

Statistical Mechanics

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Chapter 1

Introduction

Macroscopic amounts of matter manifest themselves in a vast variety of different phases. Besides gases, liquids, and solids, there are Bose-Einstein condensates, gels, liquid crystals, superfluids, and superconductors (including both the traditional metallic low-temperature superconductors and the more recently discovered ceramic high-temperature superconductors). There are other even more exotic forms of condensed matter such as nuclear matter inside dense neutron stars, and perhaps quark matter deep inside their cores, the quark-gluon plasma that existed during the first microsecond after the big bang, and the plasma of other elementary particles that filled the early universe.

The fundamental constituents of all these forms of matter are quite well understood in the standard model of particle physics: they are the quarks that are bound inside protons and neutrons, which in turn form the atomic nucleus, the electrons that surround the nucleus, as well as more exotic elementary particles such as the short-lived muons or the very weakly interacting neutrinos. Also the fundamental forces are quite well understood: the strong interactions that bind quarks inside protons and neutrons are mediated by gluons, the weak interactions responsible e.g. for radioactive decay are mediated by heavy W - and Z -bosons, electromagnetic interactions are mediated by massless photons, and then there is gravity — the weakest force in the universe.

Although the basic constituents of matter as well as the fundamental forces between them are well understood, it is in general extremely difficult to derive the complex properties of condensed matter from first principles. The enormous number of basic degrees of freedom that are participating in the dynamics of condensed matter makes it practically impossible to understand them in detail

from first principles. For example, a gas of N particles moving in 3-dimensional space has $3N$ microscopic degrees of freedom. A macroscopic sample of gas particles easily contains Avogadro's number of particles, $N_A \approx 6 \times 10^{23}$, an enormous number of degrees of freedom. If we know all forces that the gas particles exert on each other, and if we know the initial positions and velocities of all gas particles, e.g. classical mechanics can be used to describe the gas. The time evolution of the gas particles then results as the solution of Newton's equations, which is a system of $3N$ coupled ordinary second order differential equations. In practice, it is impossible to solve such a gigantic system of equations. Already the determination of the initial conditions alone is practically impossible. Even if we would be able to overcome all these problems, the solution of Newton's equation would provide us with a set of $3N$ functions describing the particle coordinates as functions of time. Hence, although the fundamental theories of physics — classical or quantum mechanics — in principle allow us to deal explicitly with all microscopic degrees of freedom, in practice this is neither possible nor particularly useful. Who wants to know exactly how each individual degree of freedom evolves as a function of time?

It is much more adequate to describe the gas by macroscopic quantities that are averages over many microscopic degrees of freedom. Such averaged quantities are, for example, the energy or particle number density. Remarkably, we don't need to know in detail how the system works microscopically before we can make statements about those macroscopic quantities. For example, in the nineteenth century physicists knew much less about the basic constituents of matter than we do today, and still they were able to develop the very successful theory of thermodynamics. The large number of particles in a gas undergoes chaotic motion. The kinetic energy of this motion manifests itself as heat. To a large extent thermodynamics is the science of heat. No matter how complicated a system is microscopically, it will always obey energy conservation. Consequently, heat appears as a form of energy in the first law of thermodynamics, which just represents energy conservation.

While it is easy to convert mechanical energy into heat (e.g. by using the friction between a rotating stick and a wooden plate), it is impossible to completely convert heat back into mechanical energy (e.g. by heating a stick and wooden plate and waiting for the stick to start rotating). A machine that would completely convert heat into mechanical energy is known as a perpetuum mobile of the second kind. Although it would obey energy conservation (and hence the first law of thermodynamics), it would violate the second law of thermodynamics, which states that entropy (a measure of disorder) never decreases. Hence, a perpetuum mobile of the second kind can indeed not exist. In the nineteenth century

engineers were interested in converting heat into mechanical energy, for example, using steam engines. Indeed, originally one motivation for the development of thermodynamics was the need to understand the dynamics of steam engines. Even though heat cannot be converted completely into mechanical energy, it can be converted to some extent. The most efficient engine for doing this is going through a so-called Carnot process. Remarkably, even if we would not understand how the gas works at microscopic scales (which was true for nineteenth century engineers), we can compute the efficiency of a Carnot machine.

Thermodynamics is limited to understanding the most basic features of a macroscopic system which follow from basic principles like energy conservation and entropy increase. Statistical mechanics is more ambitious and tries to derive thermodynamic properties from the underlying microscopic physics. At microscopic scales physics is governed by quantum mechanics. Hence, to some extent we will be dealing with quantum statistical mechanics. In general it will be difficult to derive the averaged thermodynamic quantities exactly from the microscopic dynamics. This is particularly hard if the averages of microscopic quantities still vary in space or with time. In that case, the system would not be in thermodynamic equilibrium. If, on the other hand, the system is in equilibrium, its macroscopic features are characterized by a small number of averages which are themselves constant. Even then, for interacting systems it is in general impossible to derive those averages exactly from the microscopic degrees of freedom. We will hence start with simple systems like ideal, i.e. non-interacting, gases and proceed to interacting systems later.

Chapter 2

Kinetic Theory of the Classical Ideal Gas

As an introduction to the subject of statistical mechanics, let us study gases consisting of weakly interacting atoms or molecules. The atoms or molecules of a gas move more or less independent of each other. One can use an idealization to describe this situation: in an ideal gas, the atoms or molecules move independently as free particles, except during collisions which are assumed to be completely elastic. In practice it is completely impossible (and fortunately unnecessary) to describe all the degrees of freedom (of order 10^{23}) in detail. It is much more practical to describe the gas particles from a statistical point of view. Their average force on the walls of a container determines the pressure of the gas, and the average kinetic energy of the particles determines the temperature. Pressure and temperature are directly measurable physical quantities which characterize the gas much better than a list of all positions and momenta of the gas particles. Pressure, temperature, and density of a gas are related to each other by the ideal gas law. When a gas is heated, it increases its internal energy (and hence its temperature) and it may also expand and thereby do work. The energy balance of a gas is summarized in the first law of thermodynamics which reflects nothing but energy conservation. To get acquainted with gases, we will first consider their elementary constituents: atoms and molecules, and study some of their properties.

2.1 Atoms and Molecules

Atoms consist of an atomic nucleus and a number of electrons. The nucleus consists of Z positively charged protons and N neutrons and has a size of the order of 10^{-14} m. The whole atom is electrically neutral because there are also Z negatively charged electrons forming a cloud surrounding the nucleus. The size of the electron cloud (and of the entire atom) is of the order of 10^{-10} m. The mass of a neutron or proton is one atomic mass unit $M_n \approx M_p = 1u = 1.66 \times 10^{-24}$ g, while the electron mass is much smaller ($M_e = 9.04 \times 10^{-28}$ g). Hence, the mass of the atom is almost entirely concentrated in the nucleus and we can write it as $M_A = (Z + N)u$.

To understand the physics of the electron cloud as well as of the nucleus we need quantum mechanics. However, at moderate temperatures the energy is insufficient to ionize the atoms and we can treat the atoms as point-like and structureless. This is exactly what we do for a monatomic ideal gas. Of course, this is an idealization. In particular, at very high temperatures the electrons could be removed from the atomic nucleus and the system becomes a plasma (as e.g. the matter that exists in the sun). At yet much higher temperatures even the atomic nucleus itself would dissolve into quarks and gluons and we would end up in a quark-gluon plasma — the state of matter that existed during the first microsecond after the big bang.

The simplest atom is the hydrogen atom H . It consists of one proton (the nucleus) and one electron in the cloud and has a mass $M_H = 1u$. The electrons are bound to the atomic nucleus by electromagnetic forces. These forces also bind atoms to molecules. For example, two hydrogen atoms may form a hydrogen molecule H_2 , by sharing their electron cloud. The diatomic hydrogen molecule has a mass $M_{H_2} = 2u$. Table 2.1 summarizes some properties of atoms and molecules.

How many water molecules are contained in 1 cm^3 of water? We know that 1 liter = 10^3 cm^3 of water weighs 1 kg. Hence, 1 cm^3 of water weighs 1 g. One water molecule weighs $18u$, so the number of water molecules in 1 cm^3 of water is

$$N = \frac{1\text{g}}{18u} = \frac{1\text{g}}{2.98 \times 10^{-23}\text{g}} = 3.36 \times 10^{22}. \quad (2.1.1)$$

Consequently, 18 g of water contain Avogadro's number

$$N_A = 18N = 6.02 \times 10^{23} \quad (2.1.2)$$

of water molecules. An amount of matter that contains N_A basic units (atoms

Particle	notation	Z	N	M_A
hydrogen atom	H	1	0	$1u$
helium atom	He	2	2	$4u$
nitrogen atom	N	7	7	$14u$
oxygen atom	O	8	8	$16u$
hydrogen molecule	H ₂	2	0	$2u$
nitrogen molecule	N ₂	14	14	$28u$
oxygen molecule	O ₂	16	16	$32u$
water molecule	H ₂ O	10	8	$18u$

Table 2.1: *Basic Properties of some atoms and molecules.*

or molecules) of some substance is called one mole of that substance. One mole of water weighs 18 g, and in general one mole of a substance weighs the number of its basic units in grams. For example, one mole of oxygen gas (O₂) weighs 32 g, while one mole of helium gas (He) weighs 4 g. The first contains N_A oxygen molecules, the second N_A helium atoms.

2.2 Pressure and Temperature of the Ideal Gas

Let us consider a container of volume $V = L_x \times L_y \times L_z$ containing an ideal gas consisting of N particles (atoms or molecules) of mass M . The number density of gas particles is then given by $n = N/V$ and the mass density is $\rho = NM/V = Mn$. The gas particles perform a random, chaotic motion, and each has its own velocity \vec{v}_a . The particles collide with each other and with the walls of the container. For an ideal gas we assume that all these collisions are completely elastic.

Let us consider the average force that the gas exerts on the walls of the container. This will lead to an expression for the pressure of the gas. When particle number a collides with the wall (perpendicular to the x -direction) its velocity \vec{v}_a changes to \vec{v}'_a . Since the collision is elastic we have $v'_{ax} = -v_{ax}$. Hence, during the collision particle a transfers an impulse $J_{ax} = 2Mv_{ax}$ to the wall (in the perpendicular x -direction). What is the probability for particle a hitting the wall during a time interval Δt ? In order to be able to reach the wall within Δt , the particle must at most be a distance $\Delta x_a = v_{ax}\Delta t$ away from the wall. Since the wall has area $A = L_y \times L_z$, it must be inside a volume $A\Delta x_a$. Since the total volume is V , the probability to be within the volume $A\Delta x_a$ is $A\Delta x_a/V$. Still, the particle will not necessarily hit the wall, even if it is within

the volume $A\Delta x_a$. In half of the cases it will move away from the wall. Hence, the probability for particle a to hit the wall during the time Δt is only

$$\frac{1}{2} \frac{A\Delta x_a}{V} = \frac{1}{2} \frac{Av_{ax}\Delta t}{V}. \quad (2.2.1)$$

The force (impulse per time) exerted on the wall by particle a is hence given by

$$F_{ax} = \frac{2Mv_{ax}}{\Delta t} \frac{1}{2} \frac{Av_{ax}\Delta t}{V} = \frac{A}{V} Mv_{ax}^2, \quad (2.2.2)$$

and the total force exerted by all particles is

$$F_x = \sum_{a=1}^N F_{ax} = \frac{A}{V} \sum_{a=1}^N Mv_{ax}^2 = \frac{A}{V} N \langle Mv_x^2 \rangle. \quad (2.2.3)$$

We have introduced the average over all particles

$$\langle Mv_x^2 \rangle = \frac{1}{N} \sum_{a=1}^N Mv_{ax}^2. \quad (2.2.4)$$

The force (perpendicular to the wall) per unit area of the wall is the pressure which is hence given by

$$p = \frac{F_x}{A} = \frac{N}{V} \langle Mv_x^2 \rangle = \frac{N}{V} \frac{2}{3} \left\langle \frac{M}{2} v^2 \right\rangle. \quad (2.2.5)$$

Here we have introduced the velocity squared $v^2 = v_x^2 + v_y^2 + v_z^2$ and we have used symmetry to argue that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. Now we can write

$$pV = N \frac{2}{3} \left\langle \frac{M}{2} v^2 \right\rangle. \quad (2.2.6)$$

In other words, the pressure of the gas is proportional to the average kinetic energy of the gas particles $\langle \frac{1}{2} Mv^2 \rangle$. Pressure is measured in Pascal (1 Pa = 1 N/m²) and the typical atmospheric pressure is about 10⁵ Pa.

The absolute temperature T of the gas is defined by

$$\frac{3}{2} k_B T = \left\langle \frac{M}{2} v^2 \right\rangle. \quad (2.2.7)$$

Up to the numerical factor $\frac{3}{2} k_B$ the temperature is just the average kinetic energy of the gas particles. The Boltzmann constant k_B is present to match the different units of temperature and energy. If we (or Boltzmann and his colleagues)

had decided to measure temperature in Joules (J), k_B could have been dropped. However, temperature is traditionally measured in degrees Kelvin (K) and

$$k_B = 1.38 \times 10^{-23} \text{ J/K}. \quad (2.2.8)$$

From its definition it is clear that the absolute temperature must be positive, i.e. $T \geq 0$, because $v^2 \geq 0$. Only if all gas particles are at rest we have $T = 0$. This corresponds to the absolute zero of temperature (0 K). In degrees Celsius this corresponds to -273.16 C.

With the above definition of temperature we now obtain

$$pV = Nk_B T. \quad (2.2.9)$$

This is the ideal gas law. Sometimes it is also written as

$$pV = \mathcal{N}RT, \quad (2.2.10)$$

where $\mathcal{N} = N/N_A$ is the number of moles of gas, and $R = k_B N_A = 8.3$ J/K is the so-called gas constant.

A monatomic ideal gas has no internal degrees of freedom. In contrast to diatomic gases, the particles in a monatomic ideal gas are considered as point-like and cannot rotate or vibrate. The average energy $\langle E \rangle$ of a monatomic ideal gas is hence just its kinetic energy, i.e.

$$\langle E \rangle = N \left\langle \frac{M}{2} v^2 \right\rangle = \frac{3}{2} N k_B T, \quad (2.2.11)$$

and we can also write the ideal gas law as

$$pV = \frac{2}{3} \langle E \rangle. \quad (2.2.12)$$

Chapter 3

Microcanonical and Canonical Ensemble

In this chapter we introduce some powerful formalism of statistical mechanics. First we formulate classical mechanics using the Hamilton formalism. Then we introduce the concept of an ensemble and we discuss the microcanonical and the canonical ensembles. To illustrate these ideas we use the model of a particle on an energy ladder and we introduce a simple model for a heat bath.

3.1 The Hamilton Function

The previous discussion of the ideal gas was intuitive and did not use more than we know from Newtonian mechanics. It also led to the concepts of pressure and temperature. We need additional powerful concepts that will be useful also beyond ideal gases. In particular, as a preparation of quantum statistical mechanics (the quantum mechanical version of statistical mechanics) it is useful to introduce classical mechanics (and then classical statistical mechanics) in the so-called Hamilton formulation. Although perhaps less intuitive, the new formulation will turn out to be extremely useful. Later we will use the ideal gas to show explicitly that the new formalism is completely equivalent to what we derived before.

The configuration of a general classical system of particles is characterized by specifying the coordinates \vec{x}_a and the momenta \vec{p}_a of all the particles. The coordinates and momenta define the so-called phase space of the system. The total energy of any configuration of the system is given by the classical Hamilton

function

$$\mathcal{H}[x, p] = \sum_a \frac{p_a^2}{2M_a} + \sum_{a>b} V(|\vec{x}_a - \vec{x}_b|). \quad (3.1.1)$$

The first term is the total kinetic energy. Here M_a is the mass of particle number a . The second term is the total potential energy which we have assumed to be a sum of pair-potentials depending on the distance of the interacting particles. The Hamilton function describes the dynamics of the system through the Hamilton equations of motion

$$\frac{\partial \mathcal{H}}{\partial p_{ai}} = \frac{dx_{ai}}{dt}, \quad \frac{\partial \mathcal{H}}{\partial x_{ai}} = -\frac{dp_{ai}}{dt}. \quad (3.1.2)$$

For the Hamilton function from above these equations take the form

$$\frac{p_{ai}}{M_a} = \frac{dx_{ai}}{dt}, \quad \sum_b F_{abi} = \frac{dp_{ai}}{dt}. \quad (3.1.3)$$

We conclude that

$$\vec{p}_a = M_a \frac{d\vec{x}_a}{dt}, \quad (3.1.4)$$

i.e. momentum is the product of mass and velocity. Furthermore

$$F_i^{ab} = -\frac{\partial V(|\vec{x}_a - \vec{x}_b|)}{\partial x_{ai}} \quad (3.1.5)$$

is the force that particle b exerts on particle a . Taking the time derivative of the momentum and combining both equations we obtain

$$M_a \frac{d^2 \vec{x}_a}{dt^2} = \frac{d\vec{p}_a}{dt} = \sum_b \vec{F}_{ab}. \quad (3.1.6)$$

This is nothing but Newton's equation, which is hence completely equivalent to the pair of Hamilton equations of motion.

Physical quantities $\mathcal{O}[x, p]$ are functions over configuration (or phase) space. Examples of relevant physical quantities are the total energy $\mathcal{H}[x, p]$, the kinetic energy

$$\mathcal{T}[x, p] = \sum_a \frac{p_a^2}{2M_a}, \quad (3.1.7)$$

the potential energy

$$\mathcal{V}[x, p] = \sum_{a>b} V(|\vec{x}_a - \vec{x}_b|), \quad (3.1.8)$$

or the total momentum

$$\vec{\mathcal{P}}[x, p] = \sum_a \vec{p}_a. \quad (3.1.9)$$

3.2 The Concept of an Ensemble

Let us consider a gas in a container with a removable wall that separates the left from the right half of the container. Let us assume that all gas particles are initially in the left half of the container, while the right half is empty. When we remove the wall, the gas will immediately expand into the right half and will eventually reach an equilibrium state. In equilibrium, we will never find all the gas particles in the left half again, because without the wall such configurations are extremely improbable.

A classical gas evolves through configuration (or phase) space following the Hamilton (or equivalently Newton's) classical equations of motion, starting from its initial conditions. In order to understand the probabilities with which different configurations are realized during the time-evolution, one might attempt to solve the equations of motion. However, due to the enormous number of degrees of freedom and due to our limited knowledge of the initial conditions, this is completely impossible in practice. Fortunately, this is indeed not necessary.

Statistical mechanics describes the probabilities of the various configurations using the concept of an ensemble. Instead of considering a single system during its time-evolution, one considers a large number of independent identical systems (an ensemble) at one moment in time. The hypothesis of ergodicity states that in equilibrium the time-average of a single system is the same as the ensemble average over many independent identical systems. An ensemble is characterized by a probability distribution

$$\rho[x, p] = \rho(\vec{x}_1, \vec{p}_1, \vec{x}_2, \vec{p}_2, \dots, \vec{x}_N, \vec{p}_N) \geq 0, \quad (3.2.1)$$

which describes the probability to find a system in the ensemble that is in the configuration $(\vec{x}_1, \vec{p}_1), (\vec{x}_2, \vec{p}_2), \dots, (\vec{x}_N, \vec{p}_N)$. The total probability is normalized as

$$\int \mathcal{D}x \mathcal{D}p \rho[x, p] = 1. \quad (3.2.2)$$

Here the integrations extend over all of phase space, i.e.

$$\mathcal{D}x \mathcal{D}p = \frac{1}{\Delta^N} d^3 x_1 d^3 p_1 d^3 x_2 d^3 p_2 \dots d^3 x_N d^3 p_N. \quad (3.2.3)$$

Here Δ is an arbitrarily chosen volume of phase space which is introduced in order to make the integration measure dimensionless. An ensemble average of a physical quantity \mathcal{O} is given by

$$\langle \mathcal{O} \rangle = \int \mathcal{D}x \mathcal{D}p \mathcal{O}[x, p] \rho[x, p]. \quad (3.2.4)$$

Note that the arbitrarily chosen factor Δ drops out of this expression for the average.

3.3 The Microcanonical Ensemble

Depending on the physical conditions, different systems are described by different ensembles. The simplest case is the so-called microcanonical ensemble for which

$$\rho[x, p] = \frac{1}{Z(E)} \delta(\mathcal{H}[x, p] - E). \quad (3.3.1)$$

This ensemble describes an isolated system with total energy E . For example, a gas in a container with perfectly reflecting walls can be described in this way. It is completely isolated from the rest of the world and cannot exchange energy with it. Hence, the total energy of all the gas particles is necessarily conserved. Instead of considering a single isolated system during its time-evolution, the microcanonical ensemble describes a large number of independent identical systems, all with the same total energy E . In the microcanonical ensemble all configurations are equally probable, as long as they have the correct total energy E . The energy-dependent partition function $Z(E)$ of the microcanonical ensemble is a normalization factor for the total probability and is given by

$$Z(E) = \int \mathcal{D}x \mathcal{D}p \delta(\mathcal{H}[x, p] - E). \quad (3.3.2)$$

The average of the total energy in the microcanonical ensemble is given by

$$\begin{aligned} \langle \mathcal{H} \rangle &= \int \mathcal{D}x \mathcal{D}p \mathcal{H}[x, p] \rho[x, p] \\ &= \frac{1}{Z(E)} \int \mathcal{D}x \mathcal{D}p \mathcal{H}[x, p] \delta(\mathcal{H}[x, p] - E) \\ &= E \frac{1}{Z(E)} \int \mathcal{D}x \mathcal{D}p \delta(\mathcal{H}[x, p] - E) \\ &= E \int \mathcal{D}x \mathcal{D}p \rho[x, p] = E. \end{aligned} \quad (3.3.3)$$

It is interesting to consider the variance

$$\Delta \mathcal{O} = \sqrt{\langle \mathcal{O}^2 \rangle - \langle \mathcal{O} \rangle^2} \quad (3.3.4)$$

of a physical quantity \mathcal{O} . In the microcanonical ensemble the variance of the energy vanishes because

$$\langle \mathcal{H}^2 \rangle = E^2 = \langle \mathcal{H} \rangle^2. \quad (3.3.5)$$

Other physical quantities like the kinetic or potential energy will in general have a non-zero variance in the microcanonical ensemble.

3.4 The Canonical Ensemble

Many interesting physical systems are not totally isolated from the rest of the world. For example, we could put our gas container inside a bigger tank of gas at some temperature T . Now the gas inside the container can exchange energy with the surrounding gas in the tank which serves as a so-called heat bath. As a result, the gas in the container will eventually reach a new equilibrium at the same temperature as the heat bath. In the following it will be important that the heat bath is very large and can exchange an unlimited amount of energy with our physical system. In particular, when energy is absorbed by the system this will not lead to a decrease of the temperature of the heat bath.

The canonical ensemble describes a system in thermal equilibrium with a heat bath of temperature T . Since the system can exchange energy with the heat bath, the energy of the system now fluctuates (it has a variance). The distribution function of the canonical ensemble is given by

$$\rho[x, p] = \frac{1}{Z(\beta)} \exp(-\beta\mathcal{H}[x, p]), \quad (3.4.1)$$

where $\beta = 1/k_B T$ is the inverse temperature (in units of k_B). The partition function of the canonical ensemble is hence given by

$$Z(\beta) = \int \mathcal{D}x \mathcal{D}p \exp(-\beta\mathcal{H}[x, p]), \quad (3.4.2)$$

and the thermal average of a physical quantity is given by

$$\langle \mathcal{O} \rangle = \frac{1}{Z(\beta)} \int \mathcal{D}x \mathcal{D}p \mathcal{O}[x, p] \exp(-\beta\mathcal{H}[x, p]). \quad (3.4.3)$$

It is interesting to note that the thermal average of the energy can be written as

$$\begin{aligned} \langle \mathcal{H} \rangle &= -\frac{\partial \log Z(\beta)}{\partial \beta} = -\frac{1}{Z(\beta)} \frac{\partial Z(\beta)}{\partial \beta} \\ &= \frac{1}{Z(\beta)} \int \mathcal{D}x \mathcal{D}p \mathcal{H}[x, p] \exp(-\beta\mathcal{H}[x, p]). \end{aligned} \quad (3.4.4)$$

Similarly, the variance of the energy takes the form

$$\begin{aligned} (\Delta\mathcal{H})^2 &= \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial^2 \log Z(\beta)}{\partial \beta^2} \\ &= \frac{1}{Z(\beta)} \frac{\partial^2 Z(\beta)}{\partial \beta^2} - \frac{1}{Z(\beta)^2} \left(\frac{\partial Z(\beta)}{\partial \beta} \right)^2. \end{aligned} \quad (3.4.5)$$

The partition functions of the canonical and microcanonical ensembles are related by a so-called Laplace transform

$$\begin{aligned} Z(\beta) &= \int_{-\infty}^{\infty} dE Z(E) \exp(-\beta E) \\ &= \int_{-\infty}^{\infty} dE \int \mathcal{D}x \mathcal{D}p \delta(\mathcal{H}[x, p] - E) \exp(-\beta E) \\ &= \int \mathcal{D}x \mathcal{D}p \exp(-\beta \mathcal{H}[x, p]). \end{aligned} \quad (3.4.6)$$

The Laplace transform is closely related to the more familiar Fourier transform. Indeed, if we analytically continue the inverse temperature to purely imaginary values and write $\beta = it$ the above equation turns into a Fourier transform

$$Z(it) = \int_{-\infty}^{\infty} dE Z(E) \exp(-iEt). \quad (3.4.7)$$

The corresponding inverse Fourier transform takes the form

$$Z(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt Z(it) \exp(iEt). \quad (3.4.8)$$

Using the Fourier representation of the δ -function

$$\delta(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-iEt), \quad (3.4.9)$$

one can write

$$\begin{aligned} Z(E) &= \int \mathcal{D}x \mathcal{D}p \delta(\mathcal{H}[x, p] - E) \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \int \mathcal{D}x \mathcal{D}p \exp(-i(\mathcal{H}[x, p] - E)t) \\ &= \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} d\beta \int \mathcal{D}x \mathcal{D}p \exp(-\beta \mathcal{H}) \exp(\beta E) \\ &= \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} d\beta Z(\beta) \exp(\beta E). \end{aligned} \quad (3.4.10)$$

In analogy to the inverse Fourier transform of eq.(3.4.8) this is the inverse Laplace transform. It should be noted that β is to be integrated over purely imaginary values.

3.5 Particle on an Energy Ladder

To illustrate the ideas introduced before, let us consider a simple physical system — a single particle on a ladder. A classical physics realization of this model is a particle that climbs a ladder in the gravitational potential of the earth. The ladder has steps of height $z_n = z_0 n$, $n = 0, 1, 2, \dots, \infty$ with a corresponding potential energy

$$\mathcal{H}[n] = E_n = Mgz_n = Mgz_0 n = \epsilon n, \quad \epsilon = Mgz_0. \quad (3.5.1)$$

Here g is the gravitational acceleration and M is the particle mass.¹ The particle in this model has only potential (and no kinetic) energy and hence its total energy is given by E_n . It will turn out that the total energy of a quantum mechanical harmonic oscillator is also described by an energy ladder with $E_n = \hbar\omega(n + \frac{1}{2})$ where ω is the frequency of the oscillator and \hbar is Planck's constant. Until we will be familiar enough with quantum mechanics we can imagine the classical particle on the ladder. Still, the most interesting physical applications of the energy ladder emerge from the quantum harmonic oscillator.

Let us consider the canonical partition function of the particle on the ladder. Since the particle only has potential energy, its configuration is entirely specified by the step n . Hence the partition function is a sum (and not an integral) over configuration space and we obtain

$$Z(\beta) = \sum_{n=0}^{\infty} \exp(-\beta E_n) = \sum_{n=0}^{\infty} \exp(-\beta \epsilon n) = \frac{1}{1 - \exp(-\beta \epsilon)}. \quad (3.5.2)$$

Here we have used the formula for a geometric series

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1 - x}. \quad (3.5.3)$$

¹Strictly speaking this formula for the potential energy is valid only close to the earth's surface.

The average energy takes the form

$$\begin{aligned}\langle \mathcal{H} \rangle &= -\frac{\partial \log Z(\beta)}{\partial \beta} = \frac{\partial \log[1 - \exp(-\beta\epsilon)]}{\partial \beta} \\ &= \frac{\epsilon \exp(-\beta\epsilon)}{1 - \exp(-\beta\epsilon)} = \frac{\epsilon}{\exp(\beta\epsilon) - 1}.\end{aligned}\tag{3.5.4}$$

Similarly, the variance of the energy is given by

$$(\Delta \mathcal{H})^2 = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial^2 \log Z(\beta)}{\partial \beta^2} = \frac{\epsilon^2 \exp(\beta\epsilon)}{[\exp(\beta\epsilon) - 1]^2}.\tag{3.5.5}$$

Hence the ratio of the variance and the average energy is given by

$$\frac{\Delta \mathcal{H}}{\langle \mathcal{H} \rangle} = \exp\left(\frac{1}{2}\beta\epsilon\right).\tag{3.5.6}$$

Such a large variance is typical for small systems (we are dealing with a single particle), while for large systems the variance is typically much smaller than the average.

3.6 Model for a Heat Bath

Let us use the particle on the energy ladder to discuss a simple model for a heat bath. The heat bath consists of a large number of particles with energy zero or ϵ . The fraction with energy ϵ is $q \in [0, \frac{1}{2}]$. The single particle on the ladder is coupled to the heat bath. At each time-step it interacts with one of the bath particles and exchanges energy according to the following rules. If the particle on the ladder is hit by a bath particle of energy ϵ it absorbs the energy and jumps from the step n up to the step $n + 1$. We assume that the bath is infinitely large, such that the fraction q does not change when a bath particle transfers its energy to the particle on the ladder. If the particle on the ladder is hit by a bath particle of energy zero, on the other hand, the particle on the ladder steps down from step n to step $n - 1$ and transfers the energy ϵ to the bath. The only exception from this rule arises when the ladder particle is initially at the ground level $n = 0$. Then it cannot lower its energy further. It will then stay at $n = 0$ and will not transfer energy to the bath. The interaction of the particle on the ladder with the heat bath can be characterized by a transition probability between steps n and $n + 1$

$$w[n \rightarrow n + 1] = q,\tag{3.6.1}$$

(with probability q the particle on the ladder is hit by a bath particle of energy ϵ and steps up the ladder), and between the steps n and $n - 1$

$$w[n \rightarrow n - 1] = 1 - q, \quad n \geq 1, \quad (3.6.2)$$

(with probability $1 - q$ the particle on the ladder is hit by a bath particle of energy zero and steps down the ladder). Finally, if initially $n = 0$

$$w[0 \rightarrow 0] = 1 - q. \quad (3.6.3)$$

All other transition probabilities are zero, i.e.

$$w[n \rightarrow n'] = 0, \quad |n' - n| \geq 2. \quad (3.6.4)$$

For any given initial $n \geq 1$ the transition probability is correctly normalized because

$$\sum_{n'} w[n \rightarrow n'] = w[n \rightarrow n + 1] + w[n \rightarrow n - 1] = q + 1 - q = 1, \quad (3.6.5)$$

and also for $n = 0$

$$\sum_{n'} w[0 \rightarrow n'] = w[0 \rightarrow 1] + w[0 \rightarrow 0] = q + 1 - q = 1. \quad (3.6.6)$$

Let us imagine that the particle on the ladder is initially characterized by an ensemble with probability distribution $\rho_0[n]$. For example, if the particle is initially certainly on the ground we have $\rho_0[n] = \delta_{n0}$, but any other initial probability distribution would also be possible. After one time-step, i.e. after one interaction with a bath particle, the new probability distribution will be

$$\rho_1[n'] = \sum_n \rho_0[n] w[n \rightarrow n']. \quad (3.6.7)$$

Similarly, after the i -th time step, i.e. after i interactions with the bath particles

$$\rho_i[n'] = \sum_n \rho_{i-1}[n] w[n \rightarrow n']. \quad (3.6.8)$$

After a large number of time-steps, we expect that the particle on the ladder will get into thermal equilibrium with the heat bath, i.e. its probability distribution will converge to a fixed $\rho_\infty[n]$ which is characterized by

$$\rho_\infty[n'] = \sum_n \rho_\infty[n] w[n \rightarrow n']. \quad (3.6.9)$$

In particular, for $n' \geq 1$ this implies

$$\begin{aligned}\rho_\infty[n'] &= \rho_\infty[n'-1]w[n'-1 \rightarrow n'] + \rho_\infty[n'+1]w[n'+1 \rightarrow n'] \\ &= q\rho_\infty[n'-1] + (1-q)\rho_\infty[n'+1],\end{aligned}\quad (3.6.10)$$

and for $n' = 0$

$$\rho_\infty[0] = \rho_\infty[0]w[0 \rightarrow 0] + \rho_\infty[1]w[1 \rightarrow 0] = (1-q)\rho_\infty[0] + (1-q)\rho_\infty[1]. \quad (3.6.11)$$

This equation implies

$$\rho_\infty[1] = \frac{q}{1-q}\rho_\infty[0]. \quad (3.6.12)$$

Using

$$\rho_\infty[1] = q\rho_\infty[0] + (1-q)\rho_\infty[2], \quad (3.6.13)$$

this leads to

$$\rho_\infty[2] = \frac{\rho_\infty[1] - q\rho_\infty[0]}{1-q} = \left(\frac{q}{1-q}\right)^2 \rho_\infty[0]. \quad (3.6.14)$$

Generally one obtains

$$\rho_\infty[n] = \left(\frac{q}{1-q}\right)^n \rho_\infty[0]. \quad (3.6.15)$$

Remarkably, the equilibrium distribution $\rho_\infty[n]$ resembles the canonical ensemble $\rho[n]$ for which

$$\rho[n] = \frac{1}{Z(\beta)} \exp(-\beta\mathcal{H}[n]) = \frac{1}{Z(\beta)} \exp(-\beta E_n) = \exp(-\beta\epsilon n)\rho[0], \quad (3.6.16)$$

if one identifies

$$\frac{q}{1-q} = \exp(-\beta\epsilon) \Rightarrow q = \frac{1}{\exp(\beta\epsilon) + 1}. \quad (3.6.17)$$

3.7 Canonical Ensemble for Particles on a Ladder

We will now consider not just one but N distinguishable particles on the energy ladder. The configuration $[n]$ of the system is then specified by the heights $z_a = n_a z_0$ (with $a \in \{1, 2, \dots, N\}$) of each of the N particles. The corresponding Hamilton function is given by

$$\mathcal{H}[n] = \sum_{a=1}^N E_a = \epsilon \sum_{a=1}^N n_a, \quad (3.7.1)$$

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and the canonical partition function

$$Z(\beta) = \sum_{[n]} \exp(-\beta\mathcal{H}[n]) = \prod_{a=1}^N \sum_{n_a=0}^{\infty} \exp(-\beta\epsilon n_a) = z(\beta)^N \quad (3.7.2)$$

factorizes into single particle partition functions

$$z(\beta) = \sum_{n=0}^{\infty} \exp(-\beta\epsilon n) = \frac{1}{1 - \exp(-\beta\epsilon)}. \quad (3.7.3)$$

The average energy of the particles is given by

$$\langle \mathcal{H} \rangle = -\frac{\partial \log Z(\beta)}{\partial \beta} = -N \frac{\partial \log z(\beta)}{\partial \beta} = N \frac{\epsilon}{\exp(\beta\epsilon) - 1}, \quad (3.7.4)$$

which is just N times the average energy in the single particle case. Let us also consider the variance of the energy

$$(\Delta \mathcal{H})^2 = \frac{\partial^2 \log Z(\beta)}{\partial \beta^2} = N \frac{\partial^2 \log z(\beta)}{\partial \beta^2} = N \frac{\epsilon^2 \exp(\beta\epsilon)}{[\exp(\beta\epsilon) - 1]^2}. \quad (3.7.5)$$

The ratio of the variance and the average of the energy now takes the form

$$\frac{\Delta \mathcal{H}}{\langle \mathcal{H} \rangle} = \frac{1}{\sqrt{N}} \exp\left(\frac{1}{2}\beta\epsilon\right). \quad (3.7.6)$$

In the so-called thermodynamic limit $N \rightarrow \infty$ of a large number of particles, the fluctuations of the energy are suppressed as $1/\sqrt{N}$.

3.8 Microcanonical Ensemble for Particles on a Ladder

Let us again consider N distinguishable particles on the energy ladder. However, we will now use the microcanonical ensemble, i.e. the N particles will share a fixed amount of energy $E = M\epsilon$. Let us first determine the microcanonical partition function $Z(E) = Z(M, N)$. How many ways are there for distributing M basic units of energy ϵ among N distinguishable particles? Let us begin with the trivial case of a single particle ($N = 1$). Then that particle gets all the energy and

$$Z(M, 1) = 1. \quad (3.8.1)$$

Next we consider two particles. Then we can give n units of energy to particle 1 and the remaining $M - n$ units to particle 2, such that

$$Z(M, 2) = M + 1. \quad (3.8.2)$$

With three particles the thing gets more interesting. First, we can give n units of energy to particle 1 and we can then distribute the remaining $M - n$ units among the particles 2 and 3. There are $Z(M - n, 2) = M - n + 1$ ways of doing that and hence

$$Z(M, 3) = \sum_{n=0}^M Z(M - n, 2) = \sum_{n=0}^M (M - n + 1) = \frac{(M + 2)(M + 1)}{2}. \quad (3.8.3)$$

The general formula for N particles takes the form

$$Z(M, N) = \frac{(M + N - 1)!}{M!(N - 1)!}, \quad (3.8.4)$$

which indeed satisfies

$$Z(M, N) = \sum_{n=0}^M Z(M - n, N - 1). \quad (3.8.5)$$

What is the density of particles at step n ? In other words, what is the probability of particle 1 (or any other particle) to reach step n . The previous discussion immediately implies

$$\rho[n] = \frac{Z(M - n, N - 1)}{Z(M, N)} = \frac{(M - n + N - 2)!}{(M - n)!(N - 2)!} \frac{M!(N - 1)!}{(M + N - 1)!}. \quad (3.8.6)$$

Let us consider a system of many particles ($N \rightarrow \infty$) with a large amount of energy ($M \rightarrow \infty$), such that the energy per particle, i.e. M/N , remains fixed. We now use the Stirling formula

$$\log N! = N \log N - N, \quad (3.8.7)$$

which holds in the limit of large N . This implies

$$\begin{aligned} \log \rho[n] &= \log Z(M - n, N - 1) - \log Z(M, N) \\ &= (M - n + N - 2) \log(M - n + N - 2) - (M - n) \log(M - n) \\ &\quad - (N - 2) \log(N - 2) + M \log M \\ &\quad + (N - 1) \log(N - 1) - (M + N - 1) \log(M + N - 1) \\ &= \log \rho[0] - n \log(M + N) + n \log M + \mathcal{O}(n^2), \end{aligned} \quad (3.8.8)$$

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and hence

$$\rho[n] = \rho[0] \left(\frac{M}{M+N} \right)^n = \rho[0] \exp(-\beta \epsilon n). \quad (3.8.9)$$

Remarkably, this is the same result as for the canonical ensemble provided that we identify

$$\exp(\beta \epsilon) = 1 + \frac{N}{M} = 1 + \frac{N\epsilon}{E} \Rightarrow E = N \frac{\epsilon}{\exp(\beta \epsilon) - 1}. \quad (3.8.10)$$

The average energy in the canonical ensemble is indeed given by

$$\langle \mathcal{H} \rangle = N \frac{\epsilon}{\exp(\beta \epsilon) - 1}. \quad (3.8.11)$$

Hence, in the thermodynamical limit of many particles ($N \rightarrow \infty$) both the canonical and the microcanonical ensemble give the same physical results. In particular, just as for any N in the microcanonical ensemble, for $N \rightarrow \infty$ the variance of the total energy vanishes even in the canonical ensemble.

Chapter 4

Information and Entropy

In this chapter we introduce other useful concepts — information and information deficit as well as the closely related entropy.

4.1 Information and Information Deficit

Let us imagine that somebody places a queen at some unknown square on the chess board. How many binary questions do we need to ask in order to figure out where the queen is? First of all, the question “Where is the queen?” is not binary because a possible answer would be “On B7”, and not just “Yes” or “No”. Binary questions have only two possible answers: “Yes” or “No”. The question “Is the queen on F4?” is binary, but not necessarily the best question to ask. For example, following the strategy of checking out individual squares, in the worst case it requires 63 questions to figure out where the queen is.¹ On the other hand, if we are lucky we find the queen already after the first question. On the average, following this strategy, we would need 32 questions to locate the queen. Obviously, there is a much better strategy. First, we ask “Is the queen in the left side of the board?”. If the answer is “No”, we concentrate on the right side and ask “Is the queen in the top-half of the right side?” Depending on the answer, we check out one half of the remaining section of the board. In this way, after $\log_2 64 = 6$ questions we will always find the queen. Hence, although following the second strategy we will never find the queen after the first question,

¹Of course, we don’t need to ask the 64th question because if we got the answer “No” 63 times, we know that the queen is on the square we did not check.

on average we will find it more than five times faster than using the first strategy. Indeed the second strategy is optimal, because it minimizes the average number of binary questions.

How much information is encoded in the position of the queen? Hence, how big is our information deficit when we don't know where the queen is? By positioning the queen we can store the answer to 6 binary questions, hence the information content is 6 bits. Consequently, initially our information deficit is also 6 bits. With every binary question we reduce the deficit by one bit, until finally, after 6 questions, we have extracted all the information.

As we just defined it, information is measured in bits which encode answers to binary questions. What if the information content is not an integer number of bits? For example, let us imagine that the queen can only be placed in three possible positions. Then, following the logic from before, the information deficit should be $I_3 = \log_2 3 \approx 1.585$ bits. Following an optimal strategy, how many binary questions do we need to ask on average in order to reveal the position of the queen? We can ask "Is the queen in position 1?". In $\frac{1}{3}$ of the cases, the answer will be "Yes" and we are done in one step. In the other $\frac{2}{3}$ of the cases the answer is "No" and we ask "Is the queen in position 2?". In any case, no matter if the question is "Yes" or "No", after the second question we know where the queen is. Hence, on average we need to ask $\frac{1}{3} + \frac{2}{3} \cdot 2 = \frac{5}{3} \approx 1.667$ binary questions. Although this is not exactly equal to I_3 it is quite close ($\frac{5}{3}/I_3 \approx 1.05$). What if we place the queen in one out of five possible positions? In that case, the information deficit should be $I_5 = \log_2 5 \approx 2.322$ bits. In this case, we can ask "Is the queen in position 1 or 2?". In $\frac{2}{5}$ of the cases the answer will be "Yes", and we need one more question to figure out where the queen is. In $\frac{3}{5}$ of the cases, on the other hand, the answer will be "No". Then we can proceed as in the three-position case and will on average need $\frac{5}{3}$ more questions. Hence, in total on average we need to ask $\frac{2}{5} \cdot 2 + \frac{3}{5} \cdot (1 + \frac{5}{3}) = \frac{12}{5}$ questions, such that $\frac{12}{5}/I_5 \approx 1.03$ which is even closer to 1 than in the three-position case. In the following we will be dealing with very large configuration spaces of size $Z(E)$. Then the difference between $\log_2 Z(E)$ and the average number of binary questions required to figure out the configuration is totally negligible. Hence, in the following we will define

$$I = \log_2 Z(E) \tag{4.1.1}$$

as the information deficit, even if in general it is not an integer number of bits.

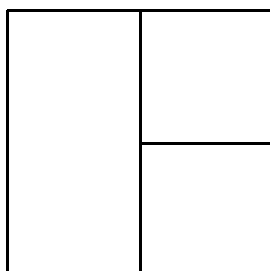
4.2 The Concept of Entropy

Entropy is another concept very closely related to information deficit. It is a measure of disorder. Entropy is defined for any ensemble, i.e. for any probability distribution $\rho[n]$, not only for ensembles describing thermal equilibrium such as the canonical or microcanonical ones. For a general ensemble the entropy is defined as

$$S = -k_B \sum_{[n]} \rho[n] \log \rho[n]. \quad (4.2.1)$$

The second law of thermodynamics states that the total entropy of the Universe always increases with time. This does not mean that the entropy of a subsystem cannot decrease. For example, we can establish some order in one part of the Universe (for example, in our brain) at the expense of increasing the entropy of the rest of the world.

To illustrate the basic idea behind entropy, let us again consider a simple example related to chess. We divide the chess board into three regions as shown in the figure:



The queen is placed on one of the 64 squares with equal probabilities. Once the queen is placed, we no longer distinguish between the squares within a given region and only ask in which region the queen is. On average, what is the minimum number of binary questions we need to ask in order to locate the queen? First, we ask if the queen is on the left side of the board. In one half of the cases the answer will be “Yes” and we are done. In the other half of the cases we ask once more “Is the queen in the top-half of the right side?”. The answer will then allow us to locate the queen after two questions. Hence, on average we need $\frac{1}{2} + \frac{1}{2}2 = \frac{3}{2}$ binary questions to locate the queen, and the information deficit is thus $I = \frac{3}{2}$. What is the corresponding entropy? The queen on the divided board is described by the following ensemble. With probability $\frac{1}{2}$ it is in region 1 (the left-half of the board) and hence $\rho[1] = \frac{1}{2}$. With probabilities $\frac{1}{4}$ the queen is in regions 2 and 3 (the top and bottom half of the right-half of the board) and

hence $\rho[2] = \rho[3] = \frac{1}{4}$. According to the previous definition, the corresponding entropy is hence given by

$$\begin{aligned} S &= -k_B(\rho[1] \log \rho[1] + \rho[2] \log \rho[2] + \rho[3] \log \rho[3]) \\ &= -k_B\left(\frac{1}{2} \log \frac{1}{2} + 2\frac{1}{4} \log \frac{1}{4}\right) = -k_B\left(\frac{1}{2} \log_2 \frac{1}{2} + \frac{1}{2} \log_2 \frac{1}{4}\right) \log 2 \\ &= k_B\left(\frac{1}{2} + \frac{1}{2} \cdot 2\right) \log 2 = k_B \frac{3}{2} \log 2 = k_B I \log 2. \end{aligned} \quad (4.2.2)$$

The final equality is not just a coincidence. As we will see later, entropy and information deficit are generally related by $S = k_B I \log 2$.

4.3 Entropy and Free Energy in the Canonical Ensemble

In the canonical ensemble the entropy is given by

$$\begin{aligned} S &= -k_B \sum_{[n]} \rho[n] \log \rho[n] \\ &= k_B \sum_{[n]} \frac{1}{Z(\beta)} \exp(-\beta \mathcal{H}[n]) [\beta \mathcal{H}[n] + \log Z(\beta)] \\ &= k_B [\beta \langle \mathcal{H} \rangle + \log Z(\beta)]. \end{aligned} \quad (4.3.1)$$

Introducing the so-called free energy F as

$$Z(\beta) = \exp(-\beta F), \quad (4.3.2)$$

and putting $\langle \mathcal{H} \rangle = E$, the entropy takes the form

$$S = k_B \beta (E - F) = \frac{1}{T} (E - F) \Rightarrow F = E - TS. \quad (4.3.3)$$

4.4 Entropy of Particles on a Ladder

Let us again consider N distinguishable particles on an energy ladder. In the canonical ensemble the free energy of N distinguishable particles on the ladder is given by

$$F = -\frac{1}{\beta} \log Z(\beta) = -\frac{N}{\beta} \log z(\beta) = \frac{N}{\beta} \log[1 - \exp(-\beta \epsilon)], \quad (4.4.1)$$

and the entropy takes the form

$$S = \frac{1}{T}(E - F) = k_B N \left\{ \frac{\beta \epsilon}{\exp(\beta \epsilon) - 1} - \log[1 - \exp(-\beta \epsilon)] \right\}. \quad (4.4.2)$$

Let us also consider the system in the microcanonical ensemble, in which the N particles share M basic units of energy ϵ . As we argued before, the corresponding microcanonical partition function is given by

$$Z(E) = Z(M, N) = \frac{(M + N - 1)!}{M!(N - 1)!}. \quad (4.4.3)$$

How many binary questions do we need to pose in order to figure out the configuration $[n]$ of the system? According to our definition, the information deficit is given by

$$I = \log_2 Z(E) = \log_2 \frac{(M + N - 1)!}{M!(N - 1)!} = \log \frac{(M + N - 1)!}{M!(N - 1)!} / \log 2. \quad (4.4.4)$$

Again, going to the thermodynamical limit $M, N \rightarrow \infty$ and using Sterling's formula one obtains

$$\begin{aligned} I &= [(M + N) \log(M + N) - M \log M - N \log N] / \log 2 \\ &= [(M + N) \left(\log M + \log\left(1 + \frac{N}{M}\right)\right) - M \log M - N \log N] / \log 2 \\ &= [(M + N) \log\left(1 + \frac{N}{M}\right) + N \log \frac{M}{N}] / \log 2 \\ &= N \left[\left(1 + \frac{M}{N}\right) \log\left(1 + \frac{N}{M}\right) + \log \frac{M}{N} \right] / \log 2 \\ &= N [\beta \epsilon - \log(\exp(\beta \epsilon) + 1)] / \log 2. \end{aligned} \quad (4.4.5)$$

We have again used

$$\begin{aligned} 1 + \frac{N}{M} &= \exp(\beta \epsilon), \quad 1 + \frac{M}{N} = \frac{\exp(\beta \epsilon)}{\exp(\beta \epsilon) - 1}, \\ \log \frac{M}{N} &= \log \frac{1}{\exp(\beta \epsilon) - 1} = -\beta \epsilon - \log[1 - \exp(-\beta \epsilon)]. \end{aligned} \quad (4.4.6)$$

Remarkably, up to a factor $k_B \log 2$ the information deficit in the microcanonical ensemble is just the entropy in the canonical ensemble. In particular, in the thermodynamical limit we can identify

$$S = k_B I \log 2. \quad (4.4.7)$$

This clarifies further the physical meaning of the entropy, it is the analog of the information deficit in the microcanonical ensemble and, in fact, it is a measure of disorder.

4.5 The Principle of Maximum Entropy

The second law of thermodynamics states that entropy never decreases. Hence, as a system approaches thermal equilibrium it should increase its entropy and finally reach an entropy maximum in thermal equilibrium. Let us assume the second law of thermodynamics and thus postulate a principle of maximum entropy. Which ensemble then has the maximum amount of entropy? In order to answer this question we assume an arbitrary ensemble characterized by a probability distribution $\rho[n]$ and we maximize the entropy

$$S = -k_B \sum_{[n]} \rho[n] \log \rho[n]. \quad (4.5.1)$$

Of course, while we maximize the entropy, we cannot violate energy conservation. Hence, we should maximize the entropy under the constraint that at least the average energy

$$\langle \mathcal{H} \rangle = \sum_{[n]} \mathcal{H}[n] \rho[n] = E \quad (4.5.2)$$

is fixed. Also the probability distribution itself must be normalized correctly to

$$\sum_{[n]} \rho[n] = 1. \quad (4.5.3)$$

The above constraints can be incorporated via two Lagrange multipliers, i.e. we should maximize

$$S' = -k_B \sum_{[n]} \rho[n] \log \rho[n] - \lambda \left(\sum_{[n]} \mathcal{H}[n] \rho[n] - E \right) - \lambda' \left(\sum_{[n]} \rho[n] - 1 \right), \quad (4.5.4)$$

such that

$$\frac{\partial S'}{\partial \rho[n]} = -k_B \log \rho[n] - k_B - \lambda \mathcal{H}[n] - \lambda' = 0, \quad (4.5.5)$$

and we obtain

$$\rho[n] = \exp(-\lambda \mathcal{H}[n]/k_B - \lambda'/k_B - 1) = \frac{1}{Z(\beta)} \exp(-\beta \mathcal{H}[n]). \quad (4.5.6)$$

Remarkably, this is just the canonical ensemble if we identify $\lambda = 1/T$. The other Lagrange multiplier is given by

$$\frac{1}{Z(\beta)} = \exp(-\lambda'/k_B - 1) = \exp(-\beta F) \Rightarrow \lambda' = \frac{F}{T} - k_B. \quad (4.5.7)$$

As we have seen earlier, the coupling to a heat bath leads to the canonical ensemble. As we see now, the canonical ensemble also arises from the principle of maximum entropy, which in turn relies on the second law of thermodynamics.

Let us also consider the principle of entropy maximization in the context of the microcanonical ensemble. In that case, energy is automatically conserved and we only need to impose $\sum_{[n]} \rho[n] = 1$, such that

$$S' = -k_B \sum_{[n]} \rho[n] \log \rho[n] - \lambda' \left(\sum_{[n]} \rho[n] - 1 \right), \quad (4.5.8)$$

and

$$\frac{\partial S'}{\partial \rho[n]} = -k_B \log \rho[n] - k_B - \lambda' = 0. \quad (4.5.9)$$

Hence, we now obtain

$$\rho[n] = \exp(-\lambda'/k_B - 1) = \frac{1}{Z(E)}. \quad (4.5.10)$$

Hence, this is indeed the microcanonical ensemble if we identify

$$\lambda' = k_B [\log Z(E) - 1] = k_B I \log 2 - k_B = S - k_B. \quad (4.5.11)$$

Hence, we see that both the canonical and the microcanonical ensemble can be derived from the principle of maximum entropy.

4.6 The Arrow of Time

Why does time flow from the past to the future? This is a very profound question that we may hope to understand by studying physics. First of all, is there a fundamental difference between the past and the future? In other words, do the fundamental laws of Nature single out a preferred direction of time or are they invariant against time-reversal? Indeed, time-reversal is a symmetry of most fundamental forces in Nature. In particular, the laws of classical mechanics or of electrodynamics are time-reversal invariant. For example, if we change the direction of all momenta of an isolated system of particles, the particles trace back the same paths they originally went through. The resulting motion is the same as the one obtained by reversing the direction of time. Indeed, Newton's laws or Maxwell's equations make no fundamental difference between the past and the future. Also the Schrödinger equation of quantum mechanics is time-reversal

invariant. Yet in this context there are subtle issues related to the quantum mechanical measurement process which we will not touch upon here.

Our present understanding of fundamental physics is based on relativistic quantum field theories which incorporate the basic principles of quantum mechanics as well as special relativity. In the context of relativistic quantum field theories one can prove the so-called *CPT* theorem, which states that the fundamental forces described by such theories are invariant under the combined transformations of charge conjugation *C*, parity *P*, and time-reversal *T*. While *T* changes the direction of time, parity changes the sign of the three spatial coordinates, and charge conjugation exchanges all particles with their antiparticles. All we know about elementary particle physics today is summarized in the so-called standard model. As a relativistic quantum field theory the standard model necessarily obeys the *CPT* theorem. The strongest fundamental forces of the standard model, namely the strong interactions (responsible for quark confinement and the binding of the atomic nucleus) and the electromagnetic interactions are even invariant under the individual symmetries *C*, *P*, and *T* — not only under the combination *CPT*. The weak interactions (e.g. responsible for radioactive decay), on the other hand, are not invariant separately under *C* and *P*, but only under the combination *CP*. Hence, using the *CPT* theorem, even the weak interactions are invariant under *T*. Still, there is a very weak force (whose physical origin is presently not very well understood) which indeed violates *CP* and thus (due to the *CPT* theorem) also *T*. This interaction involves the so-called Higgs field whose quantum — the Higgs particle — has not yet been directly verified experimentally. It is one of the physics objectives of the Large Hadron Collider (LHC) presently being built at CERN to find the Higgs particle (the start of these experiments is planned for 2007). Although the Higgs particle itself has not yet been found, the *CP*- and thus *T*-violating interaction mediated by the Higgs field has been verified experimentally in the decays of neutral *K*-mesons — elementary particles consisting of a quark and an anti-quark. It should be noted that *T*-violation in the standard model involves all three quark generations. Ordinary matter is made almost entirely of the up (u) and down (d) quarks of the first generation, with only small admixtures of the charm (c) and strange (s) quarks of the second generation. The third generation consists of the very heavy top (t) and bottom (b) quarks which can only be produced in particle accelerators. Hence, although Nature does make a fundamental difference between the past and the future (e.g. in the decay of neutral *K*-mesons), the corresponding processes are extremely rare and have practically no effect on the matter that surrounds us today. It should be noted that the weakest fundamental force — gravity — is not part of the standard model, because we presently don't understand how to treat general relativity (Einstein's classical theory of gravity) quantum mechanically.

Some attempts to go in this direction involve string theory (a possible extension of relativistic quantum field theory) which may even violate *CPT*. Still, classical gravity is perfectly *T*-invariant. We may hence conclude that, although there is indeed an extremely weak interaction that breaks time-reversal, all fundamental forces that govern the matter that surrounds us today do not distinguish the past from the future.

Still, as weak as they may be today, *CP*- and thus *T*-violating forces may have played an important role immediately after the big bang. In particular, without *T*-violation there would be no baryon asymmetry, i.e. the young Universe would have contained exactly equal amounts of matter and antimatter. In our Universe, due to *T*-violating forces, there was a very tiny surplus of matter compared to antimatter. About one second after the big bang all the antimatter annihilated with almost all the matter, thus generating the cosmic microwave background radiation which carries almost all of the entropy of the Universe today. Only the tiny surplus of matter escaped the mass extinction with the antimatter and constitutes all the matter that exists in the Universe today. In particular, it is the stuff that condensed matter (including us) is made of. Without *T*-violating forces (and thus without a baryon asymmetry) the Universe would consist entirely of cosmic background radiation. In particular, there would be nobody there to worry about things like the arrow of time.

If the fundamental forces relevant for the dynamics of the matter that surrounds us today are invariant under time-reversal, every physical process should be reversible. In other words, the phenomena that we observe when playing a movie backwards should be consistent with the fundamental laws of Nature. However, this seems obviously not to be the case. We are familiar with an egg falling down from the kitchen table, cracking open, and making a big mess; but we have never seen the mess reassemble itself to an intact egg, then jumping back up on the table. This is a consequence of the second law of thermodynamics: the total entropy of the Universe is always increasing. Ordered configurations are extremely rare compared to disordered ones. Hence, when a system starts from an ordered configuration (the intact egg on the table) and evolves in time, even if the underlying fundamental dynamics are invariant under time-reversal, it will most likely evolve towards the much more probable disordered configurations (the mess on the floor).

If this is true, why was the hen able to produce the egg in the first place? Or, for example, why are we able to put together the pieces of a puzzle? Living creatures are out of thermal equilibrium. They eat sugar (a highly ordered form of energy) and do some more or less useful things with it (like laying an egg or

putting together a puzzle). However, along with such activities they sweat and thus produce heat. In total the entropy of the Universe still increases, but a small part of the world (the egg or the puzzle) gets more ordered. Where did the sugar come from? Ultimately, the sugar is energy from sunlight converted into chemical energy through photosynthesis. So why is there sunlight? Well, there is hydrogen gas in the Universe which collapses under its own gravity and makes stars like the sun. The hydrogen gas itself formed about 400,000 years after the big bang. At that time, the Universe had expanded so much that the hot plasma of positively charged protons and negatively charged electrons had cooled down sufficiently that neutral atoms could form. Today the age of the Universe is about 13×10^9 years. After 5×10^9 more years or so, the sun will go through a red giant phase and will eventually burn out. Even if the earth survives the red giant phase and does not evaporate, this will be the end of energy supply to the earth and thus the end of life on it. At some point (in about 10^{14} years or so) even the oldest stars will be burnt out, all hydrogen in the Universe will be used up, and no new stars can be born. By then all eggs will have turned into a big mess and no new ones will be laid. There is no way out: entropy will win the game. Fortunately for us, these events will take place only in the very distant future.

What will happen to the matter of the burnt out stars and the entropy contained in them? Through gravitational attraction, the matter will ultimately collapse into black holes. Already today, the center of our and other galaxies contains a super-massive black hole. What happens to the entropy of the matter when it falls into a black hole? Or alternatively, what happens to information, e.g. when you throw your laptop into a black hole? The solution of the black hole entropy and information puzzle is still controversial. In any case, entropy or information may not be lost, but may ultimately be returned to the rest of the world in the form of Hawking radiation — photons (and other particles) produced quantum mechanically at the black hole horizon. Even the largest black hole should eventually evaporate into Hawking radiation (after 10^{100} years or so) and the Universe may ultimately be filled entirely with photons. This is probably the absolute maximum of the entropy and a true sign of death of the Universe at the end of time.

If, as far as the underlying fundamental forces are concerned, there is essentially no difference between the past and the future, why do we experience time as flowing in one direction. For example, why do we remember the past and not the future? This may just be a matter of definition: we may simply define a biological arrow of time by declaring the future as that part of time we cannot remember. Alternatively, we may define a thermodynamical arrow of time by declaring the future as the time-direction in which the total entropy

increases. Then an interesting question arises: why are the biological and the thermodynamical arrows pointing in the same direction? In other words, why do we only remember things that happened when the entropy was lower. In order to remember the past, we must store information in our brain. Obviously, this creates some order in the brain, and thus decreases its entropy. According to the second law of thermodynamics, this is possible only if we use some energy (we eat sugar), produce some heat (we sweat), and thus contribute to the overall entropy increase of the rest of the world. Computers work in a similar way: they consume energy to store and process information and they produce a lot of heat. Consequently, we can only remember (or store information about) those times at which the entropy of the rest of the world was lower. Entropy increase also explains why we are born before and not after we die. Its again the same story that leads from the egg to the big mess. Perhaps not surprisingly, when we age it becomes harder to maintain a low entropy in our brain (i.e. we forget things), and finally, when we die, our entropy has increased so much that we literally approach thermal equilibrium with the rest of the world.

Chapter 5

Canonical Ensemble for the Ideal Gas

In this chapter we apply the concept of the canonical ensemble to the classical ideal gas. This leads to the Maxwell-Boltzmann distribution as well as to the barometric height formula. While classical particles are distinguishable, due to their elementary quantum nature identical atoms or molecules are not. This has drastic consequences for the configuration space of a gas.

5.1 The Maxwell-Boltzmann Distribution

Let us now consider the canonical ensemble for the classical ideal gas. The ideal gas has only kinetic energy and its Hamilton function is given by

$$\mathcal{H}[x, p] = \sum_{a=1}^N \frac{p_a^2}{2M}. \quad (5.1.1)$$

Hence the distribution function of the canonical ensemble takes the form

$$\rho[x, p] = \frac{1}{Z(\beta)} \exp(-\beta\mathcal{H}[x, p]) = \frac{1}{Z(\beta)} \prod_{a=1}^N \exp(-\beta \frac{p_a^2}{2M}), \quad (5.1.2)$$

which is known as the Maxwell-Boltzmann distribution. Since the gas particles are independent, the distribution function factorizes into contributions from the

individual particles. Hence, the canonical partition function takes the form

$$\begin{aligned} Z(\beta) &= \int \mathcal{D}x \mathcal{D}p \exp(-\beta \mathcal{H}[x, p]) \\ &= \prod_{a=1}^N \frac{1}{\Delta} \int d^3x_a d^3p_a \exp(-\beta \frac{p_a^2}{2M}) = z(\beta)^N. \end{aligned} \quad (5.1.3)$$

Here

$$z(\beta) = \frac{1}{\Delta} \int d^3x d^3p \exp(-\beta \frac{p^2}{2M}) = \frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \quad (5.1.4)$$

is the partition function of a single gas particle, and V is the spatial volume filled by the gas.

Let us determine the average energy of the gas particles

$$\langle \mathcal{H} \rangle = -\frac{\partial \log Z(\beta)}{\partial \beta} = -N \frac{\partial \log z(\beta)}{\partial \beta} = \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T. \quad (5.1.5)$$

This confirms that the temperature of the canonical ensemble is indeed identical with the temperature that we defined before as the average kinetic energy for an ideal gas. Let us also consider the variance of the energy

$$(\Delta \mathcal{H})^2 = \frac{\partial^2 \log Z(\beta)}{\partial \beta^2} = N \frac{\partial^2 \log z(\beta)}{\partial \beta^2} = \frac{3}{2} N \frac{1}{\beta^2}. \quad (5.1.6)$$

The ratio of the variance and the average of the energy then takes the form

$$\frac{\Delta \mathcal{H}}{\langle \mathcal{H} \rangle} = \sqrt{\frac{2}{3N}}. \quad (5.1.7)$$

In the thermodynamic limit $N \rightarrow \infty$ of a large number of particles, the fluctuations of the energy are suppressed as $1/\sqrt{N}$.

5.2 Ideal Gas in a Gravitational Field

Let us consider the earth's atmosphere in the gravitational potential Mgz of the earth. The real atmosphere is a complicated dynamical system that is very nontrivial to understand. In particular, there is weather which means that the atmosphere is not in global thermal equilibrium. For example, the temperature is not constant everywhere in the atmosphere but usually decreases with the height. Here we idealize the atmosphere as an ideal gas in thermal equilibrium, i.e. with

a fixed constant temperature independent of the height. The Hamilton function of the ideal gas in the gravitational field of the earth is given by

$$\mathcal{H}[x, p] = \sum_{a=1}^N \frac{p_a^2}{2M} + \sum_{a=1}^N Mgz_a. \quad (5.2.1)$$

The distribution function of the canonical ensemble now takes the form

$$\rho[x, p] = \frac{1}{Z(\beta)} \exp(-\beta\mathcal{H}[x, p]) = \frac{1}{Z(\beta)} \prod_{a=1}^N \exp(-\beta \frac{p_a^2}{2M} - \beta Mgz_a), \quad (5.2.2)$$

and the canonical partition function is given by

$$\begin{aligned} Z(\beta) &= \int \mathcal{D}x \mathcal{D}p \exp(-\beta\mathcal{H}[x, p]) \\ &= \prod_{a=1}^N \frac{1}{\Delta} \int d^3x_a d^3p_a \exp(-\beta \frac{p_a^2}{2M} - \beta Mgz_a) = z(\beta)^N. \end{aligned} \quad (5.2.3)$$

Again the gas particles are independent and the single-particle partition function is now given by

$$z(\beta) = \frac{1}{\Delta} \int d^3x d^3p \exp(-\beta \frac{p^2}{2M} - \beta Mgz) = \frac{A}{\Delta} \frac{1}{\beta M g} \left(\frac{2\pi M}{\beta} \right)^{3/2}. \quad (5.2.4)$$

Here A is the area over which the atmosphere is considered.

Let us again determine the average energy of the gas particles

$$\langle \mathcal{H} \rangle = -\frac{\partial \log Z(\beta)}{\partial \beta} = -N \frac{\partial \log z(\beta)}{\partial \beta} = \frac{3}{2} N \frac{1}{\beta} + \frac{N}{\beta} = \frac{5}{2} N k_B T. \quad (5.2.5)$$

Similarly, the variance of the energy is given by

$$(\Delta \mathcal{H})^2 = \frac{\partial^2 \log Z(\beta)}{\partial \beta^2} = N \frac{\partial^2 \log z(\beta)}{\partial \beta^2} = \frac{5}{2} N \frac{1}{\beta^2} \quad (5.2.6)$$

and hence

$$\frac{\Delta \mathcal{H}}{\langle \mathcal{H} \rangle} = \sqrt{\frac{2}{5N}}. \quad (5.2.7)$$

What is the density of the atmosphere as a function of the height z ? To answer this question we simply identify the probability density $\rho(z)$ for a gas particle to reach the height z which is given by

$$\begin{aligned} \rho(z) &= \frac{1}{z(\beta)\Delta} \int dx dy d^3p \exp(-\beta \frac{p^2}{2M} - \beta Mgz) \\ &= \beta M g \exp(-\beta Mgz) = \rho(0) \exp(-\beta Mgz). \end{aligned} \quad (5.2.8)$$

This expression — known as the barometric height formula — describes the density decrease in the atmosphere.

5.3 Distinguishability of Classical Particles

Actual gases consist of atoms and molecules whose dynamics are governed by quantum mechanics. When we work classically some things are radically different than in quantum mechanics. For example, a classical physicist (like Boltzmann) may have thought of atoms like tiny classical billiard balls. Classical objects are distinguishable. For example, we can imagine to label each billiard ball with a number. Even if we don't enumerate the particles, we can distinguish them by their initial positions (“This is the particle that started with initial momentum \vec{p}_1 from the initial position \vec{x}_1 ”). If we have two particles a and b with positions and momenta (\vec{x}_1, \vec{p}_1) and (\vec{x}_2, \vec{p}_2) they can be in two possible configurations. In the first configuration the particle with label a has position and momentum (\vec{x}_1, \vec{p}_1) and the particle with label b has position and momentum (\vec{x}_2, \vec{p}_2) , while in the second configuration the particle with label b has position and momentum (\vec{x}_1, \vec{p}_1) and the particle with label a has position and momentum (\vec{x}_2, \vec{p}_2) . The two configurations are different because the two particles are distinguishable (by their labels a and b). Similarly, N distinguishable particles with positions and momenta $(\vec{x}_1, \vec{p}_1), (\vec{x}_2, \vec{p}_2), \dots, (\vec{x}_N, \vec{p}_N)$ can exist in $N!$ different configurations.

The previous discussion is completely correct for a gas of classical objects, e.g. the “gas” of balls on a billiard table or in a lottery machine. However, actual atoms or molecules are not classical billiard balls. Instead, they follow the rules of quantum mechanics. Most important, identical atoms or molecules are completely indistinguishable. We cannot paint a label a or b on an atom (the paint itself would consist of other atoms) or say something like “this is the atom with the blue hair”. An elementary object like an atom has only a certain number of distinguishing features. It has a momentum, an excitation energy, an angular momentum, and that's it. In particular, besides those basic physical properties, it has no label or other identifying features that could distinguish it from other identical atoms.

Let us imagine that we remove the labels from a set of classical billiard balls and paint them all with the same color. Let us further assume that they are all perfectly round, have the same radius, and have exactly the same content. Then it would also become difficult to distinguish them. However, we could still keep track of the particles by following the individual balls along their trajectories and

say something like “this is the same ball that started originally with momentum \vec{p}_1 at position \vec{x}_1 ”. Interestingly, this again does not work for actual atoms which are quantum objects. In contrast to classical physics, due to the Heisenberg uncertainty principle, in quantum mechanics one cannot simultaneously measure both momentum and position with infinite precision. A quantum particle does not even have simultaneously a well-defined position and momentum. This has far-reaching physical consequences. In particular, this means that the concept of a classical particle trajectory no longer makes sense quantum mechanically (after all, the classical trajectory simultaneously specifies both position and momentum of a particle). If the concept of a trajectory no longer makes sense, we cannot keep track of individual atoms and distinguish them in that way. It is an inescapable consequence of quantum mechanics that identical particles cannot be distinguished. Hence, the combinatorial factor $N!$ of a classical “gas” of billiard balls is absent for a system of identical atoms. Of course, different atoms (like H and O) can still be distinguished.

5.4 The Entropy of the Classical Ideal Gas

Let us consider the entropy for the classical ideal gas. First of all, the defining formula for the entropy

$$S = -k_B \sum_{[n]} \rho[n] \log \rho[n] \quad (5.4.1)$$

is not readily applicable in this case because the configuration space is not discrete but continuous. In this case, it is natural to define the entropy as

$$S = -k_B \int \mathcal{D}x \mathcal{D}p \rho[x, p] \log \rho[x, p]. \quad (5.4.2)$$

In order to see that these two expressions for the entropy are consistent, let us divide the $6N$ -dimensional phase space into elementary hypercubic cells c_n of arbitrarily chosen volume Δ^N . The cells c_n are enumerated by a discrete label n . We can then average the probability distribution over an elementary cell and introduce

$$\rho[n] = \int_{c_n} \mathcal{D}x \mathcal{D}p \rho[x, p], \quad (5.4.3)$$

which is properly normalized by

$$\sum_{[n]} \rho_n = \sum_{[n]} \int_{c_n} \mathcal{D}x \mathcal{D}p \rho[x, p] = \int \mathcal{D}x \mathcal{D}p \rho[x, p] = 1. \quad (5.4.4)$$

In the limit of small cells (i.e. $\Delta \rightarrow 0$) we have

$$\rho[n] = \rho[x, p]. \quad (5.4.5)$$

Now the original definition of the entropy is applicable and one obtains

$$S = -k_B \sum_{[n]} \rho[n] \log \rho[n] = -k_B \int \mathcal{D}x \mathcal{D}p \rho[x, p] \log(\rho[x, p]). \quad (5.4.6)$$

One should ultimately take the limit $\Delta \rightarrow 0$. In this limit the entropy diverges. This may not be too surprising, since it indeed requires an infinite number of binary questions to figure out the location of a particle in a continuous configuration space.

The divergence of the entropy of the classical ideal gas is an “ultraviolet catastrophe”, similar to the Jeans catastrophe in classical black body radiation. In that case, a black body would radiate an infinite amount of energy — obviously a nonsensical result that puzzled physicists more than a hundred years ago. The puzzle was finally solved by Planck who introduced the quantum h . The fact that $h \neq 0$ cuts-off the radiation in the ultraviolet and thus prevents the Jeans catastrophe. As we will see later, quantum mechanics also prevents the ultraviolet catastrophe of the divergent entropy of a classical gas. Indeed, we will be able to relate the volume of an elementary cell of phase space $\Delta = h^3$ with Planck’s quantum h .

In order to proceed further without switching to a quantum mechanical treatment, we will keep the phase space volume Δ small but non-zero. For the classical ideal gas we then obtain

$$\begin{aligned} S &= -k_B \int \mathcal{D}x \mathcal{D}p \rho[x, p] \log(\rho[x, p]) \\ &= k_B \frac{1}{Z(\beta)} \int \mathcal{D}x \mathcal{D}p \exp(-\beta \mathcal{H}[x, p]) \{ \log Z(\beta) + \beta \mathcal{H}[x, p] \} \\ &= \frac{1}{T} (E - F). \end{aligned} \quad (5.4.7)$$

We have identified the free energy from

$$Z(\beta) = \exp(-\beta F). \quad (5.4.8)$$

Using the previous result for $Z(\beta)$ of eqs.(5.1.3,5.1.4) we obtain

$$F = -k_B T \log Z(\beta) = -N k_B T \log z(\beta) = -N k_B T \log \left[\frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]. \quad (5.4.9)$$

Also using $E = \langle \mathcal{H} \rangle = \frac{3}{2}Nk_B T$ we finally get

$$S = \frac{3}{2}Nk_B + Nk_B \log \left[\frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]. \quad (5.4.10)$$

Again, we see that the entropy diverges in the limit $\Delta \rightarrow 0$.

5.5 Gibbs' Paradox

The previous result for the entropy of the classical ideal gas is related to the so-called Gibbs paradox. The paradox is related to the fact that in the above expression the entropy is not an extensive quantity. Extensive quantities are proportional to the system size. For example, if we increase both the number of particles N and the volume V by the same factor λ , an extensive quantity should also increase by the same factor λ . Hence, if the entropy were an extensive quantity, it should obey $S(\lambda N, \lambda V) = \lambda S(N, V)$. Since the volume V is contained in the logarithmic term of eq.(5.4.10), in this case the entropy is indeed not extensive.

Why is this paradoxical? Let us consider a container of volume V which is divided into two parts of volume $V/2$ by a removable wall. Both parts are filled with $N/2$ particles of an ideal gas at the same temperature T on both sides. Let us now remove the wall. From a macroscopic point of view not much happens. In particular, the gas remains in thermal equilibrium. When we slide the wall back in, again not much happens and we essentially return to the initial situation.¹ We say that removing the wall is a reversible (or adiabatic) process. In such a process the system stays in thermal equilibrium. According to the rules of thermodynamics, entropy is conserved in reversible (adiabatic) processes. On the other hand, after removing the wall, according to eq.(5.4.10) the entropy increases by

$$\begin{aligned} S(N, V) - 2S(N/2, V/2) &= \\ Nk_B \log \left[\frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right] - Nk_B \log \left[\frac{V}{2\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right] &= \\ Nk_B \log 2. & \end{aligned} \quad (5.5.1)$$

¹Of course, after sliding the wall back in, we cannot expect that exactly $N/2$ particles will be in each half of the container. However, for sufficiently large N this will still be the case to very high accuracy.

Indeed this seems to make sense, because after removing the wall our information deficit has increased. Compared to the situation with the wall, we now need to ask one binary question for each particle in order to figure out in which half of the container it presently is. However, this obviously contradicts the reversible nature of the above process performed with an actual gas.

What is wrong with our model of the ideal gas? And thus, how can we resolve Gibbs' paradox? As we have pointed out before, actual atoms and molecules are indistinguishable objects, while we treated the constituents of the classical ideal gas as distinguishable. What would change if we would treat these constituents as indistinguishable? Since there are $N!$ ways of enumerating N objects, we would simply have to divide the partition function by the factor $N!$. The corresponding partition function then takes the form

$$Z'(\beta) = \frac{1}{N!}Z(\beta) = \frac{1}{N!}z(\beta)^N. \quad (5.5.2)$$

When we determine the average energy $E' = \langle \mathcal{H} \rangle$ (or other thermal expectation values) the additional factor $N!$ drops out since it is absorbed into the normalization of the total probability and hence $E' = E$. However, it affects the free energy F' and thus the entropy S' . In particular, we now obtain

$$\begin{aligned} Z'(\beta) &= \frac{1}{N!}Z(\beta) = \frac{1}{N!} \exp(-\beta F) = \exp(-\beta F') \Rightarrow \\ \beta F' &= \beta F + \log N! \Rightarrow \frac{F'}{T} = \frac{F}{T} + k_B(N \log N - N), \end{aligned} \quad (5.5.3)$$

where we have used Sterling's formula. Hence, one finds

$$S' = \frac{1}{T}(E' - F') = S - k_B(N \log N - N). \quad (5.5.4)$$

Inserting the result of eq.(5.4.10) we now obtain

$$S' = \frac{5}{2}Nk_B + Nk_B \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]. \quad (5.5.5)$$

Interestingly, this expression for the entropy is indeed extensive, i.e.

$$S'(\lambda N, \lambda V) = \lambda S'(N, V). \quad (5.5.6)$$

Consequently, taking into account the fundamental indistinguishability of the true elementary constituents of the gas — namely atoms or molecules — resolves Gibbs' paradox.

5.6 Mixing Entropy

In order to further clarify these issues, let us also discuss a physically different situation. We consider again a container of total volume V divided into two parts of volume $V/2$. However, this time the gas particles in sub-volume 1 are distinguishable from those in sub-volume 2. For example, we can imagine that the particles in sub-volume 1 have mass M_1 , while those in sub-volume 2 have mass M_2 and are thus distinguishable from the particles in sub-volume 1. Still, we want to assume that the particles in each sub-volume are indistinguishable among themselves. After removing the wall, the two gases mix and both types of particles can now occupy the entire volume. If we reintroduce the wall after a while, the situation will be very different from before. In particular, gas particles of both types will occupy both sub-volumes. Hence, the process of mixing the two gases is irreversible. Indeed, the corresponding entropy increase is now given by

$$\begin{aligned}
 & S'_1(N/2, V) + S'_2(N/2, V) - S'_1(N/2, V/2) - S'_2(N/2, V/2) = \\
 & \frac{N}{2}k_B \log \left[\frac{2V}{N\Delta} \left(\frac{2\pi M_1}{\beta} \right)^{3/2} \right] + \frac{N}{2}k_B \log \left[\frac{2V}{N\Delta} \left(\frac{2\pi M_2}{\beta} \right)^{3/2} \right] \\
 & - \frac{N}{2}k_B \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M_1}{\beta} \right)^{3/2} \right] - \frac{N}{2}k_B \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M_2}{\beta} \right)^{3/2} \right] = \\
 & Nk_B \log 2.
 \end{aligned} \tag{5.6.1}$$

We see that the distinguishability of the two particle types leads to a non-zero mixing entropy.

Chapter 6

Grand Canonical Ensemble

Until now we have considered the microcanonical and canonical ensembles in which the particle number of the system was fixed. In this chapter we introduce a new ensemble in which the particle number is not fixed but is controlled by a new parameter — the chemical potential. The corresponding ensemble is the so-called grand canonical ensemble.

6.1 Introduction of the Grand Canonical Ensemble

Let us imagine an empty container in which we punch a small hole. When the container is surrounded by air, some air molecules will find the small hole and will enter the container. Soon, the container will be filled with air and an equilibrium will be reached. Still, some air molecules will enter the container but others will leave. On the average, the number of entering and exiting air molecules per unit of time is the same, but still the number of air molecules inside the container is not always the same. The atmosphere surrounding the container provides a particle reservoir, just like a heat bath provides an energy reservoir. Just like the temperature controls the average energy, a new parameter controls the average particle number. This parameter is the chemical potential. Temperature and chemical potential are so-called thermodynamical potentials. While energy and particle number are extensive quantities (they increase with the system size), the thermodynamical potentials are intensive (and thus are independent of the system size).

Let us assume that a system can exist in a countable number of configurations

$[n]$. The total energy of the system is given by $\mathcal{H}[n]$ and the total number of particles is given by $\mathcal{N}[n]$. In particular, not all configurations contain the same number of particles. The grand canonical ensemble is then defined by the probability distribution

$$\rho[n] = \frac{1}{Z(\beta, \mu)} \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]). \quad (6.1.1)$$

Here μ is the chemical potential, an energy that we hand to each particle that is willing to leave the reservoir and enter the system. The grand canonical partition function

$$Z(\beta, \mu) = \sum_{[n]} \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]) \quad (6.1.2)$$

guarantees that the probability distribution is properly normalized to

$$\sum_{[n]} \rho[n] = 1. \quad (6.1.3)$$

The thermal average of some physical quantity \mathcal{O} is given by

$$\langle \mathcal{O} \rangle = \frac{1}{Z(\beta, \mu)} \sum_{[n]} \mathcal{O}[n] \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]). \quad (6.1.4)$$

As in the canonical ensemble, the partition function can be used as a generating functional for the thermal average and the variance of the total energy and the particle number. At this point it is useful to treat β and $\beta\mu$ as independent quantities. Then one can write

$$\begin{aligned} \langle \mathcal{N} \rangle &= \frac{\partial \log Z(\beta, \mu)}{\partial(\beta\mu)} = \frac{1}{Z(\beta, \mu)} \sum_{[n]} \mathcal{N}[n] \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]), \\ (\Delta \mathcal{N})^2 &= \langle \mathcal{N}^2 \rangle - \langle \mathcal{N} \rangle^2 = \frac{\partial^2 \log Z(\beta, \mu)}{\partial(\beta\mu)^2}, \\ \langle \mathcal{H} \rangle &= -\frac{\partial \log Z(\beta, \mu)}{\partial\beta} = \frac{1}{Z(\beta, \mu)} \sum_{[n]} \mathcal{H}[n] \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]), \\ (\Delta \mathcal{H})^2 &= \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial^2 \log Z(\beta, \mu)}{\partial\beta^2}. \end{aligned} \quad (6.1.5)$$

In the grand canonical ensemble the entropy is given by

$$\begin{aligned}
S &= -k_B \sum_{[n]} \rho[n] \log \rho[n] \\
&= -\frac{k_B}{Z(\beta, \mu)} \sum_{[n]} \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]) [-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]] - \log Z(\beta, \mu)] \\
&= \frac{1}{T} [E - \mu N - k_B T \log Z(\beta, \mu)].
\end{aligned} \tag{6.1.6}$$

The analog of the free energy F in the canonical ensemble is the so-called grand canonical potential J which is defined by

$$Z(\beta, \mu) = \exp(-\beta J), \tag{6.1.7}$$

such that

$$J = E - \mu N - TS. \tag{6.1.8}$$

6.2 Grand Canonical Ensemble of Particles on a Ladder

For illustrative purposes, let us again consider the system of particles on the energy ladder, now coupled to a particle reservoir. We can view this as a simple model for the atmosphere. As before we will consider distinguishable particles. The canonical partition function takes the form

$$\begin{aligned}
Z(\beta, \mu) &= \sum_{[n]} \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n]]) \\
&= \sum_{N=0}^{\infty} Z(\beta) \exp(\beta\mu N) = \sum_{N=0}^{\infty} [z(\beta) \exp(\beta\mu)]^N \\
&= \frac{1}{1 - z(\beta) \exp(\beta\mu)} = \frac{1 - \exp(-\beta\epsilon)}{1 - \exp(-\beta\epsilon) - \exp(\beta\mu)}.
\end{aligned} \tag{6.2.1}$$

Here $z(\beta)$ is again the single particle partition function of the canonical ensemble. It should be noted that we have implicitly assumed that $\exp(\beta\mu) < 1 - \exp(-\beta\epsilon)$. Otherwise the geometric series diverges and the partition function is infinite. We now obtain

$$N = \langle \mathcal{N} \rangle = \frac{\partial \log Z(\beta, \mu)}{\partial(\beta\mu)} = \frac{\exp(\beta\mu)}{1 - \exp(-\beta\epsilon) - \exp(\beta\mu)}, \tag{6.2.2}$$

which implies

$$\exp(\beta\mu) = \frac{1 - \exp(-\beta\epsilon)}{1 + 1/N} \quad (6.2.3)$$

Similarly

$$E = \langle \mathcal{H} \rangle = -\frac{\partial \log Z(\beta, \mu)}{\partial \beta} = \frac{\exp(\beta\mu)}{1 - \exp(-\beta\epsilon) - \exp(\beta\mu)} \frac{\epsilon \exp(-\beta\epsilon)}{1 - \exp(-\beta\epsilon)}, \quad (6.2.4)$$

and therefore one finds

$$E = N \frac{\epsilon}{\exp(\beta\epsilon) - 1}, \quad (6.2.5)$$

which is exactly the same result as in the canonical ensemble. Hence, we see that just like the canonical and microcanonical ensemble, also the canonical and grand canonical ensemble are physically equivalent.

Finally, let us also calculate the grand canonical potential

$$J = -\frac{1}{\beta} \log Z(\beta, \mu) = k_B T \log \frac{1 - \exp(-\beta\epsilon) - \exp(\beta\mu)}{1 - \exp(-\beta\epsilon)}, \quad (6.2.6)$$

which then yields the entropy

$$\begin{aligned} S &= \frac{1}{T}(E - \mu N - J) \\ &= k_B \frac{\exp(\beta\mu)}{1 - \exp(-\beta\epsilon) - \exp(\beta\mu)} \left(\frac{\beta\epsilon}{\exp(\beta\epsilon) - 1} - \beta\mu \right) \\ &\quad - k_B \log \frac{1 - \exp(-\beta\epsilon) - \exp(\beta\mu)}{1 - \exp(-\beta\epsilon)}. \end{aligned} \quad (6.2.7)$$

6.3 Chemical Potential of Particles on a Ladder

Let us also derive the chemical potential from the canonical ensemble. For this purpose we consider the first law of thermodynamics which takes the form

$$dE = TdS + \mu dN. \quad (6.3.1)$$

From this we can read off the relations

$$\mu = \left. \frac{\partial E}{\partial N} \right|_S, \quad (6.3.2)$$

as well as

$$\mu = -T \left. \frac{\partial S}{\partial N} \right|_E. \quad (6.3.3)$$

Let us consider the entropy of N particles on the ladder

$$S = k_B N \left\{ \frac{\beta\epsilon}{\exp(\beta\epsilon) - 1} - \log[1 - \exp(-\beta\epsilon)] \right\}. \quad (6.3.4)$$

The average energy is given by

$$E = N \frac{\epsilon}{\exp(\beta\epsilon) - 1} \Rightarrow \exp(\beta\epsilon) = 1 + \frac{N\epsilon}{E}, \quad (6.3.5)$$

and one then obtains

$$S = k_B \left(N + \frac{E}{\epsilon} \right) \log \left(1 + \frac{N\epsilon}{E} \right) - k_B N \log \frac{N\epsilon}{E}. \quad (6.3.6)$$

It is then straightforward to show that

$$\mu = -T \frac{\partial S}{\partial N} \Big|_E = k_B T \log[1 - \exp(-\beta\epsilon)]. \quad (6.3.7)$$

Indeed, in the thermodynamical limit $\langle \mathcal{N} \rangle \rightarrow \infty$ this agrees with the result of eq.(6.2.3). Hence, we see that the canonical and grand canonical ensembles yield the same physical results for a large number of particles.

We can even go back to the microcanonical ensemble. Then the entropy is given in terms of the information deficit I as

$$S = k_B I \log 2 = k_B \log Z(E) = k_B \log Z(M, N) = k_B \log \frac{(M + N - 1)!}{M!(N - 1)!}. \quad (6.3.8)$$

Using the Stirling formula in the thermodynamical limit $M, N \rightarrow \infty$ implies

$$S = k_B [(M + N) \log(M + N) - M \log M - N \log N]. \quad (6.3.9)$$

Keeping M (and thus the energy $E = M\epsilon$) fixed, the chemical potential is then given by

$$\mu = -T \frac{\partial S}{\partial N} \Big|_M = -k_B T \log \left(1 + \frac{M}{N} \right). \quad (6.3.10)$$

Keeping in mind the earlier result

$$1 + \frac{M}{N} = \frac{1}{1 - \exp(-\beta\epsilon)}, \quad (6.3.11)$$

this again implies

$$\exp(\beta\mu) = 1 - \exp(-\beta\epsilon). \quad (6.3.12)$$

Thus, as one would expect, the grand canonical and the microcanonical ensemble are also equivalent in the thermodynamical limit.

We have produced quite a number of results for the system of particles on the energy ladder for the microcanonical, the canonical, and the grand canonical ensemble. Since these results are scattered through various chapters, here we summarize the main results in table 6.1.

Ensemble	microcanonical	canonical	grand canonical
Particle number	N	N	$\langle \mathcal{N} \rangle = [e^{\beta\mu} - e^{\beta(\mu-\epsilon)} - 1]^{-1}$
Energy	$E = M\epsilon$	$\langle \mathcal{H} \rangle = N\epsilon/(e^{\beta\epsilon} - 1)$	$\langle \mathcal{H} \rangle = \langle \mathcal{N} \rangle \epsilon / (e^{\beta\epsilon} - 1)$
Inverse temperature	$\beta = \frac{1}{\epsilon} \log(1 + \frac{N}{M})$	$\beta = \frac{1}{k_B T}$	$\beta = \frac{1}{k_B T}$
Chemical potential	$\beta\mu = -\log(1 + \frac{M}{N})$	$\beta\mu = \log(1 - e^{-\beta\epsilon})$	$\beta\mu = \frac{\mu}{k_B T}$
thermodynamical potential	information deficit $I = \log_2 \frac{(M+N-1)!}{M!(N-1)!}$	free energy $F = \frac{N}{\beta} \log(1 - e^{-\beta\epsilon})$	grand canonical potential $J = \frac{1}{\beta} \log \frac{1 - e^{-\beta\epsilon} - e^{\beta\mu}}{1 - e^{-\beta\epsilon}}$
Entropy	$S = k_B \log \frac{(M+N-1)!}{M!(N-1)!}$	$S = Nk_B \left\{ \frac{\beta\epsilon}{e^{\beta\epsilon} - 1} - \log(1 - e^{-\beta\epsilon}) \right\}$	$S = k_B \frac{e^{\beta\mu}}{1 - e^{-\beta\epsilon} - e^{\beta\mu}} \times \left(\frac{\beta\epsilon}{e^{\beta\epsilon} - 1} - \beta\mu \right) - k_B \log \frac{1 - e^{-\beta\epsilon} - e^{\beta\mu}}{1 - e^{-\beta\epsilon}}$

Table 6.1: Summary of results for particles on the energy ladder.

6.4 Chemical Potential of the Classical Ideal Gas

Just as we calculated the pressure of the ideal gas before, we will now calculate its chemical potential. As before, the starting point is the first law of thermodynamics which now reads

$$dE = TdS - pdV + \mu dN. \quad (6.4.1)$$

From this we can read off the relations

$$\mu = \frac{\partial E}{\partial N} \Big|_{S,V}, \quad (6.4.2)$$

as well as

$$\mu = -T \frac{\partial S}{\partial N} \Big|_{E,V}. \quad (6.4.3)$$

Let us consider the entropy of the classical ideal gas consisting of indistinguishable particles and express the inverse temperature as

$$\beta = \frac{1}{k_B T} = \frac{3N}{2E}. \quad (6.4.4)$$

Then we obtain

$$S = \frac{5}{2} Nk_B + Nk_B \log \left[\frac{V}{N\Delta} \left(\frac{4\pi ME}{3N} \right)^{3/2} \right], \quad (6.4.5)$$

and hence we find

$$\begin{aligned}
\mu &= -T \frac{\partial S}{\partial N} \Big|_{E,V} \\
&= -\frac{5}{2} k_B T - k_B T \log \left[\frac{V}{N\Delta} \left(\frac{4\pi M E}{3N} \right)^{3/2} \right] + N k_B T \left(\frac{1}{N} + \frac{3}{2N} \right) \\
&= -k_B T \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]. \tag{6.4.6}
\end{aligned}$$

Indeed this is an intensive quantity. It is independent of the system size because it depends only on the density $n = N/V$ and the temperature (which are both also intensive).

6.5 Grand Canonical Ensemble for the Ideal Gas

Let us again consider a classical ideal gas of indistinguishable particles. The grand canonical partition function can be written as

$$\begin{aligned}
Z(\beta, \mu) &= \sum_{N=0}^{\infty} Z(\beta) \exp(\beta\mu N) = \sum_{N=0}^{\infty} \frac{z(\beta)^N}{N!} \exp(\beta\mu N) \\
&= \exp[z(\beta) \exp(\beta\mu)] = \exp\left[\frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \exp(\beta\mu) \right]. \tag{6.5.1}
\end{aligned}$$

This implies

$$N = \langle \mathcal{N} \rangle = \frac{\partial \log Z(\beta, \mu)}{\partial(\beta\mu)} = \frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \exp(\beta\mu), \tag{6.5.2}$$

which then yields

$$\mu = k_B T \log \left[\frac{N\Delta}{V} \left(\frac{\beta}{2\pi M} \right)^{3/2} \right] \tag{6.5.3}$$

in agreement with the result obtained in the canonical ensemble. Similarly, one obtains

$$E = \langle \mathcal{H} \rangle = -\frac{\partial \log Z(\beta, \mu)}{\partial \beta} = \frac{V}{\Delta} \exp(\beta\mu) \frac{3}{2} \left(\frac{2\pi M}{\beta} \right)^{1/2} \frac{2\pi M}{\beta^2} = \frac{3}{2} N k_B T, \tag{6.5.4}$$

again in agreement with the canonical ensemble result.

The grand canonical potential is obtained as

$$J = -\frac{1}{\beta} \log Z(\beta, \mu) = -k_B T \frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \exp(\beta\mu), \quad (6.5.5)$$

and the entropy is hence given by

$$\begin{aligned} S &= \frac{1}{T}(E - \mu N - J) \\ &= \frac{5}{2} N k_B + k_B N \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]. \end{aligned} \quad (6.5.6)$$

Chapter 7

Pressure Ensemble

In this chapter we discuss the pressure ensemble in which the volume is not fixed but controlled by an intensive thermodynamical parameter — the pressure.

7.1 Introduction of the Pressure Ensemble

In the canonical ensemble the average energy is controlled by the temperature. In the grand canonical ensemble, in addition, the particle number is controlled by the chemical potential. In both cases, the physical system exchanges an extensive quantity (the energy or the particle number) with a reservoir. This exchange is controlled by an intensive thermodynamical potential (the temperature or the chemical potential). Another extensive quantity is the volume of the system. In the pressure ensemble, the system can exchange volume with a reservoir. This exchange is controlled by another intensive thermodynamical potential — the pressure. The pressure ensemble is, for example, realized by a gas in a container that is closed by a movable piston. By moving the piston, the volume of the system is traded against the volume of the rest of the world, controlled by the ambient pressure.

The pressure ensemble is defined by the probability distribution

$$\rho[n] = \frac{1}{Z(\beta, p)} \exp(-\beta[\mathcal{H}[n] + p\mathcal{V}[n]]). \quad (7.1.1)$$

Here p is the pressure and $\mathcal{V}[n]$ is the volume occupied by a given configuration

$[n]$. The partition function of the pressure ensemble takes the form

$$Z(\beta, p) = \sum_{[n]} \exp(-\beta[\mathcal{H}[n] + p\mathcal{V}[n]]). \quad (7.1.2)$$

As usual, the thermal average of a physical quantity \mathcal{O} is given by

$$\langle \mathcal{O} \rangle = \frac{1}{Z(\beta, p)} \sum_{[n]} \mathcal{O}[n] \exp(-\beta[\mathcal{H}[n] + p\mathcal{V}[n]]). \quad (7.1.3)$$

The partition function can be used as a generating functional for the thermal average and the variance of the volume. Then it is useful to treat β and βp as independent quantities, and one obtains

$$\begin{aligned} \langle \mathcal{V} \rangle &= -\frac{\partial \log Z(\beta, p)}{\partial(\beta p)} = \frac{1}{Z(\beta, p)} \sum_{[n]} \mathcal{V}[n] \exp(-\beta[\mathcal{H}[n] + p\mathcal{V}[n]]), \\ (\Delta \mathcal{V})^2 &= \langle \mathcal{V}^2 \rangle - \langle \mathcal{V} \rangle^2 = \frac{\partial^2 \log Z(\beta, p)}{\partial(\beta p)^2}. \end{aligned} \quad (7.1.4)$$

In the pressure ensemble the entropy is given by

$$\begin{aligned} S &= -k_B \sum_{[n]} \rho[n] \log \rho[n] \\ &= -\frac{k_B}{Z(\beta, p)} \sum_{[n]} \exp(-\beta[\mathcal{H}[n] + p\mathcal{V}[n]]) [-\beta[\mathcal{H}[n] + p\mathcal{V}[n]] - \log Z(\beta, p)] \\ &= \frac{1}{T} [E + pV + k_B T \log Z(\beta, p)]. \end{aligned} \quad (7.1.5)$$

The analog of the free energy F in the pressure ensemble is the so-called free enthalpy G which is defined by

$$Z(\beta, p) = \exp(-\beta G), \quad (7.1.6)$$

such that

$$G = E + pV - TS. \quad (7.1.7)$$

7.2 The Pressure of the Classical Ideal Gas

We have seen earlier that the kinetic theory of the classical ideal gas yields the ideal gas law $pV = Nk_B T$. Now we want to reproduce this result using the

canonical ensemble. In order to compress a gas at pressure p by a volume dV one must do the work $-pdV$. If the compression is adiabatic (i.e. reversible, without entropy change) the work is entirely converted into internal energy of the gas and

$$dE = -pdV. \quad (7.2.1)$$

This is a special case (with $dS = 0$) of the first law of thermodynamics

$$dE = TdS - pdV, \quad (7.2.2)$$

which expresses nothing but energy conservation. The pressure can now be determined as

$$p = -\left.\frac{\partial E}{\partial V}\right|_{S,N}, \quad (7.2.3)$$

or alternatively as

$$p = T\left.\frac{\partial S}{\partial V}\right|_{E,N}, \quad (7.2.4)$$

The subscripts S , N , and E specify which quantities are kept fixed during the compression. Let us use the previous equation to determine the pressure of the ideal gas. We then indeed obtain

$$p = Nk_B T \frac{\partial \log V}{\partial V} \Rightarrow pV = Nk_B T. \quad (7.2.5)$$

7.3 The Pressure Ensemble for the Classical Ideal Gas

Let us once more consider a classical ideal gas of indistinguishable particles, this time in the pressure ensemble. The corresponding partition function then takes the form

$$\begin{aligned} Z(\beta, p) &= \beta p \int_0^\infty dV Z(\beta) \exp(-\beta p V) = \beta p \int_0^\infty dV \frac{z(\beta)^N}{N!} \exp(-\beta p V) \\ &= \beta p \int_0^\infty dV \frac{1}{N!} \left[\frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]^N \exp(-\beta p V) \\ &= \frac{1}{N!} \left[\frac{1}{\beta p \Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]^N \Gamma(N+1). \end{aligned} \quad (7.3.1)$$

Here $\Gamma(N+1) = N!$ is the gamma-function, such that

$$Z(\beta, p) = \left[\frac{1}{\beta p \Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]^N. \quad (7.3.2)$$

This implies

$$V = \langle \mathcal{V} \rangle = -\frac{\partial \log Z(\beta, p)}{\partial(\beta p)} = \frac{N}{\beta p}, \quad (7.3.3)$$

and thus leads again to the ideal gas law $pV = Nk_B T$. Similarly, we obtain

$$E = \langle \mathcal{H} \rangle = -\frac{\partial \log Z(\beta, p)}{\partial \beta} = \frac{3}{2} Nk_B T, \quad (7.3.4)$$

again in agreement with the canonical ensemble result.

The free enthalpy is given by

$$G = -\frac{1}{\beta} \log Z(\beta, p) = \frac{N}{\beta} \log \left[\beta p \Delta \left(\frac{\beta}{2\pi M} \right)^{3/2} \right], \quad (7.3.5)$$

such that the entropy takes the form

$$\begin{aligned} S &= \frac{1}{T} (E + pV - G) \\ &= \frac{5}{2} Nk_B + Nk_B \log \left[\frac{1}{\beta p \Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]. \end{aligned} \quad (7.3.6)$$

Scattered through various chapters, we have derived a variety of relations for the classical ideal gas for indistinguishable particles. Table 7.1 summarizes these results.

7.4 Overview of Different Ensembles

If necessary, one can define further ensembles. Basically any other conserved extensive quantity besides energy, particle number, or the volume of the available space can be exchanged with a reservoir and thus be controlled by an appropriate intensive parameter analogous to T , μ , or p . Along with any new ensemble come new physical quantities analogous to the free energy F , like the grand canonical potential J and the free enthalpy G . The subject of statistical mechanics may sometimes seem rather formal because one may be overwhelmed by a zoo of different quantities whose physical meaning may not always be clear immediately. However, as one continues to work with these concepts, one will appreciate their physical relevance. Table 7.2 summarizes the ensembles and associated physical quantities introduced so far.

Physical quantity	Classical ideal gas of indistinguishable particles
Energy	$E = \frac{3}{2}Nk_B T$
Inverse temperature	$\beta = 1/k_B T = 3N/2E$
Volume	$V = Nk_B T/p$
Pressure	$p = Nk_B T/V$
Entropy (canonical)	$S = Nk_B \left\{ \frac{5}{2} + \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right] \right\}$
Free energy	$F = -Nk_B T \left\{ 1 + \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right] \right\}$
Chemical potential	$\mu = -k_B T \log \left[\frac{V}{N\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]$
Particle number (grand canonical)	$N = \frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \exp(\beta\mu)$
Entropy (grand canonical)	$S = \frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \exp(\beta\mu) k_B \left(\frac{5}{2} - \beta\mu \right)$
Grand canonical potential	$J = -\frac{V}{\Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \exp(\beta\mu) k_B T$
Entropy (pressure)	$S = \frac{5}{2}Nk_B + Nk_B \log \left[\frac{1}{\beta p \Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]$
Free enthalpy	$G = -Nk_B T \log \left[\frac{1}{\beta p \Delta} \left(\frac{2\pi M}{\beta} \right)^{3/2} \right]$

Table 7.1: *Physical quantities for the classical ideal gas of indistinguishable particles.*

Ensemble	microcanonical	canonical
fixed parameters	E, N, V	β, N, V
Boltzmann factor	1	$\exp(-\beta\mathcal{H})$
partition function	$Z(E)$	$Z(\beta)$
thermal averages	fixed E	$\langle H \rangle = -\frac{\partial \log Z(\beta)}{\partial \beta}$
entropy	$S = k_B I \log 2$	$S = \frac{E}{T} + k_B \log Z(\beta)$
thermodynamical potential	information deficit $I = \log_2 Z(E)$	free energy $F = E - TS$
Ensemble	grand canonical	pressure
fixed parameters	β, μ, V	β, N, p
Boltzmann factor	$\exp(-\beta[\mathcal{H} - \mu\mathcal{N}])$	$\exp(-\beta[\mathcal{H} + p\mathcal{V}])$
partition function	$Z(\beta, \mu)$	$Z(\beta, p)$
thermal averages	$\langle N \rangle = \frac{\partial \log Z(\beta, \mu)}{\partial(\beta\mu)}$	$\langle V \rangle = -\frac{\partial \log Z(\beta, p)}{\partial(\beta p)}$
entropy	$S = \frac{1}{T}(E - \mu N) + k_B \log Z(\beta, \mu)$	$S = \frac{1}{T}(E + pV) + k_B \log Z(\beta, p)$
thermodynamical potential	grand canonical potential $J = E - \mu N - TS$	free enthalpy $G = E + pV - TS$

Table 7.2: Comparison of various ensembles.

Chapter 8

Equilibrium Thermodynamics

Thermodynamics is a phenomenological science developed in the 19th century before the microscopic structure of matter was understood. With our present understanding of statistical mechanics based on microscopic systems of atoms or molecules we can attempt to derive thermodynamics from the underlying microscopic physics. Here we consider statistical systems in thermal equilibrium.

8.1 The First Law of Thermodynamics

The first law of thermodynamics is just a consequence of energy conservation. Already in the 19th century physicists knew that the internal energy of a gas can essentially change in two ways. Either the gas does some work (the goal of the steam engine designers of those days) or it is heated (a necessary prerequisite to let the engine work). The energy balance of a gas can hence be written as

$$dE = \delta W + \delta Q, \tag{8.1.1}$$

Here dE is an infinitesimal change of the internal energy and

$$\delta W = -pdV \tag{8.1.2}$$

is an infinitesimal amount of work done by the gas. If the gas expands by a small volume $dV > 0$ at some pressure p it exerts a force on a movable piston. For example, if the piston is moved by a distance dx and has a cross sectional area A we have $dV = Adx$. The pressure $p = F/A$ is a force per area, and hence the

work (force times distance) is given by

$$Fdx = \frac{F}{A}Adx = pdV. \quad (8.1.3)$$

The gas is doing work pdV for us. The corresponding energy is lost to the gas and shows up as $-pdV$ in the internal energy balance of the gas itself. In order to make the gas do work for us we must supply some energy by heating it. The corresponding term δQ in the energy balance of the gas is the heat supplied from outside.

8.2 Expansion of a Classical Ideal Gas

Let us first consider the expansion of a gas without heat transfer ($\delta Q = 0$). This is called adiabatic expansion. The first law of thermodynamics then takes the form

$$dE = -pdV. \quad (8.2.1)$$

For a classical ideal gas we have

$$E = \frac{3}{2}Nk_B T = \frac{3}{2}pV, \quad (8.2.2)$$

such that

$$dE = \frac{3}{2}(pdV + dpV) = -pdV \Rightarrow \frac{3}{2}dpV = -\frac{5}{2}pdV \Rightarrow \frac{dp}{p} = -\frac{5}{3}\frac{dV}{V}. \quad (8.2.3)$$

Integrating both sides of this equation we obtain

$$\int_{p_i}^{p_f} \frac{dp}{p} = -\frac{5}{3} \int_{V_i}^{V_f} \frac{dV}{V} \Rightarrow \log \frac{p_f}{p_i} = -\frac{5}{3} \log \frac{V_f}{V_i} \Rightarrow \frac{p_f}{p_i} = \left(\frac{V_i}{V_f} \right)^{5/3}. \quad (8.2.4)$$

Here p_i and V_i are the initial pressure and volume (before the expansion) and p_f and V_f are the final pressure and volume (after the expansion). It should be noted that if $V_f > V_i$ then $p_f < p_i$, i.e. adiabatic expansion implies a pressure decrease. Using

$$p_i V_i = Nk_B T_i, \quad p_f V_f = Nk_B T_f, \quad (8.2.5)$$

the initial and final temperatures T_i and T_f are related by

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f} \right)^{2/3}, \quad (8.2.6)$$

such that adiabatic expansion also implies cooling.

Now we want to consider expansion without cooling. This is possible only if we transfer heat from outside. We want to supply enough energy to keep the temperature constant. Such a process is known as isothermal expansion. In order to maintain a constant temperature (according to $E = \frac{3}{2}Nk_B T$) the internal energy E must remain unchanged. In that case the first law of thermodynamics takes the form

$$dE = \delta W + \delta Q = 0 \Rightarrow \delta Q = pdV = Nk_B T \frac{dV}{V}. \quad (8.2.7)$$

The total work done by the gas then equals the heat transferred to the gas and is given by

$$W = Nk_B T \int_{V_i}^{V_f} \frac{dV}{V} = Nk_B T \log \frac{V_f}{V_i}. \quad (8.2.8)$$

8.3 Heat and Entropy Change

Let us consider the pressure ensemble. Then we have

$$\rho[n] = \frac{1}{Z(\beta, p)} \exp(-\beta[\mathcal{H}[n] + p\mathcal{V}[n]]), \quad (8.3.1)$$

and

$$\begin{aligned} E = \langle \mathcal{H} \rangle &= \sum_{[n]} \mathcal{H}[n] \rho[n] \Rightarrow dE = \sum_{[n]} \mathcal{H}[n] d\rho[n], \\ V = \langle \mathcal{V} \rangle &= \sum_{[n]} \mathcal{V}[n] \rho[n] \Rightarrow dV = \sum_{[n]} \mathcal{V}[n] d\rho[n]. \end{aligned} \quad (8.3.2)$$

It should be noted that $\mathcal{H}[n]$ and $\mathcal{V}[n]$ are completely fixed for a given configuration n and hence $d\mathcal{H}[n] = d\mathcal{V}[n] = 0$. For the heat we thus obtain

$$\delta Q = dE + pdV = \sum_{[n]} (\mathcal{H}[n] + p\mathcal{V}[n]) d\rho[n]. \quad (8.3.3)$$

Heat is a disordered form of energy contained in the chaotic motion of the atoms or molecules of a gas. When we heat a gas, the motion of its constituents becomes more chaotic which should increase the entropy. Hence, we expect a relation between heat and entropy change. Let us consider the entropy

$$S = -k_B \sum_{[n]} \rho[n] \log \rho[n]. \quad (8.3.4)$$

In the pressure ensemble an infinitesimal entropy change is then given by

$$\begin{aligned}
dS &= -k_B \sum_{[n]} (d\rho[n] \log \rho[n] + \rho[n] d \log \rho[n]) \\
&= -k_B \sum_{[n]} d\rho[n] (\log \rho[n] + 1) \\
&= -k_B \sum_{[n]} d\rho[n] (-\log Z(\beta, p) - \beta(\mathcal{H}[n] + p\mathcal{V}[n])) \\
&= \frac{1}{T} \sum_{[n]} d\rho[n] (\mathcal{H}[n] + p\mathcal{V}[n]).
\end{aligned} \tag{8.3.5}$$

Here we have used

$$\sum_{[n]} d\rho[n] = 0, \tag{8.3.6}$$

which results from the normalization condition $\sum_{[n]} \rho[n] = 1$. Hence, we can now identify

$$\delta Q = TdS, \tag{8.3.7}$$

i.e. heat transfer indeed implies a change of the entropy. The first law of thermodynamics can now be written as

$$dE = TdS - pdV. \tag{8.3.8}$$

A change of the thermodynamical state of a system is called adiabatic if $\delta Q = TdS = 0$, i.e. for adiabatic processes the entropy is conserved.

For a generalized ensemble which allows both volume and particle exchange the first law of thermodynamics is given by

$$dE = TdS - pdV + \mu dN. \tag{8.3.9}$$

The last term represents a contribution to the internal energy due to the addition of particles with energy μ (the chemical potential) per particle. The above equation immediately implies other relations of a similar form. In particular, the changes of the free energy, the grand canonical potential, and the free enthalpy take the form

$$\begin{aligned}
dF &= d(E - TS) = -SdT - pdV + \mu dN, \\
dJ &= d(E - TS - \mu N) = -SdT - pdV - Nd\mu, \\
dG &= d(E - TS + pV) = -SdT + Vdp + \mu dN.
\end{aligned} \tag{8.3.10}$$

8.4 Equations of State

The thermodynamical behavior of some substance can be characterized by its equations of state. The so-called caloric equation of state takes the form

$$E = E(T, N, V). \quad (8.4.1)$$

For a classical ideal gas the caloric equation of state takes the form

$$E = \frac{3}{2}Nk_B T. \quad (8.4.2)$$

Similarly, the so-called thermal equation of state is given by

$$p = p(T, N, V). \quad (8.4.3)$$

For the classical ideal gas the thermal equation of state takes the form

$$p = \frac{Nk_B T}{V}. \quad (8.4.4)$$

Finally, the so-called chemical equation of state is given by

$$\mu = \mu(T, N, V), \quad (8.4.5)$$

which for a classical ideal gas takes the form

$$\mu = k_B T \log \left[\frac{N\Delta}{V} \left(\frac{\beta}{2\pi M} \right)^{3/2} \right]. \quad (8.4.6)$$

In general, these equations of state can be derived from the expression for the entropy $S = S(E, N, V)$. Using the first law of thermodynamics in the form

$$dS = \frac{1}{T}(dE + pdV - \mu dN) \quad (8.4.7)$$

one obtains

$$\frac{1}{T} = \frac{\partial S}{\partial E}|_{N,V}, \quad \frac{p}{T} = \frac{\partial S}{\partial V}|_{E,N}, \quad \frac{\mu}{T} = -\frac{\partial S}{\partial N}|_{E,V}. \quad (8.4.8)$$

This is indeed how we derived the equations of state for the classical ideal gas.

8.5 Thermodynamic Coefficients

As we mentioned before, thermodynamics may sometimes seem like a zoo of different physical quantities with fancy names whose physical meaning may not always be instantly clear. Here we will list a number of such quantities. We begin with the specific heat, both at constant volume

$$C_V = \frac{\delta Q}{\delta T}|_{N,V} = T \frac{\partial S}{\partial T}|_{N,V}, \quad (8.5.1)$$

and at constant pressure

$$C_p = \frac{\delta Q}{\delta T}|_{N,p} = T \frac{\partial S}{\partial T}|_{N,p}. \quad (8.5.2)$$

The specific heats determine the amount of heat δQ that is required to raise the temperature by the amount δT , either keeping the volume or the pressure constant. Using the first law of thermodynamics in the form

$$TdS = dE + pdV - \mu dN \quad (8.5.3)$$

we can write

$$C_V = T \frac{\partial S}{\partial T}|_{N,V} = \frac{\partial E}{\partial T}|_{N,V}. \quad (8.5.4)$$

For example, for a classical ideal gas we thus obtain

$$C_V = \frac{3}{2}Nk_B. \quad (8.5.5)$$

One can write

$$(\Delta\mathcal{H})^2 = -\frac{\partial\langle\mathcal{H}\rangle}{\partial\beta}|_{N,V} = -\frac{\partial E}{\partial T}|_{N,V} \frac{dT}{d\beta} = k_B T^2 C_V, \quad (8.5.6)$$

which shows that $C_V \geq 0$.

Another useful quantity is the compressibility which measures the relative change of the volume $-\delta V/V$ that results from a pressure increase δp . One distinguishes the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial p}|_{T,N} \quad (8.5.7)$$

at fixed temperature, and the adiabatic compressibility

$$\kappa_S = -\frac{1}{V} \frac{\partial V}{\partial p}|_{N,S} \quad (8.5.8)$$

at fixed entropy.

Yet another quantity is the expansion coefficient which measures the relative increase of the volume $\delta V/V$ due to a temperature increase δT . The isobaric expansion coefficient

$$\alpha_p = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_{N,p}, \quad (8.5.9)$$

is defined at constant pressure. Finally, we introduce the isochoric tension coefficient

$$\beta_V = \frac{1}{p} \frac{\partial p}{\partial T} \Big|_{N,V} \quad (8.5.10)$$

defined at constant volume.

One can relate the thermodynamic coefficients by using some identities for Jacobi determinants of two functions $f(x, y)$ and $g(x, y)$ of two independent variables x and y

$$\frac{\partial(f, g)}{\partial(x, y)} = \det \begin{pmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{pmatrix} = \frac{\partial f}{\partial x} \frac{\partial g}{\partial y} - \frac{\partial f}{\partial y} \frac{\partial g}{\partial x}, \quad (8.5.11)$$

which obey

$$\frac{\partial(f, g)}{\partial(x, y)} = \frac{\partial(f, g)}{\partial(u, v)} \frac{\partial(u, v)}{\partial(x, y)}, \quad (8.5.12)$$

as well as

$$\frac{\partial(f, g)}{\partial(x, y)} = -\frac{\partial(g, f)}{\partial(x, y)} = -\frac{\partial(f, g)}{\partial(y, x)} = \frac{\partial(g, f)}{\partial(y, x)}. \quad (8.5.13)$$

We also have

$$\frac{\partial(f, y)}{\partial(x, y)} = \frac{\partial f}{\partial x} \frac{\partial y}{\partial y} - \frac{\partial f}{\partial y} \frac{\partial y}{\partial x} = \frac{\partial f}{\partial x} \Big|_y, \quad (8.5.14)$$

and

$$\frac{\partial(f, g)}{\partial(x, y)} \frac{\partial(x, y)}{\partial(f, g)} = 1. \quad (8.5.15)$$

Using these identities we obtain

$$\begin{aligned} \frac{C_p}{C_V} &= \frac{\frac{\partial S}{\partial T} \Big|_{N,p}}{\frac{\partial S}{\partial T} \Big|_{N,V}} = \frac{\frac{\partial(S,p)}{\partial(T,p)}}{\frac{\partial(S,V)}{\partial(T,V)}} = \frac{\partial(p, S)}{\partial(p, T)} \frac{\partial(V, T)}{\partial(V, S)} \\ &= \frac{\partial(p, S)}{\partial(V, S)} \frac{\partial(V, T)}{\partial(p, T)} = \frac{\frac{\partial(V,T)}{\partial(p,T)}}{\frac{\partial(V,S)}{\partial(p,S)}} = \frac{\frac{\partial V}{\partial p} \Big|_{T,N}}{\frac{\partial V}{\partial p} \Big|_{S,N}} = \frac{\kappa_T}{\kappa_S}. \end{aligned} \quad (8.5.16)$$

Chapter 9

Nonequilibrium Thermodynamics

Until now we have concentrated on systems in thermal equilibrium. Such systems are described by the equilibrium ensembles discussed earlier. In this chapter we will study statistical systems out of thermal equilibrium.

9.1 Extremality of the Entropy in Equilibrium

We have seen earlier that the canonical and microcanonical ensembles represent extrema of the entropy. We will now show the same for a general equilibrium ensemble characterized by the probability distribution

$$\rho[n] = \frac{1}{Z(\beta, \mu, p)} \exp(-\beta[\mathcal{H}[n] - \mu\mathcal{N}[n] + p\mathcal{V}[n]]). \quad (9.1.1)$$

We will compare this ensemble of thermal equilibrium with a general ensemble characterized by $\rho'[n]$. We want to imagine that $\rho'[n]$ describes the system on its way to thermal equilibrium. Since the energy, the particle number, and the volume are conserved quantities we want to assume that their average values

remain unchanged, i.e.

$$\begin{aligned}
E &= \sum_{[n]} \mathcal{H}[n] \rho[n] = \sum_{[n]} \mathcal{H}[n] \rho'[n] = E', \\
N &= \sum_{[n]} \mathcal{N}[n] \rho[n] = \sum_{[n]} \mathcal{N}[n] \rho'[n] = N', \\
V &= \sum_{[n]} \mathcal{V}[n] \rho[n] = \sum_{[n]} \mathcal{V}[n] \rho'[n] = V'.
\end{aligned} \tag{9.1.2}$$

We now want to show that $S' \leq S$, i.e. that the entropy assumes its maximum value in thermal equilibrium. For this purpose we first show that

$$\sum_{[n]} \rho'[n] (\log \rho[n] - \log \rho'[n]) \leq 0. \tag{9.1.3}$$

Using $\log x \leq x - 1$, this follows from

$$\begin{aligned}
\sum_{[n]} \rho'[n] (\log \rho[n] - \log \rho'[n]) &= \sum_{[n]} \rho'[n] \log \frac{\rho[n]}{\rho'[n]} \\
&\leq \sum_{[n]} \rho'[n] \left(\frac{\rho[n]}{\rho'[n]} - 1 \right) = \sum_{[n]} (\rho[n] - \rho'[n]) = 0.
\end{aligned} \tag{9.1.4}$$

Using this inequality, we can now write

$$\begin{aligned}
S' &= -k_B \sum_{[n]} \rho'[n] \log \rho'[n] \\
&\leq -k_B \sum_{[n]} \rho'[n] \log \rho[n] \\
&= -k_B \sum_{[n]} \rho'[n] (-\log Z(\beta, \mu, p) - \beta(\mathcal{H}[n] - \mu\mathcal{N}[n] + p\mathcal{V}[n])) \\
&= k_B \log Z(\beta, \mu, p) + \frac{1}{T} (E' - \mu N' + pV') \\
&= k_B \log Z(\beta, \mu, p) + \frac{1}{T} (E - \mu N + pV) \\
&= -k_B \sum_{[n]} \rho[n] (-\log Z(\beta, \mu, p) - \beta(\mathcal{H}[n] - \mu\mathcal{N}[n] + p\mathcal{V}[n])) \\
&= S,
\end{aligned} \tag{9.1.5}$$

which indeed shows that keeping the averages E , N and V fixed, the equilibrium ensemble has the largest entropy.

9.2 Time Evolution and Poisson Brackets

Let us consider a system of N classical particles evolving in phase space $[x, p] = (\vec{x}_1, \vec{p}_1, \vec{x}_2, \vec{p}_2, \dots, \vec{x}_N, \vec{p}_N)$ according to their Hamilton equations of motion

$$\frac{\partial \mathcal{H}}{\partial p_{ai}} = \frac{dx_{ai}}{dt}, \quad \frac{\partial \mathcal{H}}{\partial x_{ai}} = -\frac{dp_{ai}}{dt}. \quad (9.2.1)$$

Let us now consider a general ensemble characterized by the probability distribution $\rho[x, p]$. The probability distribution then evolves according to the equation

$$\begin{aligned} \frac{d\rho}{dt} &= \sum_{ai} \left(\frac{\partial \rho}{\partial x_{ai}} \frac{dx_{ai}}{dt} + \frac{\partial \rho}{\partial p_{ai}} \frac{dp_{ai}}{dt} \right) \\ &= \sum_{ai} \left(\frac{\partial \rho}{\partial x_{ai}} \frac{\partial \mathcal{H}}{\partial p_{ai}} - \frac{\partial \rho}{\partial p_{ai}} \frac{\partial \mathcal{H}}{\partial x_{ai}} \right) = \{\rho, \mathcal{H}\}. \end{aligned} \quad (9.2.2)$$

Here we have introduced the so-called Poisson bracket

$$\{\mathcal{A}, \mathcal{B}\} = \sum_{ai} \left(\frac{\partial \mathcal{A}}{\partial x_{ai}} \frac{\partial \mathcal{B}}{\partial p_{ai}} - \frac{\partial \mathcal{A}}{\partial p_{ai}} \frac{\partial \mathcal{B}}{\partial x_{ai}} \right) \quad (9.2.3)$$

of two functions $\mathcal{A}[x, p]$ and $\mathcal{B}[x, p]$ over phase space. The Poisson bracket is the classical analog of the quantum mechanical commutator and plays a central role in modern (post-Newtonian) formulations of classical mechanics. Also the equations of motion themselves can be expressed as

$$\begin{aligned} \frac{dx_{ai}}{dt} &= \{x_{ai}, \mathcal{H}\} = \sum_{bj} \left(\frac{\partial x_{ai}}{\partial x_{bj}} \frac{\partial \mathcal{H}}{\partial p_{bj}} - \frac{\partial x_{ai}}{\partial p_{bj}} \frac{\partial \mathcal{H}}{\partial x_{bj}} \right) \\ &= \sum_{bj} \delta_{ab} \delta_{ij} \frac{\partial \mathcal{H}}{\partial p_{bj}} = \frac{\partial \mathcal{H}}{\partial p_{ai}}, \\ \frac{dp_{ai}}{dt} &= \{p_{ai}, \mathcal{H}\} = \sum_{bj} \left(\frac{\partial p_{ai}}{\partial x_{bj}} \frac{\partial \mathcal{H}}{\partial p_{bj}} - \frac{\partial p_{ai}}{\partial p_{bj}} \frac{\partial \mathcal{H}}{\partial x_{bj}} \right) \\ &= -\sum_{bj} \delta_{ab} \delta_{ij} \frac{\partial \mathcal{H}}{\partial x_{bj}} = -\frac{\partial \mathcal{H}}{\partial x_{ai}}. \end{aligned} \quad (9.2.4)$$

9.3 Conservation of Probability

Any probability distribution should be properly normalized, i.e.

$$\int \mathcal{D}x \mathcal{D}p \rho[x, p] = 1. \quad (9.3.1)$$

Of course, the probability should remain normalized during the time evolution. This is automatically the case if the probability distribution obeys a continuity equation

$$\frac{d\rho}{dt} + \delta j = 0, \quad (9.3.2)$$

where $j[x, p]$ is a probability current in phase space. Indeed, using the evolution equation for $\rho[x, p]$ we can identify

$$j = \rho \left(-\frac{\partial \mathcal{H}}{\partial p_{1i}}, \frac{\partial \mathcal{H}}{\partial x_{1i}}, \dots, -\frac{\partial \mathcal{H}}{\partial p_{Ni}}, \frac{\partial \mathcal{H}}{\partial x_{Ni}} \right), \quad (9.3.3)$$

because

$$\delta j = \sum_{ai} \left(\frac{\partial j_{x_{ai}}}{\partial x_{ai}} + \frac{\partial j_{p_{ai}}}{\partial p_{ai}} \right) = \sum_{ai} \left(-\frac{\partial \rho}{\partial x_{ai}} \frac{\partial \mathcal{H}}{\partial p_{ai}} + \frac{\partial \rho}{\partial p_{ai}} \frac{\partial \mathcal{H}}{\partial x_{ai}} \right) = -\frac{d\rho}{dt}. \quad (9.3.4)$$

Using Gauss' law in phase space we thus obtain

$$\frac{d}{dt} \int \mathcal{D}x \mathcal{D}p \rho = \int \mathcal{D}x \mathcal{D}p \frac{d\rho}{dt} = - \int \mathcal{D}x \mathcal{D}p \delta j = 0. \quad (9.3.5)$$

9.4 Conservation of Entropy

Let us consider the time evolution of the entropy

$$S = -k_B \int \mathcal{D}x \mathcal{D}p \rho \log \rho. \quad (9.4.1)$$

For this purpose we consider

$$\begin{aligned} \frac{dS}{dt} &= -k_B \int \mathcal{D}x \mathcal{D}p \frac{d\rho}{dt} (\log \rho + 1) \\ &= k_B \int \mathcal{D}x \mathcal{D}p \delta j (\log \rho + 1) \\ &= -k_B \int \mathcal{D}x \mathcal{D}p j \delta (\log \rho + 1). \end{aligned} \quad (9.4.2)$$

In the last step we have performed a partial integration in the multi-dimensional phase space. The resulting gradient takes the form

$$\delta (\log \rho + 1) = \frac{1}{\rho} \delta \rho = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial x_{1i}}, \frac{\partial \rho}{\partial p_{1i}}, \dots, \frac{\partial \rho}{\partial x_{Ni}}, \frac{\partial \rho}{\partial p_{Ni}} \right), \quad (9.4.3)$$

such that

$$\begin{aligned} j\delta(\log \rho + 1) &= \sum_{ai} \left(-\frac{\partial \mathcal{H}}{\partial p_{ai}} \frac{\partial \rho}{\partial x_{ai}} + \frac{\partial \mathcal{H}}{\partial x_{ai}} \frac{\partial \rho}{\partial p_{ai}} \right) \\ &= -\sum_{ai} \left(\frac{\partial \rho}{\partial x_{ai}} \frac{dx_{ai}}{dt} + \frac{\partial \rho}{\partial p_{ai}} \frac{dp_{ai}}{dt} \right) = -\frac{d\rho}{dt}. \end{aligned} \quad (9.4.4)$$

Hence, using the conservation of probability, we obtain

$$\frac{dS}{dt} = -k_B \int \mathcal{D}x \mathcal{D}p \, j\delta(\log \rho + 1) = k_B \int \mathcal{D}x \mathcal{D}p \, \frac{d\rho}{dt} = 0. \quad (9.4.5)$$

In view of the second law of thermodynamics ($\frac{dS}{dt} \geq 0$) this result is very puzzling. First, one might argue that the above calculation is meaningless, because the above expression for the entropy is rather formal and indeed infinite in the limit of vanishing volume element of phase space ($\Delta \rightarrow 0$). As it was mentioned before, this ultraviolet catastrophe of the classical theory will be automatically cured by going to quantum mechanics. Then the volume of an elementary cell of phase space $\Delta = h^3 > 0$ is indeed non-zero and given in terms of Planck's quantum h . As we will see later, the above result of entropy conservation persists at the quantum level. We should hence indeed conclude that, taking into account all its microscopic constituents, the total entropy of a closed system is indeed conserved. What does the second law of thermodynamics then really mean?

9.5 A Model with Entropy Increase

Let us consider a simple model in which the second law of thermodynamics, i.e. entropy increase ($\frac{dS}{dt} \geq 0$), can indeed be proved. The model consists of a single particle moving on a line of discrete points $x = na$. Here $n \in \mathbb{Z}$ labels the point and a is the distance between neighboring points. The possible configurations $[n]$ are thus labeled by the integer n . At all positions $x = na$, i.e. in all configurations $[n]$, the particle has the same energy. Hence, in thermodynamical equilibrium we are dealing with a microcanonical ensemble. Instead of imposing a deterministic continuous Hamiltonian time evolution, we assume that the particle moves from point to point by a probabilistic dynamics in discrete time steps. In each time step, the particle can either stay where it is (i.e. $n' = n$) or it can hop to a neighboring point (i.e. $n' = n + 1$ or $n' = n - 1$). The probabilities for the hops are described by a transition probability $w[n \rightarrow n']$ as follows

$$w[n \rightarrow n + 1] = w[n \rightarrow n - 1] = p, \quad w[n \rightarrow n] = 1 - 2p. \quad (9.5.1)$$

All other transition probabilities are zero and $p \in [0, \frac{1}{2}]$. Let us now assume that there is an ensemble of particles with some initial probability distribution $\rho_0[n]$. In a discrete time step the probability distribution changes according to

$$\rho_i[n'] = \sum_n \rho_{i-1}[n] w[n \rightarrow n'] = p(\rho_{i-1}[n'+1] + \rho_{i-1}[n'-1]) + (1-2p)\rho_{i-1}[n']. \quad (9.5.2)$$

Introducing

$$\tilde{\rho}_{i-1}[n] = \frac{1}{2}(\rho_{i-1}[n+1] + \rho_{i-1}[n-1]), \quad (9.5.3)$$

we thus obtain

$$\rho_i[n] = 2p\tilde{\rho}_{i-1}[n] + (1-2p)\rho_{i-1}[n]. \quad (9.5.4)$$

After $i-1$ time steps the entropy is given by

$$S_{i-1} = -k_B \sum_{[n]} \rho_{i-1}[n] \log \rho_{i-1}[n]. \quad (9.5.5)$$

We now want to show that $S_i \geq S_{i-1}$. For this purpose we use the concavity of the function

$$s(\rho) = -\rho \log \rho, \quad (9.5.6)$$

which is guaranteed by

$$\frac{d^2 s}{d\rho^2} = -\frac{d}{d\rho}(\log \rho + 1) = -\frac{1}{\rho} \leq 0. \quad (9.5.7)$$

The concavity of $s(\rho)$ implies that

$$s(\tilde{\rho}_i[n]) = s(2p\tilde{\rho}_{i-1}[n] + (1-2p)\rho_{i-1}[n]) \geq 2ps(\tilde{\rho}_{i-1}[n]) + (1-2p)s(\rho_{i-1}[n]), \quad (9.5.8)$$

such that

$$S_i \geq 2p\tilde{S}_{i-1} + (1-2p)S_{i-1}. \quad (9.5.9)$$

Here we have defined

$$\tilde{S}_{i-1} = -k_B \sum_{[n]} \tilde{\rho}_{i-1}[n] \log \tilde{\rho}_{i-1}[n]. \quad (9.5.10)$$

In the next step we again use the concavity of $s(\rho)$ which also implies

$$s(\tilde{\rho}_{i-1}[n]) = s\left(\frac{\rho_{i-1}[n+1] + \rho_{i-1}[n-1]}{2}\right) \geq \frac{1}{2}(s(\rho_{i-1}[n+1]) + s(\rho_{i-1}[n-1])), \quad (9.5.11)$$

such that

$$\tilde{S}_{i-1} \geq \frac{1}{2}(S_{i-1} + S_{i-1}) = S_{i-1}, \quad (9.5.12)$$

and hence

$$S_i \geq 2p\tilde{S}_{i-1} + (1-2p)S_{i-1} \geq S_{i-1}. \quad (9.5.13)$$

Indeed, in this model with probabilistic dynamics the entropy is always increasing. Obviously, the evolution of our ensemble is irreversible — the entropy will never decrease again. This is perhaps surprising because the elementary time-steps are reversible, i.e. the probability for the particle to jump backward is the same as to jump forward.

9.6 A Model for Diffusion

The previous model describes a simple diffusion process. We will now derive the diffusion equation by taking a continuum limit of the model. In particular, we relate the discrete time steps i with a continuous time variable $t = i\epsilon$, where ϵ is the duration of a single discrete time step. We can then rewrite the evolution equation for the probability distribution as

$$\frac{\rho_i[n'] - \rho_{i-1}[n']}{\epsilon} = \frac{pa^2}{\epsilon} \frac{\rho_{i-1}[n'+1] + \rho_{i-1}[n'-1] - 2\rho_{i-1}[n']}{a^2}. \quad (9.6.1)$$

Taking the space and time continuum limits $a \rightarrow 0$ and $\epsilon \rightarrow 0$ and keeping the so-called diffusion coefficient

$$\gamma = \frac{pa^2}{\epsilon} \quad (9.6.2)$$

fixed, the above differences turn into derivatives and we obtain the continuum diffusion equation

$$\frac{\partial \rho}{\partial t} = \gamma \frac{\partial^2 \rho}{\partial x^2}. \quad (9.6.3)$$

Here we have identified $\rho(x, t) = \rho_i[n]$ with $x = na$ and $t = i\epsilon$. The continuum probability distribution is normalized as

$$\frac{1}{a} \int dx \rho(x, t) = \sum_n \rho_i[n] = 1. \quad (9.6.4)$$

Indeed the distribution remains properly normalized during the diffusion process because

$$\frac{d}{dt} \int dx \rho(x, t) = \int dx \frac{\partial \rho}{\partial t} = \gamma \int dx \frac{\partial^2 \rho}{\partial x^2} = \frac{\partial \rho}{\partial x} \Big|_{-\infty}^{\infty} = 0. \quad (9.6.5)$$

Also one can write a continuity equation

$$\frac{\partial \rho}{\partial t} + \delta j = \frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0, \quad (9.6.6)$$

where the probability current density is given by

$$j = -\gamma \frac{\partial \rho}{\partial x}. \quad (9.6.7)$$

In the continuum limit the entropy can be identified as

$$S(t) = S_i = -k_B \sum_n \rho_i[n] \log \rho_i[n] = -\frac{k_B}{a} \int dx \rho(x, t) \log \rho(x, t). \quad (9.6.8)$$

Hence, one obtains

$$\begin{aligned} \frac{dS}{dt} &= -\frac{k_B}{a} \int dx \frac{\partial \rho}{\partial t} (\log \rho + 1) = \frac{k_B}{a} \int dx \frac{\partial j}{\partial x} (\log \rho + 1) \\ &= -\frac{k_B}{a} \int dx j \frac{\partial}{\partial x} (\log \rho + 1) = \frac{k_B \gamma}{a} \int dx \frac{1}{\rho} \left(\frac{\partial \rho}{\partial x} \right)^2 \geq 0. \end{aligned} \quad (9.6.9)$$

As expected from the discrete model, we hence confirm that also in the continuum diffusion model the entropy always increases.

9.7 Approach to Equilibrium

It is straightforward to verify the following solution of the diffusion equation

$$\rho(x, t) = \frac{a}{\sqrt{4\pi\gamma t}} \exp\left(-\frac{x^2}{4\gamma t}\right). \quad (9.7.1)$$

In particular, at $t = 0$ the probability distribution reduces to $\rho(x, 0) = a\delta(x)$. Afterward the distribution is Gaussian with a width increasing proportional to \sqrt{t} . The average distance squared that a particle reaches after a time t is given by

$$\langle x(t)^2 \rangle = 2\gamma t. \quad (9.7.2)$$

Let us also calculate the entropy as a function of time. It is convenient to first compute

$$\frac{dS}{dt} = \frac{k_B \gamma}{a} \int dx \frac{1}{\rho} \left(\frac{\partial \rho}{\partial x} \right)^2 = \frac{k_B}{2t}, \quad (9.7.3)$$

which then implies a logarithmic behavior of the entropy itself

$$S(t) - S(\epsilon) = \frac{k_B}{2} \log \frac{t}{\epsilon}. \quad (9.7.4)$$

In particular, for late times the entropy increases without bound. This indeed makes sense, since the information deficit keeps increasing as the particles diffuse to infinity. Hence, this system never reaches thermodynamical equilibrium.

Let us now consider the same system in a finite volume. In that case, the particles cannot diffuse to infinity and we indeed expect to approach thermodynamical equilibrium. For simplicity we impose periodic boundary conditions over the interval $x \in [0, L]$. The solution of the diffusion equation then takes the form

$$\rho(x, t) = \frac{a}{\sqrt{4\pi\gamma t}} \sum_{m \in \mathbb{Z}} \exp\left(-\frac{(x - mL)^2}{4\gamma t}\right). \quad (9.7.5)$$

For $t \rightarrow \infty$ the solution approaches $\rho(x, t) = \frac{a}{L}$ and the entropy turns into

$$S(\infty) = -\frac{k_B}{a} \int_0^L dx \rho \log \rho = k_B \log \frac{L}{a}. \quad (9.7.6)$$

Chapter 10

The Ising Model

The Ising model is one of the simplest models in classical statistical mechanics and still it is applicable to a wide variety of physical systems. It describes idealized magnets, the mixing of fluids, critical opalescence in boiling water at high pressure, and even special features of the quark-gluon plasma that filled the early Universe.

10.1 Definition and Basic Properties

Let us consider the simplest classical spin model — the so-called Ising model. Here the word spin does not mean that we deal with quantized angular momenta. All we do is work with classical spin variables that take values $s_x = \pm 1$. The Ising spins are located on the sites of a d -dimensional spatial cubic lattice. The Ising model is characterized by its classical Hamilton function (not a quantum Hamilton operator) which simply specifies the energy of any configuration of spins. The Ising Hamilton function includes a sum of nearest neighbor contributions

$$\mathcal{H}[s] = -J \sum_{\langle xy \rangle} s_x s_y - \mu B \sum_x s_x, \quad (10.1.1)$$

with a ferromagnetic coupling constant $J > 0$ that favors parallel spins, plus a coupling to an external magnetic field B . The classical partition function of this system is given by

$$Z = \sum_{[s]} \exp(-\beta \mathcal{H}[s]) = \prod_x \sum_{s_x = \pm 1} \exp(-\beta \mathcal{H}[s]). \quad (10.1.2)$$

The sum over all spin configurations corresponds to an independent summation over all possible orientations of individual spins. Thermal averages are computed by inserting appropriate observables $\mathcal{O}[s]$. For example, the magnetization is given by

$$\mathcal{M}[s] = \sum_x s_x, \quad (10.1.3)$$

and its thermal expectation value is given by

$$\langle \mathcal{M} \rangle = \frac{1}{Z} \sum_{[s]} \mathcal{M}[s] \exp(-\beta \mathcal{H}[s]) = \frac{\partial \log Z}{\partial(\beta \mu B)}. \quad (10.1.4)$$

The magnetic susceptibility is defined as

$$\chi = \frac{1}{L^d} (\langle \mathcal{M}^2 \rangle - \langle \mathcal{M} \rangle^2) = \frac{1}{L^d} \frac{\partial^2 \log Z}{\partial(\beta \mu B)^2}, \quad (10.1.5)$$

where L^d is the spatial volume. Similarly, the spin correlation function is defined as

$$\langle s_x s_y \rangle = \frac{1}{Z} \sum_{[s]} s_x s_y \exp(-\beta \mathcal{H}[s]). \quad (10.1.6)$$

At large distances the so-called connected spin correlation function typically decays exponentially

$$\langle s_x s_y \rangle_c = \langle s_x s_y \rangle - \langle s_x \rangle \langle s_y \rangle \sim \exp(-|x - y|/\xi), \quad (10.1.7)$$

where ξ is the correlation length. The susceptibility is the connected correlation function summed over all pairs of points x and y , i.e.

$$\chi = \frac{1}{L^d} \sum_{x,y} \langle s_x s_y \rangle_c. \quad (10.1.8)$$

At general temperatures the correlation length is typically just a few lattice spacings. When one models real materials, the Ising model would generally be a great over-simplification, because real magnets, for example, not only have nearest-neighbor couplings. Still, the details of the Hamilton function at the scale of the lattice spacing are not always important. There is a critical temperature T_c at which ξ diverges and universal behavior arises. At this temperature a second order phase transition occurs. Then the details of the model at the scale of the lattice spacing are irrelevant for the long-range physics that takes place at the scale of ξ . In fact, at their critical temperatures real materials behave just like the simple Ising model. This is why the Ising model is so interesting. It is just

a very simple member of a large universality class of different models, which all share the same critical behavior. This does not mean that they have the same values of their critical temperatures. However, their correlation lengths diverge at the critical temperature with the same exponent ν , i.e.

$$\xi \propto |T - T_c|^{-\nu}, \quad (10.1.9)$$

their magnetizations go to zero at the critical temperature with the same exponent β

$$\langle \mathcal{M} \rangle \propto |T - T_c|^\beta, \quad T \leq T_c, \quad (10.1.10)$$

and their susceptibilities diverge with the same exponent γ

$$\chi \propto |T - T_c|^{-\gamma}, \quad (10.1.11)$$

i.e. the critical exponents ν , β , and γ are identical for different systems in the same universality class.

10.2 Mean Field Theory

Understanding critical behavior is a highly nontrivial issue. For example, there is no generally applicable analytic method that allows us to determine critical exponents exactly. An exception are theories in one or two dimensions. As we will see, in one dimension the Ising model can be solved easily. In two dimensions the so-called conformal symmetry allows exact calculations. In the 3-dimensional case the so-called ϵ -expansion at least provides a systematic expansion whose convergence is, however, not always guaranteed. In the next chapter we will learn about the Monte Carlo method which provides an alternative numerical tool to understand critical phenomena. To illustrate critical behavior we want to use an approximate method — mean field theory. Its results become exact in the limit of infinitely many dimensions, but should not be trusted quantitatively in the physically most relevant case $d = 3$. The idea behind mean field theory is to assume that a spin s_x that interacts with its fluctuating nearest neighbors s_y can simply be coupled to a constant averaged mean value $\langle s \rangle_m$ for the spin. The mean field approximation to the Hamilton function takes the form

$$\mathcal{H}_m[s] = -J \sum_x s_x d \langle s \rangle_m - \mu B \sum_x s_x = -\mu B_{\text{eff}} \sum_x s_x, \quad (10.2.1)$$

where

$$\mu B_{\text{eff}} = \mu B + dJ \langle s \rangle_m, \quad (10.2.2)$$

is an effective magnetic field acting on the spin s_x . In the full theory the magnetic field generated by the neighboring spins fluctuates with the values of the spins s_y . In mean field theory one neglects these fluctuations and treats the magnetic field as an averaged constant.

In the mean field approximation the partition function can now be evaluated easily

$$\begin{aligned} Z_m &= \sum_{[s]} \exp(-\beta\mathcal{H}_m[s]) = \prod_x \sum_{s_x=\pm 1} \exp(\beta\mu B_{\text{eff}} \sum_x s_x) \\ &= \left[\sum_{s_{x_0}=\pm 1} \exp(\beta\mu B_{\text{eff}} s_{x_0}) \right]^V = [2 \cosh(\beta\mu B_{\text{eff}})]^V, \end{aligned} \quad (10.2.3)$$

where x_0 is any arbitrarily chosen lattice point and $V = L^d$ is the volume (the total number of lattice sites). The factor d is just the number of bonds per spin in d dimensions. Since B_{eff} depends on the mean field value of the spin $\langle s \rangle_m$ the calculation is not yet complete. The next step is to determine the average spin from a consistency condition. In mean field theory we have

$$\begin{aligned} \langle s \rangle_m &= \frac{1}{Z_m} \sum_{[s]} s_{x_0} \exp(-\beta\mathcal{H}_m[s]) \\ &= \frac{1}{Z_m} \left[\sum_{s_{x_0}=\pm 1} s_{x_0} \exp(\beta\mu B_{\text{eff}} s_{x_0}) \right] [2 \cosh(\beta\mu B_{\text{eff}})]^{V-1} \\ &= \tanh(\beta\mu B_{\text{eff}}) = \tanh(\beta(\mu B + dJ\langle s \rangle_m)). \end{aligned} \quad (10.2.4)$$

This is the consistency condition for $\langle s \rangle_m$.

Next we assume that the external magnetic field is switched off, i.e. $B = 0$. Then the consistency condition takes the form

$$\langle s \rangle_m = \tanh(\beta dJ \langle s \rangle_m). \quad (10.2.5)$$

For $d\beta J < 1$ this has only the trivial solution $\langle s \rangle_m = 0$. However, for $d\beta J > 1$ there is, in addition, a solution with $\langle s \rangle_m \neq 0$. This solution describes spontaneous symmetry breaking: without any bias by an external magnetic field, the spins decide collectively to point in a common direction. The nontrivial solution appears at a critical temperature T_c that is given by

$$d\beta_c J = 1 \Rightarrow T_c = \frac{dJ}{k_B}. \quad (10.2.6)$$

Above this temperature the spin system is in the so-called symmetric (or unbroken) phase with $\langle s \rangle_m = 0$, while for $T < T_c$ the system is in the broken (or

ordered) phase in which spontaneous symmetry breaking occurs and $\langle s \rangle_m \neq 0$. The two phases are separated by a phase transition. The value of the average spin determines whether the system is in the unbroken or in the ordered phase. Hence, $\langle s \rangle$ is known as an order parameter.

It remains to be shown that the nontrivial solution is indeed physically realized. For that purpose we compare the free energies of the two phases. In the symmetric phase we have $B_{\text{eff}} = 0$ and hence

$$Z_m = [2 \cosh(\beta \mu B_{\text{eff}})]^V = 2^V = \exp(-\beta F_s), \quad (10.2.7)$$

In the broken phase, on the other hand, we have $|B_{\text{eff}}| > 0$ and hence

$$\exp(-\beta F_b) > \exp(-\beta F_s) \Rightarrow F_b < F_s. \quad (10.2.8)$$

Since the free energy of the broken phase is smaller than the one of the symmetric phase, the broken phase is thermodynamically stable for $T < T_c$.

Next we compute the average spin (magnetization per lattice site) for temperatures below but close to T_c . Expanding the consistency condition for small $\langle s \rangle_m$

$$\langle s \rangle_m = \tanh(\beta d J \langle s \rangle_m) \approx \beta d J \langle s \rangle_m - \frac{1}{3} (\beta d J \langle s \rangle_m)^3, \quad (10.2.9)$$

one obtains

$$\beta d J \langle s \rangle_m = \sqrt{3(\beta d J - 1)} \Rightarrow \langle s \rangle_m \propto \sqrt{T_c - T} = |T - T_c|^\beta. \quad (10.2.10)$$

Here β is the critical exponent introduced before. Its mean field value $\beta = 1/2$ is not exact. Since the order parameter goes to zero continuously at T_c , the phase transition is of second order.

At a first order phase transition, on the other hand, the order parameter makes a discontinuous jump. The Ising model undergoes a first order phase transition at $T < T_c$ when one changes the external magnetic field B from positive to negative values. At $B = 0$ the magnetization changes abruptly from $+\langle s \rangle_m$ to $-\langle s \rangle_m$.

10.3 Exact Results for the 1-dimensional Ising Model

Mean field theory nicely illustrates the qualitative behavior of the Ising model but it yields only approximate results. In this section we will derive some exact

results for the Ising model in one dimension. The 1-dimensional Ising model is easy to solve analytically. Its partition function (for $B = 0$) is given by

$$Z = \prod_x \sum_{s_x = \pm 1} \exp(\beta J \sum_{\langle xy \rangle} s_x s_y). \quad (10.3.1)$$

We consider a lattice with L sites and with periodic boundary conditions (i.e. $s_{x+L} = s_x$). Introducing bond variables

$$b_{\langle xy \rangle} = s_x s_y = \pm 1, \quad (10.3.2)$$

the partition function can be rewritten as

$$Z = 2 \prod_{\langle xy \rangle} \sum_{b_{\langle xy \rangle} = \pm 1} \exp(\beta J \sum_{\langle xy \rangle} b_{\langle xy \rangle}) \delta_{\prod_{\langle xy \rangle} b_{\langle xy \rangle}, 1}. \quad (10.3.3)$$

The constraint

$$\prod_{\langle xy \rangle} b_{\langle xy \rangle} = 1, \quad (10.3.4)$$

that is enforced by the Kronecker δ -function is a consequence of periodic boundary conditions. The δ -function can be rewritten as

$$\delta_{\prod_{\langle xy \rangle} b_{\langle xy \rangle}, 1} = \frac{1}{2} \sum_{m=0,1} \left(\prod_{\langle xy \rangle} b_{\langle xy \rangle} \right)^m. \quad (10.3.5)$$

Hence, the partition function takes the form

$$Z = \sum_{m=0,1} \prod_{\langle xy \rangle} \sum_{b_{\langle xy \rangle} = \pm 1} \exp(\beta J b_{\langle xy \rangle}) b_{\langle xy \rangle}^m = \{ [2 \cosh(\beta J)]^L + [2 \sinh(\beta J)]^L \}. \quad (10.3.6)$$

This exact result differs from the mean field result of eq.(10.2.3).

Let us also compute the correlation function $\langle s_x s_y \rangle$. For this purpose we write the spin correlation as a string of bond variables

$$s_x s_y = \prod_{\langle wz \rangle} b_{\langle wz \rangle}. \quad (10.3.7)$$

The product extends over all bonds $\langle wz \rangle$ connecting the points x and y . The correlation function is then given by

$$\begin{aligned} \langle s_x s_y \rangle &= \frac{1}{Z} \sum_{m=0,1} \prod_{\langle xy \rangle} \sum_{b_{\langle xy \rangle} = \pm 1} \prod_{\langle wz \rangle} b_{\langle wz \rangle} \exp(\beta J b_{\langle xy \rangle}) b_{\langle xy \rangle}^m \\ &= \frac{1}{Z} \{ [2 \cosh(\beta J)]^{L-n} [2 \sinh(\beta J)]^n \\ &+ [2 \sinh(\beta J)]^{L-n} [2 \cosh(\beta J)]^n \}. \end{aligned} \quad (10.3.8)$$

Here $n = |x - y|$ is the distance between the points x and y .

The susceptibility is now obtained from

$$\begin{aligned}
 \chi &= \frac{1}{L} \sum_{x,y} \langle s_x s_y \rangle \\
 &= \sum_{n=0}^{L-1} \frac{1}{Z} \{ [2 \cosh(\beta J)]^{L-n} [2 \sinh(\beta J)]^n \\
 &\quad + [2 \sinh(\beta J)]^{L-n} [2 \cosh(\beta J)]^n \}. \tag{10.3.9}
 \end{aligned}$$

Applying the formula for an incomplete geometric series

$$\sum_{n=0}^{L-1} x^n = \frac{1 - x^L}{1 - x} \tag{10.3.10}$$

for $x = \tanh(\beta J)$ as well as $x = \coth(\beta J)$ one obtains

$$\begin{aligned}
 \chi &= \frac{1}{Z} \left\{ [2 \cosh(\beta J)]^L \frac{1 - \tanh^L(\beta J)}{1 - \tanh(\beta J)} + [2 \sinh(\beta J)]^L \frac{1 - \coth^L(\beta J)}{1 - \coth(\beta J)} \right\} \\
 &= \frac{1 - \tanh^L(\beta J)}{1 + \tanh^L(\beta J)} \exp(2\beta J). \tag{10.3.11}
 \end{aligned}$$

10.4 Exact Results for the 2-dimensional Ising Model

Next we consider the 2-dimensional Ising model. In that case the bond variables around an elementary lattice square with four sites w , x , y , and z satisfy the constraint

$$b_{\langle wx \rangle} b_{\langle xy \rangle} b_{\langle yz \rangle} b_{\langle zw \rangle} = 1. \tag{10.4.1}$$

For each lattice square we introduce a variable m_{\square} that implements this constraint via

$$\delta_{b_{\langle wx \rangle} b_{\langle xy \rangle} b_{\langle yz \rangle} b_{\langle zw \rangle}, 1} = \frac{1}{2} \sum_{m_{\square}=0,1} (b_{\langle wx \rangle} b_{\langle xy \rangle} b_{\langle yz \rangle} b_{\langle zw \rangle})^{m_{\square}}. \tag{10.4.2}$$

We now introduce the dual lattice with sites \tilde{x} at the centers of the squares \square . The variable m_{\square} can then be interpreted as a spin variable,

$$s_{\tilde{x}} = 1 - 2m_{\square} = \pm 1, \tag{10.4.3}$$

on the dual lattice. Summing over the bond variable $b_{\langle xy \rangle}$ on the original lattice then induces an interaction between the dual spins $s_{\tilde{x}}$ and $s_{\tilde{y}}$ at the centers of the two squares $\square_{\tilde{x}}$ and $\square_{\tilde{y}}$ that share the bond $\langle xy \rangle$. We have

$$\sum_{b_{\langle xy \rangle} = \pm 1} \exp(\beta J b_{\langle xy \rangle}) b_{\langle xy \rangle}^{m_{\square_{\tilde{x}}} + m_{\square_{\tilde{y}}}} = \exp(-\tilde{\beta} \tilde{h}(s_{\tilde{x}}, s_{\tilde{y}})), \quad (10.4.4)$$

which defines a Hamilton function

$$\tilde{H}[s] = \sum_{\langle \tilde{x}\tilde{y} \rangle} \tilde{h}(s_{\tilde{x}}, s_{\tilde{y}}). \quad (10.4.5)$$

One obtains

$$\begin{aligned} \exp(-\tilde{\beta} \tilde{h}(1, 1)) &= \exp(-\tilde{\beta} \tilde{h}(-1, -1)) = 2 \cosh(\beta J), \\ \exp(-\tilde{\beta} \tilde{h}(1, -1)) &= \exp(-\tilde{\beta} \tilde{h}(-1, 1)) = 2 \sinh(\beta J). \end{aligned} \quad (10.4.6)$$

In the original Ising model the ratio of the two Boltzmann factors was

$$\exp(-\beta h(1, -1)) / \exp(-\beta h(1, 1)) = \exp(-2\beta J). \quad (10.4.7)$$

Similarly, the ratio of the two dual Boltzmann factors is

$$\exp(-\tilde{\beta} \tilde{h}(1, -1)) / \exp(-\tilde{\beta} \tilde{h}(1, 1)) = \tanh(\beta J) = \exp(-2\tilde{\beta} \tilde{J}). \quad (10.4.8)$$

This equation determines the coupling constant \tilde{J} of a dual Ising model. When the original Ising model is in the high-temperature phase (βJ small) the dual Ising model is in the low-temperature phase ($\tilde{\beta} \tilde{J}$ large) and vice versa. The exact critical temperature $T_c = 1/k_B \beta_c$ of the 2-dimensional Ising model follows from the self-duality condition

$$\tanh(\beta_c J) = \exp(-2\beta_c J), \quad (10.4.9)$$

which again differs from the mean field result of eq.(10.2.6).

10.5 Cluster Representation

In this section we will rewrite the Ising model in terms of spin and bond variables. Parallel spins connected by activated bonds form correlated clusters, while spins in different clusters are uncorrelated. The susceptibility can be expressed in terms of the cluster sizes. The cluster representation of the Ising model gives rise to an extremely efficient Monte Carlo algorithm — the so-called cluster algorithm.

We begin by introducing bond variables $b_{\langle xy \rangle} = 0, 1$ which are different from the ones introduced before. An activated bond has $b_{\langle xy \rangle} = 1$ while a deactivated bond has $b_{\langle xy \rangle} = 0$. We can now write

$$\exp(-\beta h(s_x, s_y)) = \sum_{b_{\langle xy \rangle}=0,1} \exp(-\beta h(s_x, s_y, b_{\langle xy \rangle})), \quad (10.5.1)$$

with

$$\begin{aligned} \exp(-\beta h(s, s, 1)) &= \exp(\beta J) - \exp(-\beta J), \\ \exp(-\beta h(s, s, 0)) &= \exp(-\beta J), \\ \exp(-\beta h(s, -s, 1)) &= 0, \\ \exp(-\beta h(s, -s, 0)) &= \exp(-\beta J), \end{aligned} \quad (10.5.2)$$

for $s = \pm 1$, such that indeed

$$\begin{aligned} \exp(-\beta h(s, s)) &= \exp(\beta J) \\ &= \exp(-\beta h(s, s, 1)) + \exp(-\beta h(s, s, 0)), \\ \exp(-\beta h(s, -s)) &= \exp(-\beta J) \\ &= \exp(-\beta h(s, -s, 1)) + \exp(-\beta h(s, -s, 0)). \end{aligned} \quad (10.5.3)$$

Note that a bond can be activated only if the two connected spins are parallel. It should also be noted that the Boltzmann weight of a deactivated bond is independent of the spin configuration, i.e.

$$\begin{aligned} \exp(-\beta h(1, 1, 0)) &= \exp(-\beta h(1, -1, 0)) = \\ \exp(-\beta h(-1, 1, 0)) &= \exp(-\beta h(-1, -1, 0)) = \exp(-\beta J). \end{aligned} \quad (10.5.4)$$

This implies that the spin configuration decomposes into clusters of parallel spins. The spins connected by activated bonds belong to the same cluster. Spins in the same cluster are hence parallel, while spins in different clusters are uncorrelated. It should be noted that spins completely unconnected to other spins form a cluster by themselves. In this way, each spin belongs to exactly one cluster.

The cluster decomposition of a spin configuration has interesting consequences. In particular, when all spins of a given cluster are flipped, the Boltzmann weight of the spin and bond configuration remains the same. This means that there are 2^{N_C} equally probable configurations, which are obtained by independently flipping all N_C clusters in the configuration. From this fact one can derive a cluster representation of the susceptibility. First, the total magnetization is a sum of cluster magnetizations

$$\mathcal{M}[s] = \sum_x s_x = \sum_C \mathcal{M}_C, \quad (10.5.5)$$

where the cluster magnetization is given by

$$\mathcal{M}_C = \sum_{x \in C} s_x. \quad (10.5.6)$$

In a finite volume the average magnetization always vanishes (even in the broken phase), i.e.

$$\langle \mathcal{M} \rangle = \left\langle \sum_C \mathcal{M}_C \right\rangle = 0, \quad (10.5.7)$$

since each cluster of spins can be flipped which leads to a change of sign of the magnetization. Similarly, the susceptibility can be expressed as

$$\begin{aligned} \chi &= \frac{1}{L^d} \langle \mathcal{M}^2 \rangle = \frac{1}{L^d} \left\langle \left(\sum_C \mathcal{M}_C \right)^2 \right\rangle \\ &= \frac{1}{L^d} \left\langle \sum_{C_1, C_2} \mathcal{M}_{C_1} \mathcal{M}_{C_2} \right\rangle = \frac{1}{L^d} \left\langle \sum_C \mathcal{M}_C^2 \right\rangle. \end{aligned} \quad (10.5.8)$$

In the last step we have used the fact that two different clusters C_1 and C_2 are uncorrelated, i.e. $\mathcal{M}_{C_1} \mathcal{M}_{C_2}$ averages to zero under cluster flip. Consequently, only the square of the magnetization of the individual clusters \mathcal{M}_C^2 determines the susceptibility. Since all spins of a cluster are parallel, up to a sign the cluster magnetization is given by the cluster size $|C|$, i.e.

$$\mathcal{M}_C = \pm |C| = \pm \sum_{x \in C} 1. \quad (10.5.9)$$

Hence, the susceptibility can also be written as

$$\chi = \frac{1}{L^d} \left\langle \sum_C |C|^2 \right\rangle. \quad (10.5.10)$$

This shows that the cluster size is directly related to a physical quantity. In this sense the clusters are indeed physical objects.

Chapter 11

The Monte Carlo Method

A powerful numerical technique to solve problems in statistical mechanics is the so-called Monte Carlo method. The idea is to compute expectation values by generating spin configurations numerically. Of course, the partition function is an extremely large sum, such that doing it with numerical brute force is completely hopeless. In the Monte Carlo method predominantly those spin configurations are generated that have the largest contribution to the partition function. In fact, the Boltzmann factor $\exp(-\beta\mathcal{H}[s])$ is used as the probability to generate the spin configuration $[s]$. This method is also known as importance sampling.

11.1 The Concept of a Markov Chain

In a Monte Carlo simulation one generates a sequence of spin configurations

$$[s^{(1)}] \rightarrow [s^{(2)}] \rightarrow \dots \rightarrow [s^{(N)}], \quad (11.1.1)$$

which form a so-called Markov chain, by applying an algorithm that turns the configuration $[s^{(i)}]$ into $[s^{(i+1)}]$. The initial configuration $[s^{(1)}]$ is either picked at random or selected otherwise. Ultimately, nothing should depend on this choice. After a (possibly large) number M of Monte Carlo iterations (applications of the algorithm) an equilibrium is reached, and the system has forgotten about the initial configurations. Only the configurations generated after equilibration are used in the actual calculation. To estimate the expectation value of some observable one averages its values over all configurations of the Monte Carlo

sample

$$\langle \mathcal{O} \rangle = \lim_{N \rightarrow \infty} \frac{1}{N - M} \sum_{i=M+1}^N \mathcal{O}[s^{(i)}]. \quad (11.1.2)$$

In the limit $N \rightarrow \infty$ the calculation becomes exact. At finite $N - M$ one makes a calculable statistical error that decreases in proportion to $1/\sqrt{N - M - 1}$. Hence, to increase the numerical accuracy by a factor of two one must run the Monte Carlo algorithm four times as long. The Boltzmann factor $\exp(-\beta\mathcal{H}[s])$ is not explicitly included in the above sum. It is implicitly included, because the configurations in the Markov chain occur with probability $\exp(-\beta\mathcal{H}[s])$.

11.2 Ergodicity and Detailed Balance

To demonstrate that a particular Monte Carlo algorithm converges to the correct equilibrium distribution it is sufficient to show that it is ergodic and obeys detailed balance. Ergodicity means that, starting from an arbitrary initial configuration, the algorithm can, at least in principle, reach any other spin configuration. This condition is obviously necessary, because the correct value for the expectation value can be obtained only if all spin configurations are included. Detailed balance means that

$$\exp(-\beta\mathcal{H}[s])w[s, s'] = \exp(-\beta\mathcal{H}[s'])w[s', s]. \quad (11.2.1)$$

Here $w[s, s']$ is the transition probability for the algorithm to turn the configuration $[s]$ into $[s']$. A Monte Carlo algorithm is completely characterized by the corresponding $w[s, s']$. Since the algorithm definitely generates a new configuration the proper normalization is

$$\sum_{[s']} w[s, s'] = 1. \quad (11.2.2)$$

When the Monte Carlo algorithm converges to an equilibrium distribution $p[s]$ of spin configurations, this distribution is an eigenvector of $w[s, s']$ with eigenvalue 1, i.e.

$$\sum_{[s]} p[s]w[s, s'] = p[s']. \quad (11.2.3)$$

Now we want to show that the canonical Boltzmann distribution

$$p[s] = \exp(-\beta\mathcal{H}[s]) \quad (11.2.4)$$

is indeed an eigenvector of $w[s, s']$ if the algorithm obeys detailed balance. We find

$$\begin{aligned}
 \sum_{[s]} \exp(-\beta\mathcal{H}[s])w[s, s'] &= \sum_{[s]} \exp(-\beta\mathcal{H}[s'])w[s', s] \\
 &= \exp(-\beta\mathcal{H}[s']) \sum_{[s]} w[s', s] \\
 &= \exp(-\beta\mathcal{H}[s']). \tag{11.2.5}
 \end{aligned}$$

Assuming ergodicity one can show that only one eigenvector with eigenvalue 1 exists, and that the equilibrium distribution is therefore unique.

11.3 The Metropolis Algorithm

A simple example of an algorithm that is ergodic and obeys detailed balance is the so-called Metropolis algorithm. In this algorithm a new configuration $[s']$ is randomly chosen based on the old configuration $[s]$. If the energy of the new configuration is smaller than the energy of the old configuration, the new configuration is accepted, i.e.

$$\mathcal{H}[s'] < \mathcal{H}[s] \Rightarrow w[s, s'] = 1. \tag{11.3.1}$$

On the other hand, if the new energy is larger, the new configuration is accepted only with a certain probability, i.e.

$$\mathcal{H}[s'] > \mathcal{H}[s] \Rightarrow w[s, s'] = \exp(-\beta(\mathcal{H}[s'] - \mathcal{H}[s])). \tag{11.3.2}$$

Otherwise the old configuration is kept. This algorithm obeys detailed balance. Let us consider two configurations $[s]$ and $[s']$. We can assume that $\mathcal{H}[s'] < \mathcal{H}[s]$ such that $w[s, s'] = 1$. Then of course, $\mathcal{H}[s] > \mathcal{H}[s']$ such that $w[s', s] = \exp(-\beta(\mathcal{H}[s] - \mathcal{H}[s']))$, and hence

$$\begin{aligned}
 \exp(-\beta\mathcal{H}[s])w[s, s'] &= \exp(-\beta\mathcal{H}[s]) \\
 &= \exp(-\beta\mathcal{H}[s']) \exp(-\beta(\mathcal{H}[s] - \mathcal{H}[s'])) \\
 &= \exp(-\beta\mathcal{H}[s'])w[s', s]. \tag{11.3.3}
 \end{aligned}$$

We still need to specify how a new configuration is proposed. In the Ising model one visits the spins one by one and proposes to flip them. The resulting change of the energy is calculated by investigating the neighboring spins. Then

following the Metropolis algorithm, it is decided whether a given spin is flipped or not. When all spins on the lattice have been updated in this way, one has completed one Metropolis sweep. It is obvious that any spin configuration can, at least in principle, be reached in this way, i.e. the Metropolis algorithm is indeed ergodic. A typical Monte Carlo simulation consists of a large number of sweeps, say 1 million, for example.

11.4 Error Analysis

Since any practical Monte Carlo simulation has a finite length, the results are not exact but are affected by statistical errors. Hence, an important part of every Monte Carlo calculation is the error analysis. An ideal Monte Carlo algorithm (which does not really exist in practice) would generate a Markov chain of statistically independent configurations. If the Monte Carlo data for an observable \mathcal{O} are Gaussian distributed, the standard deviation from their average (i.e. their statistical error) is given by

$$\Delta\mathcal{O} = \frac{1}{\sqrt{N - M - 1}} \langle (\mathcal{O} - \langle \mathcal{O} \rangle)^2 \rangle = \frac{1}{\sqrt{N - M - 1}} (\langle \mathcal{O}^2 \rangle - \langle \mathcal{O} \rangle^2). \quad (11.4.1)$$

In order to reduce the statistical error by a factor of two, the number of independent equilibrated configurations $N - M$ must hence be increased by a factor of four.

Practical Monte Carlo algorithms (like the Metropolis algorithm) are not ideal, i.e. they do not generate statistically independent configurations. In particular, the Metropolis algorithm is rather simple, but not very efficient. Since the new configuration is generated from the previous configuration in the Markov chain, subsequent configurations are correlated. This implies that the actual statistical error is larger than the above naive estimate of the standard deviation. In order to detect the autocorrelation of the Monte Carlo data, it is useful to bin these data. For this purpose one averages a number N_b of subsequent measurements and treats this average as a statistically independent result. One then computes the standard deviation based on the $(N - M)/N_b$ statistically independent averages. Of course, if the bin size N_b is too small, the averages are still correlated and the corresponding standard deviation still underestimates the true statistical error. When one increases the bin size N_b , the corresponding standard deviation increases until subsequent bin averages are indeed statistically independent. Once the standard deviation has reached a plateau (by increasing N_b), one has obtained a reliable estimate of the true statistical error.

In order to estimate the number τ of Monte Carlo iterations that separate statistically independent spin configuration, it is also useful to determine the autocorrelation function of some observable \mathcal{O}

$$\langle \mathcal{O}^{(i)} \mathcal{O}^{(i+t)} \rangle = \lim_{N \rightarrow \infty} \frac{1}{N - M - t} \sum_{i=M+1}^{N-t} \mathcal{O}[s^{(i)}] \mathcal{O}[s^{(i+t)}] \propto \exp(-t/\tau). \quad (11.4.2)$$

The autocorrelation time τ of the Metropolis algorithm actually increases when one approaches a second order phase transition. At a second order phase transition the correlation length ξ diverges. One finds so-called critical slowing down

$$\tau \propto \xi^z, \quad (11.4.3)$$

where z is a dynamical critical exponent characterizing the efficiency of a Monte Carlo algorithm. For the Metropolis algorithm one finds $z \approx 2$, which leads to a very bad critical slowing down behavior. This is a good motivation to turn to the much more efficient cluster algorithms which can reach $z \approx 0$.

11.5 The Swendsen-Wang Cluster Algorithm

The Swendsen-Wang cluster algorithm is a Monte Carlo method based on the cluster representation of the Ising model, i.e. it operates on both spins and bonds. First, an initial spin configuration is selected. Then each bond is activated or deactivated, depending on the orientation of the adjacent spins. If the two spins connected by the bond are anti-parallel the bond is deactivated. On the other hand, if the two spins are parallel the bond can be activated or deactivated. The corresponding Boltzmann weights are given by

$$\begin{aligned} \exp(-\beta h(s, s, 1)) &= \exp(\beta J) - \exp(-\beta J), \\ \exp(-\beta h(s, s, 0)) &= \exp(-\beta J), \end{aligned} \quad (11.5.1)$$

where $s = \pm 1$. Hence, the probability for activating the bond is

$$p = \frac{\exp(-\beta h(s, s, 1))}{\exp(-\beta h(s, s, 1)) + \exp(-\beta h(s, s, 0))} = 1 - \exp(-2\beta J). \quad (11.5.2)$$

Once each bond is activated or deactivated, one identifies the clusters of sites connected by activated bonds. By construction all spins in a common cluster are parallel. Each cluster is flipped (i.e. all spins in the cluster change sign) with 50 percent probability. This completes one sweep of the cluster algorithm. Then the procedure is repeated, i.e. the bonds are updated again.

As a benefit of the cluster algorithm we can make use of the cluster representation of the susceptibility

$$\chi = \frac{1}{L^d} \left\langle \sum_C |C|^2 \right\rangle \quad (11.5.3)$$

in order to obtain a so-called improved estimator. Instead of measuring just $\mathcal{M}[s]^2$ for the given spin configuration, we sum the squares of all cluster sizes $|C|$. Effectively, this increases the statistics by a factor 2^{N_C} , where N_C is the number of clusters in the configuration.

Let us first show that the cluster algorithm is ergodic. There is a finite (although perhaps very small) probability that no bonds are activated. Then each spin forms its own cluster. By flipping these individual spin clusters one can obviously reach any possible spin configuration.

We still need to show that the cluster algorithm obeys detailed balance, i.e.

$$\exp(-\beta\mathcal{H}[s])w[s, s'] = \exp(-\beta\mathcal{H}[s'])w[s', s]. \quad (11.5.4)$$

It is sufficient to consider just one pair of neighboring spins. If the two spins are anti-parallel they necessarily belong to different clusters. After cluster flip they will be parallel with 50 percent probability. In the next sweep the bond between them will then be activated with probability p and deactivated with probability $(1-p)$. The probability to turn back into the original anti-parallel configuration is then $\frac{1}{2}(1-p)$. The corresponding detailed balance relation then takes the form

$$\begin{aligned} \exp(-\beta h(s, -s))\frac{1}{2} &= \exp(-\beta h(s, s))\frac{1}{2}(1-p) \Rightarrow \\ \exp(-\beta J)\frac{1}{2} &= \exp(\beta J)\frac{1}{2}\exp(-2\beta J), \end{aligned} \quad (11.5.5)$$

which is indeed satisfied. With the other 50 percent probability the originally anti-parallel spins will remain anti-parallel. In that case, the bond between them cannot be activated and thus with 50 percent probability we return to the original configuration. Detailed balance is then trivially satisfied. Finally, let us assume that the two spins are originally parallel. Then we need to distinguish between two cases. First, we assume that the two spins are already indirectly connected through other activated bonds. In that case, it is irrelevant if the direct bond between them is activated or not. The two spins remain parallel and detailed balance is trivially satisfied. Next, we assume that the two parallel spins are not indirectly connected by activated bonds. Then the direct bond between them is activated with probability p and the spins remain parallel. With probability

$(1-p)$ the bond is deactivated and the spins remain parallel only with 50 percent probability. Again, detailed balance is then trivially satisfied. With the other 50 percent probability the two spins will become anti-parallel. Then they cannot be connected by an activated bond and they return into the parallel configuration with 50 percent probability. The detailed balance relation then again takes the form

$$\begin{aligned} \exp(-\beta h(s, s)) \frac{1}{2} (1-p) &= \exp(-\beta h(s, -s)) \frac{1}{2} \Rightarrow \\ \exp(\beta J) \frac{1}{2} \exp(-2\beta J) &= \exp(-\beta J) \frac{1}{2}. \end{aligned} \quad (11.5.6)$$

Thus, in all cases detailed balance is indeed satisfied.

11.6 The Wolff Cluster Algorithm

The Wolff cluster algorithm is an interesting (and sometimes even more efficient) variant of the Swendsen-Wang algorithm. The Swendsen-Wang algorithm is a multi-cluster algorithm, i.e. all clusters in a configuration are identified and on average half of them are flipped. The Wolff cluster algorithm, on the other hand, is a single-cluster algorithm, i.e. a site is selected at random and only the one cluster attached to this site is identified in this configuration. In contrast to the Swendsen-Wang algorithm, the single cluster is then flipped with 100 percent probability. In this case, no effort is wasted for identifying clusters which are then not flipped. After the single cluster is flipped, a new bond configuration is generated and the whole procedure is repeated.

As for the Swendsen-Wang algorithm, for the Wolff cluster algorithm one can also construct an improved estimator for the susceptibility. While in the multi-cluster algorithm all clusters contribute $|C|^2$ to the susceptibility, in the single-cluster algorithm the cluster is selected with a probability $|C|/L^d$ (proportional to its size $|C|$). Hence, bigger clusters are selected more frequently than smaller ones and one must correct for this bias. Hence, in the single-cluster algorithm the improved estimator for the susceptibility takes the form

$$\chi = \frac{1}{L^d} \left\langle |C|^2 \frac{L^d}{|C|} \right\rangle = \langle |C| \rangle. \quad (11.6.1)$$

Chapter 12

Quantum Statistical Mechanics

Until now we have investigated classical statistical mechanics. From now on we will incorporate the principles of quantum mechanics into our considerations, and hence we will move on to quantum statistical mechanics. Remarkably, the structure of statistical mechanics is sufficiently general that, unlike other physical theories, it does not undergo radical changes upon quantization. In particular, the same ensembles of thermodynamical equilibrium also make sense at the quantum level.

12.1 Canonical Ensemble in Quantum Statistics

In classical statistical mechanics we have introduced the canonical ensemble via its probability distribution

$$\rho[n] = \frac{1}{Z} \exp(-\beta\mathcal{H}[n]), \quad (12.1.1)$$

where $\mathcal{H}[n]$ is the classical Hamilton function of a system in the configuration $[n]$. The probability distribution is normalized to

$$\sum_{[n]} \rho[n] = 1, \quad (12.1.2)$$

such that the canonical partition function is given by

$$Z = \sum_{[n]} \exp(-\beta\mathcal{H}[n]). \quad (12.1.3)$$

The thermal average of a physical quantity \mathcal{O} is then given by

$$\langle \mathcal{O} \rangle = \frac{1}{Z} \sum_{[n]} \mathcal{O}[n] \exp(-\beta \mathcal{H}[n]). \quad (12.1.4)$$

While a classical system is characterized by its Hamilton function \mathcal{H} , a quantum system is characterized by its Hamilton operator H . The Hamilton operator can be viewed as a matrix in the Hilbert space of the theory. The solution of the time-independent Schrödinger equation

$$H\chi_n(\vec{x}) = E_n\chi_n(\vec{x}), \quad (12.1.5)$$

determines the energy eigenvalues E_n and the corresponding energy eigenstates $\chi_n(\vec{x})$. Quantum statistical mechanics is defined via the so-called statistical operator or density matrix

$$\rho = \frac{1}{Z} \exp(-\beta H), \quad (12.1.6)$$

where the exponential of the Hamiltonian is defined by the corresponding power series. In quantum statistical mechanics the density matrix ρ plays the same role as the probability distribution $\rho[n]$ in classical statistical mechanics. In particular, we can define the matrix element

$$\begin{aligned} \rho[n] &= \int d^3x \chi_n(\vec{x})^* \rho \chi_n(\vec{x}) = \int d^3x \chi_n(\vec{x})^* \frac{1}{Z} \exp(-\beta H) \chi_n(\vec{x}) \\ &= \frac{1}{Z} \exp(-\beta E_n) \int dx \chi_n(\vec{x})^* \chi_n(\vec{x}) = \frac{1}{Z} \exp(-\beta E_n). \end{aligned} \quad (12.1.7)$$

Here we have used the normalization condition for the quantum mechanical wave function

$$\int d^3x \chi_n(\vec{x})^* \chi_n(\vec{x}) = 1. \quad (12.1.8)$$

The quantity $\rho[n]$ shall be interpreted as the probability to find the quantum system (which is again a member of an ensemble) in the state n . In analogy to classical statistical mechanics we now demand that

$$\sum_n \rho_n = 1, \quad (12.1.9)$$

which implies

$$Z = \sum_n \exp(-\beta E_n) \quad (12.1.10)$$

for the quantum statistical partition function. In particular, we see that the quantum mechanical state n plays the same role as the classical configuration

[n]. Similarly, the quantum mechanical Hilbert space is analogous to the classical configuration or phase space. The sum over all states in the Hilbert space can also be written as a trace, i.e.

$$Z = \text{Tr} \exp(-\beta H). \quad (12.1.11)$$

In this notation the normalization condition for the density matrix reads

$$\text{Tr} \rho = 1, \quad (12.1.12)$$

and the thermal average of a quantum mechanical observable (described by a Hermitean operator O) takes the form

$$\langle O \rangle = \text{Tr}[O\rho] = \frac{1}{Z} \text{Tr}[O \exp(-\beta H)]. \quad (12.1.13)$$

If O is diagonal in the basis of the energy eigenstates, i.e. if the observable O and the energy are simultaneously measurable with arbitrary precision, one can write

$$\langle O \rangle = \frac{1}{Z} \sum_n O[n] \exp(-\beta E_n), \quad (12.1.14)$$

where

$$O[n] = \int d^3x \chi_n(\vec{x})^* O \chi_n(\vec{x}) \quad (12.1.15)$$

is the matrix element of the operator O in the state n .

In analogy to classical statistical mechanics, for the thermal average of the energy we can again write

$$E = \langle H \rangle = \text{Tr}[H\rho] = \frac{1}{Z} \text{Tr}[H \exp(-\beta H)] = -\frac{\partial \log Z}{\partial \beta}. \quad (12.1.16)$$

Also the entropy is defined analogous to the classical case and is given by

$$S = -k_B \text{Tr} \rho \log \rho. \quad (12.1.17)$$

In the canonical ensemble we hence obtain

$$S = -k_B \frac{1}{Z} \text{Tr}[\exp(-\beta H)(-\beta H - \log Z)] = \frac{E}{T} - k_B \log Z. \quad (12.1.18)$$

Again introducing the free energy F as

$$Z = \exp(-\beta F) \Rightarrow F = \frac{1}{\beta} \log Z, \quad (12.1.19)$$

we obtain

$$S = \frac{E}{T} - \frac{F}{T} \Rightarrow F = E - TS, \quad (12.1.20)$$

exactly as in classical statistical mechanics.

In classical mechanics we have seen that the time-evolution of a general probability distribution is given by the Poisson bracket

$$\frac{d\rho}{dt} = \{\rho, \mathcal{H}\}. \quad (12.1.21)$$

Similarly, the quantum mechanical evolution equation for a general density matrix is

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H]. \quad (12.1.22)$$

In the canonical ensemble with $\rho = \exp(-\beta H)/Z$ we have $[\rho, H] = 0$ such that $d\rho/dt = 0$. This shows that the canonical ensemble describes a stationary time-independent distribution, which is what one expects in thermal equilibrium.

12.2 Canonical Ensemble for the Harmonic Oscillator

Let us illustrate quantum statistical mechanics using the harmonic oscillator. All we need to know at this point is its quantum mechanical energy spectrum

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) = \varepsilon\left(n + \frac{1}{2}\right), \quad (12.2.1)$$

where ω is the angular frequency of the oscillator and $n = 0, 1, 2, \dots, \infty$. Just as for the classical particle on the energy ladder, the energies of the quantum mechanical eigenstates of the harmonic oscillator are equally spaced. The quantum statistical partition function is given by

$$Z = \text{Tr} \exp(-\beta H) = \sum_{n=0}^{\infty} \exp(-\beta E_n) = \frac{\exp(-\beta\varepsilon/2)}{1 - \exp(-\beta\varepsilon)}. \quad (12.2.2)$$

Up to the irrelevant constant factor $\exp(-\beta\varepsilon/2)$ this is identical with the classical partition function of the particle on the ladder. Hence, we can use everything we have learned earlier about the classical particle on the energy ladder and reinterpret it in the context of the quantum mechanical harmonic oscillator.

Chapter 13

Hot Quantum Gases in the Early Universe

Quantum mechanical particles come as two fundamentally different types — bosons and fermions — which differ in both their spin and their statistics. Bosons have integer and fermions have half-integer spin (an intrinsic angular momentum of a particle). Furthermore, bosons have a wave function that is symmetric against particle permutations, while fermions have antisymmetric wave functions. As a consequence, an arbitrary number of bosons but at most one fermion can occupy a given quantum state. This gives rise to two fundamentally different forms of quantum statistics. Bosons obey the so-called Bose-Einstein statistics, while fermions obey Fermi-Dirac statistics. To illustrate these issues we will consider hot quantum gases in the early Universe.

13.1 Bose-Einstein Statistics and Background Radiation

Historically the first theoretical formula of quantum physics was Planck's law for black body radiation. For example, the cosmic background radiation — a remnant of the big bang — is of the black body type. Planck was able to explain the energy distribution of black body radiation by assuming that light of angular frequency $\omega = 2\pi\nu$ is absorbed and emitted by matter only in discrete amounts of energy

$$E = \hbar\omega. \tag{13.1.1}$$

Nowadays, we would associate Planck's radiation formula with a rather advanced field of quantum physics. Strictly speaking, it belongs to the quantum statistical mechanics of the theory of the free electromagnetic field, i.e. it is part of quantum field theory — clearly a subject of graduate courses. It is amazing that theoretical quantum physics started with such an advanced topic. Still, we will try to understand Planck's radiation formula in what follows.

Thermodynamics deals with systems of many particles that are in thermal equilibrium with each other and with a thermal bath. The energies of the individual states are statistically distributed, following a Boltzmann distribution for a given temperature T . The thermal statistical fluctuations are of a different nature than those related to quantum uncertainty. Thermal fluctuations are present also at the classical level, and e.g. reflect our inability to treat a system with a large number of particles exactly. Following the classical concept of reality, this is possible, at least in principle. In practice, it is, however, much more appropriate to use a classical statistical description. In the thermodynamics of photons, i.e. in quantum statistical mechanics, we deal with thermal and quantum fluctuations at the same time.

A system of photons in thermal equilibrium has been with us from the beginning of our Universe. Immediately after the big bang the energy density — and hence the temperature — was extremely high, and all kinds of elementary particles (among them photons, electrons and their anti-particles — positrons — as well as neutrinos and anti-neutrinos) have existed as an extremely hot gas filling all of space. These particles interacted with each other e.g. via Compton scattering. As the Universe expanded, the temperature decreased and electrons and positrons annihilated into a lot of photons. A very small fraction of the electrons (actually all the ones in the Universe today) exceeded the number of positrons and thus survived annihilation. At this time — a few seconds after the big bang — no atom had ever been formed. As a consequence, there were no characteristic colors of selected spectral lines. This is what we mean when we talk about the cosmic photons as black body radiation. About 300000 years after the big bang the Universe had expanded and cooled so much that electrons and atomic nuclei could settle down to form neutral atoms. At that time the Universe became transparent. The photons that emerged from the mass extinction of electrons and positrons were left alone, and are still floating through our Universe. Of course, in the last 14 billion years the Universe has expanded further and the cosmic photon gas has cooled down accordingly. Today the temperature of the cosmic background radiation is 2.735 K. It is amazing that this temperature is to very high accuracy the same, no matter what corner of the Universe the photons come from. This was first explained by Alan Guth from MIT using the idea of

the inflationary Universe.

How does one measure the temperature of a system of photons? The temperature is defined via the Boltzmann distribution, in our case by the intensity of radiation with a certain frequency. Hence, by measuring the photon spectrum one can determine the temperature. This is exactly what the antennae of WMAP satellite (the Wilkinson Microwave Anisotropy Probe) are doing. Equipped with the idea of Planck, let us now derive this spectrum theoretically. For simplicity we replace the Universe by a large box of spatial size $L \times L \times L$ with periodic boundary conditions. This is only a technical trick that will allow us to simplify the calculation. At the end we let $L \rightarrow \infty$. We will proceed in three steps. First we work classically, and classify all possible modes of the electromagnetic field in the box. Then we switch to quantum mechanics and populate these modes with photons. Finally, we do quantum statistical mechanics by summing over all quantum states using Boltzmann's distribution.

What are the modes of the electromagnetic field in an L^3 periodic box? First of all, we can classify them by their wave vector \vec{k} , which is now restricted to discrete values

$$\vec{k} = \frac{2\pi}{L}\vec{m}, \quad m_i \in \mathbb{Z}. \quad (13.1.2)$$

The frequency of this mode is given by

$$\omega = |\vec{k}|c. \quad (13.1.3)$$

Each of the modes can exist in two polarization states.

Now we turn to quantum mechanics and populate the classical modes with photons. As we have learned, a mode of frequency ω can host photons of energy

$$E(\vec{k}) = \hbar\omega = \hbar|\vec{k}|c \quad (13.1.4)$$

only. Photons are bosons. This means that an arbitrary number of them can occupy a single mode of the electromagnetic field. Electrons and neutrinos, for example, behave very differently. They are fermions, i.e. at most one of them can occupy a single mode. All elementary particles we know are either fermions or bosons. We can completely classify a quantum state of the electromagnetic field by specifying the number of photons $n(\vec{k}) \in \{0, 1, 2, \dots\}$ occupying each mode (characterized by wave vector \vec{k} and polarization, which we suppress in our notation). It is important to note that it does not matter "which photon" occupies which mode. Individual photons are indistinguishable from each other, they are like perfect twins. Hence specifying their number per mode determines their state completely.

Now that we have classified all quantum states of the electromagnetic field by specifying the photon occupation numbers for all modes, we can turn to quantum statistical mechanics. Then we must evaluate the partition function by summing over all states. Since the modes are completely independent of one another, the partition function

$$Z = \prod_{\vec{k}} Z(\vec{k}) \quad (13.1.5)$$

factorizes into partition functions for each individual mode. Here we consider a single mode partition function

$$Z(\vec{k}) = \sum_{n(\vec{k})=0}^{\infty} \exp(-n(\vec{k})E(\vec{k})/k_B T) = \sum_{n(\vec{k})=0}^{\infty} \exp(-\beta n(\vec{k})\hbar|\vec{k}|c). \quad (13.1.6)$$

Each mode state is weighted by its Boltzmann factor $\exp(-n(\vec{k})E(\vec{k})/k_B T)$, which is determined by its total energy of photons $n(\vec{k})E(\vec{k})$ occupying that mode and by the temperature T . Now we make use of the well-known summation formula for a geometric series

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}. \quad (13.1.7)$$

Using $x = \exp(-\beta\hbar|\vec{k}|c)$ we obtain the partition function corresponding to Bose-Einstein statistics

$$Z(\vec{k}) = \frac{1}{1 - \exp(-\beta\hbar|\vec{k}|c)}. \quad (13.1.8)$$

We are interested in the statistical average of the energy in a particular mode, which is given by

$$\begin{aligned} \langle n(\vec{k})E(\vec{k}) \rangle &= \frac{1}{Z(\vec{k})} \sum_{n(\vec{k})=0}^{\infty} n(\vec{k})E(\vec{k}) \exp(-\beta n(\vec{k})E(\vec{k})) \\ &= -\frac{\partial \log Z(\vec{k})}{\partial \beta} = \frac{\hbar|\vec{k}|c}{\exp(\beta\hbar|\vec{k}|c) - 1}. \end{aligned} \quad (13.1.9)$$

Finally, we are interested in the average total energy as a sum over all modes

$$\langle E \rangle = 2 \sum_{\vec{k}} \langle n(\vec{k})E(\vec{k}) \rangle \rightarrow 2 \left(\frac{L}{2\pi}\right)^3 \int d^3k \langle n(\vec{k})E(\vec{k}) \rangle. \quad (13.1.10)$$

Here a factor 2 arises due to the two polarization states. In the last step we have performed the infinite volume limit $L \rightarrow \infty$. Then the sum over discrete modes

turns into an integral. It is no surprise that our result grows in proportion to the volume L^3 . We should simply consider the energy density $\rho = \langle E \rangle / L^3$. We can now perform the angular integration and also replace $|\vec{k}| = \omega/c$ to obtain

$$\rho = \frac{1}{\pi^2 c^3} \int_0^\infty d\omega \frac{\hbar \omega^3}{\exp(\beta \hbar \omega) - 1}. \quad (13.1.11)$$

Before we do the integral we read off the energy density per unit frequency for modes of a given angular frequency ω

$$\frac{d\rho(\omega)}{d\omega} = \frac{1}{\pi^2 c^3} \frac{\hbar \omega^3}{\exp(\hbar \omega / k_B T) - 1}. \quad (13.1.12)$$

This is Planck's formula that was at the origin of quantum mechanics. If you have followed the above arguments: congratulations, you have just mastered a calculation in quantum field theory!

Since we have worked quite hard to produce this important result, let us discuss it in some detail. Let us first consider the classical limit $\hbar \rightarrow 0$. Then we obtain the classical Rayleigh-Jeans law

$$\frac{d\rho(\omega)}{d\omega} = \frac{\omega^2 k_B T}{\pi^2 c^3}. \quad (13.1.13)$$

Integrating this over all frequencies gives a divergent result from the high frequency end of the spectrum. This is the so-called ultraviolet Jeans catastrophe. The classical thermodynamics of the electromagnetic field gives an unphysical result. Now we go back to Planck's quantum result and perform the integral over all frequencies ω . This gives the Stefan-Boltzmann law

$$\rho = \frac{\pi^2 k_B^4 T^4}{15 \hbar^3 c^3}, \quad (13.1.14)$$

which is not only finite, but also agrees with experiment. Again, in the classical limit the result would be divergent. It is interesting that for high temperatures and for low frequencies, i.e. for $k_B T \gg \hbar \omega$, Planck's formula also reduces to the classical result. Quantum effects become important only in the low temperature and high frequency regimes.

Now we can understand how WMAP measures the temperature of the cosmic background radiation. The energy density is measured for various frequencies, and is then compared with Planck's formula, which leads to a high precision determination of T . The WMAP data tell us a lot about how our Universe began. In fact, the early history of the Universe is encoded in the photons left over from the big bang. Sometimes one must understand the very small, before one can understand the very large.

13.2 Thermodynamical Distributions

Let us define the Bose-Einstein distribution function

$$f(\vec{k}) = \frac{1}{\exp(\beta\hbar|\vec{k}|c) - 1}. \quad (13.2.1)$$

Then we can write the energy and number density of a free photon gas as

$$\begin{aligned} \rho &= \frac{\langle E \rangle}{L^3} = \frac{2}{(2\pi)^3} \int d^3k \hbar|\vec{k}|c f(\vec{k}), \\ n &= \frac{\langle N \rangle}{L^3} = \frac{2}{(2\pi)^3} \int d^3k f(\vec{k}). \end{aligned} \quad (13.2.2)$$

Let us now consider a more general system of free relativistic particles of mass m . The energy of a particle then is

$$E = \sqrt{(|\vec{p}|c)^2 + (mc^2)^2} = \sqrt{(\hbar kc)^2 + (mc^2)^2}. \quad (13.2.3)$$

Here the momentum $\vec{p} = \hbar\vec{k}$ characterizes the state of the particle. The particle may also have a spin \vec{S} . The component of the spin in the direction of momentum is the so-called helicity, which is given by $S_k = -S, \dots, S$, i.e. for a particle with spin S there are $g = 2S + 1$ helicities. The spin determines the statistics of particles. Particles with integer spin are bosons, while particles with half-integer spin are fermions. A particle state can hence be characterized by \vec{k} and S_k . Photons (and other massless particles) are slightly different. Photons are bosons with spin $S = 1$ but they only have two helicities $S_k = \pm 1$, i.e. $g = 2$. These are the two polarization states that entered the derivation of Planck's formula.

Now let us consider massive bosons. An arbitrary number of bosons can occupy the same state, and the grand canonical partition function thus takes the form

$$Z(\beta, \mu) = \text{Tr} \exp(-\beta(H - \mu N)). \quad (13.2.4)$$

The chemical potential is a useful concept only if particle number is conserved. This is not always the case in relativistic theories. In particular, in an interacting photon gas particle number is not conserved. For example, we have said that the cosmic background radiation originated from a mass extinction of particles — namely the annihilation of electrons and their anti-particles (positrons). In this process an enormous number of photons has been created. Photon number hence was not conserved in this process. Therefore a chemical potential for photons is in general not a useful concept. The number of other bosons, however, may be conserved. In such cases, it is appropriate to introduce a chemical potential μ .

The trace in eq.(13.2.4) extends over all possible states

$$\begin{aligned}
Z(\beta, \mu) &= \prod_{\vec{k}, S_k} \sum_{n(\vec{k}, S_k)=0}^{\infty} \exp(-\beta \sum_{\vec{k}, S_k} n(\vec{k}, S_k) (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)) \\
&= \prod_{\vec{k}, S_k} \left(\sum_{n(\vec{k}, S_k)=0}^{\infty} \exp(-\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu) n(\vec{k}, S_k)) \right) \\
&= \prod_{\vec{k}, S_k} \frac{1}{1 - \exp(-\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))}. \tag{13.2.5}
\end{aligned}$$

Let us compute the expectation value of the particle number

$$\begin{aligned}
\langle N \rangle &= \frac{1}{Z(\beta, \mu)} \text{Tr}[N \exp(-\beta(H - \mu N))] \\
&= \frac{\partial \log Z(\beta, \mu)}{\partial(\beta\mu)} \\
&= \frac{\partial}{\partial(\beta\mu)} \sum_{\vec{k}, S_k} \log \frac{1}{1 - \exp(-\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))} \\
&= g \sum_{\vec{k}} \frac{\exp(-\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))}{1 - \exp(-\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))} \\
&= g \sum_{\vec{k}} \frac{1}{\exp(\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)) - 1} \tag{13.2.6}
\end{aligned}$$

Up to now we have summed over momenta, i.e. we have assumed that we are in a finite volume $V = L^3$, e.g. with periodic boundary conditions, and thus with wave numbers

$$\vec{k} = \frac{2\pi}{L} \vec{n}, \quad \vec{n} \in \mathbb{Z}^3. \tag{13.2.7}$$

In the infinite volume limit we obtain

$$\sum_{\vec{k}} \rightarrow \left(\frac{L}{2\pi}\right)^3 \int d^3k, \tag{13.2.8}$$

such that the particle density takes the form

$$n = \frac{\langle N \rangle}{L^3} = \frac{g}{(2\pi)^3} \int d^3k f(\vec{k}), \tag{13.2.9}$$

where

$$f(\vec{k}) = \frac{1}{\exp(\beta (\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)) - 1} \tag{13.2.10}$$

is a generalization of the Bose-Einstein distribution of eq.(13.2.1) to bosons with non-zero mass m at non-zero chemical potential μ . Correspondingly, one finds for the energy density

$$\rho = \frac{\langle H \rangle}{L^3} = \frac{g}{(2\pi)^3} \int d^3k \sqrt{(\hbar kc)^2 + (mc^2)^2} f(\vec{k}). \quad (13.2.11)$$

Let us now repeat the calculation for fermions. Since at most one fermion can occupy a given quantum state, one obtains

$$\begin{aligned} Z(\beta, \mu) &= \prod_{\vec{k}, S_k} \left(\sum_{n(\vec{k}, S_k)=0}^1 \exp(-\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)n(\vec{k}, S_k)) \right) \\ &= \prod_{\vec{k}, S_k} (1 + \exp(-\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))). \end{aligned} \quad (13.2.12)$$

The corresponding expectation value of the particle number is

$$\begin{aligned} \langle N \rangle &= \frac{\partial}{\partial(\beta\mu)} \sum_{\vec{k}, S_k} \log(1 + \exp(-\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))) \\ &= g \sum_{\vec{k}} \frac{\exp(-\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))}{1 + \exp(-\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu))} \\ &= g \sum_{\vec{k}} \frac{1}{\exp(\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)) + 1} \end{aligned} \quad (13.2.13)$$

From this we obtain the particle density

$$n = \frac{\langle N \rangle}{L^3} = \frac{g}{(2\pi)^3} \int d^3k f(\vec{k}), \quad (13.2.14)$$

now with the so-called Fermi-Dirac distribution

$$f(\vec{k}) = \frac{1}{\exp(\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)) + 1}. \quad (13.2.15)$$

Let us also consider the non-relativistic limit of the Bose-Einstein and Fermi-Dirac distributions. Then $k_B T \ll mc^2$ and hence

$$f(\vec{k}) = \frac{1}{\exp(\beta(\sqrt{(\hbar kc)^2 + (mc^2)^2} - \mu)) \pm 1} \sim \exp(-\beta(mc^2 + \frac{\hbar^2 k^2}{2m} - \mu)), \quad (13.2.16)$$

which is just the Boltzmann distribution well-known from classical statistical mechanics. This implies

$$n = g \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \exp(-\beta(mc^2 - \mu)), \quad \rho = mc^2 n. \quad (13.2.17)$$

Let us now consider massless fermions with a negligible chemical potential ($\mu \ll k_B T$), and with spin 1/2 ($g = 2$). Then

$$\begin{aligned} n &= \frac{2}{(2\pi)^3} 4\pi \int_0^\infty dk k^2 \frac{1}{\exp(\beta\hbar kc) + 1} = \frac{4}{(2\pi)^2} \frac{1}{\beta^3 \hbar^3 c^3} \left(1 - \frac{1}{4}\right) \Gamma(3) \zeta(3) \\ &= \frac{3\zeta(3) k_B^3 T^3}{2\pi^2 \hbar^3 c^3}, \\ \rho &= \frac{2}{(2\pi)^3} 4\pi \int_0^\infty dk k^2 \frac{\hbar kc}{\exp(\beta\hbar kc) + 1} = \frac{4}{(2\pi)^2} \frac{1}{\beta^4 \hbar^3 c^3} \left(1 - \frac{1}{8}\right) \Gamma(4) \zeta(4) \\ &= \frac{7\pi^2 k_B^4 T^4}{120 \hbar^3 c^3}. \end{aligned} \quad (13.2.18)$$

13.3 Entropy Conservation and Neutrino Temperature

The second law of thermodynamics states that entropy never decreases — and indeed usually increases. In general, an expanding system — for example, an exploding gas — will not be in thermodynamical equilibrium. The expansion of the Universe, however, is slow and the system remains in thermodynamical equilibrium while it expands and cools. Such processes are called adiabatic. For them the total entropy is conserved, and they are, in fact, reversible. The entropy in a volume $V = L^3$ is given by

$$S = \frac{E}{T} - \frac{F}{T} = \frac{\rho + p}{T} L^3. \quad (13.3.1)$$

For a gas of relativistic particles (either bosons or fermions) the energy and pressure are related by the equation of state

$$p = \frac{1}{3} \rho, \quad (13.3.2)$$

and hence

$$S = \frac{4}{3} \frac{\rho}{T} L^3. \quad (13.3.3)$$

Different particle species will remain in thermal equilibrium, only if they interact with each other often enough. Since the Universe expands, particle densities become smaller and smaller, and ultimately the various particle species decouple from each other. Still, one may assign a temperature T_i to each particle species i . We want to compare these temperatures with the one of the photons $T = T_\gamma$, which today is 2.735 K. If the various particle species have different temperatures we obtain

$$S = \frac{2\pi^2 k_B^4}{45\hbar^3 c^3} \left(\sum_{\text{bosons}} g_i T_i^3 + \sum_{\text{fermions}} \frac{7}{8} g_i T_i^3 \right) L^3. \quad (13.3.4)$$

We will use the conservation of entropy to determine the temperature of the neutrinos in the Universe. Let us go back to about 1 sec after the big bang. At that time we have a system of electrons, positrons, photons, and neutrinos. The neutrinos are no longer in thermal equilibrium with the other particles at that moment, because they interact only weakly. Before that time neutrinos, electrons, positrons, and photons had the same temperature T . When electrons and positrons annihilate, their entropy goes into the photons, which thus get heated up to a higher temperature T_γ . Before the electron-positron annihilation we have

$$S = \frac{2\pi^2 k_B^4}{45\hbar^3 c^3} (g_\gamma + \frac{7}{8}(g_e + g_{\bar{e}} + g_{\nu_e} + g_{\nu_\mu} + g_{\nu_\tau})) (TL)^3 = \frac{2\pi^2 k_B^4}{45\hbar^3 c^3} (4 + \frac{7}{8}5 \times 2) (TL)^3. \quad (13.3.5)$$

After the electron-positron annihilation all entropy is in photons and neutrinos. The neutrino temperature has decreased to T_ν and the size of the Universe is now L' such that

$$T_\nu L' = TL. \quad (13.3.6)$$

The entropy is then given by

$$\begin{aligned} S &= \frac{2\pi^2 k_B^4}{45\hbar^3 c^3} (g_\gamma (T_\gamma L')^3 + \frac{7}{8} (g_{\nu_e} + g_{\nu_\mu} + g_{\nu_\tau}) (T_\nu L')^3) \\ &= \frac{2\pi^2 k_B^4}{45\hbar^3 c^3} (2(T_\gamma L')^3 + \frac{7}{8}3 \times 2(T_\nu L')^3). \end{aligned} \quad (13.3.7)$$

Using entropy conservation we obtain

$$\begin{aligned} (T_\gamma L')^3 + \frac{7}{8}3(T_\nu L')^3 &= (1 + \frac{7}{8}5)(T_\nu L')^3 \Rightarrow \\ \left(\frac{T_\gamma}{T_\nu}\right)^3 &= 1 + \frac{7}{8}2 = \frac{11}{4} \Rightarrow T_\nu = \left(\frac{4}{11}\right)^{1/3} T_\gamma. \end{aligned} \quad (13.3.8)$$

During the following expansion of the Universe these temperatures are simply red-shifted, but their ratio remains fixed. The photons still interact with charged

matter until they decouple about 300000 years after the big bang, when neutral atoms are formed. The number of photons is, however, much larger than the number of charged particles, such that the interactions cannot change the temperature of the photons. Since one observes the cosmic background radiation at a temperature $T_\gamma = 2.7$ K, we expect a cosmic neutrino background of temperature $T_\nu = 1.9$ K. Unfortunately, neutrinos interact so weakly that the cosmic neutrino background radiation has not yet been detected. Detecting it would be very interesting, because it would tell us something about the so-called lepton number asymmetry of the Universe.

Chapter 14

Lattice Vibrations

In this chapter we discuss the vibrations of the crystal lattice of a solid. We will model the vibrations of a cubic lattice of heavy atomic nuclei (actually ions) with coupled harmonic oscillators. The resulting quantum mechanical model can be solved analytically and gives rise to quantized lattice vibrations, known as phonons. Just as photons, phonons are bosons which may form an ideal Bose gas. However, unlike photons, they do not have a linear energy-momentum dispersion relation for large values of the momentum. At low temperature T , the phonon gas determines the specific heat of solids, which is proportional to T^3 . This behavior was first derived by Peter Debye in 1912. In our considerations, we will completely ignore the electrons that propagate in the background of the crystal lattice of ions. However, there are interesting effects that result from the coupling of electrons and phonons. In particular, at very low temperatures the electromagnetic repulsion between two electrons, which is mediated by the exchange of photons, may be overcome by an attractive interaction mediated by phonons. This attraction gives rise to the formation of Cooper pairs of electrons, i.e. two electrons form a boson. The condensation of Cooper pair bosons gives rise to superconductivity of metals at very low temperatures. In this chapter, ignoring the electrons, we concentrate entirely on the physics of phonons. For simplicity, we will first consider a model in one dimension. In this context, we will also discuss in which sense phonons may be considered as “particles”. Since they are actually quantized waves, following Frank Wilczek, it may be more appropriate to call them “wavicles”. In particular, in contrast to particles, a priori, phonons and other wavicles (such as photons or electrons) do not have a well-defined position and are thus not localizable in the usual sense. Remarkably, the model that we use to describe a vibrating solid has both a particle and a wavicle interpretation.

The resulting particle-wavicle complementarity should not be confused with the particle-wave duality sometimes discussed in the quantum mechanics textbook literature.

14.1 A 1-dimensional Model for Ions Forming a Crystal

The ions inside a solid form a regular crystal lattice. We will consider a simple analytically solvable model in which the ions are described as point particles of mass M . As a warm-up exercise, let us first consider the problem in one spatial dimension. The ions are then described by their positions x_n . Here the index $n \in \mathbb{Z}$ enumerates the ions according to their order in the crystal. In particular, the equilibrium position of the ion with label n is na , where a is the crystal lattice spacing. In the model the ions are coupled only to their nearest neighbors on the lattice via a harmonic oscillator potential. The Hamiltonian of the lattice model is then given by

$$H = \sum_{n \in \mathbb{Z}} \left[\frac{p_n^2}{2M} + \frac{1}{2} M \omega_0^2 (x_{n+1} - x_n - a)^2 \right]. \quad (14.1.1)$$

As a next step, we introduce the displacement of each ion from its equilibrium position

$$y_n = x_n - na, \quad (14.1.2)$$

such that

$$H = \sum_{n \in \mathbb{Z}} \left[\frac{p_n^2}{2M} + \frac{1}{2} M \omega_0^2 (y_{n+1} - y_n)^2 \right], \quad (14.1.3)$$

and we perform a discrete Fourier transform of the variables y_n with respect to their index n , i.e.

$$\tilde{y}(k) = \sum_{n \in \mathbb{Z}} y_n \exp(-ikna). \quad (14.1.4)$$

The wave number k takes values in the periodic Brillouin zone $k \in]-\pi/a, \pi/a]$. Note that indeed $\tilde{y}(k + 2\pi/a) = \tilde{y}(k)$. Since the original variables y_n are real-valued (and the corresponding quantum mechanical operator is thus Hermitian), one obtains $\tilde{y}(-k) = \tilde{y}(k)^\dagger$. The inverse Fourier transform takes the form

$$y_n = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \tilde{y}(k) \exp(ikna). \quad (14.1.5)$$

Let us now rewrite the potential energy of our model in terms of the Fourier transformed variables $\tilde{y}(k)$, i.e.

$$\begin{aligned}
 V &= \sum_{n \in \mathbb{Z}} \frac{1}{2} M \omega_0^2 (y_{n+1} - y_n)^2 \\
 &= \left(\frac{a}{2\pi} \right)^2 \frac{1}{2} M \omega_0^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk' \tilde{y}(k)^\dagger \tilde{y}(k') \\
 &\times \sum_{n \in \mathbb{Z}} [\exp(ik(n+1)a) - \exp(ikna)] [\exp(-ik'(n+1)a) - \exp(-ik'na)] \\
 &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{2} M \omega_0^2 \hat{k}^2 a^2 \tilde{y}(k)^\dagger \tilde{y}(k). \tag{14.1.6}
 \end{aligned}$$

Here we have used

$$\frac{a}{2\pi} \sum_{n \in \mathbb{Z}} \exp(i(k-k')na) = \delta(k-k'), \tag{14.1.7}$$

as well as

$$2 - \exp(ika) - \exp(-ika) = 2[1 - \cos(ka)] = \left(2 \sin \frac{ka}{2} \right)^2 = \hat{k}^2 a^2. \tag{14.1.8}$$

In the last step we have introduced

$$\hat{k} = \frac{2}{a} \sin \frac{ka}{2}. \tag{14.1.9}$$

Similarly, we consider the kinetic energy

$$T = \sum_{n \in \mathbb{Z}} \frac{p_n^2}{2M}, \quad p_n = -i\hbar \frac{d}{dy_n}. \tag{14.1.10}$$

By again applying the Fourier transform, we obtain

$$\tilde{p}(k) = \sum_{n \in \mathbb{Z}} p_n \exp(-ikna), \quad \tilde{p}(-k) = \tilde{p}(k)^\dagger, \tag{14.1.11}$$

and correspondingly

$$p_n = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \tilde{p}(k) \exp(ikna). \tag{14.1.12}$$

The kinetic energy can now be written as

$$\begin{aligned}
T &= \sum_{n \in \mathbb{Z}} \frac{p_n^2}{2M} \\
&= \left(\frac{a}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk' \frac{1}{2M} \tilde{p}(k)^\dagger \tilde{p}(k') \sum_{n \in \mathbb{Z}} \exp(i(k-k')na) \\
&= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{2M} \tilde{p}(k)^\dagger \tilde{p}(k).
\end{aligned} \tag{14.1.13}$$

Finally, the Hamilton operator takes the form

$$H = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \left[\frac{1}{2M} \tilde{p}(k)^\dagger \tilde{p}(k) + \frac{1}{2} M \omega_0^2 \hat{k}^2 a^2 \tilde{y}(k)^\dagger \tilde{y}(k) \right]. \tag{14.1.14}$$

This represents a set of harmonic oscillators (one for each value of the wave number k) with the k -dependent frequency

$$\omega(k) = \omega_0 |\hat{k}| a = 2\omega_0 \left| \sin \frac{ka}{2} \right|. \tag{14.1.15}$$

While two individual ions would oscillate against each other with a fixed frequency ω_0 , the crystal as a whole supports vibrations of arbitrary frequency $\omega(k)$ between 0 and $2\omega_0$.

14.2 Phonon Creation and Annihilation Operators

The quantized vibrations of a solid are known as phonons. In the context of a single harmonic oscillator, we are familiar with raising and lowering operators. This suggests to introduce

$$a(k) = \frac{1}{\sqrt{2}} \left(\alpha(k) \tilde{y}(k) + \frac{i\tilde{p}(k)}{\alpha(k)\hbar} \right), \quad a(k)^\dagger = \frac{1}{\sqrt{2}} \left(\alpha(k) \tilde{y}(k)^\dagger - \frac{i\tilde{p}(k)^\dagger}{\alpha(k)\hbar} \right), \tag{14.2.1}$$

with

$$\alpha(k) = \sqrt{\frac{M\omega(k)}{\hbar}}. \tag{14.2.2}$$

We then obtain

$$\begin{aligned}
[a(k), a(k')^\dagger] &= -\frac{i\alpha(k)}{2\alpha(k')\hbar} [\tilde{y}(k), \tilde{p}(k')^\dagger] + \frac{i\alpha(k')}{2\alpha(k)\hbar} [\tilde{p}(k), \tilde{y}(k')^\dagger] \\
&= -\frac{i\alpha(k)}{2\alpha(k')\hbar} [\tilde{y}(k), \tilde{p}(-k')] + \frac{i\alpha(k)}{2\alpha(k')\hbar} [\tilde{p}(k), \tilde{y}(-k')].
\end{aligned} \tag{14.2.3}$$

The commutation relations of the coordinates and momenta are given by

$$[y_n, y_m] = 0, [p_n, p_m] = 0, [y_n, p_m] = i\hbar\delta_{nm}, \quad (14.2.4)$$

which implies

$$\begin{aligned} [\tilde{y}(k), \tilde{p}(-k')] &= \sum_{n,m \in \mathbb{Z}} [y_n, p_m] \exp(-ikna + ik'ma) \\ &= i\hbar \sum_{n \in \mathbb{Z}} \exp(i(k' - k)na) = i\hbar \frac{2\pi}{a} \delta(k - k'). \end{aligned} \quad (14.2.5)$$

This finally leads to

$$[a(k), a(k')^\dagger] = \frac{2\pi}{a} \delta(k - k'). \quad (14.2.6)$$

Similarly, we also have

$$[a(k), a(k')] = 0, [a(k)^\dagger, a(k')^\dagger] = 0. \quad (14.2.7)$$

Using

$$\begin{aligned} a(k)^\dagger a(k) &= \frac{1}{2} \left(\alpha(k) \tilde{y}(k)^\dagger - \frac{i\tilde{p}(k)^\dagger}{\alpha(k)\hbar} \right) \left(\alpha(k) \tilde{y}(k) + \frac{i\tilde{p}(k)}{\alpha(k)\hbar} \right) \\ &= \frac{1}{2} \left(\alpha(k)^2 \tilde{y}(k)^\dagger \tilde{y}(k) + \frac{\tilde{p}(k)^\dagger \tilde{p}(k)}{\alpha(k)^2} \right) \\ &\quad + \frac{i}{2\hbar} [\tilde{y}(-k) \tilde{p}(k) - \tilde{p}(-k) \tilde{y}(k)], \end{aligned} \quad (14.2.8)$$

the Hamilton operator now takes the form

$$\begin{aligned} H &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \hbar\omega(k) \left(a(k)^\dagger a(k) - \frac{i}{2\hbar} [\tilde{y}(k), \tilde{p}(-k)] \right) \\ &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \hbar\omega(k) \left(a(k)^\dagger a(k) + \frac{N}{2} \right) \\ &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \hbar\omega(k) \left(n(k) + \frac{N}{2} \right). \end{aligned} \quad (14.2.9)$$

The number of ions N (which is infinite in the infinite volume limit) arises from

$$\frac{2\pi}{a} \delta(k) = \sum_{n \in \mathbb{Z}} \exp(-ikna) \Rightarrow \frac{2\pi}{a} \delta(0) = \sum_{n \in \mathbb{Z}} 1 = N. \quad (14.2.10)$$

We have introduced the phonon number operator

$$n(k) = a(k)^\dagger a(k), \quad (14.2.11)$$

which determines the number of phonons occupying a given mode with wave number k .

14.3 Phonons in One Dimension

Just as a quantum state of the electromagnetic field is characterized by a photon number $n(\vec{k})$ for each mode \vec{k} , a quantum state of the vibrating solid is characterized by a phonon number $n(k)$ for each mode k . The ground state $|0\rangle$ of the solid has $n(k) = 0$ for all modes, i.e. for all k

$$a(k)|0\rangle = 0. \quad (14.3.1)$$

It is interesting to note that even in the absence of phonons, i.e. when $n(k) = 0$ for all k , the solid has a non-vanishing zero-point energy. Let us calculate the total ground state energy of a solid consisting of N ions, which then has a finite length $L = Na$. Just as in the derivation of Planck's formula, before we take the limit $L \rightarrow \infty$, we may introduce periodic boundary conditions which quantize the allowed k -values to $k = 2\pi m/L$ with $m \in \mathbb{Z}$, such that

$$E_0 = \sum_k \frac{1}{2} \hbar \omega(k) \rightarrow \frac{L}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{2} \hbar \omega(k). \quad (14.3.2)$$

In the infinite volume limit, the ground state energy density thus takes the form

$$\rho_0 = \frac{E_0}{L} = \frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{2} \hbar \omega(k) = \frac{\hbar \omega_0}{2\pi a}. \quad (14.3.3)$$

In the following we will ignore the ground state energy because it just corresponds to an overall constant energy shift.

When one performs a similar calculation for the electromagnetic field using quantum field theory, one finds that it also has a non-zero energy density in its ground state. The state of the electromagnetic field without any photons is known as the vacuum. Hence, quantum field theory predicts that there is a non-zero vacuum energy density. Since the analog of the lattice spacing a , which plays the role of a short distance cut-off, is sent to zero in quantum field theory, the vacuum energy in quantum field theory even diverges. This is related to the cosmological constant problem, one of the big unsolved puzzles in theoretical physics. Why is the observed vacuum energy, which manifests itself on cosmic scales, by about 120 orders of magnitude smaller than any calculation in quantum field theory would suggest?

The single-phonon states describing a phonon of momentum $p = \hbar k$ result from

$$|k\rangle = a(k)^\dagger |0\rangle. \quad (14.3.4)$$

These states have an energy difference to the ground state of

$$E(k) = \hbar\omega(k) = 2\hbar\omega_0 \left| \sin \frac{ka}{2} \right|. \quad (14.3.5)$$

Interestingly, at least for small momenta $p = \hbar k$, just like photons, phonons also have a linear energy-momentum dispersion relation, i.e. $E(k) = \hbar|k|c$. In this case, however, c is not the velocity of light. Instead

$$c = \omega_0 a \quad (14.3.6)$$

is the velocity of sound. After all, phonons are just quantized sound waves propagating inside a solid. Unlike for photons, the phonon energy-momentum dispersion relation becomes flat for large momenta at the edge of the Brillouin zone. As a result, the velocity of sound

$$c(k) = \frac{dE}{dp} = \omega_0 a \cos \frac{ka}{2}. \quad (14.3.7)$$

is k -dependent.

Let us also consider states describing two phonons with momenta $p_1 = \hbar k_1$ and $p_2 = \hbar k_2$, which are given as

$$|k_1 k_2\rangle = a(k_1)^\dagger a(k_2)^\dagger |0\rangle. \quad (14.3.8)$$

Since $[a(k_1)^\dagger, a(k_2)^\dagger] = 0$ one obtains

$$|k_1 k_2\rangle = |k_2 k_1\rangle, \quad (14.3.9)$$

i.e. the state is symmetric under the exchange of the two phonons. This means that, just like photons, phonons are bosons. Consequently, the phonon number of a given mode is unrestricted and takes values $n(k) = 0, 1, 2, \dots, \infty$.

14.4 From Particles to “Wavicles”

Just as photons are quantized electromagnetic waves, phonons are quantized lattice vibrations. It is common to talk about photons and phonons as “particles”. However, they are not genuine particles in the sense of Newton, that can be described by their position and momentum. Of course, as we learned from Heisenberg, at the quantum level the position and momentum of a particle cannot be measured simultaneously with arbitrary precision. It is important to understand that quantized wave “particles”, such as photons and phonons, are

qualitatively different. A priori, their position is not even defined. While we have started with a model of ions, which are genuine particles in the sense of Newton, the phonons are collective vibrational excitations of the ion system. While the position of a phonon is not even defined, its momentum $p = \hbar k$ as well as its energy $E(k) = \hbar\omega(k)$ make perfect sense. In order to distinguish quantized wave “particles” from genuine particles a la Newton, Frank Wilczek sometimes speaks of “wavicles”. Since there is confusion in some quantum mechanics textbooks about particle-wave duality, the distinction between particles and wavicles may be quite useful. Once we have understood the difference, we may return to common terminology and also call the wavicles “particles”.

Let us try to define the position of a photon or phonon. While one would not speak about the position of a classical electromagnetic wave or a sound wave (since they exist in whole regions of space simultaneously), we can, for example, detect single photons in the cells of our retina. This means that a “wavicle” has been localized in a certain region of space. This may imply that one could be able to define its position after all. Since we have defined momentum eigenstates $|k\rangle$ for a phonon, quantum mechanics would suggest to define a corresponding position eigenstate as

$$|m\rangle = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk |k\rangle \exp(ikma). \quad (14.4.1)$$

Defining the creation operator

$$a_m^\dagger = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk a(k)^\dagger \exp(ikma), \quad (14.4.2)$$

one would then obtain

$$|m\rangle = a_m^\dagger |0\rangle. \quad (14.4.3)$$

Also introducing the annihilation operator

$$a_m = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk a(k) \exp(-ikma), \quad (14.4.4)$$

one finds the commutation relation

$$\begin{aligned} [a_m, a_n^\dagger] &= \left(\frac{a}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk' [a(k), a(k')^\dagger] \exp(i(k'n - km)a) \\ &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \exp(ik(n - m)a) = \delta_{mn}, \end{aligned} \quad (14.4.5)$$

as well as

$$[a_m, a_n] = 0, \quad [a_m^\dagger, a_n^\dagger] = 0. \quad (14.4.6)$$

This seems to suggest that we have indeed found a useful definition of an operator that creates a phonon in the position eigenstate $|n\rangle$. Hence, let us consider the operator a_m^\dagger in more detail. Using the definition of $a(k)^\dagger$ we obtain

$$a_m^\dagger = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{\sqrt{2}} \left(\alpha(k) \tilde{y}(k)^\dagger - \frac{i\tilde{p}(k)^\dagger}{\alpha(k)\hbar} \right) \exp(ikma). \quad (14.4.7)$$

Since a_m^\dagger is the Fourier transform of the sum of two products, it can be expressed as a convolution

$$a_m^\dagger = \sum_{n \in \mathbb{Z}} \left(f_{m-n} y_n - g_{m-n} \frac{i}{\hbar} p_n \right). \quad (14.4.8)$$

Since this expression involves a sum over all ion labels n , a_m^\dagger is not at all localized at a single position m in the crystal lattice. In particular, the quantities

$$\begin{aligned} f_m &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{\alpha(k)}{\sqrt{2}} \exp(ikma) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \sqrt{\frac{M\omega(k)}{2\hbar}} \exp(ikma), \\ g_m &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{\sqrt{2}\alpha(k)} \exp(ikma) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \sqrt{\frac{\hbar}{2M\omega(k)}} \exp(ikma), \end{aligned} \quad (14.4.9)$$

are non-local, i.e. they decay only slowly as $|m| \rightarrow \infty$. In particular, for large $|m|$ one finds

$$f_m \sim \frac{1}{\sqrt{|m|^3}}, \quad g_m \sim \frac{1}{\sqrt{|m|}}. \quad (14.4.10)$$

Some values for f_m and g_m (in units of $\alpha_0 = \sqrt{M\omega_0/\hbar}$) are listed in table 1. In contrast to particles which are point-like objects (but do respect the position-momentum uncertainty relation), wavicles are inherently non-local objects. In particular, if we want to create a phonon at a position m in the crystal, we must excite ion oscillations everywhere in the crystal in a particularly coordinated manner. Hence, when we use the standard terminology and refer to phonons as “particles”, we should not forget that, a priori, they do not even have a position and are thus not localizable in the usual sense.

We can take two complementary points of views on the dynamics of the vibrating solid. On the one hand, we can use a particle description, in which we work with a wave function that depends on the coordinates of the individual ions

$ m $	f_m/α_0	$g_m\alpha_0$
0	0.762759	0.834627
1	- 0.152552	0.278209
2	- 0.050850	0.198721
3	- 0.027381	0.162590
4	- 0.017717	0.140911
5	- 0.012655	0.126078

Table 14.1: *Some values for f_m and g_m in units of $\alpha_0 = \sqrt{M\omega_0/\hbar}$.*

in the crystal. On the other hand, we can also use a wavicle description, in which we characterize a state of the vibrating solid by specifying the phonon occupation numbers $n(k)$ for all modes k . It should be pointed out that this has nothing to do with the particle-wave duality discussed in the textbook literature, which sometimes gives rise to confusion. The two views on the vibrating solid are a manifestation of what one might call particle-wavicle complementarity. Remarkably, in this case, one can really describe the same physical phenomena using either a particle or a wavicle description.

Today, the most fundamental description of Nature is provided by the Standard Model of particle physics, which is a relativistic quantum field theory. In the Standard Model, photons, electrons, and other elementary “particles” arise as wavicles. Hence, our current understanding suggests that the most fundamental objects in Nature are indeed wavicles, which arise from the quantized oscillations of fields. In this sense, it would be more appropriate to speak about wavicle rather than particle physics. In the case of the vibrating solid, the phonon “field” is determined by the positions x_n of the ion particles, thus giving rise to particle-wavicle complementarity. Such complementarity does not exist in the Standard Model. However, one may wonder whether a particle (instead of a wavicle or field) description might again be possible, perhaps at an even more fundamental level. A currently more popular but very speculative way of thinking is that not particles but strings might be the most fundamental degrees of freedom in Nature.

14.5 Specific Heat of a 1-dimensional “Solid”

Let us now consider the canonical ensemble. Just as for photons, the phonon partition function factorizes into a product of mode partition functions

$$Z = \prod_k Z(k), \quad (14.5.1)$$

with the single mode partition function given by

$$Z(k) = \sum_{n(k)=0}^{\infty} \exp(-\beta n(k)E(k)) = \frac{1}{1 - \exp(-\beta E(k))}. \quad (14.5.2)$$

The average energy stored in a mode is then given by

$$\langle n(k)E(k) \rangle = -\frac{\partial \log Z(k)}{\partial \beta} = \frac{E(k)}{\exp(\beta E(k)) - 1}. \quad (14.5.3)$$

In the infinite volume limit, the average total energy density then takes the form

$$\begin{aligned} \rho &= \frac{\langle E \rangle}{L} = \frac{1}{L} \sum_k \langle n(k)E(k) \rangle \rightarrow \frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} dk \langle n(k)E(k) \rangle \\ &= \frac{1}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{E(k)}{\exp(\beta E(k)) - 1}. \end{aligned} \quad (14.5.4)$$

The expression for the specific heat is then given by

$$c_V = \frac{C_V}{L} = \frac{1}{L} \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \rho}{\partial T} = \frac{1}{2\pi k_B T^2} \int_{-\pi/a}^{\pi/a} dk \frac{E(k)^2 \exp(\beta E(k))}{[\exp(\beta E(k)) - 1]^2}. \quad (14.5.5)$$

Unlike in the photon case, which yields the Stefan-Boltzmann law, in the phonon case the corresponding integral cannot be done analytically. However, we may consider very low temperatures. Then only a few phonons with low frequency can be excited and the energy can be approximated by $E(k) = \hbar|k|c$. In addition, the integral can safely be extended to $k \in \{-\infty, \infty\}$ because the integrand is exponentially suppressed for large values of k , such that

$$\rho = \frac{1}{\pi} \int_0^{\infty} dk \frac{\hbar k c}{\exp(\beta \hbar k c) - 1} = \frac{\pi k_B^2 T^2}{6\hbar c}. \quad (14.5.6)$$

This is the analog of the Stefan-Boltzmann law for 1-dimensional phonons at very low temperatures. The corresponding specific heat is given by

$$c_V = \frac{\partial \rho}{\partial T} = \frac{\pi k_B^2 T}{3\hbar c}. \quad (14.5.7)$$

Unlike photons, at higher temperatures phonons will show a different behavior because their energy deviates from $\hbar|k|c$ and the momentum integral is cut off at π/a . These effects become particularly noticeable when phonons of the highest frequency $\omega(\pi/a) = 2\omega_0$ become thermally excited. The energy of such phonons is $E(\pi/a) = 2\hbar\omega_0$. Hence, when the temperature becomes of the order of the Debye temperature

$$T_D = \frac{E(\pi/a)}{k_B} = \frac{2\hbar\omega_0}{k_B}, \quad (14.5.8)$$

we should expect deviations from the low-temperature behavior. In the high-temperature limit $T \gg T_D$ one obtains $\exp(\beta E(k)) - 1 \approx \beta E(k)$ the specific heat then takes the form

$$c_V = \frac{1}{2\pi k_B T^2} \int_{-\pi/a}^{\pi/a} dk \frac{1}{\beta^2} = \frac{k_B}{a}, \quad (14.5.9)$$

and thus reaches a constant in the high-temperature limit. In the following we will generalize these considerations to the realistic case of three dimensions.

14.6 Fluctuations in a 1-dimensional “Solid”

One may suspect that our simple model could also explain the thermal expansion of solids. As we will see now, this is not the case. Indeed, one must include anharmonic corrections to the harmonic oscillator potentials between the ions, in order to describe the thermal expansion. Anharmonic forces give rise to phonon-phonon interactions, which implies that phonons then no longer form an ideal gas. Here we limit ourselves to the simple harmonic oscillator model in which phonons are free particles.

In order to investigate the thermal expansion of our model solid, let us compute the thermal average of the distance

$$\langle x_n - x_m \rangle = \langle y_n - y_m \rangle + (n - m)a, \quad (14.6.1)$$

between the two ions at positions n and m in the crystal. We now use

$$\begin{aligned} y_n - y_m &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \tilde{y}(k) [\exp(ikna) - \exp(ikma)] \\ &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{1}{\sqrt{2\alpha(k)}} [a(k) + a(-k)^\dagger] [\exp(ikna) - \exp(ikma)], \end{aligned} \quad (14.6.2)$$

and consider the thermal average

$$\begin{aligned}\langle a(k) \rangle &= \frac{1}{Z} \text{Tr} \{ a(k) \exp(-\beta H) \} \\ &= \frac{1}{Z(k)} \sum_{n(k)=0}^{\infty} \langle n(k) | a(k) | n(k) \rangle \exp(-\beta \hbar \omega(k) n(k)) = 0.\end{aligned}\tag{14.6.3}$$

Here $|n(k)\rangle$ denotes a state with $n(k)$ phonons occupying the mode k . Since $a(k)$ lowers and $a(k)^\dagger$ raises the phonon number by 1, i.e.

$$\begin{aligned}a(k) |n(k)\rangle &= \sqrt{n(k)} |n(k) - 1\rangle, \\ a(k)^\dagger |n(k)\rangle &= \sqrt{n(k) + 1} |n(k) + 1\rangle,\end{aligned}\tag{14.6.4}$$

one obtains $\langle n(k) | a(k) | n(k) \rangle = 0$. Similarly, one finds $\langle n(k) | a(-k)^\dagger | n(k) \rangle = 0$. Hence, also $\langle y_n - y_m \rangle = 0$ and we thus obtain

$$\langle x_n - x_m \rangle = (n - m)a,\tag{14.6.5}$$

such that the average distance of two ions is temperature-independent and just corresponds to the equilibrium distance $(n - m)a$.

Let us also calculate the average distance squared

$$\langle (x_n - x_m)^2 \rangle = \langle (y_n - y_m)^2 \rangle + (n - m)^2 a^2,\tag{14.6.6}$$

where we have used $\langle y_n - y_m \rangle = 0$. We now obtain

$$\begin{aligned}(y_n - y_m)^2 &= \left(\frac{a}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk' \tilde{y}(k)^\dagger \tilde{y}(k') [\exp(-ikna) - \exp(-ikma)] \\ &\times [\exp(ik'na) - \exp(ik'ma)] \\ &= \left(\frac{a}{2\pi}\right)^2 \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk' \frac{[a(k)^\dagger + a(-k)][a(k') + a(-k')^\dagger]}{2\alpha(k)\alpha(k')} \\ &\times [\exp(-ikna) - \exp(-ikma)] [\exp(ik'na) - \exp(ik'ma)].\end{aligned}\tag{14.6.7}$$

The thermal average $\langle [a(k)^\dagger + a(-k)][a(k') + a(-k')^\dagger] \rangle$ vanishes if $k \neq k'$. Hence, we only need to consider $\langle a(k)^\dagger a(k) \rangle$ as well as $\langle a(k)a(k)^\dagger \rangle$ (which is the same as

$\langle a(-k)a(-k)^\dagger \rangle$. First, we obtain

$$\begin{aligned}
\langle a(k)^\dagger a(k) \rangle &= \frac{1}{Z} \text{Tr} \left[a(k)^\dagger a(k) \exp(-\beta H) \right] \\
&= \frac{1}{Z(k)} \sum_{n(k)=0}^{\infty} \langle n(k) | a(k)^\dagger a(k) | n(k) \rangle \exp(-\beta \hbar \omega(k) n(k)) \\
&= \frac{1}{Z(k)} \sum_{n(k)=0}^{\infty} n(k) \exp(-\beta \hbar \omega(k) n(k)) \\
&= \frac{\exp(-\beta \hbar \omega(k))}{1 - \exp(-\beta \hbar \omega(k))}. \tag{14.6.8}
\end{aligned}$$

Similarly, we find

$$\begin{aligned}
\langle a(k)a(k)^\dagger \rangle &= \frac{1}{Z} \text{Tr} \left[a(k)a(k)^\dagger \exp(-\beta H) \right] \\
&= \frac{1}{Z(k)} \sum_{n(k)=0}^{\infty} \langle n(k) | a(k)a(k)^\dagger | n(k) \rangle \exp(-\beta \hbar \omega(k) n(k)) \\
&= \frac{1}{Z(k)} \sum_{n(k)=0}^{\infty} [n(k) + 1] \exp(-\beta \hbar \omega(k) n(k)) \\
&= \frac{1}{1 - \exp(-\beta \hbar \omega(k))}. \tag{14.6.9}
\end{aligned}$$

This finally implies

$$\begin{aligned}
\langle (y_n - y_m)^2 \rangle &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{\langle [a(k)^\dagger + a(-k)][a(k) + a(-k)^\dagger] \rangle}{2\alpha(k)^2} \\
&\times [\exp(-ikna) - \exp(-ikma)] [\exp(ikna) - \exp(ikma)] \\
&= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{\hbar \langle [a(k)^\dagger + a(-k)][a(k) + a(-k)^\dagger] \rangle}{2M\omega(k)} \\
&\times 2[1 - \cos(k(n-m)a)] \\
&= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{2\hbar \sin^2(k(n-m)a)}{M\omega(k)} \frac{1 + \exp(-\beta \hbar \omega(k))}{1 - \exp(-\beta \hbar \omega(k))}. \tag{14.6.10}
\end{aligned}$$

This integral can not be solved in closed form. Still, one can consider the high-

temperature limit in which one obtains

$$\begin{aligned} \langle (y_n - y_m)^2 \rangle &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{4 \sin^2(k(n-m)a)}{\beta M \omega(k)^2} \\ &= \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \frac{\sin^2(k(n-m)a)}{\beta M \omega_0^2 \sin^2(ka/2)} = \frac{2}{\beta M \omega_0^2} |n-m|. \end{aligned} \quad (14.6.11)$$

In fact, at any non-zero temperature, for large separation $|n-m|$ one finds $\langle (y_n - y_m)^2 \rangle \sim |n-m|$. The linear increase of this expectation value at large distances is due to the fact that $\omega(k) \approx |k|c_0$ vanishes at zero momentum. Even in two dimensions the corresponding expectation value still increases, although only logarithmically, while in three and more dimensions it approaches a constant at large separation $|n-m|$. The linear respectively logarithmic increase in one and two dimensions, which arises as a consequence of the so-called Hohenberg-Mermin-Wagner theorem, implies that strict crystalline order exists only in three or more dimensions.

The Hohenberg-Mermin-Wagner theorem has incorrectly been invoked to argue that structures like graphene — a 2-dimensional sheet of carbon atoms arranged to form a honeycomb lattice — cannot even exist, unless they are attached to some substrate. However, free-standing graphene does indeed exist. In fact, the Nobel prize 2010 was awarded to Andre Geim and Konstantin Novoselov from Manchester University for “producing, isolating, identifying and characterizing graphene”. Just producing a single sheet of graphite alone may actually not be that difficult. After all, when we draw or write with a pencil, graphite is cleaved into thin layers that end up on the paper. Some of these may contain only a few sheets or even just a single sheet of graphite, i.e. graphene. In fact, the Hohenberg-Mermin-Wagner theorem does not imply that a 2-dimensional crystal like graphene cannot exist. It only means that perfect crystalline order cannot persist over arbitrarily large distances. Since actual graphene sheets always have a finite size, the theorem is not in conflict with any observations.

14.7 A 3-dimensional Model for Ions in a Crystal

The atomic nuclei inside a solid form a regular crystal lattice. We will now extend our simple model from one to three dimensions. We assume that the ions of mass M with position vector $\vec{x}_{\vec{n}}$ form a cubic lattice. Here the index $\vec{n} \in \mathbb{Z}^3$ enumerates the ions according to their position in the crystal. In particular, the equilibrium position of the ion with label \vec{n} is $\vec{n}a$. Ions are again coupled only to their nearest

neighbors on the lattice via a harmonic oscillator potential. The Hamiltonian of the lattice model is then given by

$$\begin{aligned} H &= \sum_{\vec{n} \in \mathbb{Z}^3} \left[-\frac{\hbar^2}{2M} \Delta_{\vec{n}} + \frac{1}{2} M \omega^2 \sum_{i=1,2,3} (\vec{x}_{\vec{n}+\vec{i}} - \vec{x}_{\vec{n}} - \vec{i}a)^2 \right] \\ &= \sum_{\vec{n} \in \mathbb{Z}^3} \left[-\frac{\hbar^2}{2M} \Delta_{\vec{n}} + \frac{1}{2} M \omega^2 \sum_{i=1,2,3} (\vec{y}_{\vec{n}+\vec{i}} - \vec{y}_{\vec{n}})^2 \right]. \end{aligned} \quad (14.7.1)$$

Here \vec{i} denotes a unit-vector in the spatial i -direction,

$$\vec{y}_{\vec{n}} = \vec{x}_{\vec{n}} - \vec{n}a, \quad (14.7.2)$$

and

$$\Delta_{\vec{n}} = \frac{\partial^2}{\partial y_{\vec{n}1}^2} + \frac{\partial^2}{\partial y_{\vec{n}2}^2} + \frac{\partial^2}{\partial y_{\vec{n}3}^2} \quad (14.7.3)$$

is the Laplacian with respect to the position $\vec{y}_{\vec{n}}$. The discrete Fourier transform

$$\tilde{y}_j(\vec{k}) = \sum_{\vec{n} \in \mathbb{Z}^3} y_{\vec{n}j} \exp(-i\vec{k} \cdot \vec{n}a), \quad j \in \{1, 2, 3\}, \quad (14.7.4)$$

has the inverse

$$y_{\vec{n}j} = \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \tilde{y}_j(\vec{k}) \exp(i\vec{k} \cdot \vec{n}a), \quad (14.7.5)$$

where $B =]-\pi/a, \pi/a]^3$ denotes the 3-dimensional Brillouin zone. In analogy to the 1-dimensional case, we now obtain the potential energy as

$$\begin{aligned} V &= \sum_{\vec{n} \in \mathbb{Z}^3} \frac{1}{2} M \omega_0^2 \sum_{i=1,2,3} (\vec{y}_{\vec{n}+\vec{i}} - \vec{y}_{\vec{n}})^2 \\ &= \left(\frac{a}{2\pi} \right)^6 \frac{1}{2} M \omega_0^2 \int_B d^3k \int_B d^3k' \sum_{j=1,2,3} \tilde{y}_j(\vec{k})^\dagger \tilde{y}_j(\vec{k}') \\ &\quad \times \sum_{i=1,2,3} \sum_{\vec{n} \in \mathbb{Z}^3} [\exp(i\vec{k} \cdot (\vec{n} + \vec{i})a) - \exp(i\vec{k} \cdot \vec{n}a)] \\ &\quad \times [\exp(-i\vec{k}' \cdot (\vec{n} + \vec{i})a) - \exp(-i\vec{k}' \cdot \vec{n}a)] \\ &= \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \frac{1}{2} M \omega_0^2 \sum_{i=1,2,3} \hat{k}_i^2 a^2 \sum_{j=1,2,3} \tilde{y}_j(\vec{k})^\dagger y_j(\vec{k}). \end{aligned} \quad (14.7.6)$$

Here we have used

$$\left(\frac{a}{2\pi} \right)^3 \sum_{\vec{n} \in \mathbb{Z}^3} \exp(i(\vec{k} - \vec{k}') \cdot \vec{n}a) = \delta(\vec{k} - \vec{k}'), \quad (14.7.7)$$

as well as

$$2 - \exp(ik_ia) - \exp(-ik_ia) = 2[1 - \cos(k_ia)] = \left(2 \sin \frac{k_ia}{2}\right)^2 = \hat{k}_i^2 a^2. \quad (14.7.8)$$

with

$$\hat{k}_i = \frac{2}{a} \sin \frac{k_ia}{2}. \quad (14.7.9)$$

This gives rise to the phonon dispersion relation in three dimensions

$$E(\vec{k}) = \hbar\omega(\vec{k}) = 2\hbar\omega_0 \sqrt{\sum_{i=1,2,3} \sin^2 \frac{k_ia}{2}}. \quad (14.7.10)$$

By applying the Fourier transform also to the momenta, i.e.

$$\begin{aligned} \tilde{p}_j(\vec{k}) &= \sum_{\vec{n} \in \mathbb{Z}^3} p_{\vec{n}j} \exp(-i\vec{k} \cdot \vec{n}a), \\ p_{\vec{n}j} &= \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \tilde{p}_j(\vec{k}) \exp(i\vec{k} \cdot \vec{n}a), \end{aligned} \quad (14.7.11)$$

one writes the kinetic energy as

$$\begin{aligned} T &= \sum_{\vec{n} \in \mathbb{Z}^3} \frac{\vec{p}_{\vec{n}}^2}{2M} \\ &= \left(\frac{a}{2\pi}\right)^6 \int_B d^3k \int_B d^3k' \frac{1}{2M} \sum_{j=1,2,3} \tilde{p}_j(\vec{k})^\dagger \tilde{p}_j(\vec{k}') \sum_{\vec{n} \in \mathbb{Z}^3} \exp(i(\vec{k} - \vec{k}') \cdot \vec{n}a) \\ &= \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \frac{1}{2M} \sum_{j=1,2,3} \tilde{p}_j(\vec{k})^\dagger \tilde{p}_j(\vec{k}). \end{aligned} \quad (14.7.12)$$

Altogether, the Hamilton operator takes the form

$$\begin{aligned} H &= \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \sum_{j=1,2,3} \left[\frac{1}{2M} \tilde{p}_j(\vec{k})^\dagger \tilde{p}_j(\vec{k}) + \frac{1}{2} M \omega_0^2 \hat{k}_j^2 a^2 \tilde{y}_j(\vec{k})^\dagger \tilde{y}_j(\vec{k}) \right] \\ &= \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \hbar\omega(\vec{k}) \sum_{j=1,2,3} \left(n_j(\vec{k}) + \frac{N}{2} \right). \end{aligned} \quad (14.7.13)$$

Here we have introduced the number operator

$$n_j(\vec{k}) = a_j(\vec{k})^\dagger a_j(\vec{k}), \quad (14.7.14)$$

for phonons with momentum $\vec{p} = \hbar\vec{k}$ and polarization $j = 1, 2, 3$. The phonon creation and annihilation operators take the form

$$\begin{aligned} a_j(\vec{k}) &= \frac{1}{\sqrt{2}} \left(\alpha(\vec{k}) \tilde{y}_j(\vec{k}) + \frac{i}{\alpha(\vec{k})\hbar} \tilde{p}_j(\vec{k}) \right), \\ a_j(\vec{k})^\dagger &= \frac{1}{\sqrt{2}} \left(\alpha(\vec{k}) \tilde{y}_j(\vec{k})^\dagger - \frac{i}{\alpha(\vec{k})\hbar} \tilde{p}_j(\vec{k})^\dagger \right), \end{aligned} \quad (14.7.15)$$

and they obey the commutation relations

$$\begin{aligned} [a_i(\vec{k}), a_j(\vec{k}')^\dagger] &= \left(\frac{2\pi}{a} \right)^3 \delta(\vec{k} - \vec{k}') \delta_{ij}, \\ [a_i(\vec{k}), a_j(\vec{k}')] &= 0, \quad [a_i(\vec{k})^\dagger, a_j(\vec{k}')^\dagger] = 0. \end{aligned} \quad (14.7.16)$$

14.8 Specific Heat of 3-dimensional Solids

In real solids, which are somewhat more complicated than our simple model, longitudinal and transverse phonons in general have different dispersion relations. In the simple harmonic oscillator model, on the other hand, all three phonon polarization states have the same energy-momentum dispersion relation $E(\vec{k}) = \hbar\omega(\vec{k})$. Again, for small momenta $\vec{p} = \hbar\vec{k}$, we obtain $E(\vec{k}) = \hbar|\vec{k}|c$, with the velocity of sound given by $c = \omega_0 a$. The canonical partition function now takes the form

$$Z = \prod_{j=1,2,3} \prod_{\vec{k}} Z(\vec{k}), \quad (14.8.1)$$

with the single mode partition function given by

$$Z(\vec{k}) = \sum_{n(\vec{k})=0}^{\infty} \exp(-\beta n(\vec{k}) E(\vec{k})) = \frac{1}{1 - \exp(-\beta E(\vec{k}))}. \quad (14.8.2)$$

The average energy stored in a mode reads

$$\langle n(\vec{k}) E(\vec{k}) \rangle = - \frac{\partial \log Z(\vec{k})}{\partial \beta} = \frac{E(\vec{k})}{\exp(\beta E(\vec{k})) - 1}. \quad (14.8.3)$$

Consequently, in the infinite volume limit, the average total energy density results as

$$\begin{aligned}\rho &= \frac{\langle E \rangle}{L^3} = \frac{3}{L^3} \sum_{\vec{k}} \langle n(\vec{k}) E(\vec{k}) \rangle \rightarrow \frac{3}{(2\pi)^3} \int_B d^3k \langle n(\vec{k}) E(\vec{k}) \rangle \\ &= \frac{3}{(2\pi)^3} \int_B d^3k \frac{E(\vec{k})}{\exp(\beta E(\vec{k})) - 1}.\end{aligned}\quad (14.8.4)$$

Here the factor 3 arises due to the three polarizations of phonons. Correspondingly, the expression for the specific heat now takes the form

$$c_V = \frac{C_V}{L^3} = \frac{3}{L^3} \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \rho}{\partial T} = \frac{3}{(2\pi)^3 k_B T^2} \int_B d^3k \frac{E(\vec{k})^2 \exp(\beta E(\vec{k}))}{[\exp(\beta E(\vec{k})) - 1]^2}.\quad (14.8.5)$$

At low temperatures, we can approximate $E(\vec{k}) \approx \hbar|\vec{k}|c$. Extending the momentum integral from B to \mathbb{R}^3 we then obtain

$$\rho = \frac{3}{2\pi^2} \int_0^\infty dk k^2 \frac{\hbar k c}{\exp(\beta \hbar k c) - 1} = \frac{\pi^2 k_B^4 T^4}{10 \hbar^3 c^3}.\quad (14.8.6)$$

Up to a factor $3/2$, which is due to three polarizations of phonons versus two polarizations of photons, this is just the Stefan-Boltzmann law. The corresponding specific heat is given by

$$c_V = \frac{\partial \rho}{\partial T} = \frac{2\pi^2 k_B^4 T^3}{5 \hbar^3 c^3}.\quad (14.8.7)$$

The T^3 -dependence is characteristic for the phonon contribution to the specific heat of solids. As we will see in the next chapter, electrons, which we have ignored until now, contribute to c_V in proportion to T .

As in one dimension, at higher temperatures phonons display a different behavior because their energy deviates from $\hbar|\vec{k}|c$ and the momentum integral extends over the finite Brillouin zone B only. In the high-temperature limit $T \gg T_D$ one again obtains $\exp(\beta E(\vec{k})) - 1 \approx \beta E(\vec{k})$ such that

$$c_V = \frac{3}{(2\pi)^3 k_B T^2} \int_B d^3k \frac{1}{\beta^2} = \frac{3k_B}{a^3}.\quad (14.8.8)$$

The fact that, at large temperatures, the specific heat reaches this T -independent value is known as the Dulong-Petit law.

Chapter 15

Electrons in Solids

While we have neglected electrons in the previous chapter, in this chapter we will neglect phonons and concentrate on the electrons. In fact, we will now impose a rigid crystal lattice by hand and will discuss the motion of the electrons in the background of the crystal lattice. In this chapter, the ions and thus the crystal lattice are not allowed to vibrate and are thus considered to be static. The crystal lattice of static ions gives rise to a periodic external potential for the electrons. The minima of this periodic potential are centered at the static ions, which exert an attractive force on the electrons. Instead of being localized near an individual ion, electrons will tunnel from ion to ion, and may thus move through the entire crystal. A periodic potential gives rise to quantum mechanically allowed energy levels which form continuous energy bands. Different bands may be separated by gaps of forbidden values of the energy. In a crystal, the Coulomb repulsion between electrons is screened by the positively charged ions. Hence, at least as a first approximation, it is reasonable to treat electrons in a solid as non-interacting.

In order to capture some important aspects of these dynamics, we will again make a very simple (and in fact over-simplified) model which, however, can then be solved analytically. In this model, which is a simple variant of the so-called single-band Hubbard model, electrons are not even considered in the continuous space between lattice points. Instead, they are restricted to hop between discrete lattice points with a hopping amplitude that reflects the tunneling rate of electrons between neighboring ions. Since electrons are fermions, they follow the Pauli exclusion principle and thus behave drastically differently than bosons. Since only one fermion can occupy a given mode, even at zero temperature some modes of non-zero energy must be populated by fermions. The surface in momentum space up to which modes are occupied with fermions at zero temperature is

known as the Fermi surface. If there are unoccupied states arbitrarily close to the Fermi surface, the system is a metal. On the other hand, if the Fermi surface coincides with a band-gap, the system is an insulator. The electron dynamics is strongly influenced by the lattice geometry. For example, massive electrons propagating on a 2-dimensional honeycomb lattice, such as in graphene, have peculiar properties reminiscent of (almost) massless fermions such as neutrinos.

It should be noted that interesting effects are missed when one ignores phonons. In particular, in metals at very low temperatures, phonons mediate an attractive interaction between electrons that can overcome the screened Coulomb repulsion. As a result, two electrons are bound into Cooper pairs, which are bosons. The Cooper pair condensation of these bosons then leads to superconductivity, i.e. to the complete absence of electric resistance at temperatures below a few degrees Kelvin. In 1972 John Bardeen, Leon Neil Cooper, and Robert Schrieffer received the Nobel prize for the explanation of metallic superconductivity. In addition to metallic superconductors, there are also the so-called high-temperature superconductors which remain superconducting up to temperatures as high as 100 degrees Kelvin. Johannes Bednorz and Karl Müller were awarded the Nobel prize of 1987 for the discovery of these materials. Remarkably, high-temperature superconductors are not metals but are related to so-called Mott insulators. In these systems, the electrons cannot be treated as non-interacting particles, but are instead strongly correlated. The dynamical mechanism responsible for high-temperature superconductivity remains a subject of very intense research in condensed matter physics. Most experts agree, that the exchange of phonons alone cannot be responsible for this intriguing phenomenon. In any case, even understanding metallic superconductivity in the framework of the Bardeen-Cooper-Schrieffer (BCS) theory is beyond the scope of these lectures.

15.1 Electron Creation and Annihilation Operators

Just like phonons, electrons can be described by creation and annihilation operators. However, since electrons are fermions while phonons are bosons, the creation and annihilation operators for electrons obey anti-commutation rather than commutation relations. In addition, while phonons have three polarization directions, electrons have two spin orientations $s = \pm\frac{1}{2} = \uparrow, \downarrow$. Let us first consider creation and annihilation operators in the simplest context of just a single lattice site. Then there is no lattice site index and we only need to consider the spin s . The operator that annihilates an electron of spin s at the given lattice site is denoted by c_s , while the corresponding creation operator is c_s^\dagger . The Pauli

principle of electrons is encoded in the following anti-commutation relations

$$\{c_s, c_{s'}^\dagger\} = \delta_{ss'}, \quad \{c_s, c_{s'}\} = 0, \quad \{c_s^\dagger, c_{s'}^\dagger\} = 0. \quad (15.1.1)$$

In general the anti-commutator of two operators A and B is given by

$$\{A, B\} = AB + BA. \quad (15.1.2)$$

Interestingly, the anti-commutation relations are sufficient to implicitly define how the operators c_s and c_s^\dagger are acting. In other words, in order to work with these operators, we need not know anything more than their anti-commutation relations. As a consequence of the anti-commutation relations, two electrons of the same spin cannot occupy the same lattice point. In particular, if we try to create two electrons of the same spin s at the same lattice site by acting with $(c_s^\dagger)^2$, we obtain

$$c_s^{\dagger 2} = \frac{1}{2}\{c_s^\dagger, c_s^\dagger\} = 0. \quad (15.1.3)$$

Similarly, one can never annihilate two electrons of the same spin at the same lattice site because

$$c_s^2 = \frac{1}{2}\{c_s, c_s\} = 0. \quad (15.1.4)$$

Let us first consider the vacuum $|0\rangle$, i.e. a state without electrons. This state is annihilated by both c_\uparrow and c_\downarrow , i.e.

$$c_\uparrow|0\rangle = 0, \quad c_\downarrow|0\rangle = 0. \quad (15.1.5)$$

By acting with the individual creation operators, we can now create states with a single electron of either spin up or down

$$c_\uparrow^\dagger|0\rangle = |\uparrow\rangle, \quad c_\downarrow^\dagger|0\rangle = |\downarrow\rangle. \quad (15.1.6)$$

Assuming that the vacuum is normalized to 1, i.e. $\langle 0|0\rangle = 1$, we can convince ourselves that the 1-particle states are also correctly normalized

$$\begin{aligned} \langle \uparrow | \uparrow \rangle &= \langle 0 | c_\uparrow c_\uparrow^\dagger | 0 \rangle = \langle 0 | 1 - c_\uparrow^\dagger c_\uparrow | 0 \rangle = \langle 0 | 0 \rangle = 1, \\ \langle \downarrow | \downarrow \rangle &= \langle 0 | c_\downarrow c_\downarrow^\dagger | 0 \rangle = \langle 0 | 1 - c_\downarrow^\dagger c_\downarrow | 0 \rangle = \langle 0 | 0 \rangle = 1. \end{aligned} \quad (15.1.7)$$

Furthermore, the two 1-particle states are orthogonal

$$\langle \uparrow | \downarrow \rangle = \langle 0 | c_\uparrow c_\downarrow^\dagger | 0 \rangle = -\langle 0 | c_\downarrow^\dagger c_\uparrow | 0 \rangle = 0. \quad (15.1.8)$$

The normalization and orthogonality relations can be summarized as

$$\langle s | s' \rangle = \delta_{ss'}, \quad s, s' = \uparrow, \downarrow. \quad (15.1.9)$$

Finally, we can also construct a 2-particle state

$$c_{\uparrow}^{\dagger}c_{\downarrow}^{\dagger}|0\rangle = c_{\uparrow}^{\dagger}|\downarrow\rangle = |\uparrow\downarrow\rangle, \quad (15.1.10)$$

which is again correctly normalized because

$$\langle\uparrow\downarrow|\uparrow\downarrow\rangle = \langle\downarrow|c_{\uparrow}c_{\uparrow}^{\dagger}|\downarrow\rangle = \langle\downarrow|1 - c_{\uparrow}^{\dagger}c_{\uparrow}|\downarrow\rangle = 1. \quad (15.1.11)$$

Similarly, we obtain

$$c_{\downarrow}^{\dagger}c_{\uparrow}^{\dagger}|0\rangle = c_{\downarrow}^{\dagger}|\uparrow\rangle = |\downarrow\uparrow\rangle. \quad (15.1.12)$$

However, this is not a new 2-particle state, since

$$|\downarrow\uparrow\rangle = c_{\downarrow}^{\dagger}c_{\uparrow}^{\dagger}|0\rangle = -c_{\uparrow}^{\dagger}c_{\downarrow}^{\dagger}|0\rangle = -|\uparrow\downarrow\rangle. \quad (15.1.13)$$

Due to the Pauli principle, which reflects the fact that electrons are indistinguishable particles, there is only one 2-particle state. In particular, the states

$$|\uparrow\uparrow\rangle = c_{\uparrow}^{\dagger}c_{\uparrow}^{\dagger}|0\rangle = 0, \quad |\downarrow\downarrow\rangle = c_{\downarrow}^{\dagger}c_{\downarrow}^{\dagger}|0\rangle = 0, \quad (15.1.14)$$

simply vanish. As a result, the fermionic Hilbert space for electrons of spin up and spin down at a single lattice site just consists of the four states $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$, and $|\uparrow\downarrow\rangle$, which are normalized and mutually orthogonal. A Hilbert space that consists of sectors with different particle numbers is also known as a Fock space.

It is interesting to note that the operator

$$n = n_{\uparrow} + n_{\downarrow} = c_{\uparrow}^{\dagger}c_{\uparrow} + c_{\downarrow}^{\dagger}c_{\downarrow} \quad (15.1.15)$$

counts the number of electrons, i.e.

$$\begin{aligned} n|0\rangle &= (c_{\uparrow}^{\dagger}c_{\uparrow} + c_{\downarrow}^{\dagger}c_{\downarrow})|0\rangle = 0, \\ n|\uparrow\rangle &= (c_{\uparrow}^{\dagger}c_{\uparrow} + c_{\downarrow}^{\dagger}c_{\downarrow})|\uparrow\rangle = c_{\uparrow}^{\dagger}|0\rangle = |\uparrow\rangle, \\ n|\downarrow\rangle &= (c_{\uparrow}^{\dagger}c_{\uparrow} + c_{\downarrow}^{\dagger}c_{\downarrow})|\downarrow\rangle = c_{\downarrow}^{\dagger}|0\rangle = |\downarrow\rangle, \\ n|\uparrow\downarrow\rangle &= (c_{\uparrow}^{\dagger}c_{\uparrow} + c_{\downarrow}^{\dagger}c_{\downarrow})|\uparrow\downarrow\rangle = c_{\uparrow}^{\dagger}|\downarrow\rangle - c_{\downarrow}^{\dagger}|\uparrow\rangle = |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle = 2|\uparrow\downarrow\rangle. \end{aligned} \quad (15.1.16)$$

The various states may alternatively be labeled by their occupation numbers $n_{\uparrow}, n_{\downarrow} \in \{0, 1\}$, such that

$$|n_{\uparrow}n_{\downarrow}\rangle = \left(c_{\uparrow}^{\dagger}\right)^{n_{\uparrow}} \left(c_{\downarrow}^{\dagger}\right)^{n_{\downarrow}} |0\rangle, \quad (15.1.17)$$

and hence

$$|00\rangle = |0\rangle, \quad |10\rangle = c_{\uparrow}^{\dagger}|0\rangle = |\uparrow\rangle, \quad |01\rangle = c_{\downarrow}^{\dagger}|0\rangle = |\downarrow\rangle, \quad |11\rangle = c_{\uparrow}^{\dagger}c_{\downarrow}^{\dagger}|0\rangle = |\uparrow\downarrow\rangle. \quad (15.1.18)$$

Finally, let us introduce the spin operator

$$\vec{S} = \sum_{ss'} c_s^\dagger \frac{\vec{\sigma}_{ss'}}{2} c_{s'}, \quad (15.1.19)$$

where $\vec{\sigma}$ is the vector of Pauli matrices

$$\vec{\sigma} = (\sigma^1, \sigma^2, \sigma^3) = \left(\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right). \quad (15.1.20)$$

Note that we have omitted the multiplicative factor of \hbar in our definition of the spin. Let us now investigate the commutation relations of the spin operators

$$\begin{aligned} [S^i, S^j] &= \left[\sum_{ss'} c_s^\dagger \frac{\sigma_{ss'}^i}{2} c_{s'}, \sum_{rr'} c_r^\dagger \frac{\sigma_{rr'}^j}{2} c_{r'} \right] \\ &= \frac{1}{4} \sum_{ss'rr'} \sigma_{ss'}^i \sigma_{rr'}^j \left(c_s^\dagger c_{s'} c_r^\dagger c_{r'} - c_r^\dagger c_{r'} c_s^\dagger c_{s'} \right) \\ &= \frac{1}{4} \sum_{ss'rr'} \sigma_{ss'}^i \sigma_{rr'}^j \left(c_s^\dagger [\delta_{s'r} - c_r^\dagger c_{s'}] c_{r'} - c_r^\dagger [\delta_{r's} - c_s^\dagger c_{r'}] c_{s'} \right) \\ &= \frac{1}{4} \sum_{ss'rr'} \sigma_{ss'}^i \sigma_{s'r'}^j c_s^\dagger c_{r'} - \frac{1}{4} \sum_{ss'rr'} \sigma_{rs}^j \sigma_{ss'}^i c_r^\dagger c_{s'} \\ &= \frac{1}{4} \sum_{ss'rr'} c_s^\dagger \sigma_{ss'}^i \sigma_{s'r'}^j c_{r'} - \frac{1}{4} \sum_{ss'rr'} c_r^\dagger \sigma_{rs}^j \sigma_{ss'}^i c_{s'} \\ &= \frac{1}{4} \sum_{ss'rr'} c_s^\dagger \left(\sigma_{ss'}^i \sigma_{s'r'}^j - \sigma_{ss'}^j \sigma_{s'r'}^i \right) c_{r'} \\ &= i\varepsilon_{ijk} \frac{1}{2} \sum_{ss'rr'} c_s^\dagger \sigma_{s'r'}^k c_{r'} = i\varepsilon_{ijk} S^k. \end{aligned} \quad (15.1.21)$$

Here we have used the commutation relation for the Pauli matrices

$$[\sigma^i, \sigma^j] = 2i\varepsilon_{ijk} \sigma^k, \quad (15.1.22)$$

to verify the standard commutation relation for the electron spin operators

$$[S^i, S^j] = i\varepsilon_{ijk} S^k. \quad (15.1.23)$$

Let us now act with the 3-component of the spin operator

$$S^3 = \sum_{ss'} c_s^\dagger \frac{\sigma_{ss'}^3}{2} c_{s'} = \frac{1}{2} \left(c_\uparrow^\dagger c_\uparrow - c_\downarrow^\dagger c_\downarrow \right) = \frac{1}{2} (n_\uparrow - n_\downarrow), \quad (15.1.24)$$

on the four states in Fock space

$$S^3|0\rangle = 0, \quad S^3|\uparrow\rangle = \frac{1}{2}|\uparrow\rangle, \quad S^3|\downarrow\rangle = -\frac{1}{2}|\downarrow\rangle, \quad S^3|\uparrow\downarrow\rangle = 0. \quad (15.1.25)$$

Next, we will consider a rigid cubic lattice of sites $\vec{x} = \vec{n}a$, where a is the lattice spacing and $\vec{n} = (n_1, n_2, n_3) \in \mathbb{Z}^3$ is a vector pointing to a lattice site. We will make a simple model in which electrons can only exist at the discrete lattice sites \vec{x} and not in the continuous space between lattice sites. In fact, we should think of an electron at site \vec{x} as an electron in a state localized near the ion at position \vec{x} . The operator that creates an electron of spin s at the lattice site \vec{x} is denoted by $c_{\vec{x},s}^\dagger$ while the corresponding annihilation operator is given by $c_{\vec{x},s}$. The anti-commutation relations then take the form

$$\{c_{\vec{x},s}, c_{\vec{x}',s'}^\dagger\} = \delta_{\vec{x}\vec{x}'}\delta_{ss'}, \quad \{c_{\vec{x},s}, c_{\vec{x}',s'}\} = 0, \quad \{c_{\vec{x},s}^\dagger, c_{\vec{x}',s'}^\dagger\} = 0. \quad (15.1.26)$$

Correspondingly, the number operator for electrons at the site \vec{x} is given by

$$n_{\vec{x}} = \sum_s c_{\vec{x},s}^\dagger c_{\vec{x},s}, \quad (15.1.27)$$

while the total number of electrons in the crystal is measured by the operator

$$N = \sum_{\vec{x}} n_{\vec{x}}. \quad (15.1.28)$$

Similarly, the spin operator for electrons at the site \vec{x} is given by

$$\vec{S}_{\vec{x}} = \sum_{ss'} c_{\vec{x},s}^\dagger \frac{\vec{\sigma}_{ss'}}{2} c_{\vec{x},s'}, \quad (15.1.29)$$

while the spin of the entire crystal is measured by the operator

$$\vec{S} = \sum_{\vec{x}} \vec{S}_{\vec{x}}. \quad (15.1.30)$$

The vacuum state $|0\rangle$ (which does not contain any electrons) is now characterized by

$$c_{\vec{x},s}|0\rangle = 0, \quad (15.1.31)$$

for all lattice sites \vec{x} and both spins $s = \uparrow, \downarrow$. All states in the Fock space can then be obtained as linear combinations of the states

$$|\psi\rangle = \prod_{\vec{x}} \left(c_{\vec{x},\uparrow}^\dagger\right)^{n_{\vec{x}\uparrow}} \left(c_{\vec{x},\downarrow}^\dagger\right)^{n_{\vec{x}\downarrow}} |0\rangle. \quad (15.1.32)$$

Here $n_{\vec{x}\uparrow}, n_{\vec{x}\downarrow} \in \{0, 1\}$ are occupation numbers that characterize the state $|\psi\rangle$. In order to make the product of creation operators unambiguously defined, one must order the lattice sites \vec{x} in some arbitrary but fixed manner. Different orderings just lead to different overall signs of the state $|\psi\rangle$.

15.2 A Model for Electrons Hopping on a Lattice

When an electron tunnels from a state localized near an ion at the site \vec{x} to another state localized near a neighboring ion at the site $\vec{x} + \vec{a}$, in the model this manifests itself as a hopping of the electron from the discrete lattice site \vec{x} to $\vec{x} + \vec{a}$. A simple Hamilton operator that describes hopping between nearest-neighbor lattice sites is given by

$$H = -t \sum_{\vec{x}, i, s} \left(c_{\vec{x}, s}^\dagger c_{\vec{x} + \vec{a}, s} + c_{\vec{x} + \vec{a}, s}^\dagger c_{\vec{x}, s} \right). \quad (15.2.1)$$

The Hamiltonian first annihilates an electron of spin s at the site \vec{x} and then recreates it at the neighboring lattice site $\vec{x} + \vec{a}$ with the same spin. Here the hopping parameter t controls the tunneling amplitude between neighboring lattice sites. Since electron hopping does not change the total number N of electrons, one has $[H, N] = 0$. Similarly, since the hopping is spin-independent, one can show that the total spin is also conserved, i.e. $[H, \vec{S}] = 0$.

Just like for phonons, in order to diagonalize the Hamiltonian for the electrons, we perform a Fourier transformation and we obtain

$$\tilde{c}_s(\vec{k}) = \sum_{\vec{x}} c_{\vec{x}, s} \exp(-i\vec{k} \cdot \vec{x}), \quad \tilde{c}_s(\vec{k})^\dagger = \sum_{\vec{x}} c_{\vec{x}, s}^\dagger \exp(i\vec{k} \cdot \vec{x}). \quad (15.2.2)$$

The corresponding anti-commutation relations then take the form

$$\begin{aligned} \{c_s(\vec{k}), c_{s'}(\vec{k}')^\dagger\} &= \sum_{\vec{x}, \vec{x}'} \{c_{\vec{x}, s}, c_{\vec{x}', s'}^\dagger\} \exp(-i\vec{k} \cdot \vec{x} + i\vec{k}' \cdot \vec{x}') \\ &= \sum_{\vec{x}, \vec{x}'} \delta_{\vec{x}\vec{x}'} \delta_{ss'} \exp(-i\vec{k} \cdot \vec{x} + i\vec{k}' \cdot \vec{x}') \\ &= \sum_{\vec{x}} \exp(i(\vec{k}' - \vec{k}) \cdot \vec{x}) \delta_{ss'} = \left(\frac{2\pi}{a}\right)^3 \delta(\vec{k} - \vec{k}') \delta_{ss'}. \end{aligned} \quad (15.2.3)$$

Similarly, one obtains

$$\{c_s(\vec{k}), c_{s'}(\vec{k}')\} = 0, \quad \{c_s(\vec{k})^\dagger, c_{s'}(\vec{k}')^\dagger\} = 0. \quad (15.2.4)$$

By an inverse Fourier transform we obtain

$$c_{\vec{x}, s} = \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \tilde{c}_s(\vec{k}) \exp(i\vec{k} \cdot \vec{x}), \quad c_{\vec{x}, s}^\dagger = \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \tilde{c}_s(\vec{k})^\dagger \exp(-i\vec{k} \cdot \vec{x}). \quad (15.2.5)$$

Here $B =] -\frac{\pi}{a}, \frac{\pi}{a}]$ again denotes the periodic Brillouin zone of the cubic lattice. The Hamilton operator then takes the form

$$\begin{aligned}
H &= -t \sum_{\vec{x}, i, s} \left(c_{\vec{x}, s}^\dagger c_{\vec{x} + \vec{i}a, s} + c_{\vec{x} + \vec{i}a, s}^\dagger c_{\vec{x}, s} \right) \\
&= -t \left(\frac{a}{2\pi} \right)^6 \int_B d^3k \int_B d^3k' \sum_s \tilde{c}_s(\vec{k})^\dagger \tilde{c}_s(\vec{k}') \\
&\times \sum_{\vec{x}, i} \left[\exp\left(-i\vec{k} \cdot \vec{x} + i\vec{k}' \cdot (\vec{x} + \vec{i}a)\right) + \exp\left(-i\vec{k}' \cdot (\vec{x} + \vec{i}a) + i\vec{k} \cdot \vec{x}\right) \right] \\
&= -t \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \sum_s \tilde{c}_s(\vec{k})^\dagger \tilde{c}_s(\vec{k}) \sum_i [\exp(ik_i a) + \exp(-ik_i a)] \\
&= \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \sum_s \hbar\omega(\vec{k}) \tilde{c}_s(\vec{k})^\dagger \tilde{c}_s(\vec{k}) \\
&= \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \sum_s \hbar\omega(\vec{k}) n_s(\vec{k}). \tag{15.2.6}
\end{aligned}$$

Here we have introduced the number operator

$$n_s(\vec{k}) = \tilde{c}_s(\vec{k})^\dagger \tilde{c}_s(\vec{k}). \tag{15.2.7}$$

The dispersion relation of electrons propagating in the cubic crystal is given by

$$E(\vec{k}) = \hbar\omega(\vec{k}) = -t \sum_i [\exp(ik_i a) + \exp(-ik_i a)] = -2t \sum_i \cos(k_i a). \tag{15.2.8}$$

Similarly, the total number of electrons is given by

$$\begin{aligned}
N &= \sum_{\vec{x}, s} c_{\vec{x}, s}^\dagger c_{\vec{x}, s} \\
&= \left(\frac{a}{2\pi} \right)^6 \int_B d^3k \int_B d^3k' \sum_s \tilde{c}_s(\vec{k})^\dagger \tilde{c}_s(\vec{k}') \sum_x \exp\left(i(\vec{k}' - \vec{k}) \cdot \vec{x}\right) \\
&= \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \sum_s \tilde{c}_s(\vec{k})^\dagger \tilde{c}_s(\vec{k}) = \left(\frac{a}{2\pi} \right)^3 \int_B d^3k \sum_s n_s(\vec{k}). \tag{15.2.9}
\end{aligned}$$

15.3 Grand Canonical Ensemble and Fermi Surface

Let us now consider the grand canonical partition function

$$Z = \text{Tr} \exp(-\beta[H - \mu N]), \tag{15.3.1}$$

where μ is the chemical potential. Introducing a finite volume L^3 with periodic boundary conditions, the partition function can be written as a product over independent modes with discrete wave number vectors $\vec{k} = 2\pi\vec{m}/L$ (with $\vec{m} \in \mathbb{Z}^3$)

$$Z = \prod_{s=\uparrow,\downarrow} \prod_{\vec{k}} Z_s(\vec{k}). \quad (15.3.2)$$

The single-mode partition function takes the form

$$Z_s(\vec{k}) = \sum_{n_s(\vec{k})=0}^1 \exp\left(-\beta[\hbar\omega(\vec{k}) - \mu]n_s(\vec{k})\right) = 1 + \exp\left(-\beta[\hbar\omega(\vec{k}) - \mu]\right). \quad (15.3.3)$$

The average occupation number of a given mode is then given by

$$\langle n_s(\vec{k}) \rangle = \frac{\partial \log Z_s(\vec{k})}{\partial(\beta\mu)} = \frac{1}{\exp\left(\beta[\hbar\omega(\vec{k}) - \mu]\right) + 1}. \quad (15.3.4)$$

Here the derivative is with respect to $\beta\mu$ only, which leaves the pure β -dependence unaffected. At zero temperature, i.e. at $\beta \rightarrow \infty$, the chemical potential determines which modes are occupied by a fermion and which ones are not. In particular, if $E(\vec{k}) = \hbar\omega(\vec{k}) < \mu$, the average occupation number is $\langle n_s(\vec{k}) \rangle = 1$, i.e. the mode is occupied with one fermion, while for modes with $E(\vec{k}) = \hbar\omega(\vec{k}) > \mu$ the mode is empty because then $\langle n_s(\vec{k}) \rangle = 0$. The 2-dimensional surface in the 3-dimensional Brillouin zone for which

$$E(\vec{k}) = \hbar\omega(\vec{k}) = \mu, \quad (15.3.5)$$

is known as the Fermi surface. At zero temperature, the Fermi surface separates occupied from empty modes. The energy $E_F = \mu$ of states at the Fermi surface is known as the Fermi energy. At zero temperature, the volume enclosed by the Fermi surface determines the expectation value of the density of electrons

$$\frac{\langle N \rangle}{L^3} = 2 \left(\frac{a}{2\pi}\right)^3 \int_{B, E(\vec{k}) < E_F} d^3k. \quad (15.3.6)$$

Here the prefactor 2 is due to spin. Denoting the momentum of an electron as $\vec{p} = \hbar\vec{k}$, the Fermi velocity is defined as the following gradient evaluated at the Fermi surface

$$\vec{v}_F = \vec{\nabla}_p E(\vec{p}) = \vec{\nabla}_k \omega(\vec{k}). \quad (15.3.7)$$

For small wave numbers $|\vec{k}|$, the dispersion relation can be approximated as

$$E(\vec{k}) = \hbar\omega(\vec{k}) = -2t \sum_i \left(1 - \frac{k_i^2 a^2}{2}\right) = -6t + \frac{\hbar^2 \vec{k}^2}{2M}, \quad (15.3.8)$$

where

$$M = \frac{\hbar^2}{2ta^2} \quad (15.3.9)$$

plays the role of an effective electron mass. The effective mass can be larger or smaller than the electron mass in vacuum by about a factor of 10. In some exotic so-called heavy fermion materials the effective mass can even be up to a factor 1000 larger than the electron mass in vacuum. Let us consider the chemical potential

$$\mu = -6t + \varepsilon \quad (15.3.10)$$

with a small value of ε , which then implies

$$E(\vec{k}) - \mu = \frac{\hbar^2 \vec{k}^2}{2M} - \varepsilon. \quad (15.3.11)$$

The Fermi surface then is a sphere of radius

$$k_F = \frac{\sqrt{2M\varepsilon}}{\hbar}. \quad (15.3.12)$$

Consequently, the average density of electrons is given by

$$\frac{\langle N \rangle}{L^3} = 2 \left(\frac{a}{2\pi} \right)^3 \frac{4\pi}{3} k_F^3 = \frac{k_F^3 a^3}{3\pi^2}. \quad (15.3.13)$$

In this case, the Fermi velocity is simply given by

$$v_F = \frac{p_F}{M} = \frac{\hbar k_F}{M}. \quad (15.3.14)$$

Here $p_F = \hbar k_F$ is known as the Fermi momentum.

The question whether a material is an insulator or a conductor depends on the value of the chemical potential, which controls the number of electrons. The number of mobile electrons in a given material depends on the type of atoms or molecules which the material consists of. In our simple model of free electrons the single-particle energies can vary between $-6t$ and $6t$, while lower or higher energies are forbidden. In real solids, the allowed energy levels form several energy bands, while our model has just a single band. The value of the chemical potential determines whether an energy band is completely or only partially filled. If the chemical potential is above the upper band edge $6t$, the band is completely filled. In our model, this is the case when there are two electrons (one with spin up and one with spin down) per lattice site. In that case, there are no available states of higher energy which electrons could occupy when an external electric field is applied. Hence, materials with completely filled energy bands are insulators. Materials with only partially filled bands, on the other hand, are metals. In that case, when one applies an external electric field, electrons can be lifted to higher previously unoccupied energy levels and can thus contribute to the conductivity.

15.4 Electrons and the Specific Heat of Metals

Let us now consider the contribution of electrons to the specific heat of a metal at small temperature and chemical potential. The average energy density of electrons is then given by

$$\frac{\langle E \rangle}{L^3} = -\frac{\partial \log Z}{\partial \beta} = \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \frac{\hbar\omega(\vec{k})}{\exp(\beta[\hbar\omega(\vec{k}) - \mu]) + 1}. \quad (15.4.1)$$

Similarly, the average number density of electrons is given by

$$\frac{\langle N \rangle}{L^3} = \frac{\partial \log Z}{\partial(\beta\mu)} = \left(\frac{a}{2\pi}\right)^3 \int_B d^3k \frac{1}{\exp(\beta[\hbar\omega(\vec{k}) - \mu]) + 1}. \quad (15.4.2)$$

At small temperature and small μ we can use

$$\hbar\omega(\vec{k}) - \mu = \frac{\hbar^2 \vec{k}^2}{2M} - \varepsilon, \quad (15.4.3)$$

and we can extend the integration over all of \mathbb{R}^3 such that

$$\frac{\langle E - \mu N \rangle}{L^3} = \frac{a^3}{2\pi^2} \int_0^\infty dk \frac{k^2 \left(\frac{\hbar^2 k^2}{2M} - \varepsilon\right)}{\exp\left(\beta \left[\frac{\hbar^2 k^2}{2M} - \varepsilon\right]\right) + 1}. \quad (15.4.4)$$

In the small-temperature limit, this integral can be expanded in powers of T and one obtains

$$\frac{\langle E \rangle}{L^3} = \frac{\pi^2 k_B T^2}{4T_F}, \quad k_B T_F = \frac{p_F^2}{2M}, \quad (15.4.5)$$

where T_F is the so-called Fermi temperature. In typical metals the Fermi temperature is around $T_F \approx 40000\text{K}$. The specific heat then results as

$$c_V = \frac{1}{L^3} \frac{\partial \langle E \rangle}{\partial T} = \frac{\pi^2 k_B T}{2T_F}. \quad (15.4.6)$$

In contrast to the T^3 behavior of an ideal Bose gas of phonons, the specific heat of the ideal Fermi gas of electrons is proportional to T . This implies that, at low temperatures, the specific heat of metals is dominated by electrons, while at higher temperatures it is dominated by phonons. In insulators the electrons are in a completely filled band and can thus not be easily excited to higher energy levels. Consequently, electrons do not contribute to the specific heat of insulators, which is hence dominated by phonons even at low temperatures.

15.5 Repulsive Hubbard Model at Half-Filling

Let us extend the simple Hamiltonian that describes the hopping of electrons between neighboring lattice sites by an interaction term between the electrons. In a solid the repulsive Coulomb repulsion between two electrons is screened by the background of positively charged ions, and therefore effectively becomes short-ranged. In the Hubbard model, the repulsion is assumed to be non-zero only if two electrons (of opposite spin) occupy the same lattice point. The corresponding Hamiltonian takes the form

$$H = -t \sum_{\vec{x}, i, s} \left(c_{\vec{x}, s}^\dagger c_{\vec{x}+\vec{i}a, s} + c_{\vec{x}+\vec{i}a, s}^\dagger c_{\vec{x}, s} \right) + U \sum_{\vec{x}} n_{\vec{x}, \uparrow} n_{\vec{x}, \downarrow}. \quad (15.5.1)$$

Here

$$n_{\vec{x}, s} = c_{\vec{x}, s}^\dagger c_{\vec{x}, s}, \quad (15.5.2)$$

counts the number of electrons with spin s at the lattice site \vec{x} . The interaction term contributes $U > 0$ if a lattice site is occupied by both a spin up and a spin down electron. It is instructive to convince oneself that the above Hamiltonian still commutes with the total spin and with the total number of electrons, i.e.

$$[H, \vec{S}] = 0, \quad [H, N] = 0, \quad (15.5.3)$$

with

$$N = \sum_{\vec{x}, s} n_{\vec{x}, s}, \quad \vec{S} = \sum_{\vec{x}, s, s'} c_{\vec{x}, s}^\dagger \frac{\vec{\sigma}_{ss'}}{2} c_{\vec{x}, s'}. \quad (15.5.4)$$

Let us consider the Hubbard model on a 2-dimensional square lattice. This model is expected to describe high-temperature superconductors which remain superconducting up to temperatures as high as 100 K or even more. Ordinary metallic low-temperature superconductors superconduct only up to temperatures of a few degrees Kelvin. While the mechanism responsible for low-temperature superconductivity is well-understood (phonon exchange leads to the binding of two electrons in Cooper pairs, which then condense), the dynamical origin of high-temperature superconductivity remains one of the greatest puzzles in modern condensed matter physics. Since nobody has been able to solve the Hubbard model (either numerically or analytically), one cannot even be sure that it contains all the ingredients that are necessary to describe high-temperature superconductivity. For example, the Hubbard model does not contain phonons. While most experts think that phonons are not essential for high-temperature superconductivity, there is no general agreement on this issue. Although high-temperature superconductors are not yet understood, their undoped precursors,

which are quantum antiferromagnets, are among the quantitatively best understood strongly correlated condensed matter systems.

Let us consider the Hubbard model at half-filling, i.e. with one electron per lattice site. Note that the Pauli principle would allow maximally two electrons per lattice site, one with spin up and one with spin down. In the limit of very large Coulomb repulsion $U \gg t$, doubly occupied lattice sites are forbidden and hence, at half-filling, there is exactly one electron on each lattice site. Since all neighboring sites are already occupied, the large Coulomb repulsion then prevents the electrons from hopping around. Since the electrons are not mobile, the system is an insulator — known as a Mott insulator. In contrast to band-insulators, Mott insulators do not have a filled lowest band. In fact, band theory which relies on the assumption of non-interacting electrons is not applicable in the presence of a very strong Coulomb repulsion.

Since each electron may have spin up or spin down independent of the other electrons, the ground state of a Mott insulator at $U = \infty$ is infinitely degenerate. Let us now make an expansion in $t/U \ll 1$ using degenerate perturbation theory. In other words, we now treat the hopping term as a small perturbation in addition to the dominant Coulomb term. Using the rules of degenerate perturbation theory, we should diagonalize the perturbation, i.e. the hopping term, in the space of degenerate states. To the linear order t the hopping term leads to a state with one empty and one doubly occupied site. This state is not among the degenerate ground states (which have exactly one electron on each lattice site). As a result, the hopping term has vanishing matrix elements between the degenerate ground states. Hence, first order perturbation theory does not remove the infinite degeneracy, and we hence proceed to second order perturbation theory. In order to obtain a non-vanishing contribution of order t^2 in second order perturbation theory, after two electron hops, we must return to one of the degenerate ground states. This is possible only if an electron hops to a neighboring site occupied by an electron of opposite spin, and then one of the electrons hops back and again fills the empty site. The intermediate state reached after the first hop contains one empty and one doubly occupied site, and is suppressed by the large Coulomb repulsion U . Hence, the contribution to the energy in second order perturbation theory is proportional to $-t^2/U$. It is important to note that this contribution arises only when two electrons of opposite spin occupy neighboring lattice sites. Otherwise, the Pauli principle forbids that both electrons occupy the same lattice site. As a result, the infinite degeneracy of ground states is lifted by a spin-spin interaction that favors anti-parallel spins. A detailed calculation shows that for $U \gg t$ the Hubbard model at half-filling reduces to the antiferromagnetic Heisen-

berg model

$$H = J \sum_{\vec{x}, i} \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x} + \vec{ia}}, \quad (15.5.5)$$

where the exchange coupling (resulting from the possible exchange of two electrons via the two hops) is given by

$$J = 2 \frac{t^2}{U} > 0. \quad (15.5.6)$$

Since J is positive, it is energetically favorable that neighboring spins are antiparallel.

Chapter 16

Magnons in Ferro- and Antiferromagnets

In this chapter we will encounter another relevant excitation in condensed matter physics, the so-called magnons or spin waves. These particles are again “wavicles”, in this case quantized fluctuations of the magnetization in a magnetic solid. The most familiar magnetic systems are ferromagnets, like iron, nickel, or cobalt. In these materials, the magnetic moments of two electrons are correlated such that they tend to point in the same direction. At sufficiently low temperatures, the electron spins (and hence the magnetic moments) get correlated over large distances and collectively point more or less in the same direction. On macroscopic scales, this manifests itself as a net magnetization of the entire crystal. The microscopic origin of ferromagnetism is somewhat complicated. In particular, it involves two bands for the electrons, as well as spin couplings between the electrons in both bands which arise due to Hund’s rules. Understanding these microscopic mechanisms is beyond the scope of these lectures. Instead, we will simply postulate a microscopic model for quantum spins — the so-called quantum Heisenberg model — to describe ferromagnets.

Interestingly, besides ferromagnets there are also antiferromagnets in which the spins of neighboring localized electrons have a tendency to point in antiparallel directions. At a sufficiently low temperature, the spins may then again get ordered. However, in this case a so-called staggered (rather than uniform) magnetization establishes itself. Quasi-two-dimensional antiferromagnets play an important role as the undoped precursors of high-temperature superconductors. Indeed, most high-temperature superconductors result from electron- or hole-

doping of an antiferromagnet. In condensed matter physics, a “hole” denotes a missing electron. Mathematically, a hole has similar properties as an anti-particle in particle physics. For example, just like a positron — the anti-particle of the electron — a hole has electric charge $+1$. As we have seen, in contrast to ferromagnetism, the microscopic origin of antiferromagnetism is relatively easy to understand and can be addressed in a single-band Hubbard model with strong electron repulsion. The tendency of neighboring localized electrons to have anti-parallel spin then results from the Pauli principle. At half-filling the Hubbard model reduces to the antiferromagnetic Heisenberg model.

16.1 Antiferromagnetic Heisenberg Model

As we have seen in the previous chapter, at half-filling the antiferromagnetic Heisenberg model reduces to the quantum Heisenberg model with the Hamiltonian

$$H = J \sum_{\vec{x}, i} \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a}. \quad (16.1.1)$$

For $J > 0$ it is energetically favorable that neighboring spins are anti-parallel. The Heisenberg model has an $SU(2)$ spin symmetry that is generated by the total spin, i.e.

$$[H, \vec{S}] = 0, \quad \vec{S} = \sum_{\vec{x}} S_{\vec{x}}. \quad (16.1.2)$$

At zero temperature, the 2-dimensional antiferromagnetic Heisenberg model develops a non-zero expectation value of the staggered magnetization

$$\vec{M}_s = \sum_{\vec{x}} (-1)^{x_1/a+x_2/a} \vec{S}_{\vec{x}}, \quad (16.1.3)$$

in its ground state. This is a result of numerical simulations. It has not been possible to find an analytic expression for the ground state and exactly derive its energy or other properties such as its staggered magnetization. The staggered magnetization is known as the order parameter of antiferromagnetism.

Fluctuations of the staggered magnetization vector manifest themselves as spin waves also known as magnons. Just as phonons are quantized lattice vibrations, antiferromagnetic magnons are quantized fluctuations of the staggered magnetization. It turns out that there are two magnon excitations (analogous to the two possible polarizations of a photon), with the dispersion relation given by

$$E(\vec{k}) = \hbar\omega(\vec{k}) = \hbar|\vec{k}|c, \quad (16.1.4)$$

for small values of $|\vec{k}|$. Just as for phonons, and in contrast to photons, the magnon dispersion relation deviates from linearity in $|\vec{k}|$ for larger values of $|\vec{k}|$, in particular near the edge of the Brillouin zone. In this case, c is the so-called spin wave velocity (which is smaller than the velocity of light). In complete analogy to photons and phonons, at low temperatures the magnon contribution to the specific heat of an antiferromagnet is determined by the linear dispersion relation. Since antiferromagnetic magnons and phonons have the same dispersion relation, and there are two magnons as well as two polarizations of photons, at low temperatures the mathematical expressions for the magnon energy density ρ and the specific heat c_V of a 3-dimensional antiferromagnet are identical with those of the photon gas, except that the velocity of light is now replaced by the spin wave velocity. In particular, one obtains

$$\rho = \frac{\pi^2 k_B^4 T^4}{15 \hbar^3 c^3}, \quad c_V = \frac{\partial \rho}{\partial T} = \frac{4\pi^2 k_B^4 T^3}{15 \hbar^3 c^3}, \quad (16.1.5)$$

which again has the T^3 behavior characteristic for the specific heat of non-interacting massless bosons with a linear dispersion relation.

16.2 Ferromagnetic Heisenberg Model

The microscopic origin of ferromagnetism is rather non-trivial. It involves electrons in two bands coupled to one another according to Hund's rule. Although it oversimplifies the underlying dynamical mechanism, here we will model ferromagnetism by a simple quantum Heisenberg model with the Hamiltonian

$$H = -J \sum_{\vec{x}, i} \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a}. \quad (16.2.1)$$

When $J > 0$, this Hamiltonian favors parallel spins. Since their Hamiltonians differ just by a minus-sign, the spectra of the ferro- and antiferromagnetic Heisenberg models are related by a sign-change. In other words, the ground state of the ferromagnet corresponds to the highest excited state of the antiferromagnet, and vice versa. Again, the ferromagnetic Heisenberg model has an $SU(2)$ spin symmetry, i.e.

$$[H, \vec{S}] = 0, \quad \vec{S} = \sum_{\vec{x}} S_{\vec{x}}. \quad (16.2.2)$$

The total spin represents the uniform magnetization, which is the order parameter of a ferromagnet. In contrast to an antiferromagnet, the order parameter of a ferromagnet (the total spin) is a conserved quantity (it commutes with the Hamiltonian).

Other than the antiferromagnetic Heisenberg model, to some extent the ferromagnetic model can be solved analytically. Let us construct a ground state of the ferromagnet

$$|0\rangle = |\uparrow\uparrow \dots \uparrow\rangle, \quad (16.2.3)$$

in which all spins are up. Introducing the sum of two neighboring spins

$$\vec{J} = \vec{S}_{\vec{x}} + \vec{S}_{\vec{x}+\vec{i}a}, \quad (16.2.4)$$

the product of the two spin vectors can be expressed as

$$\vec{J}^2 = (\vec{S}_{\vec{x}} + \vec{S}_{\vec{x}+\vec{i}a})^2 = \vec{S}_{\vec{x}}^2 + \vec{S}_{\vec{x}+\vec{i}a}^2 + 2\vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a} \Rightarrow \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a} = \frac{1}{2} [\vec{J}^2 - \vec{S}_{\vec{x}}^2 - \vec{S}_{\vec{x}+\vec{i}a}^2]. \quad (16.2.5)$$

Since the angular momentum operator \vec{J}^2 has the eigenvalue $J(J+1)$, we obtain

$$\vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a} = \frac{1}{2} \left[J(J+1) - 2\frac{3}{4} \right] = \frac{1}{2} \left[J(J+1) - \frac{3}{2} \right]. \quad (16.2.6)$$

Here we have used the fact that

$$\vec{S}_{\vec{x}}^2 = \vec{S}_{\vec{x}+\vec{i}a}^2 = \frac{1}{2} \left(\frac{1}{2} + 1 \right) = \frac{3}{4}. \quad (16.2.7)$$

In the above ground state, all nearest-neighbor spin $\frac{1}{2}$ pairs are coupled to the total spin $J = 1$ such that

$$\vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a} = \frac{1}{2} \left[J(J+1) - \frac{3}{2} \right] = \frac{1}{2} \left[2 - \frac{3}{2} \right] = \frac{1}{4}. \quad (16.2.8)$$

Consequently, we obtain

$$H|0\rangle = -J \sum_{\vec{x},i} \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a} |\uparrow\uparrow \dots \uparrow\rangle = -\frac{3JL^3}{4a^3} |0\rangle, \quad (16.2.9)$$

such that the energy of the ground state is given by

$$E_0 = -\frac{3JL^3}{4a^3}. \quad (16.2.10)$$

Here we have assumed a cubic lattice with periodic boundary conditions and L/a points in each directions. The factor 3 arises because there are $3(L/a)^3$ nearest-neighbor pairs on the lattice. The energy density of the ground state is thus given by

$$\rho_0 = \frac{E_0}{L^3} = -\frac{3J}{4a^3}. \quad (16.2.11)$$

It is important to note that the ground state has a total spin value

$$S = \frac{L^3}{2a^3}. \quad (16.2.12)$$

Hence it is $2S + 1 = L^3/a^3 + 1$ fold degenerate. In other words, on a large lattice there is an enormous number of degenerate ground states.

16.3 Magnon Dispersion Relation

Let us consider the low-energy excitations above the ground state $|0\rangle$. These are fluctuations of the magnetization known as ferromagnetic magnons. First, we construct raising and lowering operators for the individual spins

$$S_{\vec{x}}^+ = S_{\vec{x}}^1 + iS_{\vec{x}}^2, \quad S_{\vec{x}}^- = S_{\vec{x}}^1 - iS_{\vec{x}}^2, \quad (16.3.1)$$

which obey the commutation relations

$$\begin{aligned} [S_{\vec{x}}^+, S_{\vec{x}'}^-] &= -i[S_{\vec{x}}^1, S_{\vec{x}'}^2] + i[S_{\vec{x}}^2, S_{\vec{x}'}^1] = 2\delta_{\vec{x}\vec{x}'} S_{\vec{x}}^3, \\ [S_{\vec{x}}^3, S_{\vec{x}'}^+] &= [S_{\vec{x}}^3, S_{\vec{x}'}^1] + i[S_{\vec{x}}^3, S_{\vec{x}'}^2] = \delta_{\vec{x}\vec{x}'} (iS_{\vec{x}'}^2 + S_{\vec{x}}^1) = \delta_{\vec{x}\vec{x}'} S_{\vec{x}}^+, \\ [S_{\vec{x}}^3, S_{\vec{x}'}^-] &= [S_{\vec{x}}^3, S_{\vec{x}'}^1] - i[S_{\vec{x}}^3, S_{\vec{x}'}^2] = \delta_{\vec{x}\vec{x}'} (iS_{\vec{x}'}^2 - S_{\vec{x}}^1) = -\delta_{\vec{x}\vec{x}'} S_{\vec{x}}^-. \end{aligned} \quad (16.3.2)$$

As a next step, we perform a Fourier transform

$$S^+(\vec{k}) = \sum_{\vec{x}} S_{\vec{x}}^+ \exp(-i\vec{k} \cdot \vec{x}), \quad S^-(\vec{k}) = \sum_{\vec{x}} S_{\vec{x}}^- \exp(i\vec{k} \cdot \vec{x}) = S^+(\vec{k})^\dagger, \quad (16.3.3)$$

and we construct the one-magnon state

$$|\vec{k}\rangle = S^-(\vec{k})|0\rangle. \quad (16.3.4)$$

The Hamilton operator can be written in the form

$$H = -J \sum_{\vec{x}, i} \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}+\vec{i}a} = -J \sum_{\vec{x}, i} \left[\frac{1}{2} \left(S_{\vec{x}}^+ S_{\vec{x}+\vec{i}a}^- + S_{\vec{x}}^- S_{\vec{x}+\vec{i}a}^+ \right) + S_{\vec{x}}^3 S_{\vec{x}+\vec{i}a}^3 \right], \quad (16.3.5)$$

such that

$$\begin{aligned}
[H, S^-(\vec{k})] &= -J \sum_{\vec{x}, \vec{x}', i} \left[\frac{1}{2} \left(S_{\vec{x}'}^+ S_{\vec{x}'+\vec{i}a}^- + S_{\vec{x}'}^- S_{\vec{x}'+\vec{i}a}^+ \right) + S_{\vec{x}}^3 S_{\vec{x}+\vec{i}a}^3, S_{\vec{x}}^- \right] \exp(i\vec{k} \cdot \vec{x}) \\
&= -J \sum_{\vec{x}, \vec{x}', i} \left(S_{\vec{x}'}^3 \delta_{\vec{x}\vec{x}'} S_{\vec{x}'+\vec{i}a}^- + S_{\vec{x}'}^- S_{\vec{x}'+\vec{i}a}^3 \delta_{\vec{x}, \vec{x}'+\vec{i}a} \right. \\
&\quad \left. - S_{\vec{x}}^- \delta_{\vec{x}\vec{x}'} S_{\vec{x}'+\vec{i}a}^3 - S_{\vec{x}'}^3 S_{\vec{x}'+\vec{i}a}^- \delta_{\vec{x}, \vec{x}'+\vec{i}a} \right) \exp(i\vec{k} \cdot \vec{x}) \\
&= -J \sum_{\vec{x}, i} \left(S_{\vec{x}}^3 S_{\vec{x}+\vec{i}a}^- + S_{\vec{x}-\vec{i}a}^- S_{\vec{x}}^3 - S_{\vec{x}}^- S_{\vec{x}+\vec{i}a}^3 - S_{\vec{x}-\vec{i}a}^3 S_{\vec{x}}^- \right) \exp(i\vec{k} \cdot \vec{x}) \\
&= -J \sum_{\vec{x}, i} \left(S_{\vec{x}}^- S_{\vec{x}-\vec{i}a}^3 \exp(-ik_i a) + S_{\vec{x}}^- S_{\vec{x}+\vec{i}a}^3 \exp(ik_i a) \right. \\
&\quad \left. - S_{\vec{x}}^- S_{\vec{x}+\vec{i}a}^3 - S_{\vec{x}}^- S_{\vec{x}-\vec{i}a}^3 \right) \exp(i\vec{k} \cdot \vec{x}). \tag{16.3.6}
\end{aligned}$$

We now obtain

$$\begin{aligned}
[H, S^-(\vec{k})]|0\rangle &= -\frac{J}{2} \sum_{\vec{x}} S_{\vec{x}}^- \exp(i\vec{k} \cdot \vec{x}) \sum_i (\exp(-ik_i a) + \exp(ik_i a) - 2) |0\rangle \\
&= -\frac{J}{2} S^-(\vec{k}) \sum_i 2(\cos(k_i a) - 1) |0\rangle = E(\vec{k})|k\rangle, \tag{16.3.7}
\end{aligned}$$

which implies

$$H|\vec{k}\rangle = HS^-(\vec{k})|0\rangle = [H, S^-(\vec{k})]|0\rangle + S^-(\vec{k})H|0\rangle = (E(\vec{k}) + E_0)|\vec{k}\rangle, \tag{16.3.8}$$

with the magnon dispersion relation given by

$$E(\vec{k}) = -J \sum_i (\cos(k_i a) - 1). \tag{16.3.9}$$

For small values of the wave number $|\vec{k}|$ we hence obtain the quadratic energy-momentum dispersion relation

$$E(\vec{k}) = \frac{Ja^2}{2} |\vec{k}|^2. \tag{16.3.10}$$

It should be noted that the states $S(\vec{k})^- S(\vec{k}')^- |0\rangle$ are not exact two-magnon energy eigenstates. This is because magnons interact with one another and are thus in general not forming an ideal gas. Still, the magnon-magnon interactions go to zero for low magnon energies. Consequently, at least at low temperature, the magnons can still be treated as an ideal gas.

16.4 Specific Heat of a Ferromagnet

Just as photons or phonons, ferromagnetic magnons are bosons. However, they have a quadratic rather than a linear energy-momentum dispersion relation. At low temperatures, when the magnons can be treated as an ideal gas, the partition function can be written as

$$Z = \prod_{\vec{k}} Z(\vec{k}), \quad Z(\vec{k}) = \sum_{n(\vec{k})=0}^{\infty} \exp(-\beta n(\vec{k})E(\vec{k})) = \frac{1}{1 - \exp(-\beta E(\vec{k}))}. \quad (16.4.1)$$

The energy density is then given by

$$\rho = -\frac{1}{L^3} \frac{\partial \log Z}{\partial \beta} = \frac{1}{L^3} \sum_{\vec{k}} \frac{E(\vec{k})}{\exp(\beta E(\vec{k})) - 1}. \quad (16.4.2)$$

In the infinite volume limit, the sum over discrete modes turns into an integral and we obtain

$$\begin{aligned} \rho &= \frac{1}{(2\pi)^3} \int d^3k \frac{E(\vec{k})}{\exp(\beta E(\vec{k})) - 1} \\ &= \frac{Ja^2}{4\pi^2} \int_0^{\infty} dk \frac{k^4}{\exp(\beta Ja^2 k^2/2) - 1} \\ &= \frac{1}{\sqrt{2}\pi^2 (Ja^2)^{3/2}} (k_B T)^{5/2} \int_0^{\infty} dx \frac{x^{3/2}}{\exp(x) - 1} \\ &= \frac{3}{2(2\pi Ja^2)^{3/2}} \zeta\left(\frac{5}{2}\right) (k_B T)^{5/2}. \end{aligned} \quad (16.4.3)$$

Here we have extended the integration over the Brillouin zone to an integration up to infinity, which is indeed justified in the low-temperature limit. The specific heat then takes the form

$$c_V = \frac{\partial \rho}{\partial T} = \frac{15}{4(2\pi Ja^2)^{3/2}} \zeta\left(\frac{5}{2}\right) (k_B T)^{3/2}. \quad (16.4.4)$$

Calculating the specific heat at higher temperatures is non-trivial because the magnons can then no longer be treated as an ideal gas. Such calculations were pioneered by Freeman Dyson but are still an area of current research.