Eq.(7.17) we find

$$E_{\vec{k}} = (\epsilon_{\vec{k}} + Un_0) \cosh 2\theta_{\vec{k}} - Un_0 \sinh 2\theta_{\vec{k}} = \frac{\epsilon_{\vec{k}} + Un_0}{\sqrt{1 - \tanh^2 2\theta_{\vec{k}}}} - \frac{Un_0 \tanh 2\theta_{\vec{k}}}{\sqrt{1 - \tanh^2 2\theta_{\vec{k}}}} = \sqrt{\epsilon_{\vec{k}}^2 + 2\epsilon_{\vec{k}} Un_0}. \quad (7.21)$$

Finally the constant term

$$2(\epsilon_{\vec{k}} + Un_0)v_{\vec{k}}^2 - 2Un_0 u_{\vec{k}} v_{\vec{k}} = -(\epsilon_{\vec{k}} + Un_0) \cosh 2\theta_{\vec{k}} + Un_0 \sinh 2\theta_{\vec{k}} - \epsilon_{\vec{k}} + Un_0 = E_{\vec{k}} - \epsilon_{\vec{k}} - Un_0 \quad (7.22)$$

which yields the term E_0 in Eq.(7.17).

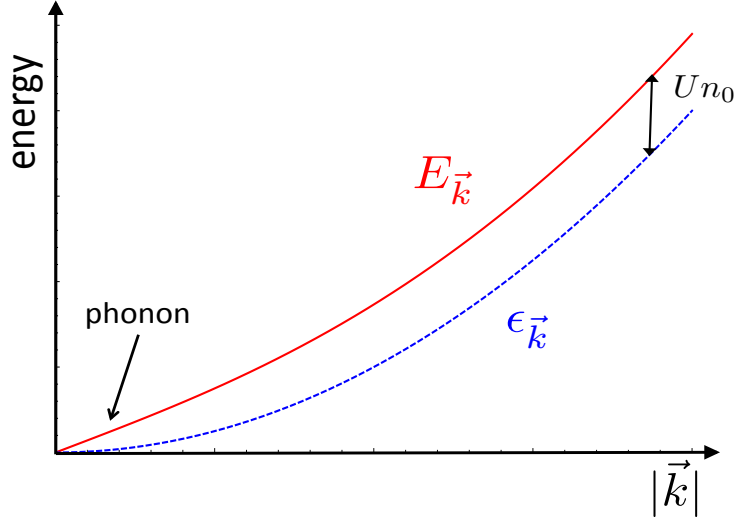


Figure 7.4: Spectrum of the Bogolyubov quasiparticles in Eqs.(7.17) and (7.25). The solid line displays $E_{\vec{k}}$ with a linear dispersion for small momenta $\vec{p} = \hbar\vec{k}$ and the dashed line shows $\epsilon_{\vec{k}}$. There are no rotons in this simple approach.

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} .⁴ Now we turn to the condensate fraction of the interacting system. How many particles condense? This can be straightforwardly calculated,

$$n_0 = n - \frac{1}{V} \sum_{\vec{k} \neq 0} \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle. \quad (7.32)$$

This is advantageous when we want to calculate now mean values for which we insert the Bogolyubov transformation in Eq.(7.23),

$$\begin{aligned} \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle &= \langle (\hat{\gamma}_{\vec{k}}^\dagger u_{\vec{k}}^* - \hat{\gamma}_{-\vec{k}} v_{\vec{k}}^*) (\hat{\gamma}_{\vec{k}} u_{\vec{k}} - \hat{\gamma}_{-\vec{k}}^\dagger v_{\vec{k}}) \rangle \\ &= |u_{\vec{k}}|^2 \langle \hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{\vec{k}} \rangle + |v_{\vec{k}}|^2 \langle \hat{\gamma}_{-\vec{k}} \hat{\gamma}_{-\vec{k}}^\dagger \rangle - u_{\vec{k}}^* v_{\vec{k}} \langle \hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{-\vec{k}}^\dagger \rangle - u_{\vec{k}} v_{\vec{k}}^* \langle \hat{\gamma}_{-\vec{k}} \hat{\gamma}_{\vec{k}} \rangle. \end{aligned} \quad (7.33)$$

Then we use the fact that the Bogolyubov quasiparticles are independent, described by the Hamiltonian in Eq.(7.17),

$$\begin{aligned} \langle \hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{\vec{k}} \rangle &= \frac{1}{e^{\beta E_{\vec{k}}} - 1}, \quad \langle \hat{\gamma}_{-\vec{k}} \hat{\gamma}_{-\vec{k}}^\dagger \rangle = 1 + \langle \hat{\gamma}_{-\vec{k}}^\dagger \hat{\gamma}_{-\vec{k}} \rangle = 1 + \frac{1}{e^{\beta E_{\vec{k}}} - 1}, \\ \langle \hat{\gamma}_{-\vec{k}} \hat{\gamma}_{\vec{k}} \rangle &= \langle \hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{-\vec{k}}^\dagger \rangle = 0. \end{aligned} \quad (7.34)$$

⁴Groundstate energy: It is rather easy to see that in the large- \vec{k} limit the integrand in E_0 (Eq.(7.25)) behaves like

$$E_{\vec{k}} - \epsilon_{\vec{k}} - U n_0 \rightarrow -\frac{m(U n_0)^2}{p^2}, \quad (7.30)$$

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

$$E'_0 = \sum_{\vec{k} \neq 0} \left[E_{\vec{k}} - \epsilon_{\vec{k}} - U n_0 + \frac{m(U n_0)^2}{p^2} \right] + N_0 \frac{U n_0}{2} = N_0 \frac{U n_0}{2} \left[1 + \frac{16}{15\pi^2 n_0} \left(\frac{U n_0 m}{\hbar^2} \right)^{3/2} \right]. \quad (7.31)$$

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.

Note that $E_{\vec{k}} = E_{-\vec{k}}$. The momentum distribution of the Bosons for $\vec{k} \neq 0$ is obviously,

$$n_{\vec{k}} = \langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle = (|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2) \frac{1}{e^{\beta E_{\vec{k}}} - 1} + |v_{\vec{k}}|^2 = \frac{1 + \chi_{\vec{k}}^2}{1 - \chi_{\vec{k}}^2} \frac{1}{e^{\beta E_{\vec{k}}} - 1} + \frac{\chi_{\vec{k}}^2}{1 - \chi_{\vec{k}}^2}. \quad (7.35)$$

The first term vanishes at $T = 0$ for all $\vec{k} \neq 0$, 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-temperature distribution function has the following behavior,

$$\langle \hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} \rangle_{T=0} = \frac{\chi_{\vec{k}}^2}{1 - \chi_{\vec{k}}^2} \approx \begin{cases} \frac{\sqrt{mUn_0}}{2\hbar k} & \hbar k \ll \sqrt{2mUn_0} \\ \frac{(mUn_0)^2}{4(\hbar k)^4} & \hbar k \gg \sqrt{2mUn_0} \end{cases} \quad (7.36)$$

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} ,

$$n_0 = n - \frac{1}{V} \sum_{\vec{k} \neq 0} \frac{\chi_{\vec{k}}^2}{1 - \chi_{\vec{k}}^2} = n - \int \frac{d^3k}{(2\pi)^3} \frac{\chi_{\vec{k}}^2}{1 - \chi_{\vec{k}}^2} = n - \frac{1}{3\pi^2} \left(\frac{mUn_0}{\hbar^2} \right)^{3/2} \quad (7.37)$$

which is valid only for sufficient weak interactions. This can be measured in terms of the characteristic length ξ , defined as

$$\frac{\hbar^2 k'^2}{2m} = Un_0 \quad \text{with} \quad k'\xi = 1 \quad \Rightarrow \quad \xi^2 = \frac{\hbar^2}{2mUn_0} \quad (7.38)$$

which leads to the condition

$$3\pi^2 n \gg \left(\frac{mUn_0}{\hbar^2} \right)^{3/2} \quad \Rightarrow \quad n\xi^3 \gg 1. \quad (7.39)$$

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

$$\int \frac{dk}{2\pi} \frac{\chi_k^2}{1 - \chi_k^2} \quad \rightarrow \quad \infty \quad (7.40)$$

diverges due to the k^{-1} dependence of the integrand for small k (see Eq.(7.36)). 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.(7.17),

$$U = \langle \mathcal{H}' \rangle = E_0 - \mu N_0 + \sum_{\vec{k} \neq 0} E_{\vec{k}} \langle \hat{\gamma}_{\vec{k}}^\dagger \hat{\gamma}_{\vec{k}} \rangle = E_0 - \mu N_0 + \sum_{\vec{k} \neq 0} \frac{E_{\vec{k}}}{e^{\beta E_{\vec{k}}} - 1} \approx N \frac{\pi^2}{30n} \left(\frac{m}{Un_0 \hbar^2} \right)^{3/2} (k_B T)^4 \quad (7.41)$$

for $k_B T \ll Un_0$. Note that in this limit we look at Bosons with a linear energy-momentum dispersion, like photons or phonons which in three dimensions yield $U \propto T^4$. The low-temperature heat capacity is then accordingly

$$C = \frac{dU}{dT} = N \frac{2\pi^2}{15n} k_B \left(\frac{m}{Un_0 \hbar^2} \right)^{3/2} (k_B T)^3 \quad (7.42)$$

which is different from the Bose-Einstein condensate with $C \propto T^{3/2}$.

7.1.3 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,

$$\begin{aligned} \mathcal{H} = \int d^3r \left\{ \frac{\hbar^2}{2m} (\vec{\nabla} \hat{\Psi}^\dagger(\vec{r})) (\vec{\nabla} \hat{\Psi}(\vec{r})) + [V(\vec{r}) - \mu] \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}(\vec{r}) \right\} \\ + \frac{1}{2} \int d^3r d^3r' \hat{\Psi}^\dagger(\vec{r}) \hat{\Psi}^\dagger(\vec{r}') U \delta(\vec{r} - \vec{r}') \hat{\Psi}(\vec{r}') \hat{\Psi}(\vec{r}) \end{aligned} \quad (7.43)$$

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,

$$i\hbar \frac{\partial}{\partial t} \hat{\Psi}(\vec{r}, t) = [\hat{\Psi}(\vec{r}, t), \mathcal{H}] = \left[-\frac{\hbar^2 \vec{\nabla}^2}{2m} + V(\vec{r}) - \mu + U \hat{\Psi}^\dagger(\vec{r}, t) \hat{\Psi}(\vec{r}, t) \right] \hat{\Psi}(\vec{r}, t). \quad (7.44)$$

If the external potential varies very slowly or is even constant we will replace the field operator by the Bogolyubov approximation discussed in Sect. 4.7.2 and obtain the equation

$$i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r}, t) = \left(-\frac{\hbar^2 \vec{\nabla}^2}{2m} + V(\vec{r}) - \mu + U |\psi_0(\vec{r}, t)|^2 \right) \psi_0(\vec{r}, t), \quad (7.45)$$

which is called *Gross-Pitaevskii equation*. This equation is obtained by variation from the energy functional

$$E = \int d^3r \left[\frac{\hbar^2}{2m} |\vec{\nabla} \psi_0(\vec{r})|^2 + \{V(\vec{r}) - \mu\} |\psi_0(\vec{r})|^2 + \frac{U}{2} |\psi_0(\vec{r})|^4 \right] \quad (7.46)$$

through

$$i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r}, t) = \frac{\delta E}{\delta \psi_0(\vec{r}, t)}. \quad (7.47)$$

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 $\mu = U n_0$ as in Eq.(7.15).

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,

$$\psi_0(\vec{r}) = \sqrt{n_0} + \eta(\vec{r}), \quad (7.48)$$

with $|\eta(\vec{r})|^2 \ll n_0$. Inserted into the Gross-Pitaevskii equation (Eq.(7.45)) we obtain to linear order in $\eta(\vec{r})$,

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2 \eta(\vec{r}) + 2U n_0 \eta(\vec{r}) = -V(\vec{r}) (\sqrt{n_0} + \eta(\vec{r})). \quad (7.49)$$

We now consider point-like defect, $V(\vec{r}) = V_0 \delta(\vec{r})$ which yields the following long distance ($r \gg \xi$) behavior,

$$\eta(\vec{r}) = \eta_0 \frac{e^{-r/\sqrt{2}\xi}}{r} \quad \text{with} \quad \xi^2 = \frac{\hbar^2}{2mU n_0} \quad (7.50)$$

the same length as introduced in Eq.(7.38) and $\eta_0 \approx mV_0 \sqrt{n_0} / 2\pi \hbar^2$.

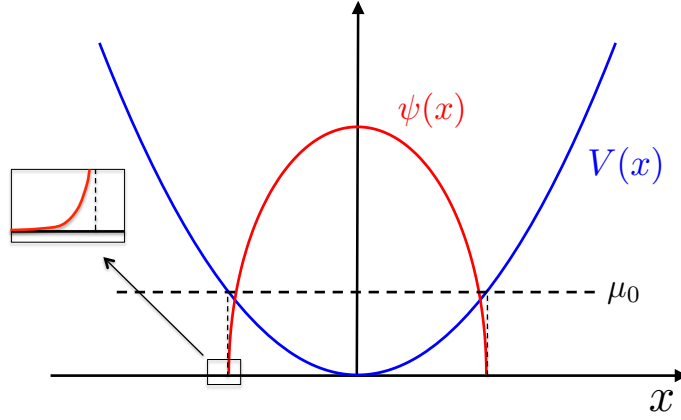


Figure 7.5: Bose-Einstein condensate trapped in a harmonic potential $V(x) \propto x^2$. The Thomas-Fermi approximation yields a condensate concentrated around the center of the potential well. Note that the approximation is only justified for large condensate densities ($n_0 \xi^3 \gg 1$). Thus, near 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,

$$\psi(\vec{r}) = \left(\frac{\mu_0 - V(\vec{r})}{U} \right)^{1/2} \quad (7.51)$$

with $\mu_0 = Un_0$ the chemical potential where $V(\vec{r}) = 0$. This is called the *Thomas-Fermi approximation*⁵. 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,

$$\begin{aligned} \frac{\partial}{\partial t} |\psi_0(\vec{r}, t)|^2 &= -\frac{\hbar}{2mi} [\psi_0^*(\vec{r}, t) \vec{\nabla}^2 \psi_0(\vec{r}, t) - \psi_0(\vec{r}, t) \vec{\nabla}^2 \psi_0^*(\vec{r}, t)] \\ &= -\vec{\nabla} \cdot \frac{\hbar}{2mi} [\psi_0^*(\vec{r}, t) \vec{\nabla} \psi_0(\vec{r}, t) - \psi_0(\vec{r}, t) \vec{\nabla} \psi_0^*(\vec{r}, t)] \end{aligned} \quad (7.55)$$

⁵*Spatial modulation:* To illustrate the effect of slow variation we assume a weak periodic potential $V(x) = V_0 \cos(qx)$. Inserting this potential into Eq.(7.49) we obtain the effectively one-dimensional differential equation,

$$-\frac{\hbar^2}{2m} \eta''(x) + 2Un_0 \eta(x) = -V_0 \sqrt{n_0} \cos(qx) \quad (7.52)$$

where we neglect the last term on the right-hand side. We then obtain

$$\eta(x) = -\frac{V_0 \sqrt{n_0} \cos(qx)}{Un_0(\xi^2 q^2 + 2)}. \quad (7.53)$$

"Slow variation" corresponds to $\xi q \ll 1$ which we may now compare with the Thomas-Fermi approximation in Eq.(7.51) with $\mu_0 = Un_0$,

$$\psi(x) = \left[n_0 - \frac{V_0}{U} \cos(qx) \right]^{1/2} \approx \sqrt{n_0} - \frac{V_0 \sqrt{n_0}}{2Un_0} \cos(qx) = \sqrt{n_0} + \eta(x) \quad (7.54)$$

as obtained above in this limit.

which we may rewrite as

$$\frac{\partial \rho(\vec{r}, t)}{\partial t} + \vec{\nabla} \cdot \vec{j}(\vec{r}, t) = 0 \quad \text{with} \quad \begin{cases} \rho(\vec{r}, t) = |\psi_0(\vec{r}, t)|^2 \\ \vec{j}(\vec{r}, t) = \frac{\hbar}{2mi} [\psi_0^*(\vec{r}, t) \vec{\nabla} \psi_0(\vec{r}, t) - \psi_0(\vec{r}, t) \vec{\nabla} \psi_0^*(\vec{r}, t)] . \end{cases} \quad (7.56)$$

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.

$$\vec{j}(\vec{r}) = \frac{\hbar}{m} n_0 \vec{\nabla} \phi(\vec{r}) = n_0 \vec{v}_s(\vec{r}) \quad (7.57)$$

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

$$E(\vec{v}_s) = V \left[\frac{m}{2} \vec{v}_s^2 n_0 - \frac{U n_0^2}{2} \right] \quad (7.58)$$

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 $v_c = \sqrt{U n_0 / m} = c_s$ as found in the Bogolyubov theory in Eq.(7.29).

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

$$\oint \vec{v}_s \cdot d\vec{s} = \frac{\hbar}{m} \oint \vec{\nabla} \phi \cdot d\vec{s} = \frac{\hbar}{m} 2\pi n_\phi \quad (7.59)$$

with n_ϕ being an integer. Thus the current $j = n_0 v_s$ 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

$$\psi_0(r_\perp, \theta, z) = \sqrt{n_0} f(r_\perp) e^{i\theta n_\phi} \quad (7.60)$$

for a line along the z -axis with (r_\perp, θ) being the cylindrical coordinates perpendicular to z . The function $f(r_\perp)$ goes to zero on the line $r_\perp = 0$ like $f(r_\perp) \propto r_\perp^{n_\phi}$ 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 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 latter, however, is larger. To be concrete we place the vortex along the rotation axis of a cylindrical vessel of radius R . Then

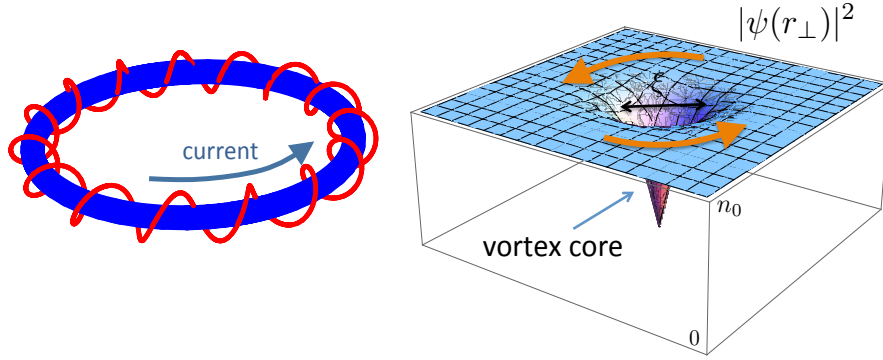


Figure 7.6: Phase winding and vortex: Left panel: phase winding (red line) around the torus leads to a current. As the phase has close the current is quantized. Right panel: Vortex structure of $|\psi(r_\perp)|^2$ with a core of linear extension $\sim \xi$.

the energy per unit length is given by

$$\begin{aligned}
 E_{\text{vortex}} &= \int_{r \leq \xi} d^2r E[\psi(\vec{r})] + \int_{r > \xi} d^2r E[\psi(\vec{r})] \\
 &\approx E_{\text{core}} + \int_{\xi}^R dr_\perp r_\perp \int_0^{2\pi} d\theta \frac{\hbar^2}{2m} \frac{1}{r_\perp^2} \left| \frac{\partial \psi(r_\perp, \theta)}{\partial \theta} \right|^2 = E_{\text{core}} + \frac{\hbar^2 n_0}{2m} 2\pi n_\phi^2 \ln \left(\frac{R}{\xi} \right),
 \end{aligned} \tag{7.61}$$

The first part is the energy expense due to the vortex core, where the depletion of the condensate leads to a loss of condensation energy

$$E_{\text{core}} \approx \frac{U n_0}{2} \pi \xi^2. \tag{7.62}$$

The second part is due to the currents and dominates the vortex energy. The amazing result is that this latter 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. A further important point is that this energy grows with n_ϕ^2 indicating that vortex of lowest energy has $n_\phi = \pm 1$. Therefore vortices of higher winding numbers would separate into such vortices to reduce the energy.

7.2 Berezinskii-Kosterlitz-Thouless transition

A peculiar behavior can be found in the two-dimensional superfluids, e.g. a ^4He 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.

7.2.1 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.4.7.2. The correlation function is given

$$g(\vec{R}) = \langle \widehat{\Psi}^\dagger(\vec{r}) \widehat{\Psi}(\vec{r} + \vec{R}) \rangle. \tag{7.63}$$

In the high-temperature limit we have approximated the long-distance behavior by

$$g(\vec{R}) = \int \frac{d^2k}{(2\pi)^2} \frac{e^{i\vec{k}\cdot\vec{R}}}{e^{\beta(\epsilon_{\vec{k}}-\mu)} - 1} \approx \frac{2mk_B T}{\hbar^2} \int \frac{d^2k}{(2\pi)^2} \frac{e^{i\vec{k}\cdot\vec{R}}}{k^2 + k_0^2} \quad (7.64)$$

$$= \frac{2}{\lambda^2} K_0(k_0 R) \approx \frac{1}{\lambda^2} \sqrt{\frac{2\pi}{k_0 R}} e^{-k_0 R}$$

with $k_0^2 = -2m\mu/\hbar^2$, $\lambda = h/\sqrt{2\pi mk_B T}$ (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.(7.46), where we keep n_0 constant and restrict to the phase fluctuations. Then we obtain

$$E[\phi] = Un_0^2 \int d^2r \left[\xi^2 (\vec{\nabla}\phi)^2 - \frac{1}{2} \right] = Un_0^2 \left[\sum_{\vec{q}} \xi^2 q^2 \phi_{\vec{q}} \phi_{-\vec{q}} - \frac{V}{2} \right] \quad (7.65)$$

with the Fourier transform

$$\phi(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \quad (7.66)$$

and V here as the area of the system. Now turn to the calculation of the correlation function

$$g(\vec{R}) = n_0 \langle e^{i(\phi(0) - \phi(\vec{R}))} \rangle = n_0 e^{-\langle (\phi(0) - \phi(\vec{R}))^2 \rangle} = \left(\frac{\pi R}{r_0} \right)^{-\eta(T)} \quad (7.67)$$

where the last equality is connected with the fact that with the above energy the averaging is Gaussian.⁶ Here the correlation function still decays, but now algebraically with $\eta(T) = 2/n_0\lambda^2$

⁶ *Averaging:* In order to calculate the correlation function in Eq.(7.67) we turn the Fourier space for the phase:

$$\phi(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \quad (7.68)$$

and rewrite the energy

$$E[\phi] = Un_0^2 \xi^2 \sum_{\vec{q}} q^2 \phi_{\vec{q}} \phi_{-\vec{q}} = Un_0^2 \xi^2 \sum_{\vec{q}} q^2 (\phi_{1,\vec{q}}^2 + \phi_{2,\vec{q}}^2) \quad (7.69)$$

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

$$Z = \int \prod_{\vec{q}} d\phi_{1,\vec{q}} d\phi_{2,\vec{q}} e^{-\beta Un_0^2 \xi^2 \sum_{\vec{q}} q^2 (\phi_{1,\vec{q}}^2 + \phi_{2,\vec{q}}^2)} \quad (7.70)$$

and the correlation function can be calculated by

$$g(\vec{R}) = \frac{1}{Z} \int \prod_{\vec{q}} d\phi_{1,\vec{q}} d\phi_{2,\vec{q}} \exp \left\{ \frac{i}{\sqrt{V}} \sum_{\vec{q}} (\phi_{1,\vec{q}} + i\phi_{2,\vec{q}}) (1 - e^{i\vec{q}\cdot\vec{R}}) - \beta Un_0^2 \xi^2 \sum_{\vec{q}} q^2 (\phi_{1,\vec{q}}^2 + \phi_{2,\vec{q}}^2) \right\} \quad (7.71)$$

which can be evaluated by completing the square.

$$g(\vec{R}) = \exp \left\{ -\frac{k_B T}{Un_0^2 \xi^2} \frac{1}{V} \sum_{\vec{q}} \frac{1 - \cos \vec{q}\cdot\vec{R}}{q^2} \right\} = \exp \left\{ -\frac{k_B T}{Un_0^2 \xi^2 (2\pi)^2} \int d^2q \frac{1 - \cos \vec{q}\cdot\vec{R}}{q^2} \right\}. \quad (7.72)$$

We can again use the relation connection with the Bessel function used above and obtain

$$g(\vec{R}) = \exp \left\{ -\frac{k_B T}{Un_0^2 \xi^2 2\pi} \int_0^{\pi/r_0} dq \frac{1 - J_0(qR)}{q} \right\} = \exp \left\{ -\eta(T) \int_0^{\pi R/r_0} dx \frac{1 - J_0(x)}{x} \right\} \quad (7.73)$$

$$\approx \exp \left\{ -\eta(T) \ln \left(\frac{\pi R}{r_0} \right) \right\} = \left(\frac{\pi R}{r_0} \right)^{-\eta(T)}$$

where we introduce a cutoff for large q with $r_0 \approx n^{-1/3}$ the mean distance between the Bosons.

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.

7.2.2 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 Thouless 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

$$E = \frac{\hbar^2 n_0}{2m} 2\pi \ln \left(\frac{R}{\xi} \right) \quad (7.74)$$

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

$$F = E - TS = \left\{ \frac{\hbar^2 n_0}{2m} 2\pi - 2k_B T \right\} \ln \left(\frac{R}{\xi} \right) \quad (7.75)$$

which suggests a phase transition at

$$k_B T_{\text{KT}} = \frac{\hbar^2 n_0}{2m} \pi \quad (7.76)$$

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 total winding number of all vortices is conserved,

$$n_\psi^{(tot)} = \sum_i n_\phi^{(i)}. \quad (7.77)$$

We can discuss the gas of vortices in terms of the grand canonical ensemble.

Two vortices interact with each other by an energy

$$E_{ij} = -2 \frac{\hbar^2}{2m} 2\pi n_\phi^{(i)} n_\phi^{(j)} \ln \left| \frac{\vec{r}_i - \vec{r}_j}{\xi} \right|, \quad (7.78)$$

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

$$\mathcal{Z}_v = \sum_{N=0}^{\infty} \frac{z^N}{[(N/2)!]^2 \xi^{2N}} \sum_{\{n_\phi\}} \int d^2 r_1 \cdots d^2 r_N \exp \left[2\beta \frac{\hbar^2}{2m} 2\pi \sum_{i < j} n_\phi^{(i)} n_\phi^{(j)} \ln \left| \frac{\vec{r}_i - \vec{r}_j}{\xi} \right| \right] \quad (7.79)$$

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 $z \rightarrow 0$ 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

$$\langle |\vec{r}_1 - \vec{r}_2|^2 \rangle = \frac{1}{2\pi V \xi^2 \mathcal{Z}_v} \int_{|\vec{r}_1 - \vec{r}_2| \geq \xi} d^2 r_1 d^2 r_2 |\vec{r}_1 - \vec{r}_2|^2 \left| \frac{\vec{r}_1 - \vec{r}_2}{\xi} \right|^{-\frac{2\pi\beta\hbar^2}{m}} \quad (7.80)$$

where we renormalize by the volume (area) V 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

$$\langle |\vec{r}|^2 \rangle = \xi^{\frac{2\pi\beta\hbar^2}{2m} - 2} \int_{\xi}^{\infty} dr r^{3 - \frac{2\pi\beta\hbar^2}{2m}} = -\frac{\xi^2}{4 - \frac{2\pi\hbar^2}{mk_B T}} = \frac{\xi^2}{4} \left(\frac{T_{KT}}{T} - 1 \right)^{-1} \quad (7.81)$$

which shows that the vortex-anti-vortex separation is finite for $T < T_{KT}$ but diverges as $T \rightarrow T_{KT}$. Note that here the same transition temperature T_{KT} is found as in Eq.(7.76).

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,

$$\mathcal{H}_{XY} = J \sum_{\langle i,j \rangle} (S_i^x S_j^x + S_i^y S_j^y) = JS^2 \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j) \quad (7.82)$$

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.