PHAS0024
Statistical Physics of Matter

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Preface

Course description

This module aims to provide a secure foundation in statistical thermodynamics/ statistical mechanics, which is of great use for the study of systems that involve many particles, ranging across all fields of physics. The module:

- reviews concepts in classical thermodynamics;

- presents the basic ideas and methods appropriate for the description of systems containing very many identical particles;

- compares and contrasts the statistical mechanics of ideal gases comprised of bosons, fermions, and classical particles;

- applies the statistical framework to form an appreciation of properties of condensed matter.

Prior knowledge

Every effort is made for the module to be self-contained, *i.e.*, understandable without more than a basic knowledge of maths and physics at early undergraduate level. Formal prerequisites are the modules PHAS0002 — Maths I and PHAS0009 —Maths II, to provide the appropriate mathematical background, and PHAS1228 —Thermal Physics, to provide a basic knowledge of concepts of thermodynamics, from which many ideas of statistical thermodynamics/ statistical mechanics originate.

These lecture notes

A thorough understanding of these notes and of the problems set throughout the course will suffice to meet the examination criteria at the end of this course. These notes have evolved from prior versions as developed by Prof. Ian Ford and Prof. Alessio Serafini at University College London, including parts covered in the books *Statistical Physics: an entropic approach* by Ian Ford (Wiley 2013) and *Solid State Physics* by J. R. Hook & H. E. Hall (Wiley 1991). For further materials and information on the module, students are referred to and expected to regularly verify its online resources on the following moodle page: https://moodle.ucl.ac.uk/course/view.php?id=6761.

Problem sheets, problem solving tutorials, and assessment

Weekly problem sheets will be posted on the moodle page to provide opportunity for putting the theoretical knowledge into practice for solving specific problems. In addition, four problem sheets

will be provided to be discussed in greater detail during problem solving tutorials. You are likely to benefit most from help and feedback during these tutorials when you have made a serious attempt to address the questions on these problem sheets *before* attending the tutorials. Worked solutions will be posted after the problem solving tutorials.

You will be assessed via two short (50 minute) tests in In-Class Assessments (ICAs), which will consist of problems derived from the questions in the problem sheets and in the problem solving tutorials. The average result of these two ICAs will form 15% of your final mark, with the remaining 85% coming from the examination after Easter.

General comment

Given its level of abstraction, this module is generally considered a difficult one. Its topic is one that is unlikely to be fully appreciated at a first reading. It is also a most rewarding topic, as its concepts allow us to tackle problems in thermodynamics, solid state and soft matter physics, quantum technology and astrophysics, to name just a few examples. In brief, some perseverance may well be required, but in the end it will be worth it.

Contents

Chapter 1

The four laws

> *Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are used to it, so it doesn't bother you any more.* — Arnold Sommerfeld (1868–1951), pioneer in quantum physics.

Many great physical theories, such as classical mechanics, electromagnetism, quantum physics and relativity, provide workable solutions for 0, 1, or at best 2 particles. Examples are the Earth evolving around the sun, or the quantum-mechanical description of the hydrogen atom (1 proton and 1 electron). Even for such two particle-systems, we often simplify the problem by considering them as a single particle (e.g., Earth, electron) moving in the presumably invariable potential of the other (e.g., sun, proton). For larger systems, we can get around this limitation by considering particles that move in a coherent way (e.g., waves) or by describing single particles moving in some mean field or potential landscape that encapsulates the effects of the many other particles that may be present. Or, somewhat soul-numbing, by letting a big computer grind and hoping for the best.

Summarising this sad state of affairs, we may note that while you have learnt at school to count 1, 2, 3, 4, 5, ..., but that physicists count in a different manner: 0, 1, 2, directly followed by... "many". Yet most problems in the real world are not limited to two particles, nor are most interesting problems in science. This calls for a physical theory to deal with many particles. This theory is statistical physics, also known as statistical mechanics.

Although its application extends far beyond it, the main motivation behind the development of statistical mechanics was to provide an explanation for the thermodynamic behaviour of physical systems, through the laws of mechanics and probability. To distinguish it from the more general framework of statistical mechanics, this specific endeavour is often referred to as "statistical thermodynamics", which tries to justify the laws of thermodynamics based on the fundamental dynamical laws that govern the constituents of all physical systems. Such laws can be classical or quantum-mechanical, thus giving rise to classical or quantum statistical mechanics, as we shall see.

This chapter will serve as an opportunity to revise already encountered notions in classical thermodynamics (see PHAS0006, Thermal Physics), but also to flesh out and analyse in more detail concepts that will be instrumental in the remainder of the course. Classical thermodynamics is a self-standing physical theory based on an overwhelming body of empirical evidence. Historically, it was developed in the wake of the industrial revolution, where the focus was on building efficient engines (machines that do work), and on understanding the fundamental limitations to such machines. In a broad sense, thermodynamics deals with the flows of matter and energy (in various forms) between physical systems. Its results are encapsulated the four thermodynamic laws, here

stated in rather intuitive forms, to be refined in the next sections.

- *Zeroth law*: If two systems are in thermal equilibrium with a third system, then they are in equilibrium with each other.

- *First law*: The total energy of an isolated system remains constant (law of conservation of energy).

- *Second law*: Heat cannot flow spontaneously from a colder to a warmer body (Clausius statement, after Rudolf Clausius, 1822–1888).

- *Third law*: It is impossible to reduce the absolute temperature to zero in a finite number of steps (Nernst's unattainability principe, after Walther Nernst, 1864–1941)

1.1 State variables

The four laws make statements on what for a system of many particles may seem rather abstract concepts. For example, the first law makes a statement about *energy* as a generic quantity that specifies the macroscopic condition of a physical system. It is a key realisation of thermodynamics that the behaviour of large systems follows regularities that can be captured in so called 'state variables' or 'functions of state', of which energy is one. This very coarse-grained description is most effective for large systems, noting that — as already implied above — fundamental dynamical laws become quickly intractable when the number of elementary constituents of a physical system grows: solving and keeping track of the motion of about $N_A = 6 \times 10^{23}$ gas particles through fundamental dynamical laws is way beyond the possibility of any calculator.

Hence thermodynamics describes physical systems in terms of a set of *state variables or functions*.

These are quantities that specify the macroscopic condition of a physical system in equilibrium, without reference to any previous history. Examples are temperature T, energy E, pressure p and volume V. Note that, during a thermodynamic transformation, the change in state functions does not depend on the nature of the transformation itself, but only on the initial and final state of the system.

State variables can be (figure 1.1):

- Extensive: Scale with the amount of material in the system, such as the energy E, the volume V, and the number of constituents N.

- Intensive: Remain the same for different amounts of material in the system, such as the temperature T and the pressure p.

By contrast to state variables, *process variables*, such as heat Q and work W, describe changes to the system (*i.e.*, describe processes), but do not specify its state in equilibrium. E.g., heat is a central notion in thermodynamics. It is a fundamental quantity that can flow from one system to another when two systems are put in thermal contact.[1] It is understood that, if a heat Q flows from system A to system B, this is equivalent to a flow of $-Q$ from B to A. It is also understood that heat flowing from one system to another can somehow be measured.

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[1]Note that we are keeping certain notions, such as 'thermal contact', or even the delicate notion of 'system', at an intuitive level. Attempting to define all terms precisely in this context would greatly lengthen and bog down this discussion. This should however give a first hint of the kind of treacherous pitfalls the theory may present.
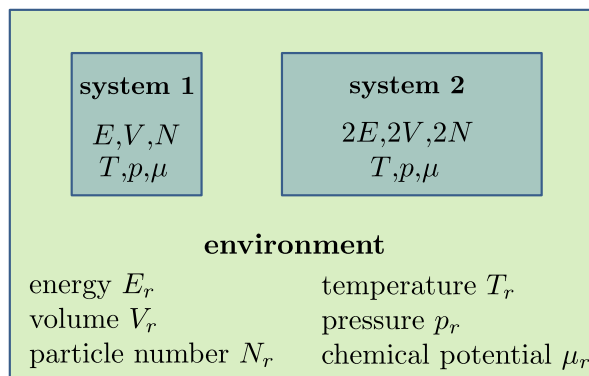
Figure 1.1: The world-view according to thermodynamics. An environment is characterised by the macroscopic properties labelled by a suffix r. The one that might be unfamiliar is chemical potential, which we discuss later. Systems coupled to this environment are characterised by similar properties, shown here without a suffix. System 2 is simply two copies of system 1 joined together. Intensive state variables do not change under such replication, but extensive variables double. Furthermore, when in equilibrium, it is the intensive state variables of the system that normally equal those of the environment, for reasons that we shall come to.

1.2 The zeroth and first laws

Based on the concepts introduced above, we can now provide a more precise statement of the zeroth law of thermodynamics. Firstly, we postulate that two systems are in thermal equilibrium if there is no heat flow between them when they are put in thermal contact. Next we note that one can just put a system A in thermal contact with a system B and observe the sign of the heat exchange: if the heat ΔQ_A flowing into A is positive, then one can stipulate that $T_A < T_B$, where T_A and T_B are the temperatures of A and B respectively. One can also, in principle, assume the existence of systems from which heat can never flow out, and set their temperature to 0. Through this definition, temperature is just an intensive property that quantifies the eagerness of a system to give away or receive heat.

> **Zeroth law of thermodynamics.** If two systems are in thermal equilibrium with a third system, then they are in equilibrium with each other. Hence, an intensive state function ("temperature", T) may be defined to decide whether two systems are in equilibrium.

We can succinctly reformulate this in terms of temperatures by the statement: if $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$.

In thermodynamics, one is largely interested in transformations (think of the steam engine), e.g., the flow of heat from one system to another. More generally, we consider cases where, after the system is prepared in a given state, certain conditions are changed and the system evolves. Throughout this course, it should be clearly stated, *we will only deal with transformations such that both the initial and the final state of the system are equilibrium states.* A system is said to be at equilibrium if none of its thermodynamic state functions change over time. This restriction is usually referred to as "equilibrium thermodynamics".[2] The "change in conditions" referred to above is responsible for a change in the equilibrium state. As we are about to see, the laws of thermodynamics are powerful instruments to predict final equilibrium states.

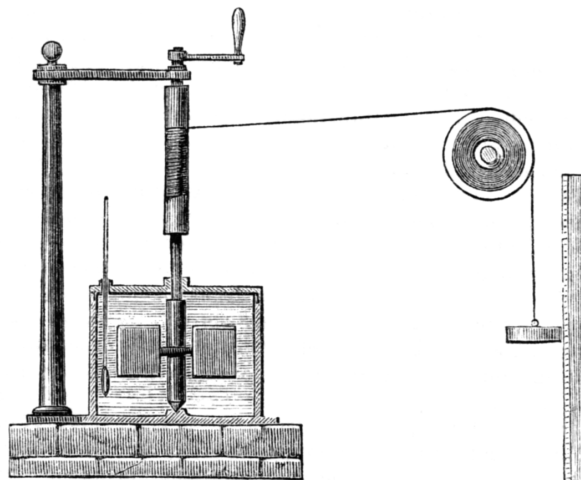[2] "Non-equilibrium" thermodynamics is still a lively field of research.

Figure 1.2: A sketch of Joule's experiment, where the work done by a falling weight is converted into heat, detected by the change in temperature of water in a tank (the "system", in our description).

As noted above, heat is not a state function, as the heat exchanged during a thermodynamic process will in general depend on the followed process, and does not provide an unambiguous specification on the initial and final state of the system. However, heat, just like work, is a form of energy. This was demonstrated in an experiment by James Joule (1818–1889), where the change in gravitational energy of a falling weight (= work done by the weight) transformed into work done by a paddles moving in a water tank, resulting in the generation of heat, as measured by an increase of the temperature of the water (figure 1.2).

Combined with the mechanical law of energy conservation (change in energy = work), this transformation can be expressed by the second law of thermodynamics, formulated as follows.

First law of thermodynamics. There is a system property ("energy", E) which can take different forms (such as heat or potential energy) and is conserved if the system is isolated from the rest of the universe. This system property is such that, if a system transformation is considered, one has

$$\mathrm{d}E = \mathrm{d}Q - \mathrm{d}W \ , \tag{1.1}$$

where $\mathrm{d}E$ is the (incremental) change in the energy of the system, $\mathrm{d}Q$ is the incoming heat (positive if heat flows into the system) and $\mathrm{d}W$ is the work done *by* the system (hence positive work implies a decrease in the energy of the system).

Since $\mathrm{d}Q$ and $\mathrm{d}W$ represent incremental changes in energy of the system due to the different transfer processes, they do not represent increments in (purported) state variables Q and W. These are not state variables: a system does not contain specific quantities of heat or work, only a certain energy. As a reminder, some treatments use $đQ$ and $đW$ when specifying heat and work increments, and refer to them as *inexact* differentials. We shall not use this notation. As long as we grasp that $\mathrm{d}Q$ and $\mathrm{d}W$ are increments of energy that specify the *course* of a certain process while $\mathrm{d}E$ is the increment in the energy state variable *resulting* from the process, the likelihood for confusion in the meaning is minimal.

Integrating equation 1.1, we can also write the first law as

$$\Delta E = \int_{E_{initial}}^{E_{final}} \mathrm{d}E' = \int_0^Q \mathrm{d}Q' - \int_0^W \mathrm{d}W' = Q - W \ , \tag{1.2}$$

where ΔE is the change in energy for a process in which there has been a heat transfer Q and a work W.

1.3 Entropy of an ideal gas

The first law, although historically groundbreaking (in relation to the discussion concerning the nature of 'heat', in the first half of the 19th century), is not with hindsight that surprising, once one acknowledges that heat is a form of energy. What makes thermodynamics stand out is the notorious second law, a piece of knowledge so iconic that, in all contexts, physicists customarily refer to it as "the" second law, without having to mention thermodynamics at all. We will define the second law in terms of the state variable entropy, a concept central to all our discussion. To introduce entropy, it is helpful to first consider some properties of the ideal classical gas.

The monatomic ideal classical gas is frequently used to illustrate aspects of thermodynamics. An ideal gas consists of particles that do not interact with each other, but only with the walls of the container in which they are confined. The equation of state described the ideal classical gas in equilibrium as follows,

$$pV = Nk_BT, \tag{1.3}$$

where p is the pressure, V is the volume, N is the number of particles, and T is the temperature of the gas. This is also known as the ideal gas law. The remaining symbol in (1.3) is Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ JK^{-1}.

Since the mean (kinetic) energy of 1 particle is given by $\langle E_1 \rangle = \frac{1}{2}m\langle v^2 \rangle$, the (average) energy of N independent particles of mass m is

$$E = \tfrac{1}{2}Nm\langle v^2 \rangle \ , \tag{1.4}$$

where $\langle v^2 \rangle$ is the mean square velocity of the particles. This result can be related to the pressure p by considering particles travelling towards a wall with a positive velocity v_x, and their change in momentum $(= -2mv_x)$ upon bouncing back from the wall, thus transferring a momentum of $2mv_x$ to the wall. Within a time $\mathrm{d}t$, this will apply to particles that are within a distance $v_x\mathrm{d}t$ from the wall, see figure 1.3. Noting that pressure is force per area and that the exerted force is the momentum transfer per infinitesimal $\mathrm{d}t$, we find[3]

$$pV = \tfrac{1}{3}Nm\langle v^2 \rangle \ . \tag{1.5}$$

Combining (1.4) and (1.5) we obtain

$$pV = \tfrac{2}{3}E \ . \tag{1.6}$$

This is a connection between the energy and pressure of an ideal gas confined to a container of volume V, which we will use hereafter.

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[3]Assuming that there are $n(v_x)\mathrm{d}v_x$ particles per unit volume with velocity between v_x and $v_x + \mathrm{d}v_x$, the force on the wall is $2m\mathcal{A}\int_0^\infty n(v_x)v_x^2\mathrm{d}v_x = 2m\mathcal{A}n_+\int_0^\infty n(v_x)v_x^2\mathrm{d}v_x / \int_0^\infty n(v_x)\mathrm{d}v_x = 2m\mathcal{A}n_+\langle v_x^2 \rangle$ where $n_+ = \int_0^\infty n(v_x)\mathrm{d}v_x$ is the total number density of particles with positive v_x (*i.e.*, travelling towards the wall). In equilibrium, this is just $\frac{1}{2}n$ where $n = N/V$ is the total particle number density. Dividing by the wall area gives the pressure in the form $p = mn\langle v_x^2 \rangle$. Assuming the system is isotropic, we note that $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}\langle v^2 \rangle$, where v is the magnitude of the velocity, leading to the result in equation 1.5.
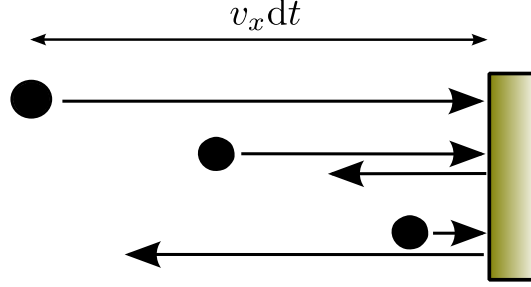
Figure 1.3: All gas particles with a positive velocity v_x, and located within a distance $v_x dt$ of a wall, collide with it in a period of time dt, giving rise to momentum transfer and hence pressure.

Inserting this result in the ideal gas law (equation 1.3), this also implies that

$$E = \tfrac{3}{2} N k_B T, \tag{1.7}$$

for the monatomic ideal classical gas. In other words, the gas particles each have — on average — a kinetic energy of $\tfrac{3}{2} k_B T$. The implication of this result is that, for an ideal gas in equilibrium, the macroscopic state variable temperature is a measure of the microscopic mean kinetic energy per particle.

To find an appropriate state variable for formulating the second law, we next consider the quantity $(dQ/T)_q$ for heat transfer from an environment into a system. The subscript q indicates that this process is *quasistatic*, meaning that the heat transfer is sufficiently slow for the system to approximately remain in the thermal equilibrium with its environment at all times. Using the first law (equation 1.1), we can write

$$\left(\frac{dQ}{T}\right)_q = \frac{dE + p dV}{T}, \tag{1.8}$$

where T is the temperature of the environment. Therefore, using the energy–pressure relation as derived above (equation 1.6),

$$\left(\frac{dQ}{T}\right)_q = \frac{3}{2}\frac{d(pV)}{T} + p\frac{dV}{T} = \frac{5}{2}p\frac{dV}{T} + \frac{3}{2}V\frac{dp}{T} = \frac{5}{2}Nk_B\frac{dV}{V} + \frac{3}{2}Nk_B\frac{dp}{p}. \tag{1.9}$$

If we sum such incremental changes over a complete quasistatic heat transfer process from equilibrium state a to equilibrium state b, we get

$$\int_a^b \left(\frac{dQ}{T}\right)_q = \left[\tfrac{5}{2}Nk_B \ln V + \tfrac{3}{2}Nk_B \ln p\right]_a^b = \left[\tfrac{3}{2}Nk_B \ln\left(pV^{5/3}\right)\right]_a^b. \tag{1.10}$$

The left hand side is a measurable quantity: the heat transferred to a system during a quasistatic process modulated by the changing inverse system temperature as the process takes place. The right hand side can be expressed in terms of the initial and final pressure and volume of the gas (p_a, V_a) and (p_b, V_b), noting that N remains the same, and we write

$$\int_a^b \left(\frac{dQ}{T}\right)_q = Nk_B \ln\left(\frac{p_b^{3/2}V_b^{5/2}}{p_a^{3/2}V_a^{5/2}}\right) = S(p_b, V_b, N) - S(p_a, V_a, N) = \int_a^b dS, \tag{1.11}$$

where we have defined a property called *entropy* (S), a name coined in 1865 by Rudolf Clausius (1822–1888), via

$$dS = \left(\frac{dQ}{T}\right)_q, \tag{1.12}$$

that for the monatomic ideal classical gas takes the form

$$S(p, V, N) = Nk_B \ln\left(\frac{p^{3/2}V^{5/2}}{C(N)}\right) . \tag{1.13}$$

The entropy S of the monatomic ideal classical gas is a state variable, since it is a function of state variables pressure and volume. The quantity C in the denominator is included to make the argument of the logarithm dimensionless. It can in principle depend on system properties that do not change as a result of the process, such as here the number of particles N. With an appropriate choice $C(N) = \hat{c}N^{5/2}$, the entropy can also be shown to be an extensive state variable,[4] *i.e.*, it scales with the amount of material, like the volume, energy, and the number of particles.

By next substituting pV using the ideal gas law (equation 1.3) into the expression for $S(p, V, N)$, we can also express the entropy as a function of T,

$$S(T, V, N) = Nk_B \ln\left(\frac{(k_BT)^{3/2}}{\hat{c}N/V}\right) . \tag{1.14}$$

1.4 The second law

In the introduction to this chapter, we have defined the second law as the Clausius statement, *i.e.*, the somewhat unspectacular observation that heat cannot flow spontaneously from a colder to a warmer body. Yet the importance of the second law can hardly be overstated. The novelist and scientist C.P. Snow (1905–1980) phrased this as follows, when lamenting the lack of scientific knowledge among his interlocutors:

> *A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the second law of thermodynamics. The response was cold: it was also negative. Yet I was asking something which is the scientific equivalent of: Have you read a work of Shakespeare's?*

To better appreciate this, we will next reformulate the Clausius statement about heat flow into a specific statement in terms of the state variable entropy. To do so, we consider a heat pump that takes heat from a system A at temperature T_A, and next transfers it to another system B at temperature T_B. The spontaneous nature of the heat flow is implied by postulating that this heat pump operates without the need of any added work W. When a small amount of heat $dQ > 0$ is *released by* A, this causes an incremental change in entropy of system A given by

$$dS_A = \frac{-dQ}{T_A} . \tag{1.15}$$

Upon transfer of this heat to system B, the entropy of system B changes by

$$dS_B = \frac{+dQ}{T_B} , \tag{1.16}$$

such that the total change in entropy, for systems A and B combined, is given by

$$dS = dS_A + dS_B = \left(\frac{1}{T_B} - \frac{1}{T_A}\right)dQ = \left(\frac{T_A - T_B}{T_AT_B}\right)dQ . \tag{1.17}$$

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[4]The appropriate choice of $C(N)$ can be derived by noting that, to be extensive, the entropy should change from $S \to 2S$ for the substitutions $N \to 2N$ and $V \to 2V$.

According to the Clausius statement, this process is not possible if $T_A < T_B$, *i.e.*, it is only possible if $T_A \geq T_B$, which is equivalent to stating that $\mathrm{d}S \geq 0$.[5] We thus arrive at the second law, formulated as follows.

Second law of thermodynamics. There is an extensive state function ("entropy") which, for an isolated system, either grows or, in ideal "reversible" transformations, is conserved. That is,

$$\mathrm{d}S \geq 0 \,, \tag{1.18}$$

where $\mathrm{d}S$ is the (here incremental) change in entropy of the system. When the inequality above reduces to an equality, the transformation is said to be reversible.

Obviously, this will also apply to larger changes in entropy, $\Delta S = \int \mathrm{d}S \geq 0$. This statement is an inequality that separates the final state of a system from its initial state, and implies discernible notions of future and past, the future being the time direction towards which entropy grows. When a process has an entropy change $\Delta S > 0$, it is irreversible (since, to reverse it, it would require a process for which $\Delta S < 0$, which is forbidden by the second law). Only processes with $\Delta S = 0$ can be reversed. Relating this time-asymmetric law to fundamental time-symmetric dynamical laws is a puzzle that still challenges researchers nowadays. Arguably, the second law is the most encompassing law of all the natural sciences. It will suffice to notice, as an example, that *all* chemical processes are ultimately governed by increases in entropy.

A well-known implication of the second law is that there is a limit on the efficiency at which heat can be used to generate work, e.g., in a steam engine. To understand this, consider heat a heat Q_A that flows from a large reservoir at constant temperature T_A, and that is converted into work W, leaving any remaining heat Q_B flow to a large reservoir at constant temperature T_B. The efficiency is of this heat engine is then given by

$$\eta = \frac{W}{Q_A} \,. \tag{1.19}$$

Similar to the case of spontaneous heat flow discussed above, the total entropy change

$$\Delta S = \frac{(-Q_A)}{T_A} + \frac{Q_B}{T_B} \geq 0 \tag{1.20}$$

because of the second law. Substituting $Q_B = Q_A - W$, we find that

$$\frac{-Q_A}{T_A} + \frac{Q_A - W}{T_B} \geq 0 \,, \tag{1.21}$$

$$Q_A \left(\frac{1}{T_B} - \frac{1}{T_A} \right) \geq \frac{W}{T_B} \,, \tag{1.22}$$

$$\eta = \frac{W}{Q_A} \leq 1 - \frac{T_B}{T_A} = \frac{T_A - T_B}{T_A} \,, \tag{1.23}$$

and 100% efficiency ($\eta = 1$) is only achieved when $T_B = 0$. As we will see below, T can only asymptotically approach 0, and in practice $\eta < 1$. In addition, if $T_A = T_B$, *i.e.*, if there is effectively only one reservoir, then $\eta = 0$. This brings us to yet another statement of the second law, namely that no device operating on a cycle may produce work from a single thermal reservoir. This is known as the Kelvin statement, after William Thomson, Lord Kelvin (1824–1907).

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[5]We do not need to worry about $T_A T_B$ being negative, as per the third law explained below.
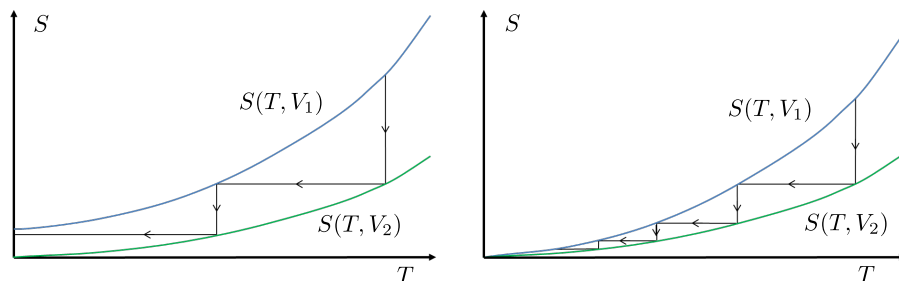
Figure 1.4: The diagram on the left shows how — in a process denied by the third law — a temperature of absolute zero would be reached by a finite sequence of cooling steps. The two curves represent the system entropy as a function of temperature at two volumes with $V_1 > V_2$. The zigzag path is followed by a sequence of isothermal compressions (moves downward), followed by quasistatic adiabatic expansions (moves to the left). If, by contrast and in agreement with the third law, an infinite number of steps is used to reach absolute zero, then $S(0, V_1) = S(0, V_2)$, as shown on the right.

1.5 The third law

In discussing the second law, we have defined only entropy differences. It will turn out that, unlike for instance energy, the absolute value of entropy will have an operational meaning in statistical mechanics. As noted in the introduction to the four laws, Nernst's unattainability principle states that it is impossible to reduce the absolute temperature to zero in a finite number of steps. In other words, zero temperature can only be reached asymptotically, $T \to 0^+$, and $T > 0$. Of course there are many technical difficulties in cooling a system, such as the elimination of leakage of heat from the environment, but the third law states that we cannot entirely remove all the thermal energy in a system, even in principle. This also has important consequences for entropy, as explained in the following.

To cool down a system, it requires a sequence of steps in which the system is each time brought into contact with a thermal reservoir to which it can transfer heat, and next thermally isolated such that the temperature of the system can evolve to a value below that of the reservoir. For example, a gas can first be compressed isothermally (in contact with the reservoir, at constant temperature T) to reduce its entropy by a reduction of the volume and concomitant heat transfer to the reservoir, see also the dependence of S on V in the expression for the ideal gas (equation 1.13). Next, the gas can be allowed to expand adiabatically (*i.e.*, thermally isolated), such that there is no heat transfer and the entropy remains (at best) constant, because of the second law (equation 1.18). In expanding adiabatically, the gas carries out work W on its environment and thus, by the first law (equation 1.1), reduces its energy and temperature (see also equation 1.7). Hence cooling can be achieved by a sequence of isothermal ($T = $ constant) and adiabatic ($Q = 0$, hence $S = $ constant) processes. In this example, the cooling occurs via changes in volume V that drive the system along the zigzag path between functions $S(T, V_1)$ and $S(T, V_2)$ starting from a finite temperature, see figure 1.4.

If the system can reach zero temperature in a finite number of such steps, then after a few compressions and expansions, the system entropy would be reduced to its value at some volume V between the two extremes, as shown on the left of figure 1.4. Therefore, the entropy could have different values at zero temperature. By contrast, in a process allowed by the third law, $T = 0$ would be reached by an infinite number of (by consequence) smaller and smaller steps, such that $S(T, V_1)$ and $S(T, V_2)$ converge to a single value, as shown on the right of figure 1.4. Stated in

terms of entropy, the third law of thermodynamics then reads:

Third law of thermodynamics. The entropy of a system at zero temperature is an absolute constant that does not depend on any other thermodynamic variable. That is,

$$\text{if } T \to 0^+ \text{ then } S \to S_0 \ , \tag{1.24}$$

where S_0 is a constant.

Quite generally, $S_0 = 0$, as we will see later, although there are some systems with non-zero (but still constant) entropy at zero temperature, not considered in these lectures. As a side note, the third law may seem incompatible with the entropy as derived for the ideal classical gas (equation 1.14), according to which S scales with $\ln T$, which diverges as the temperature approaches zero. However, we might have expected equation 1.14 to fail under these circumstances, since we suspect that for $T \to 0$, classical physics should be replaced by a quantum-mechanical treatment. With the appropriate quantum-mechanical treatment, we will find later that the ideal gas does satisfy the third law, along with showing some unexpected richness in phenomena.

1.6   Summary

Having noted that most physical systems become intractable for larger numbers of particles, we have adopted an approach in which the macroscopic state of a system is described by *state variables*, such as the energy E, volume V, number of particles N, temperature T, pressure V and entropy S. These state variables can be extensive or intensive, depending on whether their values changes with the amount of material that is considered to be in the system, or wether they are independent of it.

In terms of the state variables T, E and S and the *process variables Q and W*, we can describe the four laws of thermodynamics as follows:

- *Zeroth law*: If $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$, where T_A, T_B and T_C are the temperatures of system A, B and C, respectively.

- *First law*: $\Delta E = Q - W$, where Q represents the heat flowing into the system and W the work done by the system.

- *Second law*: For an isolated system, $\Delta S \geq 0$.

- *Third law*: If $T \to 0^+$, then $S \to S_0$, where S_0 is a constant (which for most systems is zero).

Throughout this chapter, we have considered different ways of stating these four laws and their mutual consistency. It should be clear, however, that we have not *proven* the validity of these laws; they have been postulated based on extensive experimental observations (e.g., that there is no spontaneous heat flow from a colder to a warmer body). This is not unusual for physical laws: such laws are generally not derived *ab initio*, but postulated to capture a range of experimental observations, and possibly overthrown or amended if they are found to be in contradiction with an experimental observation. It is worth noting, however, that the four laws of thermodynamics are considered particularly solid and all-encompassing. In the words of the astrophysicist Arthur Eddington (1882–1944):

> *If your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.*

Crucially, the second and third law have been formulated in terms of properties of the state variable entropy. Yet, rather strikingly, we have done so with complete disregard for the question what entropy actually means. For now, we note that it may be understood to represent *uncertainty*, and in a limited sense *disorder*, or a *lack of information* about the detail of a system. These notions will be further elaborated later.

Chapter 2

Free energy and entropy

> *I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered.* — Ludwig Boltzmann (1844–1906), pioneer in statistical mechanics.

In classical mechanics, we often use the concept of energy to determine the rest state of a particle. For example, can consider a marble that moves in a one-dimensional harmonic potential,

$$E_{pot}(x) = \tfrac{1}{2} C \left(x - x_0\right)^2 \ , \tag{2.1}$$

where C is a constant that defines how steep the potential rises, x the position of the the marble, and x_0 defines the position at which its lowest potential energy is lowest. Quite generally, the equilibrium position x_{eq} of a particle can be found by determining the minimum of the potential energy, *i.e.*,

$$\left. \frac{\mathrm{d}E_{pot}(x)}{\mathrm{d}x} \right|_{x=x_{eq}} = 0 \ , \tag{2.2}$$

which here leads to the unsurprising result that $C\left(x - x_0\right)|_{x=x_{eq}} = 0 \Rightarrow x_{eq} = x_0$.

This raises the question if a similar minimisation procedure can be applied to determine the equilibrium of a system with many moving particles, such as an ideal classical gas. Clearly, the minimisation of potential energy is of little practical use when considering an ideal classical gas — e.g., in a room full or air molecules, such a minimisation would tell us that the equilibrium position of the air molecules is on the floor, where they minimise their gravitational energy and in doing so leave any humans in the room at risk of suffocation. Therefore, some other constraints will need to be considered. In the following sections, we will define appropriate potentials that can be minimised to determine the equilibrium of a system, also leading to a better intuitive understanding of entropy.

2.1 The fundamental relation of thermodynamics

As we anticipate such potential "energies" to be expressed in terms of state variables, we start by rewriting the first law $\mathrm{d}E = \mathrm{d}Q - \mathrm{d}W$ (equation 1.1) in terms of state variables only — *i.e.*, substituting the process variables Q and W. To express $\mathrm{d}W$ in terms of state variables, we consider the mechanical work performed by an expanding gas. Presuming that the gas is contained in a cylinder with a movable piston, the work done on the gas is the applied force f times the distance moved by the piston $\mathrm{d}x$. If the expansion is slow (quasistatic), the gas is always well approximated

by an equilibrium state, and we can assume that it exerts a uniform pressure p against the piston head, of area $\mathcal{A}$, and that the force $f = p\mathcal{A}$. Hence the gas performs a work

$$\mathrm{d}W = f\mathrm{d}x = (f/\mathcal{A})(\mathcal{A}\mathrm{d}x) = p\mathrm{d}V \ , \tag{2.3}$$

where $\mathrm{d}V$ is the change in system volume brought about by the expansion. In addition, from the relation between entropy change and heat $\mathrm{d}S = \left(\frac{\mathrm{d}Q}{T}\right)_q$, we have

$$\mathrm{d}Q = T\mathrm{d}S \ , \tag{2.4}$$

where T is the temperature of the system and its environment — recall that for a quasistatic process, the system is presumed to be in thermal equilibrium with its environment. These two expressions allow us to rewrite the first law (equation 1.1)

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V \ . \tag{2.5}$$

We note that this expression is mathematically equivalent to the change of a function E that depends on two independent parameters S and V,[1]

$$\mathrm{d}E = \underbrace{\left(\frac{\partial E}{\partial S}\right)_V}_{=T} \mathrm{d}S + \underbrace{\left(\frac{\partial E}{\partial V}\right)_S}_{=-p} \mathrm{d}V \ . \tag{2.6}$$

where the subscripts V and S have been added to make explicit that the partial derivatives $\frac{\partial E}{\partial S}$ and $\frac{\partial E}{\partial V}$ are derivatives taken at constant V and S, respectively. Moreover, the energy of the gas can also change if we add more particles to it, $i.e.$, change the number of particles N. Consequently, the energy will then be a function $E(S, V, N)$ that depends on the independent parameters S, V, N, such that

$$\mathrm{d}E = \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}}_{=T} \mathrm{d}S + \underbrace{\left(\frac{\partial E}{\partial V}\right)_{S,N}}_{=-p} \mathrm{d}V + \underbrace{\left(\frac{\partial E}{\partial N}\right)_{S,V}}_{=\mu} \mathrm{d}N \ , \tag{2.7}$$

where we have defined the *chemical potential* $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$ as the change in the energy of the system upon adding another particle.[2] For an ideal classical gas, we had found (equation 1.7) that $E = \frac{3}{2}Nk_BT$, in which case $\mu = \frac{3}{2}k_BT$ represents the energy per particle. For systems with interaction particles, however, μ is generally a function of N. We can now define:

The fundamental relation of thermodynamics. The state functions E, S, T, V, p, N and μ satisfy the differential relation

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\mathrm{d}N \ . \tag{2.8}$$

In stating the fundamental relation of thermodynamics, we have implied that:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \ , \quad p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \ , \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \ . \tag{2.9}$$

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[1]For a function $f(x, y)$, we can express changes in this function as $\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y$, depending of changes in the independent parameters x, y.

[2]We here treat N as a continuous variable (rather than discrete, as the integer number N should be), an approximation that we expect to be increasingly accurate if the number of particles increases.

Indeed, we may *define* the (intensive) state variables temperature, pressure and chemical potential as partial derivatives of energy to the (extensive) state variables entropy, volume and number of particles, respectively.[3] Temperature and entropy, pressure and volume (up to a sign), and number of constituents and chemical potential are so-called *conjugate* thermodynamic variables. In the next section, we shall see how to make use of the fundamental relation to obtain criteria that identify the equilibrium state of a system given certain external conditions.

Finally, we can rewrite the fundamental relation (equation 2.8) as

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N \tag{2.10}$$

$$= \left(\frac{\partial S}{\partial E}\right)_{V,N}\mathrm{d}E + \left(\frac{\partial S}{\partial V}\right)_{E,N}\mathrm{d}V + \left(\frac{\partial S}{\partial N}\right)_{E,V}\mathrm{d}N \ , \tag{2.11}$$

such that we can define temperature, pressure and chemical potential as partial derivatives of the entropy of a system:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \ , \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \ , \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V} \ . \tag{2.12}$$

2.2 Equilibrium via minimisation of energy

Let us now go back to the example of a marble moving in a harmonic potential, as described at the beginning of this chapter. Its energy E will be a function of entropy S, volume V and number of particles N, and equilibrium is found by determining the minimum of E as a function of some parameter — here the marble position x — for a given, constant S, V, and N. In this case, it is obvious that V and N are constant, since there are no changes in volume or in number of particles $(\mathrm{d}V = \mathrm{d}N = 0)$. Yet it is instructive to more carefully consider the changes in entropy that are relevant here as the marble approaches its equilibrium position.

While moving through the potential, the marble will normally experience some friction, which will generate heat that is transferred to the environment. The first law (with $\mathrm{d}V = 0$ and thus $\mathrm{d}W = 0$ here) postulates that we can write $\mathrm{d}E = \mathrm{d}Q$ for changes in energy of the marble, where $\mathrm{d}Q$ — as usual — is defined as the heat flowing *into* the system. With our definition of $\mathrm{d}Q$ as the heat flowing into the system, the generated heat will imply a transfer of $-\mathrm{d}Q$ to the environment, where we expect $\mathrm{d}Q \le 0$.

Due to this heat transfer, the entropy of the environment increases by $\mathrm{d}S_{env} = -\mathrm{d}Q/T_{env}$, as applies for quasistatic heat transfer. We can assume that the process is quasistatic for the heat flowing into the environment, as the resulting changes are small and hence gradual for the (presumed large) environment (we can also assume T_{env} is unaffected). Note, however, that this may not be true for the (small) system of the marble, such that we can*not* generally write the change in entropy of the marble changes as $\mathrm{d}S = \mathrm{d}Q/T$. After all, the marble is *not* in equilibrium with its environment until it has settled at its equilibrium position, so this heat transfer away from the marble is not quasistatic. However, we are interested in the energy E of the marble when its entropy S is constant (just like V and N), *i.e.* when $\mathrm{d}S = 0$, and we can write the total change in entropy as

$$\mathrm{d}S_{total} = \mathrm{d}S + \mathrm{d}S_{env} = 0 - \frac{\mathrm{d}Q}{T_{env}} \quad \Rightarrow \quad \mathrm{d}S_{total} = -\frac{\mathrm{d}Q}{T_{env}} \ . \tag{2.13}$$

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[3]The extensive nature of entropy will become clearer later.

We therefore find for the energy

$$\mathrm{d}E = \mathrm{d}Q = -T_{env}\mathrm{d}S_{total} \leq 0 \;, \tag{2.14}$$

where the inequality follows from the second law, because $\mathrm{d}S_{total} \geq 0$ (and by the third law $T_{env} > 0$). So we find that $\mathrm{d}Q \leq 0$ as expected.

This simple example demonstrates and illustrates several relevant points, all implied in the laws of thermodynamics:

- for a system at constant S, V, and N, the minimisation of its energy corresponds to a maximisation of the entropy of the system and its environment;

- in approaching equilibrium, there is a change in total entropy, $\mathrm{d}S_{total} > 0$, which is associated with the generation and exchange of heat;

- this change in entropy also implies the dissipation of kinetic energy in the system, irreversibly driving the system to equilibrium (in a reversible process, the static particle in equilibrium would somehow need to regain kinetic energy and resume its oscillation in the potential);

- when such a system has reached equilibrium (with its environment), $\mathrm{d}E = \mathrm{d}Q = -T_{env}\mathrm{d}S_{total} = 0$, implying that there is no exchange of heat between the system and its environment.

Moreover, it illustrates that any practical classical dynamic system will ultimately come to a standstill if left to its own devices, at a minimum potential energy, as a consequence of the second law.

However, in this example we have ignored the thermal energy of the marble motion. When considering the ideal gas, we found that temperature could be related to the kinetic energy of a particle, where the kinetic energy is $E_{kin} \sim k_B T$ per particle (see equation 1.7). Hence as long as the system is in equilibrium with an environment (also called "reservoir" or "thermal bath") at a temperature $T > 0$, it will never reach the equilibrium energy as predicted by the minimisation of E.[4] This indicates that we may need to define another type of energy that can be minimised to determine the equilibrium of a system at a specific, constant temperature T. In this particular case, this other type of energy, or potential, would therefore need to be a function of T, and not of S like the energy E.

2.3 Legendre transformations and thermodynamic potentials

To define a potential that can be a function of independent state variables T, V, N instead of S, V, N, we consider the quantity

$$F = E - T\,S = E - \left(\frac{\partial E}{\partial S}\right)_{V,N} S \;, \tag{2.15}$$

i.e., we take the entropy S multiplied by its *conjugate* $\left(\frac{\partial E}{\partial S}\right)_{V,N} = T$, and subtract this from the energy. We can now consider any changes in this quantity, writing as before (equation 2.7)

$$\mathrm{d}F = \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}\mathrm{d}S}_{=\,T\,\mathrm{d}S} + \underbrace{\left(\frac{\partial E}{\partial V}\right)_{S,N}\mathrm{d}V}_{=\,-p\,\mathrm{d}V} + \underbrace{\left(\frac{\partial E}{\partial N}\right)_{S,V}\mathrm{d}N}_{=\,\mu\,\mathrm{d}N} - \underbrace{S\,\mathrm{d}\left(\frac{\partial E}{\partial S}\right)_{V,N}}_{=\,S\,\mathrm{d}T} - \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}\mathrm{d}S}_{=\,T\,\mathrm{d}S} \;, \tag{2.16}$$

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[4]All this applies to a classical particle. A quantum-mechanical oscillator will *always* retain some energy above the minimum potential energy, even for $T \to 0$.

where the latter two terms were obtained by applying the chain rule to $\mathrm{d}\left(\left(\frac{\partial E}{\partial S}\right)_{V,N} S\right)$. Since the first and the last term in equation 2.16 cancel, we find

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N \ . \tag{2.17}$$

demonstrating that $F = F(T, V, N)$ called the Helmholtz free energy, which is a function of independent variables T, V, and N as required.

To find the equilibrium of a system at constant T, V, N, we therefore proceed by minimising F in a similar way as we previously minimised E. Noting that we now consider the case of $\mathrm{d}T = \mathrm{d}V = \mathrm{d}N = 0$, and using the first law, we find that

$$\mathrm{d}F = \mathrm{d}E - S\,\mathrm{d}T - T\,\mathrm{d}S = \mathrm{d}Q - T\,\mathrm{d}S \ . \tag{2.18}$$

As before (see equation 2.13), we may write $\mathrm{d}S_{env} = -\mathrm{d}Q/T_{env}$, and noting that the system temperature T is now equal to the temperature of the environment T_{env}, this can be rewritten as

$$\mathrm{d}F = -T\,(\mathrm{d}S_{env} + \mathrm{d}S) = -T\,\mathrm{d}S_{total} \leq 0 \ . \tag{2.19}$$

Hence, the second law $\mathrm{d}S_{total} \geq 0$ is equivalent, under these conditions, to $\Delta F \leq 0$: for a system with a fixed temperature, fixed volume and fixed number of particles, the minimisation of F corresponds to the maximisation of the entropy .

To find F, we have made use of a so-called Legendre transformation, which is a mathematical tool to switch from a description (a function, f) in terms of an independent variable A to a description (another function, g) in terms of $a = \frac{\partial f}{\partial A}$, *i.e.*, in terms of the conjugate of A.

Legendre transform. The Legendre transform $g(a, B, C, D, \dots)$ of the function $f(A, B, C, D, \dots)$ with respect to the variable A is given by

$$g = f - \left(\frac{\partial f}{\partial A}\right)_{B,C,D,\dots} A = f - aA \ , \tag{2.20}$$

where $a = \left(\frac{\partial f}{\partial A}\right)_{B,C,D,\dots}$ is the conjugate of A.

For example, we can consider the Legendre transform

$$g\left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right) = f(A) - \left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right) A \tag{2.21}$$

of a function $f(A)$, noting that

$$\mathrm{d}g = \mathrm{d}f - A\,\mathrm{d}\left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right) - \left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right)\mathrm{d}A \tag{2.22}$$

$$= \left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right)\mathrm{d}A - A\,\mathrm{d}\left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right) - \left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right)\mathrm{d}A = -A\,\mathrm{d}\left(\tfrac{\mathrm{d}f}{\mathrm{d}A}\right) \ , \tag{2.23}$$

so g is a function of the conjugate of A only.[5] As illustrated above (equation 2.16) with the Legendre transform $F(T, V, N)$ of the energy $E(S, V, N)$, this technique can easily be generalised to functions of any number of variables, and is of great relevance to thermodynamics, of which the formal description is centred on the identification of independent state functions that in turn determine the relevant thermodynamic potentials.

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[5]Note that the partial derivatives ∂ have here been replaced by standard derivatives d, as the difference between ∂ and d becomes meaningless for a function of one variable only.

Name	Definition	Minimum describes equilibrium at fixed
Energy	E	S, V, N
Helmoltz free energy	$F = E - TS$	T, V, N
Enthalpy	$H = E + pV$	S, p, N
Gibbs free energy	$G = E + pV - TS$	T, p, N
Grand potential	$\Phi = E - TS - \mu N$	T, V, μ

Table 2.1: A list of thermodynamic potentials.

All other thermodynamic potentials can be derived by repeated Legendre transforms starting from the energy E. The minimisation of these potentials allows one to predict the equilibrium state when the independent state functions on which the potential explicitly depends are kept constant. This formalism accounts for the extraordinary predictive power of classical equilibrium thermodynamics. A zoology of standard thermodynamic potentials can be found in table 2.1. Note that all such potentials are extensive state functions.

Conveniently, the various state variables can be expressed as suitably chosen partial derivatives of these potentials. For example, noting that the grand potential $\Phi = F - \mu N$ and that $\mathrm{d}F$ is given by equation 2.17, we can write

$$\begin{aligned} \mathrm{d}\Phi &= \mathrm{d}F - \mu\,\mathrm{d}N - N\,\mathrm{d}\mu = (-S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N) - \mu\,\mathrm{d}N - N\,\mathrm{d}\mu \\ &= -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu \ , \end{aligned} \tag{2.24}$$

such that

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu} \ , \quad p = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} \ , \quad N = -\left(\frac{\partial\Phi}{\partial \mu}\right)_{T,V} \ . \tag{2.25}$$

2.4 The ideal classical gas subject to gravity

At this point, after having defined a number of so far rather abstract thermodynamics potentials, and as an introduction to statistical mechanics, it may be useful to consider a relatively simple example. We consider a room full of air molecules, such as a room we may be in at this very moment, subject to gravitation and in thermal equilibrium with its environment at temperature T. For the sake of this discussion, the precise molecular composition of air is of little relevance.

Taking into account the thermal energy of each molecule (equation 1.7), the energy E_1 of each air molecule is given by

$$E_1(h) = \tfrac{3}{2}k_B T + mgh \ , \tag{2.26}$$

where m is the mass of a molecule, $g \approx 9.8$ m s^{-2} the gravitational acceleration, and h the height above the floor, and where we assume that the the temperature T is constant. This energy is minimal when $h = 0$, leading to the prediction that the equilibrium state is one in which all molecules have condensed at the floor, depleting the rest of the room from air. This may indeed be the case if the temperature drops to sufficiently low values (below $T = 80$ K, air will liquify), but we know from daily experience that this prediction is wrong at room temperature.

Alternatively, we may consider the air as an ideal classical gas, such that ($pV = Nk_B T$, see equation 1.3)

$$p = n_V k_B T \ , \tag{2.27}$$

where n_V is the number of gas molecules per unit volume. Since we have assume T to be constant, we can calculate the derivative

$$\frac{\mathrm{d}p}{\mathrm{d}h} = \left(\frac{\mathrm{d}n_V}{\mathrm{d}h}\right) k_B T . \tag{2.28}$$

We can also find an alternative expression for $\mathrm{d}p/\mathrm{d}h$, by considering the pressure $\mathrm{d}p$ that is exerted by a layer of air between h and $h + \mathrm{d}h$, acting on the air below it over an area $\mathcal{A}$. This pressure arises because of the gravitational force f due to all molecules contained in the volume $\mathcal{A} \times \mathrm{d}h$ of the layer of air,

$$\mathrm{d}f = - \underbrace{(mg)}_{\text{force on 1 molecule}} \times \underbrace{(n_V \mathcal{A} \mathrm{d}h)}_{\text{number of molecules in volume}} , \tag{2.29}$$

where the minus sign arises because the force is pointing downwards, whereas the increase in height $h > 0$. Since the pressure $p = f/\mathcal{A}$, our expression for $\mathrm{d}p/\mathrm{d}h$ then follows from

$$\frac{\mathrm{d}p}{\mathrm{d}h} = \frac{1}{\mathcal{A}} \frac{\mathrm{d}f}{\mathrm{d}h} = -mgn_V . \tag{2.30}$$

By comparing the two expressions (Equations 2.28 and 2.30) for $\mathrm{d}p/\mathrm{d}h$ and solving the resulting differential equation, we obtain

$$\frac{\mathrm{d}n_V}{\mathrm{d}h} = \left(-\frac{mg}{k_B T}\right) n_V \quad \Rightarrow \quad n_V(h) = n_0 \exp\left(-\frac{mgh}{k_B T}\right) = \tilde{n}_0 \exp\left(-\frac{E_1(h)}{k_B T}\right) , \tag{2.31}$$

where n_0 is the density of air molecules for $h = 0$, and where we have rewritten the solution in terms of the energy $E_1(h)$ by defining the constant $\tilde{n}_0 = n_0 \exp\left(\frac{3}{2}k_B T/k_B T\right) = n_0 \exp(3/2)$. Hence we find that the distribution of air molecules in the room decays exponentially with the height h, or more precisely, with the (potential) energy of the molecules normalised to $k_B T$. This is an example of the *Boltzmann distribution*, which we will encounter again later.

At room temperature (about 300 K), $k_B T \approx 4.1 \times 10^{-21}$ J $\sim 10^{-21}$ N m, and for a height of a few meters, $mgh \sim 10^{-26}$ kg $\times$ 10 m s^{-2} $\times$ 1 m $= 10^{-25}$ N m, such that $mgh/k_B T \sim 10^{-4}$ and its exponent $\exp(10^{-4}) \approx 1$. That is, the density of air molecules at the top of the room is hardly smaller than at the bottom of the room, and we can still breathe. However, for heights of $10^3 - 10^4$ m, the drop in air density becomes much more noticeable, and at such heights it is indeed harder to breathe. At high altitudes, this leads to altitude sickness and to the need for oxygen flasks for climbing Mount Everest.

Yet this does of course not *explain* why the air molecules don't appear to follow the second law and not all approach the minimum of their potential energy at $h = 0$.

Let us therefore now consider two holed boxes in this room, box α and box β, with volumes V_α and V_β, and located at heights h_α and h_β, respectively. Air molecules will move freely in and out of these boxes, but we can safely assume that the number of molecules in these two boxes at all times will be very close to $N_\alpha = n_V(h_\alpha) V_\alpha$ and $N_\beta = n_V(h_\beta) V_\beta$. We can next ask the question what is the *probability* P that an air molecule is located in one of these boxes, e.g., in box α. This probability will simply be given by $P_\alpha(h_\alpha, V_\alpha) = N_\alpha/N$, where N is the total number of molecules in the room. Making the dependence on height and volume explicit, we can now write

$$\frac{\text{probability that a molecule is in box } \alpha}{\text{probability that a molecule is in box } \beta} = \frac{P_\alpha(h_\alpha, V_\alpha)}{P_\beta(h_\beta, V_\beta)} = \frac{V_\alpha \exp\left(-\frac{E_1(h_\alpha)}{k_B T}\right)}{V_\beta \exp\left(-\frac{E_1(h_\beta)}{k_B T}\right)} . \tag{2.32}$$

Moreover, we can discretise the room into a large number of equally spaced lattice points, with ν the volume of each lattice site, such that $V_{\alpha,\beta} = \Omega_{\alpha,\beta}\,\nu$, with Ω_α and Ω_β the number of lattice sites in box α and β, respectively. Here, we do not need to worry about lattice sites being occupied or not, since for an ideal classical gas, we have assumed that the gas molecules do not interact. With these ingredients, we can rewrite $V \exp\left(-E_1/k_B T\right) = \Omega\,\nu \exp\left(-E_1/k_B T\right) = \nu \exp\left(-(E_1 - Tk_B \ln \Omega)/k_B T\right)$. Therefore,

$$\frac{P_\alpha(h_\alpha, V_\alpha)}{P_\beta(h_\beta, V_\beta)} = \frac{\exp\left(-\frac{E_1(h_\alpha) - Tk_B \ln \Omega_\alpha}{k_B T}\right)}{\exp\left(-\frac{E_1(h_\beta) - Tk_B \ln \Omega_\beta}{k_B T}\right)} \equiv \frac{\exp\left(-F_\alpha/k_B T\right)}{\exp\left(-F_\beta/k_B T\right)} \,, \tag{2.33}$$

where we have written $F_{\alpha,\beta} = E_1(h_{\alpha,\beta}) - Tk_B \ln \Omega_{\alpha,\beta}$. This implies that even when $E_1(h_\alpha) < E_1(h_\beta)$, box β might still be the preferred location, if it contains a number of lattice sites Ω_β that is sufficiently larger than Ω_α. Overall, the preferred location will be with the smallest free energy F, instead of the smallest energy E_1. As before in the case of a constant temperature, we find that minimisation of free energy determined the equilibrium of a system.

In this discussion, we have identified $F = E - Tk_B \ln \Omega$ as the Helmholtz free energy, $F = E - T\,S$ (equation 2.17), which would suggest that we can identify $S = k_B \ln \Omega$. This is *Boltzmann's definition of entropy*, to which we will come back later. Briefly, it implies that entropy is related to the number of ways in which we can configure a system.

For our room full of air molecules, the molecules do not all gather in a small volume on the floor, because the number of lattice sites in this volume and therefore the entropy would be much smaller than the number of lattice sites in the rest of the room. In other words, by spreading over the whole room, the air molecule maximise entropy, in agreement with the second law. For this case, the room is presumed to remain at constant temperature, not constant entropy, so the maximisation of entropy corresponds to a minimisation of the Helmholtz free energy, and not (necessarily) to a minimisation of energy.

2.5   Summary

We have seen that different state variables are related via the *fundamental relation of thermodynamics*,

$$\mathrm{d}E = \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V,N}}_{=\,T} \mathrm{d}S + \underbrace{\left(\frac{\partial E}{\partial V}\right)_{S,N}}_{=\,-p} \mathrm{d}V + \underbrace{\left(\frac{\partial E}{\partial N}\right)_{S,V}}_{=\,\mu} \mathrm{d}N \,,$$

and in doing so noted that T and S, p and V, and μ and N are pairs of *conjugate* variables, where T, p and the *chemical potential* μ are intensive, and S, V and N extensive variables.

Expressed as a function of independent variables, we have the *thermodynamic potentials* energy $E(S, V, N)$, the Helmholtz free energy $F(T, V, N)$, the enthalpy $H(S, p, N)$, the Gibbs free energy $G(T, p, N)$, and the grand potential $\Phi(T, V, \mu)$. The equilibrium of a system can be found by minimising these potentials, which corresponds to maximising the entropy in accordance with the second law for the case when the independent variables of the potential are constant.

These thermodynamic potentials can be found from the energy $E(S, V, N)$ by applying *Legendre transformations*. A Legendre transformation is a mathematical tool to transform a function $f(A, B, C, D, \dots)$ into a new function $g(a, B, C, D, \dots) = f - \left(\frac{\partial f}{\partial A}\right)_{B,C,D,\dots} A$ that is not dependent on A anymore but on the *conjugate* of A, namely the partial derivative $\frac{\partial f}{\partial A}$.

For example, a marble moving in a harmonic potential will be subject to friction, generate heat that is transferred to its environment, increasing the overall entropy (second law). By the first law, this implies a loss of energy E, such that the marble eventually reaches its equilibrium at standstill at the bottom of the potential, thus minimising its energy for a given, constant value of its entropy.

In another example, air molecules in a room at constant temperature are subject to gravity. We find that in such a case, the distribution of air molecules is follows an exponential decay with height, according to $\exp\left(-E/k_B T\right)$, which is an example of the *Boltzmann distribution*, to which we will come back in the following chapters. We have argued that in this case, air molecules minimise their free energy. In doing so, we have also introduced the notion of *probability* and the *Boltzmann definition of entropy*, $S = k_B \ln \Omega$, where Ω represents — in this case — the number of ways an air molecule can be accommodated in the system. We will introduce and discuss these concepts more formally hereafter.

Chapter 3

Core concepts of statistical mechanics

God does not play dice. — Albert Einstein (1879–1955).

Statistical thermodynamics is an attempt to relate the phenomenological, macroscopic laws of classical thermodynamics to an underlying quantitative picture of molecular behaviour. Statistical mechanics is a broader term that includes dynamical systems not usually treated in thermodynamics, such as star clusters or even crowds of people. But since thermodynamics is applied to macroscopic quantities of gases, liquids, and solids, containing of the order of 10^{23} particles, this task appears rather daunting. How can we establish the behaviour of this number of particles?

However, we clearly do not need to go so far, since thermodynamic systems seem to be well enough characterised by just a handful of macroscopic quantities: energy, pressure etc, and the relationships between them. If we were to take the trouble of determining the behaviour of every molecule, then our efforts would be magnificent but pointless: the motion of every molecule surely cannot affect the equation of state. The basic assumption of statistical thermodynamics is that the detail of the molecular motion is irrelevant. This leads to the argument that a study of the *likely* or the *average* behaviour of the particles is good enough. The statistical properties at the microscale are therefore our focus of attention, and this requires us to review our understanding of probability.

3.1 The nature of probability

It is commonly stated that if we roll a die, there is a probability of 1/6 that a six will be thrown. Around this apparently simple statement has raged a couple of centuries of philosophical debate.

When we know there to be a variety of outcomes of some event, but we cannot determine which will happen, probability is something we use to weigh the outcomes in order to define our *expectation*. The probabilities we assign to the outcomes could be nothing more than a guess, in which case we would be creating an expectation that might not correlate very well with the actual event. Ideally, we should use some data, or information, to construct a set of probabilities that allow us to make good judgements about the future behaviour. This line of thought is called information theory; the use of probabilities as a basis for logical reasoning. E.g., for the die, we may expect that the 6 sides have equal probability to end facing up, hence each outcome of the die roll is the same and equal to 1/6. On the other hand, it does not sound like a very unique way of proceeding in general: how can we arrive at the best judgement?

Another point of view is that we should determine the actual frequencies with which each event should turn up in a number of trials, and use these to weigh the outcomes. Then it would seem

that we could derive an expectation that is tied to real documented behaviour, albeit from the past. However, the problem is that this is a unique approach only if we run an infinite number of trials. Otherwise the frequencies would only be estimates. If we do not have time for that many trials, there are sophisticated ways of estimating the errors. Alternatively we revert to making a judgement about the probabilities, based on the limited set of data, in other words go back to the information theoretic approach.

Whether the numerical values are generated by some sort of judgement, or from trial data, the probabilities that we actually use to weigh the events have to satisfy the same rules of arithmetic, so the distinction need not bother us too much at the moment. We can express an intuitive understanding of probability in the form of the following statements:

1. For each possible outcome i there is a positive probability $P(i)$ denoting the statistical weighing for it to arise in a trial, such as the rolling of a die.

2. The sum of the $P(i)$ for all possible outcomes of a trial is unity, *i.e.*, $\sum_i P(i) = 1$.

3. Intuitively, outcomes related through some symmetry in the system should have the same probability, hence to begin with, we guess that the probabilities for each outcome of the die roll are 1/6.

4. The probability that either outcome i *or* outcome j should occur is given by the sum $P(i) + P(j)$, as long as the two outcome are mutually exclusive. So the probability of throwing a five or a six is 1/3.

5. There is a probability $P_2(i, j)$ of joint outcomes, for example outcome i as well as outcome j. If the events are *uncorrelated*, *i.e.* the outcome of one trial is unaffected by the outcome of another, then the joint probability is the product of individual probabilities: $P_2(i, j) = P(i)P(j)$. The trials are said to be *independent*. If the outcomes are correlated, this factorisation does not apply. Thus the probability of throwing two sixes with two normal dice is $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. If, on the other hand, the dice are connected in some spooky way, such that they never produce the same number, then the probability of two sixes is zero. The two outcomes in this case are correlated. This idea extends to longer sequences, $P_3(i, j, k)$ etc. The joint probability can be expressed as a product of the probability of the first outcome times a *conditional* probability of the second outcome given the first, *i.e.*, $P_2(i, j) = P(i|j)P(j)$. The vertical line should be read as 'given'. The idea of independence is that $P(i|j) = P(i)$.

In the following, we will describe how to quite generally determine the probability of a system to be found in a particular "state", equivalent to the probability for a roll of dice to give a particular "outcome". In doing so, we will introduce various key concepts of statistical mechanics.

3.2 Microstates, macrostates and multiplicity of microstates

Although Einstein's famous quote (*God does not play dice* — stated in relation to quantum physics) suggests that this is not such a valuable endeavour, statistical mechanics involves a lot of playing dice, and we can gain some intuitive understanding of its key concepts by doing so. A standard die contains six sides with the numbers 1, 2, 3, 4, 5, 6, and has equal probability to end up with any of these sides facing upwards. If we roll two dice, we can obtain various combinations of results, e.g., (1,1), (2,5), (6,3), etc., where we distinguish between the first and the second die. For most games, the property that matters most is the sum of the two dice, *i.e.*, $1 + 1 = 2$, $2 + 5 = 7$, $6 + 3 = 9$, etc., which can range between a minimum of 2 and a maximum of 12.

We can now define (1,1), (2,5), (6,3), etc. as "microstates" of the system, formulated more generally as:

> **Microstate.** A microstate denotes a description of a system where all the values of the dynamical variables are exactly specified.

The whole set of dynamical variables of a generic system may be represented by a set of continuous and/or discrete variables that belong to a generic space often referred to as the "*phase space*" (nothing to do with a phase diagram). E.g., these variables can be all positions and momenta of the particles of a gas, all the zeros and ones in the hard disk of a computer..., or in the case of the two dice, all possible combinations of 1 and 6, which may be plotted as a two-dimensional phase space with as numbers (the sums) on a two-axis coordinate system with both the horizontal axis (one die) and the vertical axis (the other die) ranging from 1 to 6.

In statistical mechanics, one does not track every microscopic dynamical variable, which would be beyond the possibilities of any calculator. Fortunately, as discussed in the context of state variables, regularities emerge in systems involving large numbers of constituents, where statistical methods are successful. In such cases, a detailed, microscopic description is redundant in predicting collective properties. In that case, it is advantageous to consider a coarse-grained description of systems through the notion of "macrostate":

> **Macrostate.** A macrostate denotes a collection of system microstates with a common property.

For instance, a macrostate of a gas could be defined as the set of microstates of the gas with the same pressure, or the set of microstates with the same volume and temperature, or the set of microstates with the same energy (or also any other, possibly more convoluted, prescription). In the example of the two dice, a meaningful "common property" could be given — and hence a macrostate defined — by the sum of the two dice.

It then emerges immediately that some macrostates are more likely than others. For example, the macrostates of 2 and 12 are rather rare for the two dice, because for each of them, there is only one combination by which they can be obtained. That is, they are rare because each of them corresponds to only a single microstate, (1,1) and (6,6), respectively. By contrast, the most likely macrostate is 7, since there are six microstates that correspond to this macrostate, namely (1,6), (2,5), (3,4), (4,3), (5,2), and (6,1). We therefore state that the *microstate multiplicity* $\Omega = \Omega_2 = \Omega_{12} = 1$ for the macrostates that are defined by the end results 2 and 12, whereas, e.g., $\Omega_7 = 6$.[1] This brings us to the suggestion that the probability of a macrostate generally scales with its microstate multiplicity.

Moreover, in considering the rolling of two dice, we have made the implicit assumption that each distinct combination of results has the same probability to occur. That is, even though the sum result 7 may be more common than 3, the microstate (3,4) is not more likely than the microstate (1,2). As noted in our discussion on probabilities above, each of these microstates has a probability $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$, but the probability for finding the system in the macrostate 7 is given by $\Omega_7 \times \frac{1}{36} = \frac{6}{36}$, which is larger than the probability of finding the system in macrostate 3 ($\Omega_3 \times \frac{1}{36} = \frac{2}{36}$). This brings us to the following working hypothesis:

> **Principle of equal a priori probabilities.** An isolated system in equilibrium occupies each accessible microstate with the same probability.

---

[1]Note that this definition of Ω is equivalent to the one used in equation 2.33, where Ω represents the number of positions at which an air molecule can be placed within a given volume.

There are significant problems when it comes to justifying this principle in realistic physical systems. On the positive side, it is known that if a system evolves according to classical or quantum mechanical Hamiltonian dynamics, and if the probability of every microstate is initially the same, then they will remain equal in the future, a result known as Liouville's theorem. Effort has gone into investigating the *ergodic hypothesis*; the idea that such dynamics really do take a system into each and every microstate with equal frequency after an infinite amount of time. This has produced some supportive conclusions, but actually it rather misses the point, since the principle is only a working hypothesis: a simple way of arriving at predictions of behaviour, and we are prepared to modify it if need be.

And even if the dynamics were ergodic, they would generate equally frequent visits to each microstate only after an *exceedingly* long time; at least as long as the time needed to see the original configuration restored (this is called the Poincaré recurrence time and it can be estimated to be greater than the age of the universe for even quite small physical systems). Only a very small sample of the microstates will be actually be visited during a particular observation period. It is seriously crazy to claim that each microstate of a realistic dynamical system in equilibrium would actually turn up with equal *frequency* upon making measurements over a finite period. But that does not stop us using the principle of equal a priori probabilities as a *model* of the world: we just have to remember that the probabilities assigned to the microstates are not frequencies but representations of our best judgement, based on insufficient data, but guided by ideas of even-handedness in the absence of full information.

3.3   Boltzmann's entropy and the second law

Let us now go back to the example of air molecules in a room, starting with all molecules in the room contained in a small box, and the rest of the room being vacuum. When we open the box, the molecules will gain access to a much larger number of microstates — *i.e.*, different possible arrangements of the molecules in the room. By opening the box, we allow the molecules to explore this much larger phase space and fill the room. This spreading out of the air is of entirely probabilistic nature: the probability of a specific air molecule being *anywhere* in the room is simply much larger than the probability of it being within one specific small volume (such as the box), by the principle of equal a priori probabilities. By the second law, this evolution towards occupation of a larger number of microstates Ω coincides with an increase in entropy ($S \geq 0$). Note that exactly the same argument also explains why a droplet of ink in a glass of water colours the entire glass, instead of the ink molecules remaining within the small droplet volume.

Ludwig Boltzmann's (1844–1906) key insight was this association of the macroscopic state variable entropy with the number (or multiplicity) of microstates available. Based on our previous considerations of entropy and other thermodynamic parameters, we expect entropy to by an *extensive* state variable. That is, if we consider two equally sized volumes V in our room (with equal amounts of air molecules), the entropy $S_{2V} = 2S_V$. Yet in doubling the volume, we *square* the number of available microstates, $\Omega_{2V} = \Omega_{1V}^2$, since for for each single microstate of the first volume, there are Ω microstates of the second. This is the same reasoning as by which there are $6^2 = 36$ possible microstates for a roll of two dice, while there are 6 for a single dice. As a consequence, an entropy of the form $S \propto \Omega$ would not be extensive. By contrast, $\ln \Omega$ is extensive, since $\ln \Omega_{2V} = \ln \Omega_{1V}^2 = 2 \ln \Omega_{1V}$. This leads to the definition:

> **Boltzmann entropy.** The thermodynamic entropy S of a system in a macrostate with multiplicity Ω is given by
>
> $$S = k_B \ln \Omega, \tag{3.1}$$
>
> where k_B is the Boltzmann constant.

The Boltzmann constant k_B has units of Joule per Kelvin, since TS must have units of energy. That said, the presence of k_B in the expression for entropy is entirely conventional: entropies could be defined, as customary in information theory, as dimensionless (e.g. writing $S = \ln \Omega$). In thermodynamics, this would be possible and perfectly consistent if temperature were measured in units of energy rather than degrees Kelvin. The number of microstates Ω is also known as the *statistical weight*, sometimes denoted as W, as in the famous inscription "$S = k \log W$" on Boltzmann's tombstone, which can still be visited in Vienna. Sadly, Boltzmann hanged himself at the age of 52, while on vacation in Italy with his wife and daughter.

Of course, to verify the validity of Boltzmann's expression, we need to show that it reproduces known results for the thermodynamic entropy of a system such as the ideal gas expression (1.14). As we will see later, this is indeed the case.

3.4   The canonical distribution

We have postulated that *for a closed, isolated system*, the probability $P(i)$ of every microstate i is the same. This implies that the probability $P(\text{macrostate})$ for a macrostate can be related to the microstate multiplicity $\Omega(\text{macrostate})$ of that macrostate, *i.e.*,

$$P(\text{macrostate}) \propto \Omega(\text{macrostate}) , \tag{3.2}$$

This applies for a closed, isolated system, which is also denoted as a *microcanonical ensemble.*

Yet we often deal with systems that are *not closed or isolated.* In the example of the room filled with air molecules as discussed before, the room was assumed to be held at constant temperature by remaining in equilibrium with its environment. This is a case of a system in contact with a — usually presumed much larger — *reservoir.* The total of the system and the reservoir can be assumed to be a closed system in itself, with a constant energy E_{tot} and a constant number of particles N_{tot} (as well as a constant volume V_{tot}).

Let us first consider the case in which the system can exchange energy with a large reservoir, also denoted as a *canonical ensemble.* This implies that for our chosen system, the probability $P(i)$ of every system microstate is generally *not* the same, because we need to take into account that by selecting a particular microstate, the system changes the number of microstates in the reservoir Ω_r. If the system occupies a microstate with energy E, the energy available to the reservoir E_r will be changed to $E_r = E_{tot} - E$, such that we can write the probability

$$P(E) \propto \Omega_r(E_r) = \Omega_r (E_{tot} - E) \tag{3.3}$$

for the system occupying a particular microstate with energy E.[2]

Since we have assumed the reservoir to be large compared with the system (in energy, number of particles and volume), we can safely assume $E \ll E_{tot}$. Consider the energy of the reservoir E_r

---

[2]Correspondingly, as we will do below, we can write $P(E) \propto \Omega(E)\Omega_r(E_r)$ for the probability of the system occupying a particular *macrostate* with energy E, where $\Omega(E)$ denotes the multiplicity of the macrostate within the system itself. If this multiplicity $\Omega(E) = 1$, this distinction becomes irrelevant, of course.

as a continuous variable, we can then make the Taylor expansion

$$\ln \Omega_r(E_{tot} - E) = \ln \Omega_r(E_{tot}) - E \left. \frac{\partial \ln \Omega_r(E_r)}{\partial E_r} \right|_{E_r = E_{tot}} + \cdots \tag{3.4}$$

$$\approx \ln \Omega_r(E_{tot}) - \beta E , \tag{3.5}$$

where we have ignored terms in E^2 and beyond, and defined

$$\beta = \left. \frac{\partial \ln \Omega_r(E_r)}{\partial E_r} \right|_{E_r = E_{tot}} = \frac{1}{k_B} \left. \frac{\partial S_r(E_r)}{\partial E_r} \right|_{E_r = E_{tot}} = \frac{1}{k_B T} . \tag{3.6}$$

We can think of β as the value of a partial derivative for $E_r = E_{tot}$, but the Boltzmann expression $S_r = k_B \ln \Omega_r$ has allowed us to rewrite this in terms of the entropy. Hence by having expanded $\ln \Omega_r$ instead of Ω_r itself, we can directly relate the result to the entropy of the reservoir. In the final step, we have recalled that $\left(\frac{\partial S_r}{\partial E_r} \right)_{V,N} = 1/T$, where T is the temperature of the reservoir (see equation 2.12).

Substituting equations 3.5, 3.6 into our expression for the probability $P(E)$, we find

$$P(E) \propto \Omega_r(E_{tot} - E) = e^{\ln \Omega_r(E_{tot} - E)} \approx \underbrace{e^{\ln \Omega_r(E_{tot})}}_{= \text{ constant}} e^{-\beta E} \propto e^{-\beta E} \tag{3.7}$$

The latter term is called the *Boltzmann factor* and leads to the *Boltzmann (or "canonical")* *distribution* for the probability of our system to be in microstate i with energy E_i,

$$P(E_i) = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Z} , \tag{3.8}$$

where $Z = \sum_j e^{-\beta E_j}$ sums the Boltzmann factors for all microstates j, which ensures that the probability is normalised (*i.e.*, $\sum_i P(E_i) = 1$). This result agrees with the Boltzmann distribution as derived previously for the special case of an ideal gas subject to gravity (equation 2.31).

It can also be reformulated in the following, fully equivalent expression for the probability of finding a system of N particles in a *macrostate* with energy E, by explicitly taking into account that each macrostate may represent a multiplicity of microstates (*i.e.*, there may be multiple — $\Omega(E)$ — microstates $k, l, m, \ldots$ with the same energy $E \equiv E_k = E_l = E_m = \ldots$):

The canonical distribution. The probability $P(E)$ for a system in contact with a thermal reservoir to occupy the macrostate with energy E is given by

$$P(E) = \frac{\Omega(E) e^{-\beta E}}{Z} , \tag{3.9}$$

where $\Omega(E)$ is the microstate multiplicity of the system at energy E. The normalisation Z is the *canonical partition function*

$$Z = \sum_E \Omega(E) e^{-\beta E} , \tag{3.10}$$

where the summation extends over all possible values of E.

Note that the latter definition of Z is entirely equivalent with the earlier definition $Z = \sum_j e^{-\beta E_j}$ (see equation 3.8), where the summation extends over all *microstates* j. Finally, we may also rewrite the canonical distribution making use of the definition of the Helmholtz free energy $F = E -$

$TS = E - Tk_B \ln \Omega$, yielding yet another, again equivalent expression of the Boltzmann/canonical distribution,

$$P(E) = \frac{\Omega(E) \mathrm{e}^{-\beta E}}{Z} = \frac{\mathrm{e}^{-\beta(E - Tk_B \ln \Omega(E))}}{Z} \tag{3.11}$$

$$= \frac{\mathrm{e}^{-\beta F(E)}}{Z} , \tag{3.12}$$

where $Z = \sum_F \exp\left(-F/k_B T\right)$ and where the dependence of $P(E)$ on E is implied via the dependence on the Helmholtz free energy F. This demonstrate that we can use the free energy to implicitly take into account the number of microstates when we define the the probability of a macrostate of a system in thermal equilibrium with a reservoir.

3.5 The grand canonical distribution

The arguments in the previous section can easily be expanded to a system that cannot only exchange energy with a large reservoir, but also particles. In that case, we find the probability for the system to be in a particular microstate of energy E

$$P(E, N) \propto \Omega_r(E_r, N_r) = \Omega_r\left(E_{tot} - E, N_{tot} - N\right) , \tag{3.13}$$

where N is now the number of particles in the system. Noting that $E \ll E_{tot}$ and $N \ll N_{tot}$, we can Taylor expand $\ln \Omega_r\left(E_{tot} - E, N_{tot} - N\right)$ to the first order in both E and N, obtaining

$$\ln \Omega_r(E_{tot} - E, N_{tot} - N)$$
$$\approx \ln \Omega_r(E_{tot}, N_{tot}) - E \left.\frac{\partial \ln \Omega_r(E_r, N_r)}{\partial E_r}\right|_{\substack{E_r = E_{tot} \\ N_r = N_{tot}}} - N \left.\frac{\partial \ln \Omega_r(E_r, N_r)}{\partial N_r}\right|_{\substack{E_r = E_{tot} \\ N_r = N_{tot}}} \tag{3.14}$$
$$= \ln \Omega_r(E_{tot}) - \beta E + \beta \mu N ,$$

where we have defined

$$\beta \mu = - \left.\frac{\partial \ln \Omega_r(E_r, N_r)}{\partial N_r}\right|_{\substack{E_r = E_{tot} \\ N_r = N_{tot}}} = -\frac{1}{k_B} \left.\frac{\partial S(E_r, N_r)}{\partial N_r}\right|_{\substack{E_r = E_{tot} \\ N_r = N_{tot}}} , \tag{3.15}$$

where we have again made use of the Boltzmann entropy and find the result enterly consistent with the definition of the chemical potential via $\mu = -T \left(\frac{\partial S_r}{\partial N_r}\right)_{E,V}$, where T is the temperature of the reservoir (see equation 2.12).

Taking now also into account the possibility of microstate multiplicity $\Omega(E, N)$ for any macrostate of the system with energy E and number of particles N, this leads to

The grand canonical distribution. The probability $P(E, N)$ for a system in contact with a thermal reservoir at inverse temperature $\beta = 1/(k_B T)$ and chemical potential μ to occupy the macrostate with energy E and number of particles N is given by

$$P(E, N) = \frac{\Omega(E, N) e^{-\beta(E - \mu N)}}{Z_G} \ , \tag{3.16}$$

where $\Omega(E, N)$ is the system microstate multiplicity at energy E and number of particles N. The normalisation Z_G is the grand canonical partition function

$$Z_G = \sum_{E, N} \Omega(E, N) e^{-\beta(E - \mu N)} \ , \tag{3.17}$$

where the summation extends over all possible values of E and N.

The term grand canonical ensemble, therefore, refers to the preparation of a system in contact with a reservoir at given temperature and chemical potential. Notice that, if one considers a situation where N is constant, the factor $e^{\beta \mu}$ becomes an irrelevant constant (that disappears through normalisation) and one recovers the canonical distribution, which is thus in a sense a specific case of the grand canonical one.

Equivalently, using the grand potential $\Phi = E - TS - \mu N = E - T k_B \ln \Omega - \mu N$, we can rewrite the grand canonical distribution

$$P(E, N) = \frac{\Omega(E, N) e^{-\beta(E - \mu N)}}{Z_G} = \frac{e^{-\beta(E - T k_B \ln \Omega(E, N) - \mu N)}}{Z_G} \tag{3.18}$$

$$= \frac{e^{-\beta \Phi(E, N)}}{Z_G} \ , \tag{3.19}$$

where the dependence of $P(E, N)$ on E and N is now implied via its dependence on the grand potential Φ.

In other words, when a system can exchange energy and particles with a surrounding, large reservoir, its probability to be in a particular state can be expressed via Boltzmann factors $e^{-\beta E}$, $e^{-\beta F}$ or $e^{-\beta \Phi}$, depending on whether the microstate multiplity is of any relevance (*i.e.*, if $\Omega(E, N) > 1$) and on whether there is particle exchange or not (*i.e.*, if N is allowed to change).

3.6   Summary

We have introduced the following core concepts of statistical mechanics, to help us define probabilities for a general '*system*' to occupy particular '*states*':

- A *microstate* of a system denotes a description of the system where all the values of the dynamical variables are exactly specified. That is, each microstate is unique.

- A *macrostate* of a system denotes a collection of microstates that are characterised by a common property, for example by all having the same energy.

- For a closed, isolated system, we have postulated — via the *principle of equal a priori probabilities* — that each microstate is equally likely.

- This implies that the probability P of a particular macrostate is proportional to the number of microstates Ω (also denoted as *multiplicity*) that is contained within that macrostate. Stated

	Microcanonical	Canonical $T = T_r$	Grand canonical $T = T_r, \mu = \mu_r$
Constants	E, N, E_r, N_r	$E_{tot} = E + E_r$, N, N_r	$E_{tot} = E + E_r$, $N_{tot} = N + N_r$
Variables		E, E_r	E, E_r, N, N_r
$P(\text{microstate } i)$	$P(i) = P(j) \; \forall \, i, j$	$\propto \Omega_r(E_{tot} - E_i)$	$\propto \Omega_r(E_{tot} - E_i, N_{tot} - N_i)$
		$P(i) = \mathrm{e}^{-\beta E_i}/Z$	$P(i) = \mathrm{e}^{-\beta(E_i - \mu N_i)}/Z_G$
$P(\text{macrostate})$	$\propto \Omega(\text{macrostate})$	$\propto \Omega(E)\Omega_r(E_{tot} - E)$	$\propto \Omega(E, N)\Omega_r(E_{tot} - E, N_{tot} - N)$
		$P(E) = \Omega(E)\mathrm{e}^{-\beta E}/Z$	$P(E, N) = \Omega(E, N)\mathrm{e}^{-\beta(E - \mu N)}/Z_G$
		$P(F) = \mathrm{e}^{-\beta F(E)}/Z$	$P(\Phi) = \mathrm{e}^{-\beta \Phi(E,N)}/Z_G$
$S_{tot} = \text{max. for}$	constant E, V, N	constant T, V, N	constant T, V, μ

Table 3.1: Summary of characteristics of microcanonical, canonical and grand canonical ensembles, for a system with energy E and number of particles N in contact with a reservoir with energy E_r and number of particles N_r. The given probabilities P refer to probabilities for states of the system. The different ensembles for the system correspond to the maximisation of the total entropy ($S_{tot} = S + S_r$) given specific constraints for state variables of the system; and — for the canonical and grand canonical ensembles — to minimisation of the corresponding thermodynamic potentials. Note that the presence of the reservoir is irrelevant in the case of a microcanonical ensemble and that the total system (system + reservoir) is in itself treated as a microcanonical ensemble in all three cases.

differently, this probability is proportional to the number of ways in which the particular macrostate can be realised by its microscopic components.

- The Boltzmann expression for entropy postulates that $S = k_B \ln \Omega$.

- We distinguish between

  - closed, isolated systems or so called *microcanonical* ensembles;
  - systems that can exchange energy with a large *reservoir*, denoted as *canonical* ensembles;
  - and systems that can exchange both energy and particles with such a reservoir, denoted as *grand canonical* ensembles.

  The characteristics of these ensembles are summarised in table 3.1. All these ensembles can be described in terms of their respective microstates and macrostates[3].

- For a canonical ensemble, the Boltzmann factor $\mathrm{e}^{-\beta E}$ describes how the multiplicity Ω_r of the reservoir depends on the energy E of a microstate of the system. It hence defines the statistical weight and probability of the system to be in such a microstate, with $\beta = 1/k_B T$. The probability of the system to occupy a particular macrostate therefore scales with $\Omega(E)\mathrm{e}^{-\beta E} = \mathrm{e}^{-\beta F}$, with $F = E - TS$ the Helmholtz free energy of the macrostate.

---

[3]Hence a *micro*state does not necessarily refer to a *micro*canonical ensemble. The double meaning of "micro" in this (conventional) terminology may be considered somewhat unfortunate. Similarly, note that the "macro" in *macro*states does not refer to the *large* reservoir)

- For a grand canonical ensemble, this factor also contains a dependency on the number of particles in the system, via $e^{-\beta(E-\mu N)}$. The probability of the system to occupy a particular macrostate therefore scales with $\Omega(E,N)e^{-\beta(E-\mu N)} = e^{-\beta\Phi}$, with $\Phi = E - TS - \mu N$ the grand potential of the macrostate.

- Canonical and grand canonical distributions are obtained by normalising these statistical weights by, respectively, the *canonical partition function*, $Z = \sum_E \Omega(E)e^{-\beta E} = \sum_E e^{-\beta F(E)}$ and the *grand canonical partition function*, $Z_G = \sum_{E,N} \Omega(E,N)e^{-\beta(E-\mu N)} = \sum_{E,N} e^{-\beta\Phi(E,N)}$.

In the absence of microstate multiplicity and particle exchange, the most probable macrostate is the one with the lowest *energy E*, thus maximising $e^{-\beta E}$; if this macrostate contains multiple microstates, the most probable is the one with the lowest *Helmholtz free energy $F(E)$*, maximising $e^{-\beta F(E)}$;[4] and if the system can exchange both energy and particles with its environment, the most probable macrostate is the one with the lowest *grand potential* $\Phi(E.N)$, maximising $e^{-\beta\Phi(E,N)}$.

In the next chapter, we will discuss several examples of microcanonical, canonical and grand-canonical ensembles, and demonstrate how the here defined concepts can be used to calculate their properties.

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[4]Note that if $\Omega(E) = 1$, then $S(E) = k_B \ln \Omega(E) = 0$, and $F(E) = E$.

Chapter 4

Statistical mechanics in action

We now apply the principles developed in the last chapter to some reasonably realistic physical systems. We have already encountered the ideal gas as one such system. Another conceptually useful system is that of a set of N weakly coupled quantum harmonic oscillators that collectively hold Q quanta of energy. We will construct ensembles and obtain statistical information about such systems when they are in equilibrium.

In the example of a quantum harmonic oscillator with natural frequency ω has energy levels

$$E_q = (\tfrac{1}{2} + q)\hbar\omega , \tag{4.1}$$

where q is a non-negative integer. We then have total energy $E = \sum_j (\tfrac{1}{2} + q_j)\hbar\omega$, where the the integer q_j denotes the number of quanta held by the jth oscillator, such that $Q = \sum_j q_j$ is proportional to the total energy apart from a constant that contains all the zero point energies $\tfrac{1}{2}\hbar\omega$.

The oscillators are weakly coupled, in the sense that energy can be exchanged between them, but without complicating the specification of the system energy. This system is in fact very general, since it describes the case of Q energy units ϵ (here $= \hbar\omega$) to be distributed over N particles, boxes, lattice sites, binding sites, ...; and if we make the energy unit ϵ sufficiently small, its application is certainly not limited to quantum oscillators alone. Quite generally, we can think of this system as N boxes over which to distribute Q identical items. For the case of the quantum oscillators, we can assume that each box can fit any number of items.

4.1   Microcanonical ensemble and microstate enumeration

If this system is fully isolated from its environment, it is a microcanonical ensemble: the probability P_i for the system to occupy a macrostate i is given (apart from some normalisation constant) by the multiplicity Ω_i of that macrostate. So the question is how we find Ω_i. While in general this is a daunting task, we can here use a trick that is quite generally applicable to determine how many ways there are to distribute Q identical items over N boxes. Microstates of such a system can be visualised by drawing one circle per item, and by representing the boxes via $N - 1$ bars that separate them. For instance, for a system with $Q = 9$ items distributed over $N = 3$ boxes, a possible microstate is described by the sequence

$$\circ \, \circ \, \circ \, | \, \circ \, \circ \, \circ \, \circ \, | \, \circ \, \circ$$

with here in total $Q = 9$ circles separated by $N - 1 = 2$ bars.

The total number of microstates $\Omega(Q, N)$ then follows by considering how many ways there are to rearrange a total of $Q + (N - 1)$ circles and bars. If we have $Q + N - 1 = 11$ *distinguishable* items (including circles and bars), we have the choice of 11 items to put at the first position of the sequence, of the remaining 10 for the second position, of 9 for the third position, ..., such that the total number of permutations is given by $11 \times 10 \times 9 \times \cdots \times 1 = 11!$. That is, more generally, for $Q + N - 1$ distinguishable items, the number of permutations is given by the factorial $(Q + N - 1)!$.

However, this includes the $Q!$ permutations that exchange circles and the $(N - 1)!$ permutations that exchange bars within themselves. None of these permutations leads to a distinguishable microstate. For comparison, for the roll of two dice considered earlier, we count the outcome (1,1) as only one out of 36 possible outcomes. If we interchange the two dice when each has an identical number facing upwards, this does not lead to a distinguishable microstate. By contrast, the outcomes (1,2) and (2,1) are distinguishable, such that the likelyhood of a total outcome of $3 = 1 + 2 = 2 + 1$ is twice as large as that of $2 = 1 + 1$.

So we find that the total number of ways to distribute Q identical items over N boxes is given by

$$\Omega(Q, N) = \frac{(Q + N - 1)!}{Q!(N - 1)!} \;, \tag{4.2}$$

which represents the multiplicity of the macrostate that corresponds to Q items being distributed over N boxes. For the case of $Q = 9$ and $N = 3$, this yields

$$\Omega(Q = 9, N = 3) = \frac{11!}{9!2!} = 55$$

By equal a priori probabilities, each such microstate is populated with probability $1/55$. The entropy of this state is therefore $S = k_B \ln(\Omega) = k_B \ln(55)$.

Statistical mechanics wants to make predictions about physical quantities (state variables). In our example of $Q = 9$ items in $N = 3$ boxes, let us now assume that one is interested in the state variable 'population of the first box' Q_α, and let Q_β and Q_γ be the populations of the other two boxes. For example, the microstate illustrated above had $Q_\alpha = 3$, $Q_\beta = 4$ and $Q_\gamma = 2$.

We can represent these microstates in a *phase space* spanned by Q_α and Q_β, noting that $Q_\gamma = 9 - Q_\alpha - Q_\beta$ is not independent. Since Q_α, Q_β (and Q_γ) can each cover a range from zero (= empty box) to a maximum of $Q = 9$, this will look as follows,
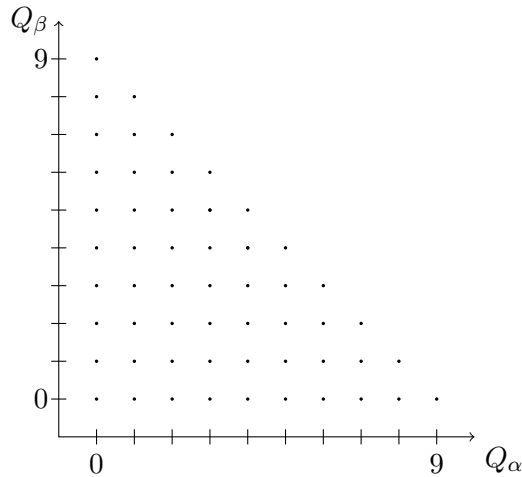
where the dots represent all 55 possible microstates. The number of microstates associated with each value of Q_α can be counted directly in the diagram above and is just $(10 - Q_\alpha)$. By applying

the principle of equal a priori probabilities, the probability $P(Q_\alpha)$ of each value of Q_α is obtained by dividing the number of microstates associated with Q_α, $(10 - Q_\alpha)$, by the total number of microstates $\Omega(Q = 9, N = 3) = 55$,

$$P(Q_\alpha) = \frac{10 - Q_\alpha}{\Omega(Q = 9, N = 3)} = \frac{10 - Q_\alpha}{55} \ . \tag{4.3}$$

Equipped with a probability distribution, we are now in a position to make statistical predictions. Given a state variable A, some relevant statistical properties are the *mean* $\langle A \rangle$ and the *standard deviation* σ, defined as the square root of $\sigma^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle (A^2 - 2A\langle A \rangle + \langle A \rangle^2) \rangle = \langle A^2 \rangle - 2\langle A \rangle^2 + \langle A \rangle^2 = \langle A^2 \rangle - \langle A \rangle^2$. In terms of the probabilities P_i, these properties are defined by

$$\langle A \rangle = \sum_i A_i P_i \ , \tag{4.4}$$

and

$$\sigma^2 = \langle A^2 \rangle - \langle A \rangle^2 = \sum_i A_i^2 P_i - \left(\sum_i A_i P_i \right)^2 \ , \tag{4.5}$$

where i labels the microstates, P_i is the equilibrium probability that the system is found in microstate i, and A_i is the value of a system property of interest when in microstate i.

With these definitions, we can now calculate

$$\langle Q_\alpha \rangle = \sum_{Q_\alpha=0}^{9} Q_\alpha P(Q_\alpha) = \sum_{Q_\alpha=0}^{9} \frac{10 - Q_\alpha}{55} Q_\alpha = \sum_{Q_\alpha=0}^{9} \frac{10}{55} Q_\alpha - \sum_{Q_\alpha=0}^{9} \frac{1}{55} Q_\alpha^2$$

$$= \frac{10}{55} \frac{9 \times 10}{2} - \frac{1}{55} \frac{9 \times 10 \times 19}{6} = 3 \ ,$$

where we used the summation formulae $\sum_{j=1}^{n} j = n(n+1)/2$ and $\sum_{j=1}^{n} j^2 = n(n+1)(2n+1)/6$. This should not come as a surprise, as we had 9 items to put into 3 boxes and, all things being equal, one should expect on average 3 per box.

The standard deviation is less trivial to foresee,

$$\sigma^2 = \langle Q_\alpha^2 \rangle - \langle Q_\alpha \rangle^2 = \sum_{Q_\alpha=0}^{9} Q_\alpha^2 P(Q_\alpha) - 9 = \sum_{Q_\alpha=0}^{9} \frac{10}{55} Q_\alpha^2 - \sum_{Q_\alpha=0}^{9} \frac{1}{55} Q_\alpha^3 - 9$$

$$= \frac{10}{55} \frac{9 \times 10 \times 19}{6} - \frac{1}{55} \frac{9^2 \times 10^2}{4} - 9 = 6 \ ,$$

where we also used $\sum_{j=1}^{n} j^3 = [n(n+1)/2]^2$. Hence, $\sigma = \sqrt{6} \approx 2.45$. The standard deviation of Q_α is therefore very large with respect to its average in this case. This is not wholly expected, because the total system we are considering is very small. We shall see in detail later that the relative uncertainty of statistical predictions (*i.e.*, the ratio between mean and standard deviation of state functions) will shrink as the system size grows, until it becomes negligible in the thermodynamic limit of infinite system size.

Factorials naturally crop up in calculations of multiplicity and they are often inconvenient in analysis. However, using *Stirling's approximation*, factorials of large numbers are readily converted into powers[1]:

---

[1]Stirling's formula may be derived by noting that $\ln m! = \ln m + \ln(m-1) + \cdots + \ln 1 = \sum_{n=1}^{m} \ln n \approx \int_1^m \ln x \, \mathrm{d}x = [x \ln x - x]_1^m \approx m \ln m - m$ for large m.

> **Stirling approximation.** To find a convenient expression of large factorials, we write
>
> $$\ln m! \approx m \ln m - m \quad \text{for } m \gg 1 . \tag{4.6}$$

Using the Stirling approximation, we can now approximate the multiplicity $\Omega(Q, N)$ (see equation 4.2) in the limit of large numbers, *i.e.*, $Q \gg 1$ and $N \gg 1$. We find

$$
\begin{aligned}
\ln \Omega(Q, N) \\
&= \ln(Q + N - 1)! - \ln Q! - \ln(N - 1)! \\
&\approx (Q + N - 1) \ln(Q + N - 1) - Q \ln Q - (N - 1) \ln(N - 1) \underbrace{-(Q + N - 1) + Q + (N - 1)}_{= 0} \\
&= \underbrace{Q \ln(Q + N - 1) - Q \ln Q}_{= Q \ln \frac{Q+N-1}{Q}} + \underbrace{(N - 1) \ln(Q + N - 1) - (N - 1) \ln(N - 1)}_{= (N-1) \ln \frac{Q+N-1}{N-1}} \\
&\approx Q \ln \left(\frac{Q + N}{Q} \right) + (N - 1) \ln \left(\frac{Q + N}{N} \right) \\
&= \ln \left(\frac{Q + N}{Q} \right)^{Q} + \ln \left(\frac{Q + N}{N} \right)^{N-1} ,
\end{aligned}
\tag{4.7}
$$

so that

$$\Omega(Q, N) \approx \left(1 + \frac{N}{Q} \right)^{Q} \left(1 + \frac{Q}{N} \right)^{N-1} . \tag{4.8}$$

In the limit of high energies, $Q/N \to \infty$, one may apply $e = \lim_{x \to 0}(1 + x)^{1/x}$ to get

$$\lim_{Q/N \to \infty} \Omega(Q, N) = e^{N} \left(\frac{Q}{N} \right)^{N-1} . \tag{4.9}$$

That is, the number of discrete, accessible microstates grows polynomially in Q for very large energies, a fact that will be useful later on.

4.2 Canonical ensemble

Whereas a microcanonical ensemble is isolated from its environment, the canonical ensemble describes the statistical properties of a system that is *not* isolated, but able to exchange energy with its environment. Specifically, we have considered the case of a system that can exchange energy with a reservoir that is considered large (*i.e.*, that has a large energy compared to the energy of the system. Note that the total of system and reservoir is again considered as isolated, and as such is a microcanonical ensemble, with each microstate of the combined system and reservoir having equal probability. For the system microstates, however, this is no longer the case, since the weighing of the microstates in the system is determined by the multiplicity of the macrostates of the reservoir. As shown in the previous chapter, this leads to the canonical (or Botlzmann distribution, equation 3.9.

Canonical ensemble average of a system property A can now be obtained by performing summations such as

$$\langle A \rangle = \frac{1}{Z} \sum_{E} A(E) \Omega(E) \exp(-\beta E), \tag{4.10}$$

where Z normalised the probability distribution and is the partition function as defined previously (equation 3.10).
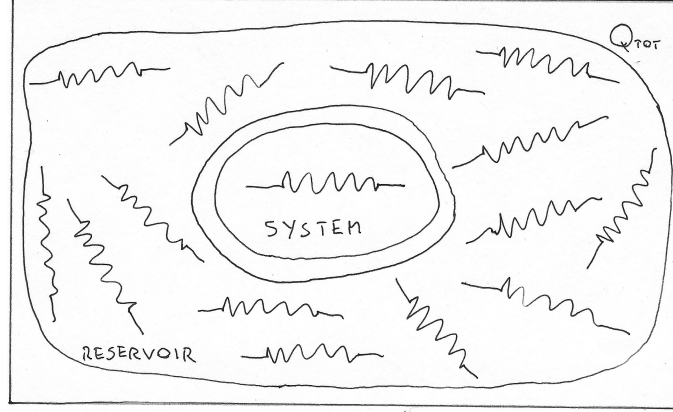
Figure 4.1: The canonical ensemble is defined by considering a system (here a single oscillator) that can exchange energy with a large reservoir (here, $N_r \gg 1$ oscillators). The system and the reservoir together form a microcanonical ensemble with fixed energy (here, $Q_{tot}\epsilon$, with $Q_{tot} \gg 1$ quanta, shared between system and reservoir).

4.2.1 Quantum harmonic oscillators

For example, consider a single quantum oscillator that is part of a large system of N_{tot} quantum oscillators, characterised by parameters $N_{tot} \gg 1$ and $Q_{tot} \gg 1$, see figure 4.1. For a single oscillator, each quantum state of the system has its own, distinguishable energy E_q, *i.e.*, $\Omega(q) = 1$ for all q. We can now determine the average energy

$$\langle E \rangle = \frac{1}{Z} \sum_{q=0}^{Q_{tot}} E_q \, e^{-\beta E_q} \ . \tag{4.11}$$

At this point, it is worth noting that we can rewrite the sum in equation 4.11 as a derivative of the partition function Z, via

$$\sum_{q=0}^{\infty} E_q \, e^{-\beta E_q} = -\sum_{q=0}^{\infty} \frac{\partial \, e^{-\beta E_q}}{\partial \beta} = -\frac{\partial}{\partial \beta} \sum_{q=0}^{\infty} e^{-\beta E_q} = -\frac{\partial Z}{\partial \beta} \ . \tag{4.12}$$

Moreover, substituting this in equation 4.11 and noting that $d \ln Z / dZ = 1/Z$, we find that

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} \ , \tag{4.13}$$

such that we readily determine the mean energy once we know the partition function Z.

Here, we recall that $E_q = (\frac{1}{2} + q)\hbar\omega$ and that the system has $Q_{tot} + 1$ microstates; if $Q_{tot} \gg 1$, the upper limit in the sum can effectively be replaced with ∞. The partition function is then given by

$$Z = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{q=0}^{\infty} \underbrace{e^{-\beta q\hbar\omega}}_{\left(e^{-\beta\hbar\omega}\right)^q \equiv x^q} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-x} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}} = \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)} \ , \tag{4.14}$$
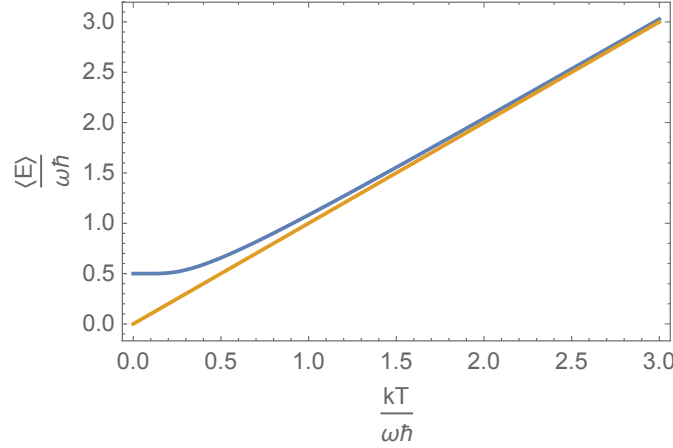
Figure 4.2: Comparison between the average canonical energy of a quantum (blue) and a classical (orange) harmonic oscillator.

where we have used the geometric series $\sum_{x=0}^{\infty} = (1-x)^{-1}$. So we have[2]

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\frac{-1}{2\sinh^2\left(\tfrac{1}{2}\beta\hbar\omega\right)}\cosh\left(\tfrac{1}{2}\beta\hbar\omega\right)\tfrac{1}{2}\hbar\omega$$

$$= \tfrac{1}{2}\hbar\omega\frac{1}{\tanh\left(\tfrac{1}{2}\beta\hbar\omega\right)} \approx \begin{cases} \tfrac{1}{2}\hbar\omega & \text{for } \beta\hbar\omega \gg 1 \\ \beta^{-1} = k_B T & \text{for } \beta\hbar\omega \ll 1 \,. \end{cases} \tag{4.15}$$

If the temperature $T \to 0$, then $\beta\hbar\omega \to \infty$ such that $\tanh\left(\tfrac{1}{2}\beta\hbar\omega\right) \to 1$ and $\langle E \rangle \to \tfrac{1}{2}\hbar\omega$, the zero point energy of a quantum oscillator. By contrast, if $k_B T \gg \hbar\omega$, then $\beta\hbar\omega \ll 1$ such that $\tanh\left(\tfrac{1}{2}\beta\hbar\omega\right) \approx \tfrac{1}{2}\beta\hbar\omega$ and we find $\langle E \rangle \approx \beta^{-1} = k_B T$. The same result follows if $\hbar\omega \to 0$, *i.e.*, when we ignore the quantisation of energy levels and recover classical behaviour. This is illustrated in figure 4.2.

4.2.2 Classical ideal gas: the Maxwell velocity distribution

As another example of a canonical ensemble, we can consider the ideal gas as discussed in section 1.3, where we found that gas particles have on average a (kinetic) energy of $\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T$ per particle, where m is the particle mass and $\langle v^2 \rangle$ the mean square velocity, see equation 1.7. We can now verify if the canonical distribution provides us with a similar result.

Firstly, we assume — as implied in the ideal-gas approximation — that we can consider all particles independently and that velocity microstates are to be found with equal density across the velocity space, *i.e.*, the number of these microstates is proportional to the volume $\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$, with $v_x^2 + v_y^2 + v_z^2 = v^2$, see also figure 4.3. However, the probability of each microstate is weighed by the Boltzmann factor, such that we find

$$P(v)\mathrm{d}v \propto \mathrm{e}^{-\beta\frac{1}{2}mv^2}\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z$$

$$\propto \mathrm{e}^{-\beta\frac{1}{2}mv^2}v^2\,\mathrm{d}v\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \tag{4.16}$$

$$\propto v^2\mathrm{e}^{-\beta\frac{1}{2}mv^2}\,\mathrm{d}v \,,$$

---

[2]For the approximations in the limits of small and large $\beta\hbar\omega$, recall that $\tanh(x) = (\mathrm{e}^x - \mathrm{e}^{-x})/(\mathrm{e}^x + \mathrm{e}^{-x})$ and consider $x \gg 1$ and $x \ll 1$. In the latter case, it helps to approximate the exponentials by first-order Taylor expansions.
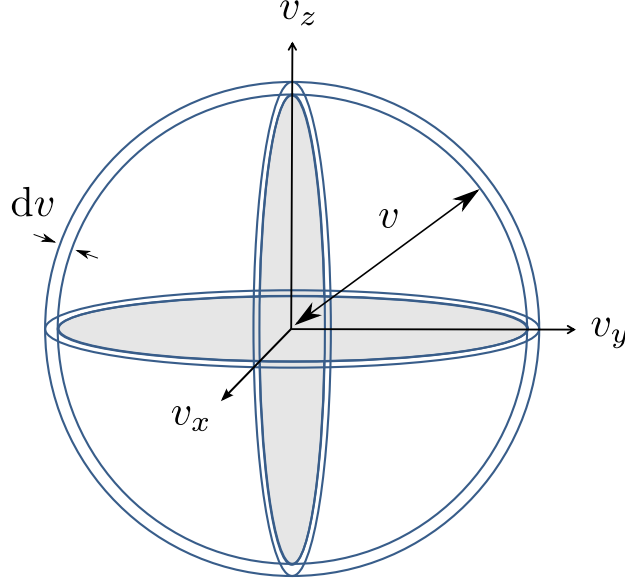
Figure 4.3: The number of microstates with speed in a range dv about a value v is proportional to the volume of a shell of radius v and thickness dv, assuming a uniform density of microstates in 3-dimensional velocity space.

where we have used polar coordinates and note that $\sin\theta\,d\theta\,d\phi = 4\pi$ does not depend on v, given that all directions are equally likely. This is the famous Maxwell velocity or Maxwell-Boltzmann distribution for the absolute value of the velocity of the ideal gas particles. Such a probability density is normalised by the single-particle canonical partition function Z:

$$Z = \int_0^\infty v^2 e^{-\beta\frac{1}{2}mv^2}\,dv \ . \tag{4.17}$$

We will not even need to determine the exact expression of Z to determine the average particle energy:

$$
\begin{aligned}
\langle \tfrac{1}{2}mv^2 \rangle &= \frac{1}{Z}\int_0^\infty \tfrac{1}{2}mv^2 \overbrace{P(v)}^{v^2 e^{-\beta\frac{1}{2}mv^2}}\,dv = \frac{1}{Z}\int_0^\infty \tfrac{1}{2}mv^4 e^{-\beta\frac{1}{2}mv^2}\,dv \\
&= \frac{1}{Z}\int_0^\infty \frac{-1}{2\beta}v^3\,d\left(e^{-\beta\frac{1}{2}mv^2}\right) = \frac{1}{Z}\underbrace{\left[\frac{-1}{2\beta}e^{-\frac{\beta}{2}mv^2}v^3\right]_0^\infty}_{=0} + \frac{3}{\beta 2Z}\underbrace{\int_0^\infty v^2 e^{-\frac{\beta}{2}mv^2}\,dv}_{=Z} \\
&= \frac{3}{2\beta} = \frac{3}{2}k_B T \ ,
\end{aligned}
\tag{4.18}
$$

where we integrated by parts and used the definition of the canonical partition function Z. This is in full agreement with the earlier result based on the ideal gas law; and the total energy of the gas is the well-known value $\frac{3}{2}Nk_B T$ (equation 1.7), since one just needs to add up the contribution given by each particle.

4.2.3 The equipartition theorem

In the previous sections, we have seen that a classical harmonic oscillator has an average energy $k_B T$ and that the average particle energy in an ideal gas is given by $\frac{3}{2} k_B T$. This suggest that there might be some more general relation between average energy $\langle E \rangle$ and $k_B T$. Both systems had in common that the energy was given — apart from a constant — by quadratic terms in position and/or velocity: $\frac{1}{2} m v^2$ for the ideal gas and $\frac{1}{2} m v^2 + \frac{1}{2} \kappa x^2$ for the (one-dimensional) harmonic oscillator (where $\kappa = m \omega^2$ is a spring constant as in Hooke's law). Let us here briefly recall that each classical particle in d dimensions is described by d pairs of position and momentum real variables, with values that go from $-\infty$ to $+\infty$, which entirely determine its dynamical state, in that they completely determine the future and past history of the particle through the solution of (second-order) Newton equations of motion.[3] In what follows, such variables will be referred to as 'phase space' variables (such is the traditional denomination, in classical mechanics, of the space of positions and momenta), bearing in mind that the same results would apply to any variables spanning the whole real line.

Let now the energy be given by some sum of phase space variables,

$$E = \sum_{j=1}^{n} \alpha_j x_j^2 \, , \tag{4.19}$$

where n is the total number of variables, α_j are constants and x_j are independent phase space variables (e.g., position x or velocity v_x along the x-axis). We can then proceed with calculating the partition function as we did for the Maxwell velocity distribution; we have already seen (equation 4.13) that the average canonical energy $\langle E \rangle$ may be obtained from Z by taking the derivative with respect to β of its logarithm, $\langle E \rangle = -\partial \ln Z / \partial \beta = -\frac{1}{Z} \partial Z / \partial \beta$.

By again assuming that the microstate multiplicity is proportional to the phase space volume, we find the following canonical partition function for the system:

$$Z = \int_{-\infty}^{+\infty} \mathrm{d}x_1 \ldots \int_{-\infty}^{+\infty} \mathrm{d}x_n \, \mathrm{e}^{-\beta \sum_{j=1}^{n} \alpha_j x_j^2} = \prod_{j=1}^{n} \int_{-\infty}^{+\infty} \mathrm{e}^{-\beta \alpha_j x_j^2} \mathrm{d}x_j \, , \tag{4.20}$$

where $\prod$ stands for the product over the j label (we have only used the properties of the exponential function) and $\beta = 1/k_B T$, as usual. Note how the partition function of independent, distinguishable variables factorises. The integral above can be solved by using the Gaussian integral

$$\int_{-\infty}^{+\infty} \mathrm{e}^{-\alpha x^2} \, \mathrm{d}x = \sqrt{\frac{\pi}{\alpha}} \, , \tag{4.21}$$

whence

$$Z = \prod_{j=1}^{n} \sqrt{\frac{\pi}{\beta \alpha_j}} = \left(\frac{\pi}{\beta} \right)^{n/2} \prod_{j=1}^{n} \alpha_j^{-1/2} \tag{4.22}$$

and

$$\ln Z = \frac{n}{2} \ln \pi - \frac{n}{2} \ln \beta + \sum_{j=1}^{n} \ln \alpha_j^{-1/2} \, . \tag{4.23}$$

So we can calculate, using equation 4.13,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{n}{2} \frac{1}{\beta} = \frac{n}{2} k_B T \, , \tag{4.24}$$

---

[3]Notice that momentum plays the same role as velocity if the mass is constant.

which shows that there is a contribution of $\frac{1}{2}k_B T$ to the mean energy for each term of independent square phase space variables, or equivalently for each so-called *degree of freedom*. This result is known as the equipartition theorem.

> **Equipartition theorem.** Each term $\alpha_j x_j^2$ in the energy, or each *degree of freedom*, contributes a term $\frac{1}{2}k_B T$ to the total average canonical energy at temperature T. Here α_j is a constant and x_j is an independent phase space variable.

This theorem is far reaching. In fact, notice first that the kinetic contribution to the energy, $\frac{p^2}{2m}$ for particle mass m, is quadratic (and indeed, by applying the theorem to such a free Hamiltonian in three dimensions one re-obtains the average energy $\frac{3}{2}Nk_B T$ of the ideal gas, as in the preceding section). For an harmonic potential $\frac{1}{2}\kappa x^2$ (or $\frac{1}{2}m\omega^2 x^2$), the equipartition theorem also predicts that for any particle in such a potential at temperature T, there will be a mean square displacement $\langle x^2 \rangle = k_B T/\kappa$, such that whenever the temperature is non-zero (always, given the third law), there is movement. This harmonic potential is also a very relevant model in practice: a system of N classical harmonic oscillators in three dimensions, with the same trapping frequency ω and mass m, has energy

$$E = \sum_{j=1}^{3N} \left(\frac{p_j^2}{2m} + \tfrac{1}{2}m\omega^2 x_j^2 \right), \tag{4.25}$$

so that the equipartition theorem states that

$$\langle E \rangle = 3Nk_B T . \tag{4.26}$$

This is a good approximated model for a solid at high temperature, where classical physics holds and one treats each atom (or ion) as a three-dimensional classical oscillator around an equilibrium position in a lattice.

4.2.4 Heat capacities

Experimentally, mean energies can be measured via heat capacities. Heat capacities are important properties of materials, so that they often serve as checkpoints to test the validity of a model or a theoretical assumption. For an ideal classical gas, two distinct heat capacities may be evaluated in two regimes:

- $C_V = \frac{\mathrm{d}Q}{\mathrm{d}T}$ *at constant volume*: $\Rightarrow$ (from the 1$^{\text{st}}$ law) $\mathrm{d}E = \mathrm{d}Q - \mathrm{d}W = \mathrm{d}Q - p\,\mathrm{d}V = \mathrm{d}Q \Rightarrow$ $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk_B$, since the mean value of E is $\frac{3}{2}Nk_B T$ (from equation 4.18 or 4.24).

- $C_p = \frac{\mathrm{d}Q}{\mathrm{d}T}$ *at constant pressure*: $\Rightarrow$ (from the 1$^{\text{st}}$ law) $\mathrm{d}E = \mathrm{d}Q - \mathrm{d}W = \mathrm{d}Q - p\,\mathrm{d}V \Rightarrow$ $C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \frac{5}{2}Nk$, where we have used the ideal gas law (equation 1.3) to find that $p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial (pV)}{\partial T}\right)_p = \frac{\partial Nk_B T}{\partial T}$.

For solid materials, we can mostly assume that the volume is constant, so with our model for a solid at high temperature, we can differentiate $\langle E \rangle$ as given by equation 4.26 with respect to T, yielding a constant heat capacity,

$$C = 3Nk_B . \tag{4.27}$$

This is indeed found a good approximation at high temperatures. Towards the absolute zero of temperature, however, classical physics breaks down, and quantum mechanics is required.
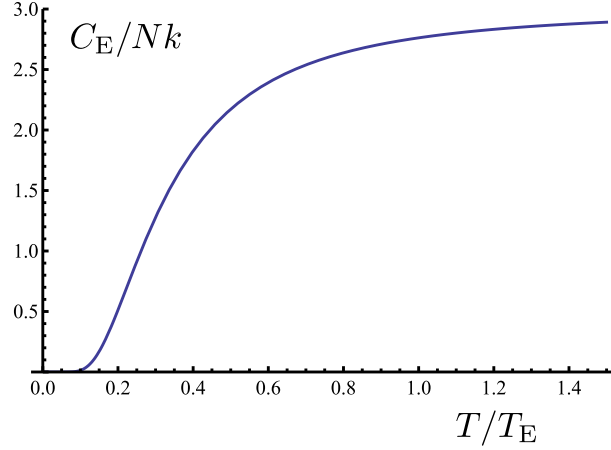
Figure 4.4: Temperature dependence of the Einstein vibrational heat capacity of a solid of N atoms, each oscillating at a common frequency ω_E, related to the Einstein temperature $T_E = \hbar\omega_E/k_B$.

So using now the mean energy of a (one-dimensional) quantum harmonic oscillator (equation 4.15) and noting that $\frac{\mathrm{d}}{\mathrm{d}x}\left(1/\tanh x\right) = -1/\sinh^2 x$, we find

$$
\begin{aligned}
C &= \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\frac{1}{2}\hbar\omega}{\tanh\left(\frac{\hbar\omega}{2k_BT}\right)}\right) \\
&= \frac{1}{2}\hbar\omega\left(\frac{-1}{\sinh^2\left(\frac{\hbar\omega}{2k_BT}\right)}\right)\left(-\frac{\hbar\omega}{2k_BT^2}\right) \\
&= \frac{\hbar^2\omega^2}{4k_BT^2\sinh^2\left(\frac{\hbar\omega}{2kT}\right)} \approx \begin{cases} 0 & \text{for } \hbar\omega/k_BT \gg 1 \\ k_B & \text{for } \hbar\omega/k_BT \ll 1 \ . \end{cases}
\end{aligned}
\tag{4.28}
$$

So at low temperatures, $C \approx 0$ since energy quantisation prevents arbitrarily small increases in energy upon small increases in temperature; and at high temperatures, $C \approx k_B$ as for the classical harmonic oscillator.

If we now consider a solid as a collection of N three-dimensional quantum harmonic oscillators that all oscillate independently at fixed lattice sites with the same (angular) frequency ω_E, we may multiply the result for a single, one-dimensional quantum oscillator (equation 4.28, above) by $3N$ and obtain

$$
C_E = \frac{3N\hbar^2\omega_E^2}{4k_BT^2\sinh^2\left(\frac{\hbar\omega_E}{2k_BT}\right)} \ ,
\tag{4.29}
$$

as originally proposed by Einstein, whence ω_E is known as the Einstein frequency. Although experimental data deviate somewhat from this particular expression at low temperature, the rough agreement was used by Einstein as evidence that the vibrational energy of a solid is indeed quantised, and that it becomes progressively 'frozen out' as the temperature is decreased. Such an application offers strong support for the validity of statistical mechanics.

In our discussion so far, we have distinguished between 'low' (quantum-mechanical) and 'high' (classical) temperature regimes, and defined these regimes quantitatively as $k_BT \ll \hbar\omega$ and $k_BT \gg \hbar\omega$, respectively. Noting this general distinction, we can now venture predictions on more sophisticated systems. For instance, consider a diatomic gas, such as O_2: one would expect a
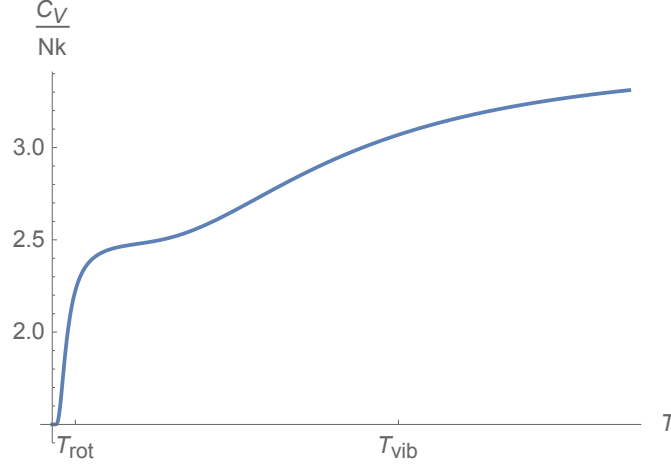
Figure 4.5: The heat capacity of the O_2 molecule has two steep changes around the rotational and vibrational temperatures T_{rot} and T_{vib} (related to the respective frequencies by $kT_{\text{rot}} = \hbar\omega_{\text{rot}}$ and $kT_{\text{vib}} = \hbar\omega_{\text{vib}}$).

contribution to the heat capacity C_V from the following energies, as derived from the equipartition theorem:

- 3 translational quadratic (kinetic) terms ($3 \times \frac{1}{2}k_BT = \frac{3}{2}k_BT$);

- 2 rotational quadratic terms ($2 \times \frac{1}{2}k_BT = k_BT$);

- 2 vibrational quadratic terms ($2 \times \frac{1}{2}k_BT = k_BT$), for the kinetic and potential energy of the harmonic oscillator that represents the bond between the two O atoms.

Indeed, O_2 has heat capacity $\frac{7}{2}k_B$ per molecule at T above 1500 K. As the temperature decreases, first the vibrational, then the rotational degrees of freedom freeze out, so that one observes two sudden transitions in the measured heat capacities, levelling to a heat capacity of $\frac{3}{2}k_B$ per molecule, in agreement with what one would predict based on a quantum harmonic oscillator model (see Fig. 4.5). Note that upon even further decrease of the temperature, the oxygen will freeze and thus stop being a gas.

4.2.5 Two-level systems in thermal equilibrium

Other very common systems in statistical mechanics are so-called two-state systems in equilibrium with a reservoir at temperature $T = 1/(k_B\beta)$. In such systems, we consider only two possible energy levels, here denoted by the energies $-\Delta$ and $+\Delta$. Some examples are the opening and closing of an ion channel in a biological membrane (with different energies for the open and for the closed state); the first two electronic levels of an atom or ion, used in quantum information, where all the other levels are energetically unfavourable or otherwise ruled out; or the up or down orientations of atomic magnetic dipoles with respect to a magnetic field in a paramagnet (where quantum mechanics dictate that these orientations are discrete, not a continuum).

In later case, the mean magnetisation is given by $M = N\mu_B\langle m_s \rangle$, where N is the number of magnetic dipoles in the material, μ_B is the Bohr magneton, $m_s = \pm 1$ is the quantum number defining the dipole orientation, and where the brackets denote a canonical average as before. The two allowed energies may then be indicated with $E_{m_s} = -m_s\mu_B B = -m_s\Delta$ for $m_s = -1, +1$,
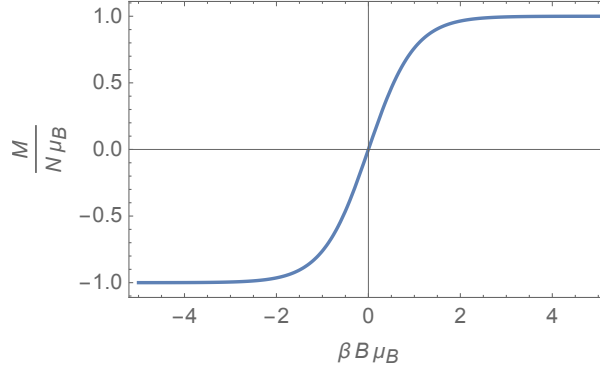
Figure 4.6: Magnetisation of a two-level paramagnet as a function of magnetic field over temperature .

where B is the magnetic field. Note the minus sign for the energies to account for the convention that we denote parallel alignment of the dipole with the magnetic field by $m_s > 0$, and antiparallel alignment with $m_s < 0$, such that the more positive m_s results in a lower energy. According to the canonical probability distribution, we then find

$$
\begin{aligned}
\langle m_s \rangle &= \frac{1}{Z} \sum_{m_s = -1,+1} m_s\, \mathrm{e}^{\overbrace{\beta m_s \Delta}^{-\beta E_{m_s}}} \\
&= \frac{(+1)\mathrm{e}^{\beta(+1)\Delta} + (-1)\mathrm{e}^{\beta(-1)\Delta}}{\mathrm{e}^{\beta(+1)\Delta} + \mathrm{e}^{\beta(-1)\Delta}} \\
&= \frac{\mathrm{e}^{\beta\Delta} - \mathrm{e}^{-\beta\Delta}}{\mathrm{e}^{\beta\Delta} + \mathrm{e}^{-\beta\Delta}} = \tanh(\beta\Delta)\,,
\end{aligned}
\tag{4.30}
$$

and the magnetisation will be proportional to this. We can again consider the limits of low and high temperature (or, equivalently, of high and low magnetic field B), defined by $k_B T \ll \mu_B B$ (*i.e.*, $\beta\Delta \gg 1$) and $k_B T \gg \mu_B B$ (*i.e.*, $\beta\Delta \ll 1$), respectively, to yield

$$
M = N\mu_B \langle m_s \rangle \approx N\mu_B \times
\begin{cases}
\pm 1 & \text{for } \mu_B B/k_B T \gg 1 \\
\mu_B B/k_B T & \text{for } \mu_B B/k_B T \ll 1\,,
\end{cases}
\tag{4.31}
$$

as also shown in figure 4.6. Hence for low temperature or high magnetic field, the magnetisation saturates, with all magnetic dipoles oriented in the same direction, aligned with the applied magnetic field B; and for high temperature or low magnetic field, the magnetisation scales linearly with B. This linear relation is a well-established experimental result known as Curie's law.

4.3 Grand canonical ensemble: Vacancies in crystals

Finally, let us now consider a case (one of many!) where we need to use the *grand* canonical distribution. This is the case of a realistic crystal at a given temperature T. In a perfect crystal, one should have one atom per lattice site, but in reality, it is quite common to have defects, called 'vacancies', *i.e.*, lattice sites where an atom is missing. To describe such a crystal, we presume that each atom is bound to a lattice site with potential energy $-E_\nu$. Fully equivalently, we can consider the energy for vacancy formation as $+E_\nu$, and consider the rest of the crystal as a gas of atoms

with zero energy (*i.e.*, we have just offset the energy scale by E_ν). This is a two-state system as discussed in section 4.2.5, with the two energies being 0 and E_ν, but now we would like to know the average number of vacancies $\langle N \rangle$ per lattice site.

A priori, we could calculate $\langle N \rangle$ by writing out the grand canonical distribution,

$$\langle N \rangle = \sum_{E,N} N P(E, N) \,, \tag{4.32}$$

but as was the case for calculating $\langle E \rangle$ (see equation 4.13), it is convenient to express it as a direct differential of the (logarithm of) the partition function. Quite generally,

$$\begin{aligned}
\langle N \rangle &= \sum_{E,N} N P(E, N) = \frac{1}{Z_G} \sum_{E,N} N \, \Omega(E, N) e^{-\beta(E - \mu N)} \\
&= \frac{1}{Z_G} \frac{1}{\beta} \frac{\partial Z_G}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln Z_G}{\partial \mu} \,.
\end{aligned} \tag{4.33}$$

Similarly, also for comparison with the canonical (as opposed to grand canonical) result $-\partial \ln Z / \partial \beta = \langle E \rangle$ (see equation 4.13), we find that

$$-\frac{\partial \ln Z_G}{\partial \beta} = -\frac{1}{Z_G} \frac{\partial Z_G}{\partial \beta} = \frac{1}{Z_G} \sum_{E,N} (E - \mu N) \, \Omega(E, N) e^{-\beta(E - \mu N)} = \langle E \rangle - \mu \langle N \rangle \,. \tag{4.34}$$

Going back to the specific case of vacancies in a crystal, we will here consider each vacancy as being independent of any other vacancies, and consider atoms that can hop between lattice sites. The situation for a single lattice site is then summed up in this table, with N denoting occupancy of vacancies:

state	N	energy
populated	0	0
vacant	1	E_ν

The partition function is therefore

$$Z_G = e^{-\beta(0 + \mu \times 0)} + e^{-\beta(E_\nu - \mu \times 1)} = 1 + e^{-\beta(E_\nu - \mu)} \tag{4.35}$$

and we find the average number of vacancies per site using equation 4.33,

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln\left(1 + e^{-\beta(E_\nu - \mu)}\right)}{\partial \mu} = \frac{1}{\beta} \frac{\beta e^{-\beta(E_\nu - \mu)}}{1 + e^{-\beta(E_\nu - \mu)}} = \frac{1}{e^{\beta(E_v - \mu)} + 1} \,. \tag{4.36}$$

Note the appearance of μ, which here represents the chemical potential of the atoms. Recall from equation 2.9 that $\mu = (\partial E / \partial N)_{S,V}$ is the change in energy per added particle; in the expression for $\langle N \rangle$, it plays the role of a reference energy for the vacancy. Since μ in general depends on the concentration of particles (here: of vacancies), this allows us — if needed — to also consider how $\langle N \rangle$ will change if we vary the concentration of vacancies in the crystal. Finally, when the temperature increases, β decreases, and equation 4.36 then predicts that it becomes more likely for a vacancy to arise at the lattice site, since $\langle N \rangle$ increases with decreasing β.

4.4 Summary

We have applied the principles of chapter 3 to some systems that are at least conceptually rather simple. Key results are as follows.

- We have define the mean of a property A of a system by $\langle A \rangle = \sum_i A_i P_i$, where P_i is the probability of finding the system in a state defined by A_i. We have also defined the standard deviation σ via $\sigma^2 = \langle A^2 \rangle - \langle A \rangle^2$, where $\langle A^2 \rangle = \sum_i A_i^2 P_i$.

- Many problems in statistical mechanics involve questions about the number of ways by which Q identical items can be distributed over N boxes. This is given by $\Omega(Q, N) = \frac{(Q+N-1)!}{Q!(N-1)!}$. In evaluating such factorials, the Stirling approximation is most useful: it states that $\ln m! \approx m \ln m - m$ for large m.

- An example of this is a set of quantum harmonic oscillators, where a number Q of equally sized energy quanta is distributed over N oscillators. Considering a single quantum harmonic oscillator that can exchange energy quanta with a large reservoir of other quantum harmonic oscillators, we have a canonical ensemble. Using the canonical (Boltzmann) distributions, we find that the mean energy of the single oscillator is given by $\langle E \rangle = \frac{1}{2}\hbar\omega/\tanh\left(\frac{1}{2}\beta\hbar\omega\right)$, which reduces to the quantum zero energy $\frac{1}{2}\hbar\omega$ at low temperatures, and to the classical result $k_B T$ at higher temperatures ($\beta\hbar\omega \ll 1$).

- In applying the canonical distribution to an ideal gas, we find the Maxwell velocity distribution, $P(v)\,\mathrm{d}v \propto v^2 \mathrm{e}^{-\beta\frac{1}{2}mv^2}\,\mathrm{d}v$.

- The equipartition theorem states that in equilibrium, there is a $\frac{1}{2}k_B T$ contribution to the mean energy of a system for each degree of freedom.

- Heat capacities ($= \partial\langle E \rangle/\partial T$ at constant volume) allow us to experimentally test different models for the mean energy of a system. For example, based on a model for quantum harmonic oscillators and the equipartition theorem, we can predict that at higher temperatures, the heat capacity becomes constant, whereas at low enough temperatures, the mean energy becomes constant and hence the heat capacity will be zero. This 'freezing out' of degrees of freedom provided early evidence for quantum mechanics.

- A large and most useful class of models is that of 'two-level' systems, which can have only two according energy states (e.g., $\pm\Delta$). By applying the canonical distribution to such systems, we find, e.g., that the mean value of a single magnetic dipoles and thus the magnetisation of a paramagnetic material scales with $\langle m_s \rangle = \tanh(\beta\Delta) = \tanh(\beta\Delta)$, which for small magnetic energies and large temperatures agrees with the experimentally well-established Curie law.

- As an example of a grand canonical ensemble, one may consider vacancies in crystals, equivalent to isolated defects that may or may not be filled up with an atom. Assuming a certain energy costs of creating a vacancy and assuming a chemical potential, the grand canonical distributions allows us to, e.g., determine the average number of vacancies per lattice site.

- It turns out that many useful mean variables in statistical mechanics can directly be obtained from the partition function. Useful examples are the mean energy $\langle E \rangle = -\partial \ln Z/\partial\beta$ for a canonical ensemble and, for a grand canonical ensemble, $\langle E \rangle - \mu\langle N \rangle = -\partial \ln Z_G/\partial\beta$ and $\langle N \rangle = \beta^{-1}\,\partial \ln Z_G/\partial\mu$.

Chapter 5

Probability and entropy

> *The laws of probability, so true in general, so fallacious in particular.* — Edward
> Gibbon (1737–1794), historian and writer.

In the previous chapter, we have considered various examples of statistical mechanics at work. However, in doing so, we have swept several aspects under the carpet. For example, we have not justified our approach to describe systems exclusively in terms of probabilities, and while Boltzmann's expression for entropy has turned out extremely useful, it leaves space for several ambiguities. Hence one may wonder if alternative formulations are possible, which may help to give a deeper understanding about the meaning of entropy.

5.1   The thermodynamic limit

As discussed in section 3.2, we have been rather bold in presuming that we can describe a system in terms of its average properties (state variables). In this section, we will explore how appropriate such an approach really is. To illustrate this, we can first again consider the role of two dice, we know that the average sum will be 7, but that the extreme outcomes 2 and 12 still occur rather regularly (each with a probability of 1/36). If we next consider how the distribution of probabilities is affected if we roll more 3, 4, ..., N dice, the probabilities of the extreme outcomes (every die showing 1 or every die showing 6) will rapidly decrease, with their probabilities given by $(1/6)^N$. This suggests that we need to worry less about extremes once the number of constituents particles of a system becomes larger.

To give this observation a more solid basis, we will again consider the canonical distribution (equation 3.9),

$$P(E) = \frac{\Omega(E, N)\mathrm{e}^{-\beta E}}{Z} \, , \tag{5.1}$$

where we have made the dependence of Ω on N explicit. Intuitively, we would expect $\Omega(E, N)$ to increase with E, as a larger energy will make more microstates accessible to the system. Indeed, considering N weakly coupled quantum harmonic oscillators, we found (equation 4.9) that $\Omega(E, N)$ is a power-like, rapidly increasing function of the number of energy quanta Q and hence of the energy E. The factor $\exp(-\beta E)$, on the other hand, is a rapidly decreasing function of E, since $\beta > 0$. As a consequence, the macrostate weighing factor $\Omega(N, E)\exp(-\beta E)$ increases with E until it reaches a peak and then falls, since exponential suppression at large E is stronger than power-law amplification.

It is very instructive to expand the weighing factor around the peak in the distribution at $E = E^*$. This is the largest, or *modal* probability over the macrostates. We write the probability distribution as

$$P(E) \propto \exp\left(\ln \Omega(E, N) - \beta E\right) \tag{5.2}$$

and determine E^* from the condition $\partial P / \partial E = 0$, equivalent to $\partial \ln P / \partial E = 0$, or

$$\frac{\partial}{\partial E}\left(\ln \Omega(E, N) - \beta E\right)\bigg|_{E=E^*} = 0 \,, \tag{5.3}$$

from which we deduce that

$$\frac{\partial \ln \Omega(E, N)}{\partial E}\bigg|_{E=E^*} = \beta \,. \tag{5.4}$$

To expand our expression for $P(E)$ (equation 5.2) around E^*, we will first consider the argument of its exponent,

$$\ln \Omega(E, N) - \beta E \approx \ln \Omega(E^*, N)$$
$$+ (E - E^*) \underbrace{\frac{\partial \ln \Omega(E, N)}{\partial E}\bigg|_{E=E^*}}_{=\beta} + \frac{(E - E^*)^2}{2} \underbrace{\frac{\partial^2 \ln \Omega(E, N)}{\partial E^2}\bigg|_{E=E^*}}_{\equiv -1/\sigma^2} - \beta E \,, \tag{5.5}$$

where we have used β as given by equation 5.4 and defined

$$\frac{1}{\sigma^2} = -\frac{\partial^2 \ln \Omega(E, N)}{\partial E^2}\bigg|_{E=E^*} \,. \tag{5.6}$$

Reinserting this result (equation 5.5) back into equation 5.2, we find

$$P(E) \propto \Omega(E, N)\, e^{-\beta E} = \exp\left(\ln \Omega(E, N) - \beta E\right)$$
$$\approx \Omega(E^*, N)\exp(-\beta E^*)\exp\left(-\frac{(E - E^*)^2}{2\sigma^2}\right) \,. \tag{5.7}$$

This has the form of a *Gaussian (or 'normal') distribution*,

$$P_G(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\exp\left(-\frac{(x - \langle x \rangle)^2}{2\sigma^2}\right) \,, \tag{5.8}$$

centred around the modal energy E^* and with the width of the distribution characterised via the standard deviation σ.

To investigate how this distributions depends on the number of constituent particles, we consider the system of N quantum harmonic oscillators of section 4.1, for which the macrostate multiplicity (equation 4.2) can be written as

$$\Omega(Q, N) = \frac{(Q + N - 1)!}{Q!(N - 1)!} \,, \tag{5.9}$$

where Q is the total number of energy quanta in the system, such that — ignoring the zero-point energy $\frac{1}{2}\hbar\omega$ for each oscillator — the total energy $E = Q\hbar\omega$. This allows us to write out $\ln \Omega(Q, N)$

and approximate it for large N and large energy E (or Q), using the Stirling approximation (equation 4.6),

$$
\begin{aligned}
\ln \Omega(Q, N) &= \ln(Q + N - 1)! - \ln Q! - \ln(N - 1)! \\
&\approx (Q + N - 1)\ln(Q + N - 1) - Q - N + 1 - Q \ln Q + Q - (N - 1)\ln(N - 1) + N - 1 \\
&= (Q + N - 1)\ln(Q + N - 1) - Q \ln Q - (N - 1)\ln(N - 1) \, ,
\end{aligned}
$$
(5.10)

$$
\frac{\partial \ln \Omega(Q, N)}{\partial Q} \approx \ln(Q + N - 1) + 1 - \ln Q - 1 = \ln\left(\frac{Q + N - 1}{Q}\right)
$$
(5.11)

and

$$
\frac{\partial^2 \ln \Omega(Q, N)}{\partial Q^2} \approx \frac{1}{Q + N - 1} - \frac{1}{Q} = \frac{N - 1}{Q(Q + N - 1)}
$$
(5.12)

With this approximation, the width of the probability distribution $P(E)$ is readily calculated,

$$
\begin{aligned}
\sigma^2 &= \left(\left.\frac{\partial^2 \ln \Omega(E, N)}{\partial E^2}\right|_{E=E^*}\right)^{-1} = (\hbar\omega)^2 \left(\left.\frac{\partial^2 \ln \Omega(Q, N)}{\partial Q^2}\right|_{Q=Q^*}\right)^{-1} \\
&\approx (\hbar\omega)^2 \frac{Q(Q + N - 1)}{N - 1}
\end{aligned}
$$
(5.13)

and for $N \gg 1$, the ratio of the standard deviation to the mean is proportional to $1/\sqrt{N}$:

$$
\left(\frac{\sigma}{E^*}\right)^2 = \frac{(\hbar\omega)^2 \, Q^*(Q^* + N)}{N} \frac{1}{(\hbar\omega Q^*)^2} \quad \Rightarrow \quad \frac{\sigma}{E^*} = \sqrt{\frac{Q^* + N}{NQ^*}} \approx \sqrt{\frac{\exp(\beta\hbar\omega)}{N}},
$$
(5.14)

where we have combined equations 5.4 and 5.11 to find that $(Q^* + N)/N \approx \exp(\beta\hbar\omega)$.

This means that the distribution becomes very sharply peaked as $N \to \infty$. This is illustrated in Figure 5.1, where for clarity E is scaled by its mean to ensure that the peak does not move as N changes. In this so-called *thermodynamic limit* where N is large, the fluctuations in macrostate are unlikely to be observable, and the system can be regarded as having a constant energy E^*. Thus on the macroscopic scale, a system described by the canonical ensemble seems to be entirely dominated by the average state variables and fluctuations are unobservable, although underlying this apparent quiescence is a continual exploration of microstates. It is simply that the exploration rarely strays away from the $E = E^*$ macrostate.

5.2   Gibbs entropy

So far, we have based our analyses on the observation that a system is most likely to adopt a macrostate that incorporates the largest microstate multiplicity Ω and thus maximises the Boltzmann entropy $S_B = k_B \ln \Omega$ (equation 3.1).[1] Possible criticisms to Boltzmann's expression of entropy are that it requires a closed system, since in an open system, the number of microstates would be infinite. Moreover, it is not generally clear how we define a microstate. When discuss simple systems such as sets of harmonic oscillators, there is no doubt that a microstate is defined by an arrangement of quanta. But how do we apply the same ideas to physical systems, notably ones

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[1]In this chapter, we will add a subscript label to distinguish between the different definitions of entropy. For example, we will write S_B for the Boltzmann entropy, instead of S previously.
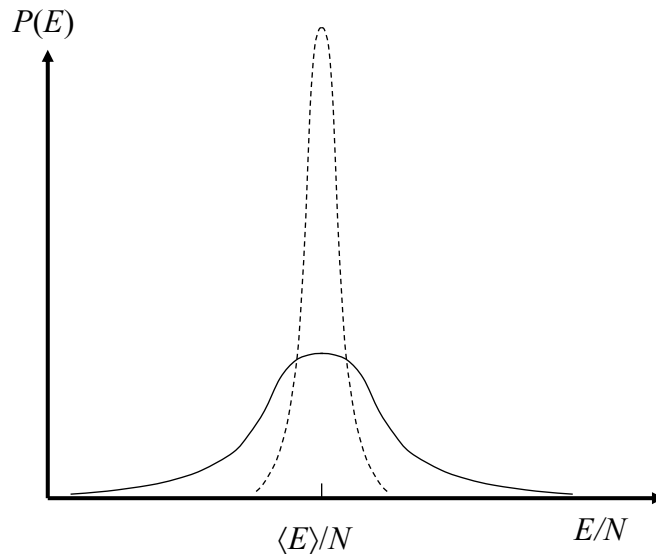
Figure 5.1: Probability distribution function of system parameter E for two system sizes N, with E scaled by the mean of the distribution, indicating how the relative width of the distribution shrinks as the system size increases. In the thermodynamic limit $N \to \infty$ the distribution becomes sharply peaked and fluctuations are of diminishing importance.

involving atoms and molecules. Is it enough to specify positions and velocities at the level of atoms, or should we dig deeper and specify the coordinates of the nuclei and electrons, or even of the protons and neutrons inside the nucleus? Surely this affects the value of the entropy? And if we did want to work with an absolute entropy, we simply do not know how many layers might lie beneath the subatomic scale. So we have to satisfy ourselves with an entropy that is defined with respect to some graining of the structure of matter.

A similar issue arises in the following circumstances. If a gas is discovered to have two isotopes, should this invalidate any previously published tables of entropy measurements? After all, from that moment on, when we perform an experiment on the gas we are aware of additional uncertainty with regard to the mass of every atom. But if the isotopic composition has no measurable effect on the thermodynamic processes of interest to us, then the answer is no: the additional microscopic degree of freedom is irrelevant and need not be taken into account in calculating the entropy.

Such problems may be avoided or at least alleviated by the Gibbs model of entropy, proposed by Josiah Willard Gibbs (1839–1903). This model assigns a set of probabilities P_j to a generic set of possible microstates of a system, here labelled with j, and next defines the entropy in terms of these probabilities:

Gibbs entropy. For a system in which each microstate j occurs with probability p_j, the entropy S is given by

$$S_G = -k_B \sum_j P_j \ln P_j \, , \tag{5.15}$$

where k_B is Boltzmann constant.

Firstly, we note that this expression is consistent with the Boltzmann entropy S_B: For a closed system, equal a-priori probabilities apply, and one has $P_j = 1/\Omega$ for all j. Inserting this in our

expression for S_G (equation 5.15), we obtain

$$S_G = -k_B \sum_{j=1}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = k_B \ln(\Omega) \sum_{j=1}^{\Omega} \frac{1}{\Omega} = k_B \ln \Omega = S_B \,, \tag{5.16}$$

which demonstrates that the Boltzmann entropy is not a distinct definition, but a special case of the Gibbs entropy.

To note the differences between the Boltzmann and Gibbs entropy, let us insert the canonical probabilities $P_j = Z^{-1} \exp(-\beta E_j)$ for a system in contact with a reservoir at temperature T (with $\beta = 1/k_B T$ as usual). We find that[2]

$$S_G = -k_B \sum_j P_j \times \left(-\frac{E_j}{k_B T} - \ln Z\right) = \frac{1}{T}\langle E\rangle + k_B \ln Z \,, \tag{5.17}$$

where the brackets indicates a canonical average. A clear indication that the Gibbs entropy differs from the Boltzmann entropy is that S_G is a function of the reservoir property T and the number of particles N. It therefore naturally applies to a system in contact with a reservoir. By contrast, S_B is a function of conserved quantity E (as well as of N), and is designed to apply to an isolated system. Of course, in the thermodynamic limit, when fluctuations about mean properties become negligible, there is an essentially unique equilibrium system energy associated with a given reservoir temperature, and the mathematical distinction between functions $S_G(N, T)$ and $S_B(E, N)$ becomes less important.

Turning to more straightforward matters, note that equation 5.17 can be rewritten as

$$-k_B T \ln Z = \langle E\rangle - TS_G, \tag{5.18}$$

and so with reference to table 2.1, and if we accept a correspondence between the thermodynamic state variable E and the statistical mean $\langle E\rangle$, we appear to be able to identify $-k_B T \ln Z$ with the Helmholtz free energy:

$$F = E - TS = -k_B T \ln Z \,. \tag{5.19}$$

As a similar result can be derived directly from the canonical distribution,[3] this correspondence lends support to the form of entropy proposed by Gibbs. Note that Z in equation 5.19 is a function of T and N, and that together with the system volume these are the natural variables for the Helmholtz free energy in classical thermodynamics.

If we employ the grand canonical microstate probabilities $P_j = Z_G^{-1} \exp(-\beta(E_j - \mu N_j))$ in the Gibbs expression for the entropy, we obtain

$$S_G = -k_B \sum_j P_j \times \left(-\frac{E_j}{k_B T} + \frac{\mu N_j}{k_B T} - \ln Z_G\right) = \frac{1}{T}\langle E\rangle - \frac{\mu\langle N\rangle}{T} + k_B \ln Z_G \,, \tag{5.20}$$

---

[2]Recall that $\sum_j P_j A_j = \langle A\rangle$ and that $\sum_j P_j = 1$.

[3]To see this, note first that $T = k_B^{-1}\beta^{-1}$ such that $dT = -k_B^{-1}\beta^{-2}d\beta$, recall from equation 2.17 that $dF = -SdT - pdV + \mu dN = k_B^{-1}\beta^{-2}Sd\beta - pdV + \mu dN$, and use the thermodynamic expression for the Helmholtz free energy (equation 2.15) $F = E - TS = E - k_B^{-1}\beta^{-1}S$. Hence we can write $d(\beta F) = \beta dF + Fd\beta = k_B^{-1}\beta^{-1}Sd\beta - \beta pdV + \beta\mu dN + Ed\beta - k_B^{-1}\beta^{-1}Sd\beta = Ed\beta - \beta pdV + \beta\mu dN$. Therefore, the partial derivative $(\partial(\beta F)/\partial\beta)|_{N,V} = E$, where as usual the subscript N, V denotes that the derivative is taken at constant N, V. This can be compared with our previous result $-\partial \ln Z/\partial\beta = \langle E\rangle$ (see equation 4.13). If we again identify the average energy $\langle E\rangle$ with the thermodynamic state variable E, we find that $\beta F = -\ln Z$, identical to the result obtained from the Gibbs entropy in equation 5.19.

where the brackets now represent a grand canonical average. This result can be rearranged into

$$- k_B T \ln Z_G = \langle E \rangle - T S_G - \mu \langle N \rangle = \Phi, \tag{5.21}$$

where $\Phi(\mu, V, T)$ is the grand potential defined in table 2.1, interpreting the system energy and particle number in that classical thermodynamic expression as grand canonical averages. This is another connection between a quantity from statistical thermodynamics (the left hand side) and a quantity from classical thermodynamics (the right hand side).

One of the appealing features of the Gibbs entropy is that it connects thermodynamic entropy directly to statistical ideas through the use of the equilibrium microstate occupation probabilities. It allows us to interpret entropy as a measure of uncertainty. To understand this, consider a system defined by a probability distribution P_j. For example, each j could refer to a possible position where we might find a particular particle. If we are absolutely certain of the position of the particle, say position i, then $P_i = 1$ and $P_{j \neq i} = 0$. Inserting this into equation 5.15, we find that the entropy is minimum, $S_G = -k_B P_j \ln P_j = k_B 1 \ln 1 = 0$. If we are completely uncertain about the position, then each $P_j = 1/\Omega$, where Ω is the number possible positions, and the Gibbs entropy is maximum, $S_G = k_B \ln \Omega$. This idea of entropy as a measure of uncertainty can be further explored using ideas from information theory, leading to the Shannon entropy as discussed in the next section.

5.3 Shannon entropy: Quantifying information

To get a handle on the problem of quantifying information, Claude Shannon (1916–2001) asked the question how many bits would be needed to reproduce a given piece of information, e.g., a message composed using an alphabet of symbols. 'Bits' refer to systems with two possible states, e.g., the 0 and 1 that underpin all information technology. Slightly rephrasing the question, he asked how many bit would be needed per symbol in the limit of an infinitely long message. To this end, he considered a probability distribution P_j, where each P_j refers to the probability of a certain symbol to occur in the message (and $\sum_j P_j = 1$ as usual).

Now, let N be the length of the message (the number of symbols sent). In the limit $N \to \infty$, each symbol j will appear exactly $N_j = P_j N$ times. To evaluate the number of possible messages in this limit, we can consider the number that would arise if all symbols were different, *i.e.*, $N!$, corrected for the number of permutations of the same symbols. That is, the number of possible messages, also known as the number of "typical sequences" , is given by

$$\frac{N!}{N_1! \, N_2! \, N_3! \dots N_j! \dots} = \frac{N!}{(P_1 N)! \, P_2 N)! \, (N_3)! \dots (N_j)! \dots} = \frac{N!}{\prod_j (P_j N)!} \; . \tag{5.22}$$

If the message is now written in bits, where each bit can assume 2 values, the total number of possible messages can also be written as $2^{N S_I}$, where N is the number of symbols as before, and S_I the number of bits per symbol. Comparing this with equation 5.22, we find

$$2^{N S_I} = \frac{N!}{\prod_j (P_j N)!} \; , \tag{5.23}$$

whence

$$NS_I = \log_2 N! - \sum_j \log_2(P_j N)! \approx \overbrace{N \log_2 N - N}^{=\sum_j P_j N \log_2 N - \sum_j P_j N} - \sum_j (P_j N) \log_2(P_j N) + \sum_j P_j N$$

$$= \sum_j P_j N \log_2 N - \sum_j P_j N \log_2(P_j N) = -\sum_j \left(\log_2 N^{P_j N} - \log_2 (P_j N)^{P_j N} \right) \qquad (5.24)$$

$$= -\sum_j \log_2 \left(\frac{P_j N}{N} \right)^{P_j N} = -N \sum_j P_j \underbrace{\log_2 P_j}_{= \ln P_j / \ln 2} ,$$

where we have used the Stirling approximation ($\log_2 N! \approx N \log_2 N - N$, equation 4.6) for large numbers and note that as usual $\sum_j P_j = 1$. Dividing equation 5.24 by N, we can therefore write:

> **Shannon entropy.** For an asymptotically long message composed of symbols j with respective probabilities of occurrence P_j, it requires a minimum number of bits S_I per symbol to convey the message without loss of information, with S_I given by:
>
> $$S_I = -\sum_j P_j \log_2 P_j = -K \sum_j P_j \ln P_j , \qquad (5.25)$$
>
> where the factor $K = (\ln 2)^{-1}$ is related to our assumption of bit (2-level) encoding.

This Shannon entropy can be compared with the Gibbs entropy $S_G = -k_B P_j \ln P_j$, where — as noted in section 3.3 — we could redefine temperature to be measured in units of $k_B T$ to eliminate k_B in the expression for entropy. That is, with the appropriate scaling for temperature (or entropy), the Gibbs and Shannon expressions for entropy are identical. Importantly, however, the Shannon entropy provides a most modern aspect of the concept of entropy, in making predictions about the minimum encoding needed to store or transfer a piece of information, e.g., how to most efficiently encode a piece of music or image into a digital format.

To illustrate this with an explicit example, consider an alphabet of three symbols, a, b and c, occurring with respective probabilities $p_a = 1/2$, $p_b = 1/4$ and $p_c = 1/4$. The translation of such an alphabet into a binary, bit one, can be enacted via the following correspondence:

$$a \leftrightarrow 00 ,$$
$$b \leftrightarrow 10 ,$$
$$c \leftrightarrow 11 ,$$

which uses 2 bits per symbol. However, the evaluation of the Shannon entropy of the alphabet yields

$$S_I = -P_a \log_2 P_a - P_b \log_2 P_b - P_c \log_2 P_c$$
$$= -\frac{1}{2} \log_2 \frac{1}{2} - \frac{1}{4} \log_2 \frac{1}{4} - \frac{1}{4} \log_2 \frac{1}{4} = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2} . \qquad (5.26)$$

Hence, since the argument above implies that such a value gives the optimal asymptotic compression rate for the alphabet in question, a better encoding, using 1.5 bits per symbol, must exist. One such optimal encoding is in fact given by

$$a \leftrightarrow 0 ,$$
$$b \leftrightarrow 10 ,$$
$$c \leftrightarrow 11 ,$$

which implies that any sequence of an even number of 1s encodes for a sequence of "c"s, any 0 that follows an uneven number of 1s refers to a "b", and any 0 that follows an even number of 1s refers to an "a". This encoding indeed uses an average of

$$P_a \times 1 \text{ bit} + P_b \times 2 \text{ bits} + P_c \times 2 \text{ bits} = \frac{1}{2} \times 1 + \frac{1}{4} \times 2 + \frac{1}{4} \times 2 = \frac{3}{2} = S_I \qquad (5.27)$$

bits per symbol. Note that if we were to reduce the number of bits further by encoding $c \leftrightarrow 1$ instead of $c \leftrightarrow 11$, we would not be able to distinguish $ca \leftrightarrow 10$ from $b \leftrightarrow 10$ anymore.

In the context of statistical mechanics, the Shannon entropy quantifies the information needed to define the state of a system. The less we know about such a system, *i.e.*, the more we are *uncertain* about the system, the more information we need to describe it and the larger S_I. This reinforces out interpretation of entropy as a measure of uncertainty of a system, as we concluded in section 5.2. Given the general aspect of the Shannon entropy, we may consider it as a general measure of the uncertainty embodied by a probability distribution, and determine the actual probabilities by maximising this uncertainty subject to any known constraints. Such an approach is based on the information theoretic interpretation of probability as a best judgement of the likelihood of outcomes, rather than as a representation of their frequencies of occurrence in trials. The maximisation may be carried out using Lagrange's method of undetermined multipliers, as illustrated below.

For example, in the microcanonical case, the only constraint to P_j is the normalisation condition $\sum_j P_j = 1$. Following the Lagrange multiplier approach, we can then maximise S_I, or equivalently $-P_j \ln P_j$ after subtraction of the constraint $\sum_j P_j = 1$ multiplied with an undetermined multiplier λ. That is, we determine the zero derivative

$$\frac{\partial}{\partial P_j} \left(\underbrace{-\sum_i P_i \ln P_i}_{\text{search to maximise entropy}} - \lambda \underbrace{\left(\sum_i P_i - 1 \right)}_{\text{with constraint that } \sum_i P_i - 1 = 0} \right) = -\ln P_j - 1 - \lambda = 0 , \qquad (5.28)$$

which implies that all the P_j are equal, $P_j = \exp\{-1 - \lambda\} \ \forall \ j$, so we recover the principle of equal a priori probabilities.

If the maximisation of S_I were carried out under the additional constraint of a known mean energy $\langle E \rangle = \sum_j E_j P_j$, we need an additional Lagrange multiplier β, and the resulting microstate probabilities would be determined from

$$\frac{\partial}{\partial P_j} \left(\sum_i P_i \ln P_i - \lambda \left(\sum_i P_i - 1 \right) - \beta \left(\sum_i P_i E_i - \langle E \rangle \right) \right) = -\ln P_j - 1 - \lambda - \beta E_j = 0 , \ (5.29)$$

which can be rewritten as

$$\ln P_j = -1 - \lambda - \beta E_j \quad \Rightarrow P_j = e^{-1-\lambda} e^{-\beta E_j} \propto e^{-\beta E_j} , \qquad (5.30)$$

where we recover the canonical distribution (equation 3.9). Notice that the parameter β in this expression derives from a Lagrange multiplier, and is to be identified through the expression $\langle E \rangle = Z^{-1} \sum_j E_j \exp(-\beta E_j)$ that relates it to the known mean energy. In contrast, in the usual derivation of the canonical ensemble, β is a property of the reservoir. In a similar way, by specifying a known mean particle number, we would be able to generate the grand canonical microstate probabilities.

Finally, for completeness, we note that there is yet another definition of entropy, similar to Shannon entropy, that is named after von Neumann and that has been used to explore uncertainty in quantum mechanics, where the probabilities of state occupation are affected by intrinsic quantum uncertainties, as well as classical statistical uncertainty. This is an important tool in the fields of quantum information processing and quantum computers.

5.4   Summary

In this chapter, we have provided a sounder base for the probabilistic approach to N-particle systems. Specifically, we have demonstrated that for systems consisting of many particles, the properties of such a system can well be described in terms of state variables, as common in thermodynamics, since fluctuations away from the modal values of these variables become negligible, in the so-called *thermodynamic limit*.

Defining entropy in terms of probabilities, the *Gibbs entropy* is $S_G = -k_B \sum_j P_j \ln P_j$, where P_j refers to microstate probabilities. The Boltzmann entropy $S_B = k_B \ln \Omega$ is a special case of the Gibbs entropy, as can be shown by assuming equal a-priori probabilities, *i.e.*, all $P_j = \Omega^{-1}$ are equal.

Using the Gibbs entropy, we have found two further examples of how thermodynamic variables can be directly derived from partition functions, in particular the Helmholtz free energy $F = -k_B T \ln Z$ and the grand potential $\Phi = -k_B T \ln Z_G$.

The *Shannon entropy* is given by $S_I = -K \sum_j P_j \ln P_j$, with $K = (\ln 2)^{-1}$, although in information theory, K is also often taken as 1. The Shannon entropy provides a measure of information content and does not make any a-priori assumptions about the probabilities P_j. In that sense, it can be seen as a more general version of the Gibbs entropy. The microcanonical, canonical and grand canonical probability distributions can all be found by maximising S_I taking into account the appropriate constraints.

Both the Gibbs and Shannon entropies direct us towards an interpretation of entropy as a measure of *uncertainty*, and less so of (as often assumed) *disorder*. Hence we can restate the second law by noting that if a system is left to its own devices, the uncertainty on its state will at best remain the same, but generally increase ($S \geq 0$).

Chapter 6

Quantum gases

One of the key successes of thermodynamics has been its description of ideal gases. As we will see later, ideal-gas descriptions applies to to a surprisingly broad range of systems of non- or weakly interacting particles that are free to move in a given volume. Via statistical mechanics, we can relate the macroscopic description of thermodynamics (*i.e.*, in terms of state variables) to properties of microscopic constituents, essentially by counting microstates. Yet we also know that at sufficiently small scales, quantum-mechanical behaviour can significantly deviate from classical physics. So it is important to consider how quantum properties emerge in statistical mechanics, with the ideal gas as an important example. We shall therefore construct a theory of quantum gases, see how it splits into two main cases, depending on the 'exchange symmetry' between particles, and recover the classical limit in the process. In doing so, we will also cover some paradoxical aspects of our treatment of classical many particle systems (the so-called Gibbs paradox) and lay the groundwork for understanding phenomena that range from superfluidity and superconductivity, via the behaviour of collapsing stars, to the electrical conductivity and semiconductivity that underpins virtually all information technology in our daily lives.

6.1 Energetics of a quantum gas

Since an ideal gas is defined as a system of non-interacting particles in a given volume (e.g., a box), we will first consider the energetics when such particles behave quantum-mechanically. The problem of N noninteracting particles in a cubic box of volume V is reducible to one of a single particle because the Hamiltonian operator in the Schrödinger equation separates into kinetic energy terms for each particle. This means that the wavefunction of the N particles is a product of wavefunctions of individual particles, or indeed a sum of such products, as we shall see. Therefore we focus attention on determining the wavefunctions and energies of a single particle in the box.

We start with

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = \epsilon\psi(x,y,z) , \tag{6.1}$$

where m is the particle mass and $\psi(x,y,z)$ is the single particle wavefunction. Writing $\psi(x,y,z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$, this separates further into equations for one-dimensional wavefunctions of the type

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_{n_x}(x)}{\mathrm{d}x^2} = \epsilon_{n_x}\psi_{n_x}(x) , \tag{6.2}$$

where the wavefunctions and energies are labelled with the index n_x, and where $\epsilon = \epsilon_{n_x} + \epsilon_{n_y} + \epsilon_{n_z}$. The boundary conditions are $\psi_{n_x}(x) = 0$ at $x = 0$ and $x = L$, where L is the length of a side of the
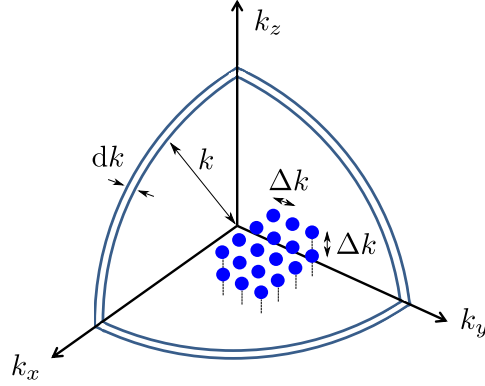
Figure 6.1: Wavefunctions describing a single particle confined to a cubic volume $V = L^3$ take the form of standing waves specified by wavevectors that form a cubic array in what is called **k**-space, with allowed components $k_j = n_j \Delta k$ defined by positive integers n_j, some of which are shown. We divide this phase space of a single particle into macrostates with a magnitude of wavevector in the range $k \to k + \mathrm{d}k$ and estimate their multiplicity by counting the number of single particle microstates within the octant shell indicated.

cubic box. The solutions are

$$\psi_{n_x}(x) \propto \sin(k_x x), \tag{6.3}$$

in terms of an x-component of the wavevector $k_x = \pi n_x / L$, with n_x a positive integer. The associated energy is

$$\epsilon_{n_x} = \frac{\hbar^2 k_x^2}{2m} = \frac{h^2 n_x^2}{8mL^2}, \tag{6.4}$$

such that the total energy is given by

$$\epsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{2m} \left(k_x^2 + k_y^2 + k_z^2 \right) = \frac{h^2}{8mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right) . \tag{6.5}$$

Note that these energy levels are not evenly spaced, in contrast to the quantised energies of a harmonic oscillator. These energies can be plotted as a function of $\{n_x, n_y, n_z\}$, such that states with equal energies lie on the surface of a sphere with radius $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$. More commonly, however, this is done in a coordinate system defined by $k_{x,y,z} = \pi n_{x,y,z}/L$, where the states can be visualised as a set of points arranged as a three-dimensional cubic lattice. In this so-called reciprocal lattice, each specified by a wavevector $\mathbf{k} = (k_x, k_y, k_z)$ with magnitude k and states with equal energies lie on the surface of a sphere with radius k. From the quantisation conditions, the nearest neighbour distance between **k**-space lattice points is $\Delta k = \Delta n \times \pi/L = 1 \times \pi/L = \pi/L$. This is illustrated in figure 6.1.

Besides the quantification of energy levels, another important result from quantum mechanics is that each particle has an internal degree of freedom, the 'spin' (intrinsic angular momentum), which can take $2s + 1$ values, where s is an integer or half integer (between $-s$ and s in integer intervals). As a consequence, each lattice point in **k**-space has $2s + 1$ distinct quantum states, *i.e.*, has a *degeneracy* of $(2s + 1)$.

6.2 One-particle partition function

As usual, the canonical partition function is given by a sum of Boltzmann factors over all available microstates. For a single particle in a box, this can be written as

$$Z_1 = \sum_{n_x, n_y, n_z} (2s+1) \mathrm{e}^{-\beta \epsilon_{\mathbf{k}}} , \tag{6.6}$$

where the spin degeneracy factor is seen to play the role of a multiplicity of microstates for the macrostate labelled by the wavevector $\mathbf{k}$. It is more convenient, however, to group the microstates into macrostates labelled by a range of the *magnitude* of the wavevector. We write

$$Z_1 = \int_0^\infty \rho(k) \mathrm{e}^{-\beta \epsilon(k)} \mathrm{d}k = \int_0^\infty g(\epsilon) \mathrm{e}^{-\beta \epsilon} \mathrm{d}\epsilon , \tag{6.7}$$

where $\rho(k) \mathrm{d}k$ is the multiplicity of microstates in the range $k \to k+\mathrm{d}k$, and $g(\epsilon)\mathrm{d}\epsilon$ is the multiplicity of microstates in the energy range $\epsilon \to \epsilon + \mathrm{d}\epsilon$. $\rho(k)$ and $g(\epsilon)$ are called densities of states.

We calculate $\rho(k)$ by counting the number of wavevector lattice points lying between spherical shells of radius k and $k + \mathrm{d}k$ in the sector of $\mathbf{k}$-space with positive wavevector components. The volume of this region, multiplied by the spin degeneracy, and divided by the volume per lattice point $(\Delta k)^3 = (\pi/L)^3$, gives the microstate multiplicity

$$\rho(k)\mathrm{d}k = (2s+1) \frac{1}{8} 4\pi k^2 \mathrm{d}k \frac{1}{(\Delta k)^3} = \frac{(2s+1)k^2 L^3}{2\pi^2} \mathrm{d}k , \tag{6.8}$$

and so we write

$$\rho(k) = \frac{(2s+1)V k^2}{2\pi^2} , \tag{6.9}$$

since L^3 is equal to the volume of the box V.

To convert this to the density of states as a function of energy, we note that the multiplicity of microstates $g(\epsilon)\mathrm{d}\epsilon$, in the energy range $\epsilon \to \epsilon + \mathrm{d}\epsilon$, should be the same as the multiplicity of microstates $\rho(k)\mathrm{d}k$ in the corresponding k range $k \to k + \mathrm{d}k$. Therefore, we have

$$g(\epsilon)\mathrm{d}\epsilon = \rho(k)\mathrm{d}k . \tag{6.10}$$

Noting that $\epsilon = \hbar^2 k^2/2m \Rightarrow k = \sqrt{2m\epsilon}/\hbar$, we find

$$g(\epsilon) = (2s+1)V \frac{k^2}{2\pi^2} \frac{\mathrm{d}k}{\mathrm{d}\epsilon} = (2s+1)\, V \left(\frac{2m\epsilon}{2\pi^2 \hbar^2}\right) \frac{1}{2\hbar} \left(\frac{2m}{\epsilon}\right)^{1/2}$$
$$= \frac{(2s+1)V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\epsilon} . \tag{6.11}$$

This density is illustrated in figure 6.2. Its nonlinearity is a consequence of the uneven spacing of the single particle energy levels alluded to in section 6.1.

The partition function representing the one-particle system is now given by

$$Z_1 = \int_0^\infty g(\epsilon) \mathrm{e}^{-\beta \epsilon} \mathrm{d}\epsilon = \frac{(2s+1)V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\epsilon}\, \mathrm{e}^{-\beta \epsilon} \mathrm{d}\epsilon . \tag{6.12}$$

To evaluate this integral, we substitute $x = \sqrt{\epsilon}$, such that $\mathrm{d}x = (2\sqrt{\epsilon})^{-1} \mathrm{d}\epsilon$ and $2x^2 \mathrm{d}x = \sqrt{\epsilon}\mathrm{d}\epsilon$. Therefore,

$$\int_0^\infty \sqrt{\epsilon}\, \mathrm{e}^{-\beta \epsilon} \mathrm{d}\epsilon = 2 \int_0^\infty x^2 \mathrm{e}^{-\beta x^2} \mathrm{d}x = \int_{-\infty}^\infty x^2 \mathrm{e}^{-\beta x^2} \mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}} , \tag{6.13}$$
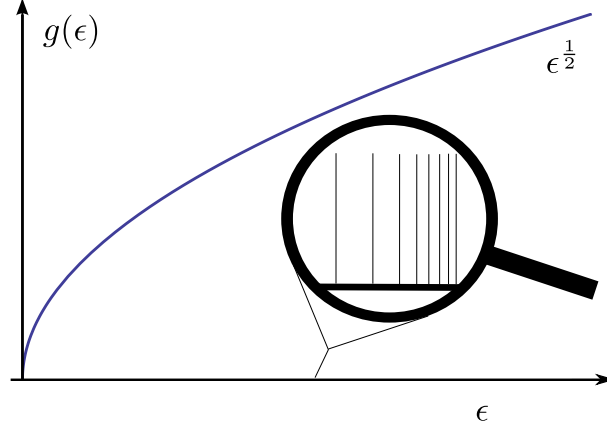
Figure 6.2: The density of states $g(\epsilon)$, with respect to energy ϵ, of a single particle in a box. The magnification of the energy axis indicates explicitly that the spectrum of states steadily becomes denser as ϵ increases.

where we have made use of a standard integral related to the variance of a centred Gaussian distribution. Inserting this result in equation 6.12, we obtain the partition function for the one-particle gas:

$$
\begin{aligned}
Z_1 &= \frac{(2s+1)V}{2^3 \pi^{3/2}} \left(\frac{2m}{\hbar^2 \beta}\right)^{3/2} = (2s+1)V \left(\frac{\pi}{2^2 \pi^2}\right)^{3/2} \left(\frac{2m}{\hbar^2 \beta}\right)^{3/2} \\
&= (2s+1)V \left(\frac{2\pi m}{(2\pi \hbar)^2 \beta^2}\right)^{3/2} = (2s+1)\frac{V}{\lambda_{\text{th}}^3} \ ,
\end{aligned}
\tag{6.14}
$$

where we define the thermal de Broglie wavelength as

$$
\lambda_{\text{th}} = \sqrt{\frac{\beta h^2}{2\pi m}} = \frac{h}{\sqrt{2\pi m k_B T}} \ .
\tag{6.15}
$$

The physical meaning of λ_{th} will become clearer later in this chapter. For now, we just note the result for Z_1 as it is, and first consider how this result is modified if we take into account multiple particles.

6.3 Multiple undistinguishable particles at a single energy level: bosons and fermions

Having determined the single-particle canonical partition function Z_1, we next consider a system that contains more than one particle. This brings us to another characteristic of quantum mechanics: when counting multi-particle states in quantum mechanics, it is important to notice that a quantum state does not change (it *is* the same) when any two identical particles are swapped: *i.e.*, for any wave-function of any number of particles $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots)$, one has:

$$
\psi(\mathbf{r}_2, \mathbf{r}_1, \ldots) = e^{i\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) \ ,
\tag{6.16}
$$

where φ is a global phase which does not change the state (here, the notation $\mathbf{r}_j$ stands for the position of a particle). By swapping once more, one must obtain the original wave function back. Therefore,

$$
\psi(\mathbf{r}_2, \mathbf{r}_1, \ldots) = e^{i2\varphi}\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) \ .
\tag{6.17}
$$

Hence $1 = e^{i2\varphi}$, such that $e^{i\varphi} = \pm 1$: the quantum mechanical wave-functions of identical particles are either completely symmetric $e^{i\varphi} = +1$ or completely anti-symmetric $e^{i\varphi} = -1$. Note here that we swapped particles 1 and 2 in the wave function, but we could have swapped any pair, so this result is general. By virtue of a classic result known as the spin-statistics theorem, it turns out that *the wave function of particles with integer spin ("bosons") is symmetric, whereas the wave-function of particles with half-integer spin ("fermions") is anti-symmetric with respect to particle exchange.*

If we now consider a wave function of two particles in the same state, defined by position ($\mathbf{r} = \mathbf{r}_1 = \mathbf{r}_2$, the exchange of particles leads to

$$\psi(\mathbf{r}_2, \mathbf{r}_1, \ldots) = +\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) \quad \Rightarrow \quad \psi(\mathbf{r}, \mathbf{r}, \ldots) = \psi(\mathbf{r}, \mathbf{r}, \ldots) \tag{6.18}$$

for bosons, revealing nothing particularly noteworthy. However, for fermions, this yields

$$\psi(\mathbf{r}_2, \mathbf{r}_1, \ldots) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots) \quad \Rightarrow \quad \psi(\mathbf{r}, \mathbf{r}, \ldots) = -\psi(\mathbf{r}, \mathbf{r}, \ldots) \quad \Rightarrow \quad \psi(\mathbf{r}, \mathbf{r}, \ldots) = 0 . \tag{6.19}$$

Hence the fermion wave function ψ is zero for any configuration in which two particles occupy the same quantum state. In other words, while a single quantum state can be occupied by an arbitrary number N of bosons, there can be no more than one fermion per quantum state, which is also known as the *Pauli exclusion principle*.

If we allocate an energy ϵ to such a state, the total energy of the system will be $N\epsilon$ and we find a grand partition function (equation 3.17)

$$Z_G^{(\epsilon)} = \sum_{N=0}^{N_{max}} e^{-\beta(\epsilon-\mu)N} \quad \text{with} \quad \begin{cases} N_{max} = \infty \text{ for bosons,} \\ N_{max} = 1 \text{ for fermions.} \end{cases} \tag{6.20}$$

The summation for $N_{\max} = \infty$ is a geometric series[1], yielding

$$Z_G^{(\epsilon)} = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}} . \tag{6.21}$$

for bosons. Clearly, the sum in equation 6.20 only converges and leads to well-defined results if $e^{-\beta(\epsilon-\mu)} < 1$, *i.e.*, $\epsilon - \mu$ must always be positive (for bosons); if we adopt the convention of defining minimum energy $\epsilon = 0$ for a system of bosons, this implies that $\mu < 0$, a fact that will prove useful later on. Having defined $Z_G^{(\epsilon)}$, it is straightforward to derive other statistical parameters of the system. In particular, we can determine the average number of particles populating the level via a partial derivative to the chemical potential μ (equation 4.33), leading to:

Bose-Einstein statistics. The mean number of bosons $\langle N \rangle^{(\epsilon)}$ occupying an energy level ϵ at temperature $T = 1/(k_B\beta)$ and chemical potential μ is given by

$$\langle N \rangle^{(\epsilon)} = \frac{1}{\beta} \frac{\partial \ln Z_G^{(\epsilon)}}{\partial \mu} = \frac{e^{-\beta(\epsilon-\mu)}}{1 - e^{-\beta(\epsilon-\mu)}} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1} . \tag{6.22}$$

This type of statistics is named after Einstein and Satyendra Bose (1894–1974), who also lend his name to bosons. Note that $\langle N \rangle_\epsilon \to \infty$ if $(\epsilon - \mu) \to 0^+$, so the occupancy of such an energy level can become very high.

The same evaluation may be repeated for fermions, for which $N_{\max} = 1$ in equation 6.20 and

$$Z_G^{(\epsilon)} = 1 + e^{-\beta(\epsilon-\mu)} , \tag{6.23}$$

leading to:

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[1] $\sum_{n=0}^{\infty} x^n = (1-x)^{-1}$ for $|x| < 1$, with here $x = e^{-\beta(\epsilon-\mu)}$.

Fermi-Dirac statistics. The mean number of fermions $\langle N \rangle^{(\epsilon)}$ occupying an energy level ϵ at temperature $T = 1/(k_B \beta)$ and chemical potential μ is given by

$$\langle N \rangle^{(\epsilon)} = \frac{1}{\beta} \frac{\partial \ln Z_G^{(\epsilon)}}{\partial \mu} = \frac{e^{-\beta(\epsilon-\mu)}}{1 + e^{-\beta(\epsilon-\mu)}} = \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \;. \tag{6.24}$$

This type of statistics is named after Enrico Fermi (1901–1954), hence the term 'fermions', and Paul Dirac (1902–1984). Since $e^{\beta(\epsilon-\mu)}$ can range between 0 and ∞ as $\beta(\epsilon-\mu)$ ranges between $-\infty$ and $+\infty$, this is consistent with our requirement that $\langle N \rangle^{(\epsilon)}$ can only range from 0 to 1 (no two fermions can occupy the same quantum state), which is very different from Bose-Einstein statistics.

Since Bose-Einstein and Fermi-Dirac statistics only differ by a sign at the denominator, we shall occasionally use the notation $(e^{\beta(\epsilon-\mu)} \mp 1)^{-1}$ to refer to both Bose–Einstein and Fermi-Dirac statistics, with the minus sign referring to Bose-Einstein statistics and the plus sign referring to Fermi-Dirac statistics.

6.4   The partition function of a quantum gas

In section 6.2, we have determined the canonical partition function Z_1 for a single-particle quantum gas and in section 6.3 the grand canonical partition function Z_G for multiple particles that can occupy a single energy level. The next step is to consider the presence of multiple states j with various energies ϵ_j, which may each be occupied by N_j particles. In doing so, it is useful to consider the partition function that results when we couple different systems A, B, C, ... each with their own partition function Z_A, Z_B, Z_C, ..., where it is useful to recall that the partition function is a sum of statistical weights.

A simple example is the roll of two dice as considered previously. For a single die, each outcome 1, 2, 3, 4, 5, 6 has an equal probability, hence equal statistical weight, say 1 as would result if we assign to each outcome a Boltzmann factor with energy 0, and the partition function for die A is given by $Z_A = \sum_{j=1}^{6} 1 = 6$. Similarly, for the other die, $Z_B = \sum_{j=1}^{6} 1 = 6$. For the roll of two dice, we find that instead of 6 different outcomes, we now have $6^2 = 36$ different combinations of outcomes (1,1), (1,2), (2,1), (1,3), etc.[2] If we again assign each of these combinations a statistical weight 1, then the partition function is the sum of 36 weights of 1, equal $36 = Z_A \times Z_B$. Note that this argument remains the same if the statistical weights for the outcomes of one die are not equal (e.g., consider a die C that has been tampered with to have faces 2, 3, 4, 5, 6 and another 6, which would still yield $Z_C = 1+1+1+1+2 \times 1 = 6$). Hence if we couple different systems A, B, C, ..., the partition function of the combined system will be $Z_A \times Z_B \times Z_C \times \ldots$. An important caveat, as we will see later, is that this only applies if the statistical weights in one system are independent of the statistical weights in other systems. In the example of the dice: if the outcome of the second die is somehow coupled to the outcome of the first, this multiplicity of partition functions would yield inaccurate results.

With this in mind, we can now construct the grand canonical partition function of the N-particle gas with multiple energy levels, writing it as the product of partition functions for the single-state system $Z_G^{(\epsilon)}$ (equation 6.20), namely

$$Z_G = \sum_{N_{\mathbf{k}_1}} e^{-\beta(\epsilon_{\mathbf{k}_1}-\mu)N_{\mathbf{k}_1}} \times \sum_{N_{\mathbf{k}_2}} e^{-\beta(\epsilon_{\mathbf{k}_2}-\mu)N_{\mathbf{k}_2}} \times \ldots = \prod_{\mathbf{k}_j} Z_G^{(\epsilon_{\mathbf{k}_j})} \;,$$

---

[2] As noted before, there can be different combinations with the same sum, e.g., $1+2=3$ and $2+1=3$, but that does not alter the number of different combinations or 'microstates'.

with $Z_G^{(\epsilon_{\mathbf{k}_j})} = \sum_{N_{\mathbf{k}_j}} \mathrm{e}^{-\beta(\epsilon_j - \mu)N_{\mathbf{k}_j}}$. The microstates are labelled by the set of populations $\{N_{\mathbf{k}_i}\}$ across the array. Notice that this avoids assigning labels to any of the particles such that we can be sure that the result will be appropriate for indistinguishable particles.

We can rewrite this in terms of a sum over the energies ϵ, but in that case we need to take into account that different values of $\mathbf{k}_j$ may result in the same energy $\epsilon_{\mathbf{k}_j}$. For example, if $\epsilon_{\mathbf{k}_1} = \epsilon_{\mathbf{k}_2} \equiv \epsilon_{\mathbf{k}}$ in equation 6.25, the first two sums can be replaced by $\left(\sum_{N_{\mathbf{k}}} \mathrm{e}^{-\beta(\epsilon_{\mathbf{k}} - \mu)N_{\mathbf{k}}}\right)^{\Omega(\epsilon_{\mathbf{k}})}$, where $\Omega(\epsilon_{\mathbf{k}})$ represents the multiplicity of energy $\epsilon_{\mathbf{k}}$ ($= 2$ in this example). We can therefore rewrite equation 6.25 as follows:

$$Z_G = \prod_\epsilon \left(Z_G^{(\epsilon)}\right)^{\Omega(\epsilon)} \tag{6.25}$$

$$\Rightarrow \ln Z_G = \sum_\epsilon \Omega(\epsilon) \ln Z_G^{(\epsilon)} \tag{6.26}$$

$$\ln Z_G \approx \int_0^\infty g(\epsilon) \ln Z_G^{(\epsilon)} \mathrm{d}\epsilon , \tag{6.27}$$

where $g(\epsilon)$ is the density of states (see equation 6.11) and where the final expression becomes exact when the discretisation of energy levels becomes negligible.

Inserting our expression for $g(\epsilon)$ (equation 6.11) and our expressions $Z_G^{(\epsilon)} = (1 - \mathrm{e}^{-\beta(\epsilon - \mu)})^{-1}$ for bosons (equation 6.21) and $Z_G^{(\epsilon)} = 1 + \mathrm{e}^{-\beta(\epsilon - \mu)}$ for fermions (equation 6.23), this can be written as

$$\ln Z_G = \frac{(2s+1)V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\epsilon} \, \ln\left(Z_G^{(\epsilon)}\right) \mathrm{d}\epsilon \tag{6.28}$$

$$= \mp\frac{(2s+1)V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\epsilon} \, \ln\left(1 \mp \mathrm{e}^{-\beta(\epsilon - \mu)}\right) \mathrm{d}\epsilon , \tag{6.29}$$

where we have adopted a unified notation through the symbol $\mp$, with the minus sign referring to bosons and the plus sign referring to fermions. With the grand canonical partition function known, other statistical parameters can readily be determined.

6.5 The entropy and pressure of a quantum gas

One important example of such a statistical parameter is obviously the entropy. As outlined in section 5.2 (equation 5.20), the Gibbs entropy provides us with a rather straightforward way to calculate this, recalling that

$$S_G = \frac{\langle E \rangle}{T} - \frac{\mu \langle N \rangle}{T} + k_B \ln Z_G , \tag{6.30}$$

With Z_G at hand, this is readily evaluated. Firstly, since $g(\epsilon)$ does not depend on β (see equation 6.11), and using equations 4.34 and 6.27), we find

$$\langle E \rangle - \mu \langle N \rangle = -\frac{\partial \ln Z_G}{\partial \beta} = \int_0^\infty g(\epsilon)\left(-\frac{\partial \ln Z_G^{(\epsilon)}}{\partial \beta}\right)\mathrm{d}\epsilon$$

$$= \int_0^\infty g(\epsilon)(\underbrace{\langle E \rangle^{(\epsilon)}}_{=\epsilon\langle N \rangle^{(\epsilon)}} - \mu\langle N \rangle^{(\epsilon)})\mathrm{d}\epsilon \tag{6.31}$$

$$= \int_0^\infty g(\epsilon)(\epsilon - \mu)\langle N \rangle^{(\epsilon)}\mathrm{d}\epsilon .$$

For completeness, we can determine the average number of particles $\langle N \rangle$ the mean energy $\langle E \rangle$ separately. Using equation 4.33 and 6.27 and noting that $g(\epsilon)$ does not depend on μ either, $\langle N \rangle$ follows from

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln Z_G}{\partial \mu} = \int_0^\infty g(\epsilon) \frac{1}{\beta} \frac{\partial \ln Z_G^{(\epsilon)}}{\partial \mu} \mathrm{d}\epsilon = \int_0^\infty g(\epsilon) \langle N \rangle^{(\epsilon)} \mathrm{d}\epsilon \,. \tag{6.32}$$

Conveniently, we already know $g(\epsilon)$ (equation 6.11) and $\langle N \rangle^{(\epsilon)}$, *i.e.*, the mean number of particles occupying a single energy level, from section 6.3 (equations 6.21 and 6.23). Substituting these in equation 6.32,

$$\langle N \rangle = \frac{V(2s+1)}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)} \mp 1} \mathrm{d}\epsilon \tag{6.33}$$

Similarly, reconsidering equation 6.31, the mean energy is given by

$$\langle E \rangle = \int_0^\infty g(\epsilon) \epsilon \langle N \rangle^{(\epsilon)} \mathrm{d}\epsilon = \frac{V(2s+1)}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} \mp 1} \mathrm{d}\epsilon \,, \tag{6.34}$$

and the entropy

$$\begin{aligned} TS_G &= \langle E \rangle - \mu \langle N \rangle + \beta^{-1} \ln Z_G \\ &= \int_0^\infty g(\epsilon) (\epsilon - \mu) \langle N \rangle^{(\epsilon)} \mathrm{d}\epsilon + \beta^{-1} \int_0^\infty g(\epsilon) \ln Z_G^{(\epsilon)} \mathrm{d}\epsilon \\ &= \int_0^\infty g(\epsilon) \left(\frac{\epsilon - \mu}{e^{\beta(\epsilon-\mu)} \mp 1} \mp \beta^{-1} \ln \left(1 \mp e^{-\beta(\epsilon-\mu)} \right) \right) \mathrm{d}\epsilon \end{aligned} \tag{6.35}$$

Another interesting result can be obtained by calculating the pressure of a quantum gas. Recalling that the pressure can be written as a partial derivative of the grand potential Φ (see equation 2.25) and that $\beta\Phi = -\ln Z_G$ (see equation 5.21), we can calculate this pressure via

$$p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = \frac{1}{\beta} \left(\frac{\partial \ln Z_G}{\partial V}\right)_{T,\mu} \tag{6.36}$$

$$= \mp \frac{1}{\beta} \frac{(2s+1)}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\epsilon} \ln\left(1 \mp e^{-\beta(\epsilon-\mu)}\right) \mathrm{d}\epsilon \,, \tag{6.37}$$

where we have used equation 6.29. This result can be integrated by parts to get

$$\begin{aligned} p &= \mp \frac{1}{\beta} \frac{(2s+1)}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{3} \left(\underbrace{\left[\epsilon^{3/2} \ln\left(1 \mp e^{-\beta(\epsilon-\mu)}\right)\right]_0^\infty}_{=0} \mp \int_0^\infty \underbrace{\frac{\epsilon^{3/2} \beta e^{-\beta(\epsilon-\mu)}}{1 \mp e^{-\beta(\epsilon-\mu)}}}_{\pm\beta\epsilon^{3/2}/\left(e^{\beta(\epsilon-\mu)}\mp 1\right)} \mathrm{d}\epsilon \right) \\ &= \frac{2}{3} \underbrace{\frac{(2s+1)}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} \mp 1} \mathrm{d}\epsilon}_{=\langle E \rangle/V} = \frac{2}{3} \frac{\langle E \rangle}{V} \,, \end{aligned} \tag{6.38}$$

where we have made use of our previous result for $\langle E \rangle$ (see equation 6.34). So we find that the pressure of a quantum gas equals $2/3$ of its energy density. Considering the thermodynamic state variables as mean values as usual, this agrees with our previous result for the classical ideal gas, where $pV = Nk_BT = \frac{2}{3}E$ (equation 1.6). That said, quantum effects do become apparent when $T \to 0$, largely because $\langle E \rangle$ does *not* follow classical behaviour under such conditions, as will be explored in the next chapters. For now, however, we will first verify our results for the quantum gas in the classical limit, where we are in for a few surprises.

6.6 The classical limit of a quantum gas

We shall refer to the classical limit of a quantum gas as the conditions under which $\langle N \rangle^{(\epsilon)} \ll 1$ for all ϵ. In such a regime, all the counting effects peculiar to due quantum mechanics (in particular the Pauli exclusion principle for fermions) become negligible, and one expects to recover the (monoatomic) classical ideal gas laws. One has, for bosons and fermions,

$$\langle N \rangle^{(\epsilon)} = \frac{1}{e^{\beta(\epsilon-\mu)} \mp 1} \ll 1 , \tag{6.39}$$

which implies $e^{\beta(\epsilon-\mu)} \gg 1$ and so $e^{-\beta(\epsilon-\mu)} \ll 1$. The grand canonical partition function of bosons $Z_G^{(\epsilon)}$ (equation 6.21) can then be approximated by a first-order Taylor expansion,

$$Z_G^{(\epsilon)} = \frac{1}{1 - e^{-\beta(\epsilon-\mu)}} \approx 1 + e^{-\beta(\epsilon-\mu)} , \tag{6.40}$$

which is the same as for fermions (see equation 6.23). *I.e.*, in the classical limit, there is no difference between bosons and fermions.

Also, by another first-order Taylor expansion in $e^{-\beta(\epsilon-\mu)}$, one finds $\ln Z_G^{(\epsilon)} \approx \ln\left(1 + e^{-\beta(\epsilon-\mu)}\right) \approx e^{-\beta(\epsilon-\mu)}$, so that the total grand canonical partition function of the systems Z_G satisfies

$$\ln Z_G = \int_0^\infty g(\epsilon) \, d\epsilon \ln Z_G^{(\epsilon)} \approx \int_0^\infty g(\epsilon) \, d\epsilon \, e^{-\beta(\epsilon-\mu)} = e^{\beta\mu} \int_0^\infty g(\epsilon) e^{-\beta\epsilon} \, d\epsilon , \tag{6.41}$$

where $g(\epsilon)$ is the energy of density single-particle levels , derived in the previous section. Intriguingly, this closely resembles the one-particle partition function of a single particle Z_1 (see equations 6.12 and 6.14) as discussed in section 6.2. In particular, in this approximation,

$$\ln Z_G = e^{\beta\mu} \underbrace{\int_0^\infty g(\epsilon) e^{-\beta\epsilon} \, d\epsilon}_{=Z_1 = V(2s+1)/\lambda_{\text{th}}^3} = e^{\beta\mu} Z_1 , \tag{6.42}$$

such that

$$Z_G = \exp\left(e^{\beta\mu} Z_1\right) = \sum_{N=0}^\infty e^{\beta\mu N} \frac{Z_1^N}{N!} , \tag{6.43}$$

where we have written the exponential as an infinite sum ($e^x = \sum_{N=0}^\infty x^N/N!$).

On the other hand, as can be shown from the general definitions of the canonical and grand canonical partition functions, one always has:

$$Z_G = \sum_{E,N} \Omega(E,N) e^{-\beta(E-\mu N)} = \sum_N e^{\beta\mu N} \underbrace{\sum_E \Omega(E,N) e^{-\beta E}}_{=Z_N} = \sum_N e^{\beta\mu N} Z_N , \tag{6.44}$$

where Z_N is the *canonical* partition function of N particles at the inverse temperature β. Compare equations 6.43) and 6.44 to obtain:

$$Z_N = \frac{Z_1^N}{N!} = \frac{1}{N!} \frac{V^N (2s+1)^N}{\lambda_{\text{th}}^{3N}} , \tag{6.45}$$

that relates the canonical partition function of N gas particles (Z_N) to the canonical partition function of a single gas particle Z_1.

At first sight, this result appears rather surprising: Given the multiplicity of partition functions as discussed at the beginning of section 6.4, we would expect the Z_N to be the product of all partition functions for the partitions functions for the individual particles Z_1, so $Z_N = Z_1^N$, which differs from equation 6.45 by a factor $N!$.

Before addressing this paradoxical result, let us first calculate the entropy of the classical ideal gas based on equation 6.45, to see how it compares with the classical result from thermodynamics, as derived in section 1.3, where we had found (see equation 1.14):

$$S(T,V,N) = Nk_B \ln\left(\frac{(k_BT)^{3/2}}{\hat{c}(N/V)}\right). \tag{6.46}$$

Firstly, we determine the mean energy from equation 6.45, using

$$\langle E\rangle = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{\partial\left(\ln \lambda_{th}\right)^{3N}}{\partial \beta} = 3N\frac{\partial}{\partial \beta}\ln\underbrace{\left(\frac{\beta h^2}{2\pi m}\right)^{1/2}}_{=\lambda_{th}} = \frac{3}{2}N\beta^{-1} = \frac{3}{2}Nk_BT, \tag{6.47}$$

fully consistent with the result for the classical ideal gas in section 1.3. Next, to determine the entropy, we make use of the expression $F = E - TS = -k_BT\ln Z$ (see equation 5.19), where as usual it is understood that $E = \langle E\rangle$ and $F = \langle F\rangle$ refer to mean values:

$$S = \frac{\langle E\rangle - \langle F\rangle}{T} = \frac{3}{2}Nk_B + k_B\ln Z_N = \frac{3}{2}Nk_B + k_BN\ln\left(\frac{(2s+1)V}{\lambda_{th}^3}\right)\underbrace{-k_B\ln N!}_{\approx -k_BN\ln N + k_BN}$$

$$\approx \frac{5}{2}Nk_B\ln \mathrm{e} + Nk_B\ln\left(\frac{(2s+1)V}{\lambda_{th}^3 N}\right) = Nk_B\ln\left(\frac{(2s+1)\mathrm{e}^{5/2}V}{\lambda_{th}^3 N}\right), \tag{6.48}$$

where we assumed $N \gg 1$ and used the Stirling approximation $\ln N! \approx N\ln N - N$ for $N \gg 1$. We have finally obtained a complete formula for the entropy of an ideal gas, usually referred to as the Sackur-Tetrode equation:

Sackur-Tetrode equation. The entropy S of a classical, monoatomic ideal gas of N indistinguishable particles of mass m and spin s, contained in a volume V at temperature T, is given by

$$S = Nk_B\ln\left(\frac{(2s+1)\mathrm{e}^{5/2}V}{\lambda_{th}^3 N}\right) = Nk_B\ln\left(\frac{(2s+1)\mathrm{e}^{5/2}(2\pi mk_BT)^{3/2}}{(N/V)h^3}\right). \tag{6.49}$$

This result has three important implications. Firstly, comparing the Sackur-Tetrode equation with the entropy as derived based on the ideal gas law 6.46, we have found an expression for the previously arbitrary constant in the latter, $\hat{c} = \mathrm{e}^{-5/2}\left(h^2/2\pi m\right)^{3/2}/(2s+1)$, and this result includes Planck's constant h in spite of being entirely classical, *i.e.*, non-quantum-mechanical! This is a reflection of the fact that classical physics cannot provide one with an absolute count of the possible configurations of a system, since classical physics allows arbitrarily small levels of coarse-graining of a system. Note, however, that entropy differences will not depend on h, as one should expect for the classical regime.

The second implication relates to the presence of $N!$ in our expression for Z_N (see equation 6.45), which is the reason for the N in the denominator of the logarithm in the Sackur-Tetrude result. Thanks to this, the entropy is extensive (see section 1.1), *i.e.*, S scales with the size of the system that we consider: if we take two separated volumes V each containing an identical ideal gas (or,

equivalently and entirely classical, a suspension of colloidal particles) each with N particles and entropy S, and next remove the separation, we would expect the entropy of the total system to remain the same, $S + S = 2S$. Hence, if $N \to 2N$ and $V \to 2V$, then $S \to 2S$, as it should. Without $N!$ in our expression for Z_N, this would not be the case, something that it known as the *Gibbs paradox*.

However, if each of the two separated volumes contain a different gas (or a different colloidal suspension), the entropy *would change* upon removing the separation, because in that case the total system will increase its entropy by mixing the two different gases (or different colloidal suspensions). Hence it is important to note it particles are distinguishable or not. In our description of a monoatomic ideal gas, such indistinguishability has here emerged as a natural consequence of the way we count states in quantum-mechanics (see equation 6.25); yet it can apply just as well for entirely classical systems such as the colloidal suspension mentioned above.

Considering again our derivation of the Sackur-Tetrode result for N indistinguishable particles in equation 6.48, as well as the Boltzmann entropy, we note that

$$S = k_B \ln \Omega = k_B \ln \underbrace{\left(\frac{(2s+1)\mathrm{e}^{3/2}V}{\lambda_{th}^3} \right)^N}_{= \, \Omega', \text{ for } N \text{ distinguishable particles}} - k_B \ln N! = k_B \ln \frac{\Omega'}{N!} \; . \tag{6.50}$$

In other words, when counting particles and (micro)states, we need to take into account whether these are distinguishable or not, as we did, for example, when counting microstates in section 4.1. In the quantum-mechanical limit, indistinguishability of identical particles is implicit. Quite generally (*i.e.*, also classically!), we should consider particles indistinguishable if they have no observable physical differences in the experimentally relevant context.

Finally, we note in the Sackler-Tetrode equation, the particle density N/V (units: per volume) is measured in terms of λ_{th} (units: volume), which suggests that there is something special when density becomes of order λ_{th}^{-3}, or equivalently when the distance between particles $\sim (V/N)^{1/3}$ becomes of order λ_{th}. To understand this, let us recall that the kinetic energy E of a gas particle can be written as $\frac{1}{2}mv^2 = p^2/2m$, and that its average value is $\frac{3}{2}k_BT$. Hence we find $p \sim \sqrt{\langle p^2 \rangle} = \sqrt{3mk_BT}$. We also know the Heisenberg uncertainty principle, $\Delta x \Delta p \gtrsim \frac{1}{2}\hbar$, which becomes relevant when $\Delta x \sim \hbar/\Delta p \sim \hbar/\sqrt{3mk_BT} \sim \sqrt{h^2/2\pi mk_BT} = \lambda_{th}$. Which brings us to the conclusion that quantum effects are likely to become noticeable when the inter-particle distance becomes of order λ_{th} or smaller, or:

Condition for quantum behaviour. A monoatomic gas of quantum particles of mass m is expected to display quantum effects when its density becomes comparable to or larger than the quantum density $n_q = \lambda_{th}^{-3}$,

$$n \gtrsim n_q \; , \tag{6.51}$$

where the thermal de Broglie wavelength is given by

$$\lambda_{th} = \frac{h}{\sqrt{2\pi mk_BT}} \; . \tag{6.52}$$

6.7   Summary

In this chapter, we have consider ideal gases from a quantum-mechanical perspective, which includes the following key concepts and results.

- For non-interacting particles in a cubic box of volume L^3, states with equal energy are characterised by having the same vectorial sum of quantum numbers $\sqrt{n_x^2 + n_y^2 + n_z^2}$ or — equivalently — the same absolute wave number $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$, where the particle energy $\epsilon_k = \hbar^2 k^2 / 2m$ and $k_{x,y,z} = \pi n_{x,y,z} / L$.

- We can now define the *density of states* as the number of states in a spherical shell of thickness $\mathrm{d}k$ in the positive quadrant of k-space, which corresponds to the number of states with energies between ϵ_k and $\epsilon_k + \mathrm{d}\epsilon_k$. As a function of k, the density of states $\rho(k)$ scales with k^2, related to the volume $4\pi k^2 \mathrm{d}k$ of the shell. As a function of ϵ, the density of states $g(\epsilon)$ scales with $\sqrt{\epsilon}$, following from $g(\epsilon)\mathrm{d}\epsilon = \rho(k)\mathrm{d}k$ and the relation $k = \sqrt{2m\epsilon}/\hbar$.

- Integrating over all energies ϵ, we obtain the single-particle partition function $Z_1 = (2s + 1)V/\lambda_{th}^3$, where $(2s + 1)$ describes the degeneracy of a quantum state for a particle with spin s. $\lambda_{th} \propto h/\sqrt{T}$ is the thermal de Broglie wavelength. When the inter-particle distance become of order of or smaller than ($\lesssim$) λ_{th}, the classical description breaks down and quantum effects are likely to dominate the particle behaviour.

- One such quantum effect is the (anti)symmetry of a many-particle wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots)$ upon exchange of two identical particles. Particles with half-integer spin, so called fermions, are described by a wave function that is antisymmetric under this operation, and obey Fermi-Dirac statistics, which implies that a single quantum state cannot be occupied by more than one fermion. Particles with integer spin, so-called bosons, are are described by a wave function that is symmetric under particle-exchange, and obey Bose-Einstein statistics; there is no restriction to the number of bosons that can (in principle) occupy a single quantum state. This can be expressed by the mean number of particles $\langle N \rangle^{(\epsilon)}$ occupying an energy level ϵ at temperature $T = 1/(k_B \beta)$ and chemical potential μ,

$$\langle N \rangle^{(\epsilon)} = \frac{1}{\mathrm{e}^{\beta(\epsilon - \mu)} \mp 1} \ ,$$

where the $-$ and $+$ in the $\mp$ sign refer to bosons and fermions, respectively.

- Translating the single-particle partition function to that for N particles, we note the multiplicity of partition functions $Z_N = Z_1^N$ *provided that the particles are independent.* If the particles are indistinguishable, however, we find $Z_N = Z_1^N / N!$, due to the indistinguishability of states with that arise due to the $N!$ possible permutations of N identical particles.

- Stated differently, via the appropriate counting of available quantum states, we find the grand canonical partition function

$$Z_G = \prod_{\mathbf{k}_j} Z_G^{(\epsilon_{\mathbf{k}_j})} \ ,$$

which leads to the observation that

$$\ln Z_G \approx \int_0^\infty g(\epsilon) \ln Z_G^{(\epsilon)} \mathrm{d}\epsilon \ ,$$

with $Z_G^{(\epsilon)}$ the partition function for a single quantum state. That is, we find $\ln Z_G$ by an integration over $Z_G^{(\epsilon)}$, weighted by the density of states $g(\epsilon)$.

- With Z_G (or $\ln Z_G$) known, thermodynamic state variables can readily be determined, e.g., mean energy, pressure and entropy. For an ideal quantum gas in the classical limit, this results in the Sackur-Tetrode entropy, the absolute value of which does depend on Planck's constant and the (quantum-mechanical) spin s. This reflects the indistinguishability of particles that is imposed by quantum mechanics.

As a more subtle point, often referred to in the context of the so-called Gibb's paradox, the appropriate entropy of a system should take into account if particles are indistinguishable in practical — *i.e.*, not necessarily quantum-mechanical — sense. This reflects our notion of entropy as a measure of the uncertainty on the microscopic parameters of the system.

Having discussed some general properties of quantum gases and described the concepts needed to understand their behaviour, we can now turn to some practical implication of quantum-statistical behaviour across different fields of physics.

Chapter 7

Quantum behaviour of boson gases

A surprisingly large range of physical systems can be treated, at least approximately, as quantum gases. In this chapter, we will focus on boson gases in different contexts and illustrate how their behaviour deviates from classical predictions. In doing so, we will establish that light consists of bosonic particles called photons and that we can also treat collective excitations — involving many particles — as individual bosons obeying Bose-Einstein statistics. We illustrate the latter point by the example of lattice vibrations in a solid. Finally, exotic phenomena such as superfluidity and superconductivity can emerge when bosons accumulate in their ground state to form a Bose-Einstein condensate.

7.1 The ultraviolet catastrophe

Historically, the development of quantum physics emerged for an important part from the failure of classical statistical mechanics to account for experimental phenomena. A crucial example of such failure is the description of black-body radiation. Black-body radiation refers to electromagnetic radiation in thermal equilibrium at temperature $T = 1/(k_B \beta)$ inside a container of volume V. Such terminology refers to the fact that, being at thermal equilibrium, black-body radiation has zero net energy flux between system and reservoir (typically, the container's absorbing and re-emitting walls). As we shall see by determining its frequency spectrum, such radiation is not "black" at all.

We intend to apply the canonical formalism to the problem in hand. In order to count configurations, one needs first to identify the degrees of freedom of light (electromagnetic radiation) in a box of volume V. Each such degree of freedom is called a "mode" of the electromagnetic field, and each mode corresponds to an independent solution of the wave equation, as derived from the classical Maxwell equations. These solutions are plane waves with nodes at the boundaries of the box, as illustrated in figure 7.1, with angular frequencies

$$\omega = 2\pi c/\lambda = kc \,, \tag{7.1}$$

where c is the speed of light, λ is the wavelength, and k the wave number. To count the number of modes, we can proceed as in sections 6.1–6.2, noting that the density of modes as a function of k (see equation 6.9) is given by

$$\rho(k) = 2 \times \frac{Vk^2}{2\pi^2} \quad \Rightarrow \quad g(\omega) = \rho(k) \underbrace{\frac{\mathrm{d}k}{\mathrm{d}\omega}}_{= c^{-1}} = \frac{V}{\pi^2 c^3} \, \omega^2 \,, \tag{7.2}$$
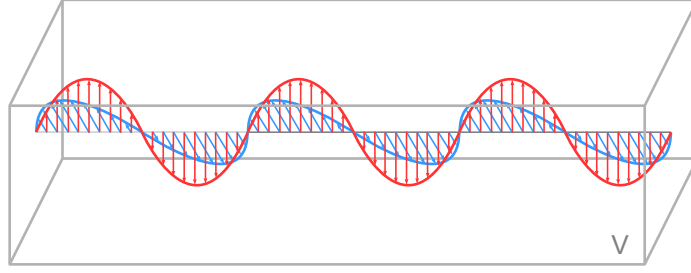
Figure 7.1: The degrees of freedom of the electromagnetic field in a volume V comprise all possible standing waves with nodes at the boundaries of the volume, propagating in all possible directions in three spatial dimensions, along two possible, orthogonal polarisations. Two such standing waves are shown above, propagating along the same direction and with the same frequency but with different polarisations, with the vectors representing electric fields. Each such standing wave may be treated as an independent quantum harmonic oscillator.

where $g(\omega)\,d\omega$ is the number of modes with frequencies between ω and $\omega + d\omega$, and where the additional factor 2 is included to account for the two orthogonal directions of the transverse waves (*i.e.*, two orthogonal polarisation directions). By noting that each mode corresponds to a different degree of freedom with energy $\propto k_B T$ as per the equipartition theorem, the total energy density in the volume

$$\frac{\langle E\rangle}{V}\bigg|_{classical} \propto k_B T \int_0^\infty g(\omega)d\omega \propto \int_0^\infty \omega^2 d\omega \to \infty \ . \tag{7.3}$$

Hence classical statistical mechanics predicts that the energy density of black-body radiation diverges, in contradiction with the first law. This result is known as the *ultraviolet catastrophe*, referring to the unphysical divergence for high ω, *i.e.*, for short λ, towards the ultraviolet range from the visible spectrum of light. This problem was resolved by assuming — as first done by Max Planck (1858–1947) — that light is discretised in energy quanta of $\hbar\omega$, such that the energy of each wave follows the behaviour of a quantum oscillator, $\hbar\omega j$ with j a positive integer, and where the zero-point energy (energy offset) $\frac{1}{2}\hbar\omega$ is irrelevant in this context. Note that in doing so, we consider these light quanta as bosons with spin $s = 0$: we can compare equation 7.2 with equation 6.9 for a quantum gas, presuming that the degeneracy $(2s + 1) = 1$.

To calculate the energy density of light in the closed volume, we can then proceed as in section 6.4, noting (see equation 6.27) that we can write the canonical partition function of the system

$$\ln Z = \int_0^\infty g(\omega) \ln Z^{(\omega)}\, d\omega = \int_0^\infty g(\omega) \ln \left(\sum_{j=0}^\infty e^{-\beta\hbar\omega j} \right) d\omega = \int_0^\infty g(\omega) \ln \left(\frac{1}{1 - e^{-\beta\hbar\omega}} \right) d\omega$$

$$= -\int_0^\infty \underbrace{g(\omega)}_{=\frac{V}{\pi^2 c^3}\omega^2} \ln\left(1 - e^{-\beta\hbar\omega}\right) d\omega = -\frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right) d\omega \ , \tag{7.4}$$

where we have used the geometric series $\sum_0^\infty x^n = (1 - x)^{-1}$ for $|x| < 1$.

With the partition function known, the mean energy follows as usual by an appropriate partial
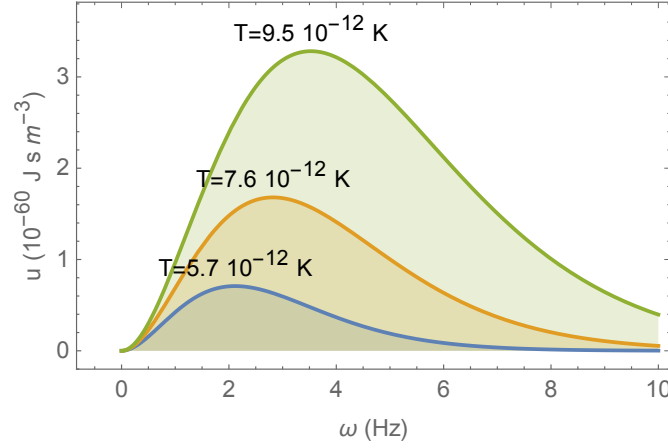
Figure 7.2: The black-body spectrum in SI units at three different temperatures. The positions of the maxima scales linearly with T (Wien's law), and the area under the curves scales with T^4 (Stefan-Boltzmann law).

derivative, and we can write the energy density in the black body as

$$\frac{\langle E \rangle}{V} = -\frac{\partial \ln Z}{\partial \beta}\frac{1}{V} = \frac{1}{\pi^2 c^3}\int_0^\infty \omega^2 \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\, d\omega = \frac{\hbar}{\pi^2 c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1}\, d\omega \tag{7.5}$$

$$= \int_0^\infty u(\omega)\, d\omega\ , \tag{7.6}$$

where we have defined the energy spectrum

$$u(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}\ . \tag{7.7}$$

This is also known as the Planck spectrum and is illustrated in figure 7.2.

On inspecting equation 7.5, we note that divergence for $\omega \to \infty$ is prevented by the exponential in the denominator, and that we would recover the classical limit if we were to (here erroneously) assume that $\beta\hbar\omega \ll 1$, such that $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$. Going further, we may rewrite the energy density as

$$\frac{\langle E \rangle}{V} = \int_0^\infty \hbar\omega\, n(\omega)\, d\omega \quad \text{with} \quad n(\omega) \propto \frac{\omega^2}{e^{\beta\omega\hbar} - 1}\ . \tag{7.8}$$

That is, the energy density follows the prediction for a gas of particles, each with energy $\hbar\omega$, with a density of states $\propto \omega^2$, that obey Bose-Einstein statistics: the factor $(e^{\beta\omega\hbar} - 1)^{-1}$ is the number occupancy $\langle N \rangle^{(\epsilon)}$ (see equation 6.22) of a quantum state of energy $\epsilon = \hbar\omega$ and zero chemical potential. The quantity $n(\omega)$ may thus be interpreted as a density of particles and, depending on the context, light behaves as an ensemble of bosonic particles, called photons, instead of waves.

Further interesting consequences follow from the analysis of the black-body spectrum. The maximum of $u(\omega)$ is at ω_{max}, which can be determined by differentiating $u(\omega)$:

$$\left.\frac{du}{d\omega}\right|_{\omega=\omega_{\text{max}}} = \frac{3\omega_{\text{max}}^2(e^{\beta\hbar\omega_{\text{max}}} - 1) - \beta\hbar\, e^{\beta\hbar\omega_{\text{max}}}\omega_{\text{max}}^3}{(e^{\beta\hbar\omega_{\text{max}}} - 1)^2} = 0\ , \tag{7.9}$$

whence

$$3(e^x - 1) - x\, e^x = 0 \tag{7.10}$$

with $x = \beta\hbar\omega_{\text{max}}$. Solving numerically, one finds $x \approx 2.821$, which leads to:

Wien's law. For electromagnetic radiation in thermal equilibrium at the temperature T, the maximum energy density occurs at the frequency

$$\omega_{\text{max}} \approx 2.821 \frac{k_B T}{\hbar} \ . \tag{7.11}$$

Note that this law, qualitatively predicted before the advent of quantum mechanics, offers a possible way to measure $\hbar$.

7.2 Stefan-Boltzmann law and the greenhouse effect

As we will see shortly, a surprising wide range of objects may — at least approximately — be considered as black bodies, which makes it relevant to determine the total light intensity that can be emitted by such a body. To this end, we first need to calculate the total energy density by completing the integration in equation 7.5,

$$\frac{\langle E \rangle}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \, d\omega = \frac{\hbar}{\pi^2 c^3} \frac{1}{\beta^4 \hbar^4} \underbrace{\int_0^\infty \frac{(\beta\hbar\omega)^3}{e^{\beta\hbar\omega} - 1} \, d(\beta\hbar\omega)}_{\int_0^\infty x^3 (e^x - 1)^{-1} dx = \pi^4/15}$$

$$= \frac{(k_B T)^4}{\pi^2 c^3 \hbar^3} \frac{\pi^4}{15} = \frac{4}{c} \sigma T^4 \ , \tag{7.12}$$

where we have used a standard integral and defined the Stefan-Boltzmann constant

$$\sigma = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} \approx 5.67 \times 10^{-8} \ \text{Wm}^{-2}\text{K}^{-4} \ . \tag{7.13}$$

The reason for this odd definition of σ, leaving out a factor $4/c$, will become clear hereafter.

The emitted light may then be found by considering the energy flux that would be emitted through a hole in the walls of the volume that contains the black-body radiation. Following the results in the previous section, we consider light as a gas of particles (photons) that each carry an energy $\hbar\omega$ and evaluate the number of photons incident at the boundary of our volume per unit area per unit time, making use of the fact that photons travel at the speed of light c. This is also an opportunity to illustrate a basic evaluation from the so-called *kinetic theory*, a useful phenomenological approach where, by simple statistical assumptions on the elementary particles forming a gas, one obtains relations between microscopic parameters (such as the velocities of such particles) and macroscopic quantities (such as the net, mean energy flux they carry).

Given an element of area dA on the boundary, it is convenient to adopt spherical polar coordinates for the velocity of the photons with polar angles θ and φ. Here θ defines the angle between the normal to dA and the velocity of the incident particles, see figure 7.3, and φ defines rotations around the normal to dA. In first instance, we will aim to calculate the number of articles incident per unit time on dA, originating from a solid angle bounded by θ, $\theta + d\theta$ and φ, $\varphi + d\varphi$.

To determine this number, we define $n(\omega) \, d\omega$, the number of particles per unit volume carrying an energy between $\hbar\omega$ and $\hbar\omega + d\hbar\omega$. Assuming that on average, the velocities of the particles are isotropic, this implies that there are $(4\pi)^{-1} n(\omega) \, d\omega \sin\theta \, d\theta \, d\varphi$ of such particles per unit volume
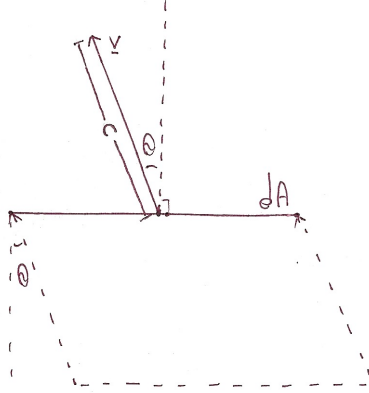
Figure 7.3: Profile view of the element of area $\mathrm{d}A$ and of the particle velocity $\mathbf{v}$, where $|\mathbf{v}|$ is the speed of light c. The spherical polar coordinate θ defines the angle between the normal to $\mathrm{d}A$ and the velocity $\mathbf{v}$. The normal to the surface, represented as a dashed line in the drawing, defines the z-axis.

with a velocity moving in the direction contained within the solid angle between θ, $\theta + \mathrm{d}\theta$ and φ, $\varphi + \mathrm{d}\varphi$.[1]

Of the particles moving in the direction contained within the solid angle between θ, $\theta + \mathrm{d}\theta$ and φ, $\varphi + \mathrm{d}\varphi$, those within the volume $c \cos\theta \, \mathrm{d}A \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi$ will reach the surface $\mathrm{d}A$ (see figure 7.3), so the total flux per unit area follows by integrating this number over θ from 0 (perpendicular to the surface) to $\pi/2$ (parallel to the surface) and over φ form $-\pi$ to $+\pi$ around the normal to the surface, and next dividing by $\mathrm{d}A$:

$$\frac{c}{4\pi} \int_0^\infty n(\omega)\mathrm{d}\omega \int_{-\pi}^{+\pi} \mathrm{d}\varphi \int_0^{\frac{\pi}{2}} \sin\theta\cos\theta \, \mathrm{d}\theta = \frac{c}{4\pi} n(\omega)\, \mathrm{d}\omega \frac{2\pi}{2} = \frac{c}{4} n(\omega)\, \mathrm{d}\omega \, . \tag{7.14}$$

Finally, to obtain the energy flux Φ due to these particles, this expression needs to be multiplied by the energy per particle (*i.e.*,per photon), $\hbar\omega$, and integrated over ω:

$$\Phi = \frac{c}{4} \int_0^\infty \hbar\omega n(\omega)\, \mathrm{d}\omega = \frac{c}{4} \frac{\langle E \rangle}{V} = \frac{c}{4} \frac{4}{c} \sigma T^4 = \sigma T^4 \, , \tag{7.15}$$

where we have used equations 7.8 and 7.12. We have thus obtained another seminal result about electromagnetic radiation in thermal equilibrium:

Stefan-Boltzmann law. A black body at temperature T irradiates energy with a flux Φ that is proportional to T^4,

$$\Phi = \sigma T^4 \, , \tag{7.16}$$

where the Stefan-Boltzmann constant σ is given by

$$\sigma = \frac{\pi^2 k^4}{60 c^2 \hbar^3} \approx 5.67 \times 10^{-8}\,\mathrm{Wm^{-2}K^{-4}} \, . \tag{7.17}$$

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[1]The integral over $\int_0^\pi \sin\theta \, \mathrm{d}\theta \int_{-\pi}^{+\pi} \mathrm{d}\varphi = 4\pi$, so we find that the integral $\int_{\theta=0}^{\theta=\pi} \int_{\varphi=-\pi}^{\varphi=+\pi} (4\pi)^{-1} n(\omega)\, \mathrm{d}\omega \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi = n(\omega)\, \mathrm{d}\omega$ yields the total number of particles per unit volume carrying an energy between $\hbar\omega$ and $\hbar\omega + \mathrm{d}\hbar\omega$, as it should.
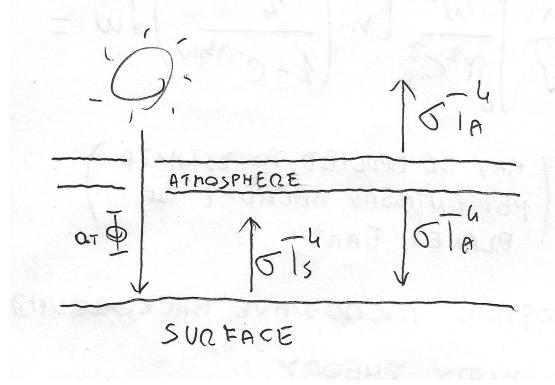
Figure 7.4: Naive depiction of energy exchanges between the Sun, the Earth's surface and the atmosphere.

The proportionality with T^4 was deduced from experimental data by Josef Stefan (1835–1893) in 1879 and given a theoretical foundation by (again) Ludwig Boltzmann five years thereafter. As shown above, the full derivation, including the value of the Stefan-Boltzmann constant σ, relies on the (quantum-mechanical) assumption of particle-behaviour of light.

The applicability of the black-body model is quite diverse and far-reaching, including the description of active stars and of the cosmic microwave background, as well as providing a simple model to understand the greenhouse effect. For the later, we may consider Earth as a black body emitting radiation, in thermal equilibrium with the incoming energy flux Φ from the Sun. The Sun itself emits black-body radiation at a temperature $T_\odot \approx 5800\,\mathrm{K}$ (the surface temperature of the Sun). The daylight flux from the Sun onto the Earth could be estimated by using the Stefan-Boltzmann law, as

$$\sigma T_\odot^4 \frac{4\pi R_\odot^2}{4\pi d^2} \approx 1.38 \times 10^3\,\mathrm{Wm}^{-2} \tag{7.18}$$

where $R_\odot$ is the radius of the Sun and d is the distance between the Sun and the Earth. On average, the incoming energy flux from the Sun turns out to be somewhat lower, $\Phi \approx 342\,\mathrm{Wm}^{-2}$, which is the value we are going to adopt.

Let us now apply the Stefan-Boltzmann law to estimate the surface temperature T_S of the Earth and to highlight the role played by the atmosphere in such an evaluation. Neglect first the atmosphere altogether. Then, aside for a 15% of incident radiation which is reflected away (this is parametrised through the surface "albedo" $a_s = 0.85$), the incident radiation must be at equilibrium with the emitted radiation, $a_s\Phi = \sigma T_S^4$, such that $T_S = (a_s\Phi/\sigma)^{1/4} \approx 268\,\mathrm{K}$, which would be freezing!

This changes substantially, however, if we introduce the atmosphere in the picture. As illustrated in Fig. 7.4, the atmosphere may be modelled as an extra layer in thermodynamic equilibrium at temperature T_A that reflects a further 15% of the incident radiation (this will result in a total albedo $a_T \approx 0.7$, which already includes reflection at the surface). We also assume that the atmosphere lets the remainder of the solar radiation through and that, by contrast, it absorbs all the radiation from the Earth's surface. The later assumption can be made plausible by taking into account the absorption spectrum of air and noting that the Earth emits radiation at lower frequencies than the Sun, because of Wien's law. With these assumptions, the atmosphere emits black-body radiation both towards and away from the Earth, and received black-body radiation

from the Earth, leading to the atmospheric energy balance

$$2\sigma T_A^4 = \sigma T_S^4 \,, \tag{7.19}$$

where T_S is the surface temperature as before. In addition, the overall balance is

$$a_T\Phi = \sigma T_A^4 \,. \tag{7.20}$$

The latter equation yields an atmospheric temperature $T_A = (a_T\Phi/\sigma)^{1/4} \approx 255\,\mathrm{K}$ which, when inserted in the former one, gives an estimate $T_S = 2^{1/4}T_A = (2a_T\Phi/\sigma)^{1/4} \approx 303\,\mathrm{K}$. In spite of the crudeness of this model, this is a very reasonable estimate of the surface temperature of the Earth, and it indicates a $35\,\mathrm{K}$ warming due to the presence of the atmosphere.

7.3 Phonons and the heat capacity of solids

In the previous sections, we have considered light as consisting of bosonic particles. Various other "particles" obeying Bose-Einstein statistics can emerge as collective excitations of larger numbers of particles. In this section, we will illustrate this with the collective excitations due to atomic vibrations in solids, which are known as "phonons". To this end, we consider a solid as an orderly lattice of N particles that are coupled by harmonic springs of spring constant C_L, such that each particle can oscillate around its equilibrium position in a harmonic potential due to the interaction with its nearest neighbours. To show how this translates into collective behaviour as results from the coupled vibrations of many atoms, we will here consider a one-dimensional chain of N such atoms, noting that a similar treatment — at the expense of more elaborate equations — applies in three dimensions.

The jth atom in such a chain will experience forces due to its interactions with neighbouring atoms $j-1$ and $j+1$, both pushing/pulling it back towards the equilibrium position. In terms of the deviation ψ_j of its equilibrium position, this yields a set of coupled equations of motion for $1 \le j \le N$,[2]

$$m\ddot{\psi}_j = -C_L(\psi_j - \psi_{j-1}) - C_L(\psi_j - \psi_{j+1}) \,, \tag{7.21}$$

where m is the mass of each atom and where we have . Note that $\psi_j - \psi_{j-1}$ is not the distance between atoms j and $j-1$, but the difference between the deviations from their equilibrium positions. We can solve such a system of N coupled equations by substituting the plane-wave ansatz

$$\psi_j = \xi \mathrm{e}^{i(\kappa j - \omega t)} \,, \tag{7.22}$$

where ξ is an arbitrary quantity with dimensions of length. This yields

$$\begin{aligned}
-m\omega^2 &= -C_L\left[(1 - \mathrm{e}^{-i\kappa}) + (1 - \mathrm{e}^{i\kappa})\right] \\
&= -2C_L(1 - \cos(\kappa)) = -4C_L\sin^2\left(\frac{\kappa}{2}\right) \,.
\end{aligned} \tag{7.23}$$

This tells us that there is a solution for every pair of values of ω and κ that satisfy this "dispersion relation", i.e., the equation relating the wave number κ and the angular frequency ω.

To identify the number of independent solutions, we can now set boundary conditions, which we shall choose to be periodic, as if the atoms were forming a closed ring. Thus, we set $x_{j+N} = x_j$, for all j, which implies $\mathrm{e}^{i\kappa N} = 1$ and

$$\kappa = z\frac{2\pi}{N} \,, \quad \text{for} \quad z \in \mathbb{Z} \,. \tag{7.24}$$

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[2] Strictly speaking, equation 7.21 is not defined for $j = 1$ or $j = N$, but this problem will be solved later by assuming appropriate boundary conditions.
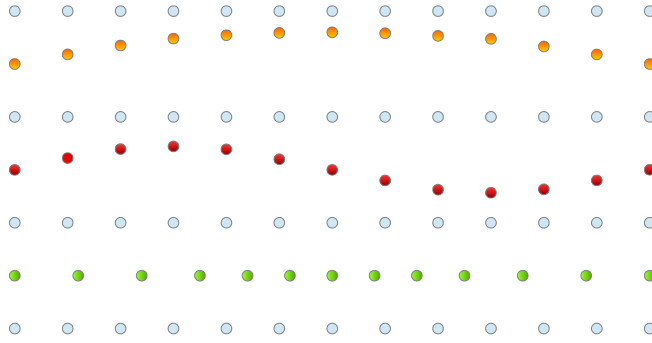
Figure 7.5: Examples of acoustic waves propagating through a lattice, represented in two rather than three dimensions, for simplicity. The orange and red waves are transverse (the orange wave's wavelength is the longest sustained by the lattice depicted, whilst the red wave's wavelength is half of it); the green wave is a longitudinal oscillation mode, where displacements with respect to the equilibrium position occur along the direction of propagation of the wave.

This equation identifies all the necessary independent solutions: only N values of z (which can be chosen between 1 and N, or $-N/2$ and $N/2 - 1$ for N even) yield different solutions. Values of κ differing by 2π would clearly give the same solution for the ψ_j's. We knew in advance the number of solutions would be N, since we are just describing the oscillations of N particles in one dimension, each of which correspond to a degree of freedom.

The analysis above may be straightforwardly extended to three spatial dimensions, obtaining $3N$ oscillatory modes: N longitudinal modes related to deviations ψ_j in the direction of the chain, and $2N$ transverse mode for deviations ψ_j perpendicular to the chain, with the only difference between the transverse and longitudinal modes being the relevant spring constant, which has to be changed from C_L to C_T.

Finally, if we are interested in variations in ψ_j that occur over distances $x \gg a$, we may write

$$\psi_j = \xi e^{i(\kappa j - \omega t)} = \xi e^{i(kaj - \omega t)} \quad \rightarrow \quad \psi(x,t) = \xi e^{i(kx - \omega t)} , \tag{7.25}$$

with a the equilibrium distance between the particles on the chain and $x = aj$. This shows that the solutions for ψ represent propagating waves, which correspond to the propagation of sound through matter. A two-dimensional depiction of the acoustic wave solution propagating through a lattice (the solid) is given in Fig. 7.5.

In the same approximation $\kappa = ka = 2\pi/\lambda \ll 1$, we find the dispersion relation (equation 7.23)

$$\omega^2 = \frac{4C_L}{m} \sin^2\left(\frac{ka}{2}\right) \approx \frac{4C_L}{m}\left(\frac{ka}{2}\right)^2 = k^2 v_L^2 , \tag{7.26}$$

where we have identified the longitudinal propagation (sound) velocity $v_L = a\sqrt{C_L/m}$. The treatment of the transverse modes is identical, up to substituting C_L with C_T to derive the speed of the transverse waves v_T.

This linear relation ($\omega = kv$) is mathematically equivalent to the dispersion relation for light ($\omega = kc$) as used in section 7.1. Conceptually, we can now associate each wave solution with a particle-like excitation, as we did previously by treating light as consisting of photons. By the same analogy, we define *phonons* as particle-like excitations that represent lattice vibrations in a solid,

and can proceed as in section 7.1 by determining a density of states $g(\omega)$, calculating the partition function and hence various state variables.

By comparison with equation 7.2 and noting that we need to accommodate two different speeds of sound, v_T and v_L, we find

$$g(\omega) = \frac{V\omega^2}{2\pi^2} \left(\frac{2}{v_T^3} + \frac{1}{v_L^3} \right) = \frac{3V\omega^2}{2\pi^2 v_s^3} , \tag{7.27}$$

where we have replaced $2c^{-3}$ in equation 7.2 (corresponding to the 2 polarisations of the transverse electromagnetic waves), substituting instead $2v_T^{-3} + v_L^{-3}$ to account for the two transverse and the one longitudinal modes of oscillation, and where we inserted the definition $3v_s^{-3} = \left(2v_T^{-3} + v_L^{-3}\right)$.

Compared to light, an other, more important difference is that the total number of modes (phonons) must be capped to $3N$, since these modes represent the oscillations of N particles in three dimensions. Peter Debye (1884–1966) handled this constraint by introducing a cut-off frequency ω_D (named after him), above which — in this simplified model — no oscillation takes place:

$$3N = \int_0^{\omega_D} g(\omega)\, \mathrm{d}\omega = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v_s^3}\, \mathrm{d}\omega = \frac{V\omega_D^3}{2\pi^2 v_s^3} , \tag{7.28}$$

which allows one to determine the Debye frequency in terms of the particle density $n = N/V$ and of the average speed of sound v_s:

$$\omega_D = v_s \left(6\pi^2 n\right)^{1/3} . \tag{7.29}$$

We continue analogously to our treatment of photons in section 7.1 (see equation 7.4), but retain the zero-point energy $\frac{1}{2}\hbar\omega$ of the quantum-harmonic oscillator, anticipating that we may also wish to consider behaviour in the low-temperature limit. Hence

$$\ln Z = \int_0^{\omega_D} g(\omega) \ln Z^{(\omega)}\, \mathrm{d}\omega = \int_0^{\omega_D} g(\omega) \ln \left(\mathrm{e}^{-\frac{1}{2}\beta\hbar\omega} \sum_{j=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega j} \right) \mathrm{d}\omega$$

$$= \int_0^{\omega_D} \underbrace{g(\omega)}_{= \frac{3V\omega^2}{2\pi^2 v_s^3}} \ln \underbrace{\left(\frac{\mathrm{e}^{-\frac{1}{2}\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}} \right)}_{= \left(2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right)^{-1}} \mathrm{d}\omega = -\frac{3V}{2\pi^2 v_s^3} \int_0^{\omega_D} \omega^2 \ln\left(2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right) \mathrm{d}\omega . \tag{7.30}$$

As previously, we can test the accuracy of this model via the heat capacity (at constant volume) and thus

$$C_V = \frac{\mathrm{d}\langle E \rangle}{\mathrm{d}T} = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{3V\hbar^2}{8\pi^2 v_s^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4}{\sinh^2\left(\frac{1}{2}\beta\hbar\omega\right)} \mathrm{d}\omega . \tag{7.31}$$

As a sanity check, we first consider the limit of high T, which in this context can be expressed as $\hbar\omega_D/k_B T \ll 1$. One can then Taylor-expand $\sinh\left(\frac{1}{2}\beta\hbar\omega\right) \approx \frac{1}{2}\beta\hbar\omega$ and find

$$C_V \approx \frac{3V k_B}{2\pi^2 v_s^3} \int_0^{\omega_D} \omega^2\, \mathrm{d}\omega = k_B \int_0^{\omega_D} g(\omega)\, \mathrm{d}\omega = 3N k_B , \tag{7.32}$$

in agreement with the classical equipartition theorem, and where we have used equation 7.28.

At low T (that is, for $\hbar\omega_D/k_B T \gg 1$), one may switch to the integration variable $x = \beta\hbar\omega$ and replace the upper integration limit ω_D with ∞, to obtain

$$
\begin{aligned}
C_V &= \frac{3V\hbar^2}{8\pi^2 v_s^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4}{\sinh^2\left(\frac{1}{2}\beta\hbar\omega\right)} \, \mathrm{d}\omega \approx \frac{3V\hbar^2 (k_B T)^5}{8\pi^2 v_s^3 k_B T^2 \hbar^5} \underbrace{\int_0^\infty \frac{x^4}{\sinh^2\left(\frac{x}{2}\right)} \, \mathrm{d}x}_{= \, 16\pi^4/15} \\
&\approx \frac{3V k_B (k_B T)^3}{8 v_s^3 \pi^2 \hbar^3} \underbrace{\int_0^\infty \frac{x^4}{\sinh^2\left(\frac{x}{2}\right)} \, \mathrm{d}x}_{= \, 16\pi^4/15} = \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3,
\end{aligned}
\tag{7.33}
$$

where we have used a standard integral and defined the Debye temperature $T_D = \hbar\omega_D/k_B$.

Heat capacities of solids at low temperatures. In the low-temperature limit of the Debye model, the heat capacity C_V of a solid is proportional to T^3:

$$
C_V \approx \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3,
\tag{7.34}
$$

where the Debye temperature is given by $T_D = \hbar\omega_D/k_B$, with the Debye frequency $\omega_D = v_s \left(6\pi^2 n\right)^{1/3}$ expressed in terms of the average speed of sound v_s and the density of atoms in the solid n.

In approaching zero for $T \to 0$ and in reproducing the classical result $3N k_B$ for high temperatures, the Debye heat capacity agrees with the Einstein heat capacity that was derived previously by considering a solid as a set of quantum harmonic oscillators (equation 4.29). It differs, however, by predicting a polynomially decaying C_V as $T \to 0$, in agreement with experimental observations.

We reiterate that the Debye result was obtained by considering the excitations of the lattice vibrations as bosonic particles (phonons) with zero chemical potential. That is, the Debye model predicts the thermal properties of solids by considering lattice vibrations as a gas of non-interacting phonons, each carrying an energy $\hbar\omega$.

7.4 Bose-Einstein condensation

In the previous sections, we have considered light and acoustic vibrations as bosons (specifically: as photons and phonons, respectively) with zero chemical potential and a zero-point energy of $\frac{1}{2}\hbar\omega$. This does not cover potentially exotic behaviour as may occur if $(\epsilon - \mu) \to 0^+$. As mentioned in section 6.3, this limit may cause the occupancy of the ground state $\langle N \rangle_\epsilon$ to reach arbitrarily high values. Such behaviour is called Bose-Einstein condensation. In this section, we will investigate the conditions under which Bose-Einstein condensates can emerge and explore their exotic physical behaviour.

As a preliminary remark, let us notice that, as the temperature goes to zero, any physical system with a given number of constituents will populate its ground state. This can be easily seen: as $T \to 0$ hence $\beta \to \infty$, the only canonical weight that does not vanish is the ground state. For a system of identical, non-interacting bosons, this implies that all of the particles will bunch in the single-particle ground state at exact zero temperature (see figure 7.6).
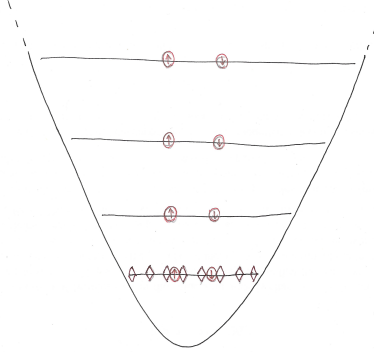
Figure 7.6: At exact zero temperature, non-interacting bosons (sepia diamonds in the picture), which are not subject to the exclusion principle, all populate the single-particle ground state, whilst spin $1/2$ fermions — the orange circles — fill energy levels up.

To study this behaviour, let us recall the expression for particle density of a boson gas (equation 6.33),

$$
\begin{aligned}
n = \frac{\langle N \rangle}{V} &= \frac{(2s+1)}{(2\pi)^2} \left(\frac{2m}{\beta \hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{\beta \epsilon}}{e^{\beta(\epsilon - \mu)} - 1} \, d\left(\beta \epsilon \right) \\
&= \frac{(2s+1)}{(2\pi)^2} \, (4\pi)^{3/2} \underbrace{\left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2}}_{= \lambda_{th}^{-3} = n_q} \int_0^\infty \frac{x^{1/2}}{e^{-\beta \mu} e^x - 1} \, dx \\
&= \frac{2(2s+1)}{\pi^{1/2}} \, n_q \int_0^\infty \frac{x^{1/2}}{e^{-\beta \mu} e^x - 1} \, dx \;,
\end{aligned}
\tag{7.35}
$$

where we have substituted $x = \beta \epsilon$ and used the definitions for the thermal de Broglie wavelength $\lambda_{\text{th}} = \sqrt{\beta h^2/(2\pi m)} = \sqrt{2\pi \beta \hbar^2/m}$ (see equation 6.15) and the quantum density $n_q = \lambda_{th}^{-3}$.

We next recall from section 6.3 that we require $\epsilon - \mu > 0$ for the grand partition function to converge. With a ground state defined as $\epsilon = 0$, this implies that $\mu < 0$ and that equation 7.35 reaches a maximum when $\mu \to 0^-$, as occurs when $T \to 0^+$ (recall from equation 2.12 that $\mu = -T \left(\partial S / \partial N \right)_{E,V}$). In that limit, the integral in equation 7.35 has an upper limit of $\int_0^\infty x^{1/2}(\exp(x) - 1)^{-1} dx \approx 1.306 \, \pi^{1/2}$, as determined by numerical evaluation. We thus find that the particle density needs to obey

$$
n \leq n_{max} = \frac{2(2s+1)}{\pi^{1/2}} n_q \int_0^\infty \frac{x^{1/2}}{e^x - 1} \, dx \approx (2s+1) \, n_q \, 2.612 \,.
\tag{7.36}
$$

However, this result is in contradiction with our earlier finding that for $(\epsilon - \mu) \to 0^+$, $\langle N \rangle_\epsilon \to \infty$ and hence $n \to \infty$. In addition, we know that non-interacting bosons should all bunch up in the ground state at zero temperature, regardless of their density. Clearly there is a flaw in our argument leading to equations 7.35 and 7.35.

The origin of this flaw lies in our description of the grand partition function as an integral, instead of as a sum over discrete energy levels (equation 6.27). That is, we have ignored the discrete nature of quantum states, which will become problematic when $k_B T$ becomes negligible compared with the energy difference between such states. The problem with this approach also becomes clear when noting that the density of states $g(\epsilon) \propto \sqrt{\epsilon} \to 0$ for $\epsilon \to 0$ for particles in a
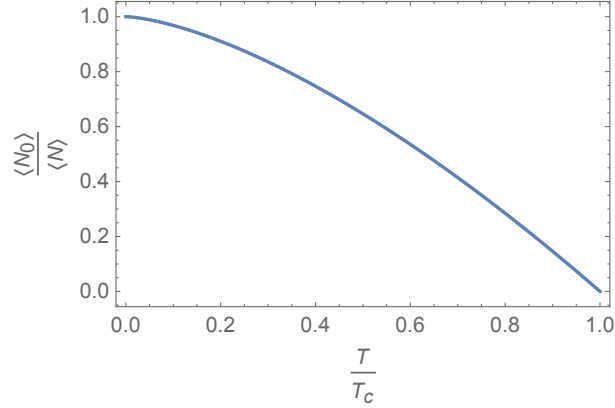
Figure 7.7: The proportion of particles occupying the ground state versus the temperature (in units of the critical temperature T_c).

box. Obviously that cannot be a suitable approximation when we wish to explore the behaviour of bosons in the ground state $\epsilon = 0$.

To better describe the behaviour of bosons at low temperature, while keeping it simple, we assume that for all situations where $n > n_{max}$, we may write

$$\langle N \rangle = \langle N \rangle_0 + n_{\max} V \;, \tag{7.37}$$

where $\langle N \rangle_0$ represents the average number of particles populating the ground state, unaccounted for by the integral in equations 7.35 and 7.35. It turns out that such a model, although somewhat artificial, works reasonably well in describing experimental data.

With this assumption and using equation 7.36, we find the relative proportion of particles in the ground state,

$$\begin{aligned}\frac{\langle N \rangle_0}{N} &= 1 - \frac{n_{\max}}{n} = 1 - \frac{1}{n}\,(2s+1)\,n_q\,2.612 \\ &= 1 - \frac{1}{n}\,(2s+1)\,2.612 \left(\frac{2\pi m k_B}{h^2}\right)^{3/2} T^{3/2} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \;,\end{aligned} \tag{7.38}$$

with

$$T_c = n^{2/3}\,\frac{h^2}{(2s+1)^{2/3}(2.612)^{2/3}\,2\pi m k_B} \;, \tag{7.39}$$

where we have reinserted the definition of $n_q = \lambda_{th}^{-3}$. The resulting behaviour is illustrated in figure 7.7

This leads us to the definition of Bose-Einstein condensation:

Bose-Einstein condensation. A Bose-Einstein condensate is attained when, for a boson gas at very low temperatures, a finite ratio of the total number of particles (and hence a macroscopic number of particles in the thermodynamic limit) occupy the single-particle ground state. This occurs suddenly when the temperature drops below a critical value T_c (given by equation 8.26).

What is distinctive and remarkable about the condensate phase? The particles in the condensate phase all occupy the same delocalised quantum wave-function, so that the collisions between the particles are suppressed to the point that the gas loses any friction (viscosity) as $T \to 0$. This explains a number of intriguing phenomena, such as:

- **Superfluidity:** This refers to the spooky behaviour of liquid helium creeping out of containers (although not properly a gas, He_4 atoms are bosons as their integer spin results from the addition of 6 spin $1/2$ fermions, and undergo a similar phase transition, to a so-called "superfluid" phase at low temperatures).

- **Superconductivity:** in a superconductor, electrons can form pairs (so-called Cooper pairs) that show bosonic behaviour (recall that the individual electrons have spin $1/2$, so are fermions). According to the Bardeen-Cooper-Schrieffer theory of superconductivity (Nobel prize 1972), these electron pairs condense in a ground state below a critical temperature T_c, thus occupying a macroscopic quantum state; resistance can only occur by scattering of individual electrons, which is only possible if sufficient energy is available to break a pair. Consequently, within certain limits, superconductors allow the flow of electric currents at zero resistance.

7.5   Summary

In this chapter, we have repeatedly used the multiplicity of individual partition functions to determine statistical properties of boson gases. This multiplicity is expressed as the additivity the logarithms of these partition functions, weighted by a density of states: $\ln Z = \int_0^\infty g(\omega) \ln Z^{(\omega)} \, d\omega$. We have seen that we can treat light as bosons, so-called photons, and that we can also use the our description of boson gases to describe collective vibrations of atoms in a solid, so-called phonons. Finally, we have explored the behaviour of a boson gas in the quantum limit at $T \to 0$. A few specific points are as follows:

- The energy density of electromagnetic radiation (*i.e.*, light) in a black-body can be written as $\langle E \rangle / V = \int_0^\infty \hbar\omega \, n(\omega) \, d\omega$, obeying Bose-Einstein statistics, $n(\omega) \propto \omega^2 / (e^{\beta\omega\hbar} - 1)$. That is, light can be considered as bosons (photons).

- By assuming light be consist of bosons with energy $\hbar\omega$, we have avoided the ultraviolet catastrophe that was found without quantisation of light: classical statistical physics predicts that the energy density in a black body diverges for larger angular frequencies ω (*i.e.*, for shorter wavelengths).

- We have found Wien's law, stating that the energy of black-body radiation occurs at a a angular frequency $\omega_{max} \propto T$, and the Stefan-Boltzmann law, stating that a black body irradiates energy at a flux $\Phi = \sigma T^4$, where σ is the Stefan-Boltzmann constant.

- Considering the Sun, the Earth and the atmosphere as black bodies, the Stefan-Boltzmann law allows us to develop a crude model to determine the temperature of the Earth and its dependence on the presence of the atmosphere, thus providing a qualitative understanding of the greenhouse effect.

- Collective lattice vibrations in a solid can be treated as bosons, called phonons, which allows us to provide an accurate prediction for the heat capacity of solids in the limits of low and high temperature. This includes the Debye heat capacity at low temperature, predicting $C_V \propto T^3$.

- As $T \to 0$, Bosons tend to accumulate in the ground state. This behaviour is not accurately captured by the approach in which we determine the partition function as a (continuous) integral instead of a (discrete) sum over different quantum states. However, we can define a number of particles in the ground state in excess to the particles described by the continuous

approximation, and find that the relative number of the particles in the ground state scales as $1 - (T/T_c)^{3/2}$. That is, there is a critical temperature below which such accumulation in the ground state emerges, forming a so-called Bose-Einstein condensate.

- Spectacular behaviour due to Bose-Einstein condensation can be observed in the form of, e.g., superfluidity and superconductivity.

Chapter 8

Quantum behaviour of Fermi gases

In the previous chapter (chapter 7), we have explored to what extent quantum effects determine the behaviour of boson gases, including the accumulation of bosons in the ground state. For fermions, however, such accumulation is prohibited by the 'exclusion principle' as discussed in section 6.3, dictating that no two fermions can occupy the same quantum state. As described below, this has profound consequences in a wide range of contexts, ranging from the stability of stars to the electronic devices that govern our daily lives.

8.1 Fermi gases at zero temperature: The Fermi energy

Given that there can be no more than one fermion in a single quantum state, a given number of non-interacting fermions will populate energy levels from the single-particle ground state upwards. At zero temperature, we can therefore define the 'Fermi energy' ϵ_F as the energy level below which all quantum states are occupied with the fermions, and above which all quantum states are empty. This is illustrated in figure 8.1, which depicts the case of spin-1/2 particles, where each energy level can be occupied by two particles with two different spin orientations. This configuration is the one with lowest energy for a system of fermions.

Mathematically, this behaviour is reflected by Fermi-Dirac statistics, which governs the population of single-particle levels for fermions . As per equation 6.24, we will define the Fermi-Dirac function (or "distribution")

$$f(\epsilon) = \langle N \rangle^{(\epsilon)} = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} = \left\{ \begin{array}{ll} 1 & \text{for } \epsilon < \mu \\ 0 & \text{for } \epsilon > \mu \end{array} \right. \quad \text{for } \beta \to \infty . \tag{8.1}$$

That is, the Fermi-Dirac distribution becomes a sharp step function as $\beta \to \infty$ (which is equivalent to $T \to 0$), since for $\beta \to \infty$, the denominator equals 1 for $\epsilon < \mu$ and diverges for $\epsilon > \mu$. Note also that $f(\epsilon) = 1/2$ for all β at $\epsilon = \mu$. The Fermi energy ϵ_F thus represents the chemical potential μ at $T = 0$. In practice, T is never exactly zero but, as can be appreciated from the plot in Fig. 8.2, this is still a very good approximation whenever $\beta \epsilon_F \gg 1$. As we shall see, this is the case in many relevant situations.

We shall refer to a gas in this low temperature regime ($\beta \epsilon_F \gg 1$) as a "degenerate" Fermi gas. This is a widespread, but somewhat unfortunate terminology, since it does not refer to a 'degeneracy' in the sense of having multiple ground states:
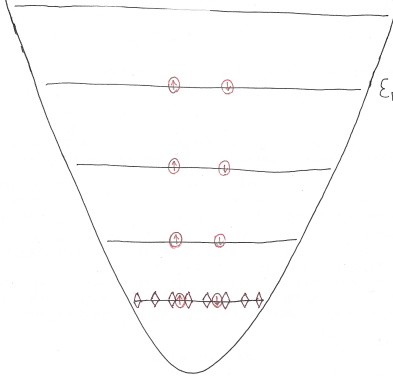
Figure 8.1: At zero temperature, bosons (the sepia diamonds in the drawing) all occupy the ground state. By contrast, fermions (the orange circles) fill up energy levels from the ground state to the Fermi energy ϵ_F. All levels above the Fermi energy are empty. The arrows denote the two possible spin orientations, up or down, of each spin $1/2$ particle, whereby two particles (of different spin) can populate the same single-particle energy level.
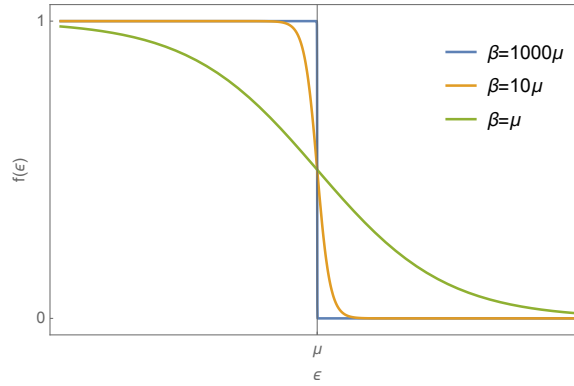

Figure 8.2: The Fermi-Dirac function $f(\epsilon)$ for different values of β, with β expressed in units of $\mu = \epsilon_F$.

Degenerate Fermi gas A 'degenerate' Fermi gas occurs when the single-particle energy eigenstates are occupied with probability 1 up to a maximum single-particle energy ϵ_F, called the 'Fermi energy', whilst all single-particle states with energy above the Fermi energy ϵ_F are empty. This occurs exactly at zero temperature and approximately when $\beta \epsilon_F \gg 1$.

As the density of particles increases, we expected more energy levels to be occupied and hence the Fermi energy ϵ_F to become larger. Mathematically, we can determine the Fermi energy of a degenerate Fermi gas by noting that

$$\langle N \rangle = \lim_{\beta \to \infty} \int_0^\infty g(\epsilon) f(\epsilon) \, \mathrm{d}\epsilon = \int_0^{\epsilon_F} g(\epsilon) \, \mathrm{d}\epsilon \ . \tag{8.2}$$

Using this result and inserting the density of states $g(\epsilon)$ for a particle in a box (equation 6.11), we

find

$$\langle N \rangle = \frac{(2s+1)V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\epsilon_F} \epsilon^{1/2} \, \mathrm{d}\epsilon = \frac{(2s+1)V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{3} \epsilon_F^{3/2} \,, \tag{8.3}$$

which allows us to express the Fermi energy as a function of the density of particles $n = \langle N \rangle / V$:

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{2s+1} \right)^{2/3} n^{2/3} \,. \tag{8.4}$$

Because of this dependence of ϵ_F on n, we can typically reach the limit $\beta \epsilon_F \gg 1$ and therefore have a degenerate Fermi gas at any temperature as long as the particle density is high enough. Henceforward, we will focus on particles with spin $s = \frac{1}{2}$, which applies, e.g., to electrons and neutrons.

We can now proceed as previously to determine other thermodynamic variables. For the average energy of a degenerate Fermi gas, we find (*cf.* equation 6.34)

$$\langle E \rangle = \lim_{\beta \to \infty} \int_0^\infty g(\epsilon) f(\epsilon) \epsilon \, \mathrm{d}\epsilon = \int_0^{\epsilon_F} g(\epsilon) \epsilon \, \mathrm{d}\epsilon$$

$$= \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\epsilon_F} \epsilon^{3/2} \, \mathrm{d}\epsilon = \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{5} \epsilon_F^{5/2} \,, \tag{8.5}$$

which in combination with equation 8.3 allows us to write the mean energy per particle $\langle E \rangle / \langle N \rangle = \frac{3}{5} \epsilon_F$. Noting that $\langle N \rangle = n V$, this yields an energy density $\langle E \rangle / V = \frac{3}{5} n \epsilon_F$.

Let us now use these results to calculate the pressure of a degenerate Fermi gas. Recall that for a classical gas (see section 1.3), we expect that $\langle E \rangle \to 0$ and $p \to 0$ when $T \to 0$ (and $\beta \to \infty$). Intuitively, this follows because we identify pressure with the momentum related to the thermally induced motion of particles in the gas. However, in this same limit (for $\beta \to \infty$, so $\beta \epsilon \gg 1$, *i.e.* the limit of a degenerate Fermi gas), we can use the relation $p = \frac{2}{3} \langle E \rangle / V$ valid for any quantum gas (see equation 6.38) and find

$$p = \frac{2}{3} \frac{\langle E \rangle}{V} = \frac{2}{3} \frac{3}{5} n \underbrace{\epsilon_F}_{= \frac{\hbar^2}{2m} (3\pi^2)^{2/3} n^{2/3}} = \frac{\hbar^2}{5m} \left(3\pi^2 \right)^{2/3} n^{5/3} \,, \tag{8.6}$$

where we have used our previous result for the Fermi energy (equation 8.4).

Hence the pressure of a Fermi gas is non-zero in the limit of $T \to 0$, which must therefore be a consequence of its quantum behaviour. As the particle density increases, we expect such quantum effects to become increasingly important. Indeed, p increases with n. If we try to constrain a gas into a smaller and smaller volume, the energy levels will rise (recall the energetics of a particle in a cubic box of size L, section 6.1) and since the Fermions cannot all bunch into the ground state, so will the Fermi energy and the pressure. Hence the non-zero pressure of a degenerate Fermi gas is a direct result of Fermi-Dirac statistics.

Having established some of the general properties of degenerate Fermi gases, we will now consider such gases in more specific contexts.

8.2 Fermi gases among the stars: stability of stellar models

As an application of the above, let us consider the stability of ageing stars. Keep in mind that, in what follows, we will have to apply pretty dramatic simplifications and that the results may not be

very quantitative. Nevertheless, the orders of magnitude we will identify through this investigation are well confirmed by astronomical observations, *a posteriori* validating the statistical approach.

Firstly, we note that stars are made of electrons, protons and neutrons, which are all spin $\frac{1}{2}$ fermions. How well may we then approximate a star as a *degenerate* Fermi gas, *i.e.*, a Fermi gas for which $\epsilon_F \gg k_B T$, in particular given the high temperatures that we expect? To answer this question, we consider conditions in the Sun, as a well known stellar situation. The Sun has a radius $R_\odot \approx 6.96 \times 10^8$ m, a mass $M_\odot \approx 2 \times 10^{30}$ kg and a surface temperature $T_\odot \approx 5.78 \times 10^3$ K.[1] We will further simplify our model by considering a star as a homogeneous sphere, such that its mass density can be straightforwardly expressed in terms of its mass M and radius R, *i.e*, $\varrho = 3M/(4\pi R^3)$, and by considering it to be entirely made of electrons and protons. Electrons, being lighter, will be the first to enter the degenerate, deep quantum regime, since the Fermi energy is inversely proportional to the fermion mass (see equation 8.4).

The density n of fermions in a star may then be estimated as

$$n = \frac{3M}{4\pi R^3 m_n} \, , \tag{8.7}$$

where $m_n = 1.67 \times 10^{-27}$ kg is a nucleon mass (to a good approximation the same for protons and neutrons). For electrons in the Sun, the Fermi energy (see equation 8.4) may therefore be estimated as

$$\epsilon_F = \frac{\hbar^2}{2m_e} \left(3\pi^2 n\right)^{2/3} = \frac{\hbar^2}{2m_e} \left(\frac{9\pi M_\odot}{4R_\odot^3 m_n}\right)^{2/3} \approx 5.19 \times 10^{-18} \text{ J} \, , \tag{8.8}$$

where $m_e \approx 9.1 \times 10^{-31}$ kg is the electron mass. We can consider the electrons in the sun as a degenerate Fermi gas, if the Fermi energy is large compared to the energy of thermal fluctuations (*i.e.*, the width of the transition in the Fermi-Dirac function),

$$k_B T_\odot \approx 7.98 \times 10^{-20} \text{ J} \, . \tag{8.9}$$

The ratio $\epsilon_F / k T_\odot$ is about 65. Recalling that the chemical potential at zero temperature is the Fermi energy ϵ_F, we see in figure 8.2 that even at a ratio $\epsilon_F/k_B T_\odot) = 10$, the Fermi–Dirac distribution is rather well approximated by a step function. Taken together, this justifies our assumption of treating electrons in a star as a zero temperature (*i.e.*, degenerate) Fermi gas. We can therefore make use of the results obtained in section 8.1.

A defining feature of stars is their large mass, which causes a large gravitational pull towards the centre of the star, driving the star towards a collapse. In relatively young stars, such a gravitational pull is countered by the energy released by nuclear fusion. However, once nuclear fusion runs out of fuel, it cannot counter the gravitational pressure any longer. What mechanism might then prevent the star from collapsing? Clearly, such a collapse will increase the density of star matter — all spin $\frac{1}{2}$ fermions — to higher and higher values, yet at some point this density will become so high that the outward pressure of the Fermi gas (see equation 8.6) may balance the gravitational pull.

From equation 8.6, we know that the outward pressure of the Fermi gas is given by

$$p = \frac{\hbar^2}{5m} \left(3\pi^2\right)^{2/3} n^{5/3} = \frac{\hbar^2}{5m} \left(3\pi^2\right)^{2/3} \left(\frac{3M}{4\pi R^3 m_n}\right)^{5/3} \, , \tag{8.10}$$

which is to be compared with the inward pressure p_G due to the gravitational pull. Note that the m in the factor $\hbar^2/5m$ can refer to nucleons (protons or neutrons) or electrons (presumed to

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[1]Here we ignore that the temperature does increase substantially in the internal layers of a star, possibly making a degenerate behaviour less likely. But the density also increases in the interior of the star, which favours the degenerate regime. We will therefore disregard this issue and just adopt the typical values stated.

be present in about equal amount as nucleons) in the star. Since the pressure is highest for the fermion with the lowest mass, we will henceforward consider the pressure due to the electron gas and therefore substitute $m \to m_e$.

To determine p_G, we again consider the star as a homogeneous sphere and consider the gravitational pull on a spherical shell of radius r and thickness dr due a homogeneous mass $\varrho\, 4\pi r^3/3$ included inside this shell (which for this purpose can be considered as a point-mass at the centre of the sphere).[2] The layer mass is $\varrho\, 4\pi r^2 dr$, such that the total force is given by

$$- \, \mathrm{d}F(r) = \frac{G}{r^2} \left(\frac{\varrho\, 4\pi r^3}{3} \right) \left(\varrho\, 4\pi r^2 \mathrm{d}r \right) = G\frac{(4\pi)^2}{3} \varrho^2 r^3 \, \mathrm{d}r \;, \tag{8.11}$$

where the minus sign in front of $\mathrm{d}F(r)$ to emphasise that this force is directed inward, *i.e.*, opposite to the direction of r. Considering the star as an accumulation of such shells with radii between 0 and the star radius R, this allows us to calculate the the gravitational pressure p_G in the centre of the star due to all the gravitational pressure of all shells. Specifically, the force $\mathrm{d}F(r)$ should be divided by the area of the shell $(4\pi r^2)$ and integrated over r between 0 and R to obtain the difference in pressure between the centre of the star at $r = 0$ and its surface at $r = R$:

$$p_G = p(0) - p(R) = \int_R^0 \frac{1}{4\pi r^2} \, \mathrm{d}F(r)$$

$$= \int_0^R G\frac{4\pi}{3} \varrho^2 r \, \mathrm{d}r = G\frac{2\pi}{3} \underbrace{\varrho^2}_{=\,(3M/(4\pi R^3))^2} R^2 = \frac{3}{8\pi}\frac{GM^2}{R^4} \;. \tag{8.12}$$

We may thus expect such stars to collapse (shrink) due to inward gravitational pull until they reach a star radius R_D at which the inward gravitational pressure is balanced by the outward pressure of the Fermi gas that makes up the star. Since they have shrunk with respect to their original size and are initially quite bright, such stars are referred to as white dwarfs. It is estimated that almost all stars will eventually become white dwarfs after they exhaust their fuel supply. The radius of a stable white dwarf can be found by comparing the two pressures above (equations 8.10 and 8.12),

$$\frac{\hbar^2}{5m_e} \left(3\pi^2 \right)^{2/3} \left(\frac{3M}{4\pi R_D^3 m_n} \right)^{5/3} = \frac{3}{8\pi}\frac{GM^2}{R^4} \;, \tag{8.13}$$

leading to:

Radius of a white dwarf. The radius R_D of a white dwarf of mass M may be estimated as

$$R_D = \frac{2}{5} \left(\frac{9\pi}{4} \right)^{2/3} \frac{\hbar^2}{GM^{1/3}m_n^{5/3}m_e} \;, \tag{8.14}$$

where G is the gravitational constant, m_n is the nucleon (proton) mass and m_e is the electron mass.

If one inserts the mass of the Sun, one would get a radius $R_D \approx 9.04 \times 10^6$ m, which is only 50% larger than the Earth and about 77 times smaller than the original radius of the Sun.

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[2]Note that this approach is similar to the approach that we use to determine the pressure below the surface of the sea, given by $\varrho_w g z$, where z is the depth under the sea surface, ϱ_w is the mass density of water and g is the gravitational acceleration, corresponding to an increase of about one atmosphere for every ten metres descent, and where we have neglected atmospheric pressure. To estimate the pressure in the centre of a star, we have replaced g by the local acceleration towards the stellar centre according to Newtonian gravitation, namely $GM(r)/r^2$, with $M(r)$ the mass included inside a radius r.

While this analysis well explains the sequence of events leading to the existence of white dwarfs, but there is a flaw in the argument, in that we have used non-relativistic estimates for the Fermi gas. However, as the mass density of a star increases, the Fermi energy goes up, and the kinetic energy of the electrons is no longer small compared with $m_e c^2$. Hence instead of the energy $\epsilon = \hbar^2 k^2 / 2m_e$, we will need to adopt the relativistic $\epsilon^2 = m_e^2 c^4 + p_e^2 c^2$, where p_e refers to the momentum of the electrons. To explore how this will affect our results, we will consider the ultra-relativistic case, in which $p_e^2 c^2 \gg m_e^2 c^4$, such that we can write the energy $\epsilon \approx p_e c = \hbar k c$. Proceeding along the lines described in section 6.2, we can determine the density of states $\rho(k) \propto k^2$ as a function of k, but since we now have $\epsilon \propto k$ instead of $\epsilon \propto k^2$ as previously found for the non-relativistic case, we now find the density of states $g(\epsilon) \propto \epsilon^2$ instead of $g(\epsilon) \propto \sqrt{\epsilon}$. With this ultra-relativistic $g(\epsilon)$, we may now recalculate the pressure of a quantum gas as outlined in equations 6.34–6.38 for the non-relativistic case, and next re-evaluate the Fermi energy and pressure of the degenerate spin-$\frac{1}{2}$ Fermi gas as described in equations 8.4 and 8.6, which leads to

$$p_{ultra-rel} = \frac{\left(3\pi^2\right)^{1/3}}{4} \, \hbar c \, n^{4/3} \; . \tag{8.15}$$

That is, as relativistic effects kick in, the pressure of the Fermi gas increases more slowly with the concentration of particles than is the case for the non-relativistic Fermi gas ($p \propto n^{5/3}$, see equation 8.10). As before, we can now compare the (ultra-relativistic) pressure (equation 8.15) with the gravitational pressure (equation 8.12),

$$\frac{\left(3\pi^2\right)^{1/3}}{4} \, \hbar c \, \left(\frac{3M}{4\pi R^3 m_n}\right)^{4/3} = \frac{3}{8\pi} \frac{G M^2}{R^4} \; , \tag{8.16}$$

with the surprising result that the radius R cancels out from this equation, and we are left with an expression for what we can interpret as the largest possible mass of a stable white dwarf according to our model:

$$M = \frac{3}{2} \frac{\sqrt{\pi}}{2^{3/2}} \left(\frac{\hbar c}{G}\right)^{3/2} m_n^{-2} \approx 1.73 M_\odot \; . \tag{8.17}$$

A more sophisticated calculation, taking into account more realistic compositions as well as a more accurate condition for hydrostatic equilibrium, would provide the celebrated Chandrasekhar mass $M_{\mathrm{Ch}} \approx 1.44 M_\odot$ (after Subrahmanyan Chandrasekhar, 1910–1995), which gives the actual upper bound to a mass of a white dwarf. Regardless of the numerical factor of order 1 in front of the estimate, it is utterly amazing that our treatment was able of providing a mass of the order of the mass of the Sun! Notice that no astronomical values were put into the last evaluation, where only the nucleon mass and fundamental physical constants play a role.

Thus, stars with a mass lower than the Chandrasekhar mass (including, notably, the Sun) contract after their active life to become a white dwarf, as the gravitational pull is not sufficiently large to overcome the pressure of the electron gas. For stars with a mass $M > M_C$, though, the collapse continues...

If the star collapses so far that the electron gas has turned relativistic, there is still a possibility that a balance can be established between gravitational pressure and the degeneracy pressure of the nuclei inside the star. These are mostly protons, which are also fermions, and since they are 1800 times more massive than electrons, they remain non-relativistic at stellar densities beyond that to be found at the Chandrasekhar limit. We might imagine that a balance between forces is achieved at a stellar radius

$$R_{\mathrm{n}} = \frac{2}{5} \left(\frac{9\pi}{4}\right)^{2/3} \frac{\hbar^2}{G M^{1/3} m_n^{8/3}} \; , \tag{8.18}$$

which is just the equation for the dwarf radius R_d in equation 8.14 with the electron mass replaced by the nucleon (proton) mass. The radius is 1800 times smaller than the dwarf radius we estimated earlier, or around 4 km. Remember that this contains 10^{30} kg of material! The mass density is ten orders of magnitude greater than that of the already crushed white dwarf, or about 10^{19} kg m^{-3} and the particle density is 10^{47} m^{-3}, such that the mean particle separation is of order 0.1 fm. An estimate of the pressure would be 10^{35} Pa!

At such an enormous pressure, it becomes favourable for protons to react with electrons to become neutrons, which are also fermions, and emit a neutrino. The star is converted into a gravitationally bound gas of neutrons at a density similar to that of the atomic nucleus. Such a stellar remnant is seriously astonishing. But is there evidence that they exist? Extraordinarily, the answer is yes: pulsars, extremely compact astronomical objects that emit pulses of radio emissions, are thought to be examples of these so-called *neutron stars*. Possessing a mass beyond the Chandrasekhar limit, these objects can be stabilised only by the degeneracy pressure of neutrons.

But immediately we can see that there is an upper limit to the mass of a neutron star. If the neutron gas goes relativistic, it will in turn become too soft to carry the burden of the gravitational pressure. What happens then is not clear. Ideally, the star would look for a similar way out, and try to form a fermion gas made up of still heavier particles from the stupendously dense nuclear material. We simply do not know what could happen, but we have an idea of another fate that might befall the star if its collapse continues too far. It might disappear behind its event horizon; or more exactly its radius R might fall below the Schwarzschild radius $R_S = 2GM_s/c^2$, which is about 1 km for the parameters considered. After this point gravity at the surface of the stellar remnant becomes so strong that even light is trapped, and the elderly star turns into a black hole.

8.3 Electron gases in metals

Moving from black holes to a somewhat more pedestrian, but still very relevant topic, let us next consider the application of degenerate Fermi gas models to metals. Metals are well-known for being good conductors of electrical currents and of heat. This property is ascribed to the role of conduction electrons: a metal may be modelled as a solid comprising a lattice of positive ions, each of which has donated one or more valence electrons that turn into a delocalised cloud (or "gas") of conduction electrons, free to roam through the metal and to carry electric currents and heat. To a fairly good approximation, conduction electrons may thus be considered as free, non-interacting particles; yet to provide an accurate description of their behaviour, we need to take Fermi-Dirac statistics into account. In the following, we will account for the conduction properties of metals by treating the valence electrons as a degenerate Fermi gas, in what is generally known as the free electron model or free electron gas model of a metal.

At first sight, this may appear a very crude approximation, since the electrons may be expected to experience strong Coulomb interactions with each other and with the lattice of positive ions. However, it turns out that, in typical metals, the *repulsive* electrostatic interactions between the electrons are screened by the *attractive* interactions with the ions. As a consequence, the conduction electrons may be treated as non-interacting particles, and the electron-electron interactions and interactions with the lattice may then largely be accounted for by attributing an "effective" mass m^* to the electrons. This effective mass is of the same order as but generally different from the bare electron mass m_e.

Having thus accounted for Coulomb interactions, we may next consider the appropriateness of the approximation $\beta\epsilon_F = \epsilon_F/(k_B T) \gg 1$ in our analysis of the degenerate Fermi gas. To do so, we

note that this approximation is equivalent to $\epsilon_F/k_B \gg T$, so we can define the 'Fermi temperature'

$$T_F = \frac{\epsilon_F}{k_B} = \frac{(3\pi^2)^{2/3}\hbar^2 n^{2/3}}{k_B \, 2m^*} \,, \tag{8.19}$$

where we have again expressed the Fermi energy in terms of the particle density (equation 8.4), taking into account that the electron spin $s = \frac{1}{2}$ and having substituted the particle mass m with the effective electron mass m^*. For typical metals, $n \sim 10^{28}$ m^{-3} (this is the value for Na with one conduction electron per atom), yielding a Fermi temperature $\sim 10^4$ K. This Fermi temperature is very large compared to room temperature $T \approx 300$ K, which justifies our treatment of the conductive electrons of metals as a degenerate Fermi gas.

The electrical conductivity σ of a metal can be estimated by a classical model (Drude model, after Paul Drude, 1863–1906). It is defined as the proportionality constant in the linear relation between the electric current $\mathbf{J}$ flowing through a metal and the applied electric field $\mathbf{E}$:

$$\mathbf{J} = \sigma\mathbf{E} \,. \tag{8.20}$$

In a metal with spatial electron density n and effective electron mass m^*, it is given by

$$\sigma = \frac{n\mathrm{e}^2\tau}{m^*} \,, \tag{8.21}$$

where τ is the average time between collisions of the electrons with the lattice.[3]

To predict the heat conductivity of a metal, we will first need to derive an expression for the heat capacity $C_V = (\partial E/\partial T)_V$ for a gas of quasi-degenerate electrons, which we will do in a rather hand-wavy fashion, to be justified *a posteriori* by comparison with experimental results. (Note that here and in the following, we drop the average signs ($\langle\rangle$) for the energy and particle numbers, for convenience, implicitly considering these as thermodynamic, *i.e.*, average variables.)

Classically, we expect the heat capacity to be $C_V = 3k_B N$ (equation 4.27), with N the number of particles. Hence a first question is what number of electrons contribute to the heat capacity here. To answer this question, we note that update and release of heat will involve energies of $\sim k_B T$. That is, only electrons at energy levels within $\epsilon_F \pm k_B T$ may contribute to the heat capacity; other energy levels are simply inaccessible for excitations due to thermal effects. To assess these electrons, we may plot the electron density as a function of energy level, which is given by the density of states $g(\epsilon)$ multiplied by the Fermi-Dirac distribution $f(\epsilon)$, see figure 8.3.

The proportion of electrons that contribute to storing thermal energy can be estimated from the width of the transition at $\mu \approx \epsilon_F$ in the Fermi distribution (equation 8.1), which can be quantified by noting that

$$f(\epsilon) = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)} + 1} = \frac{1}{\exp\left(\frac{\Delta\epsilon}{k_B T}\right) + 1} \tag{8.23}$$

varies between $(\mathrm{e}^{-1}+1)^{-1} \approx 0.73$ and $(\mathrm{e}^1+1)^{-1} \approx 0.27$ for $\Delta\epsilon$ varying between $-k_B T$ and $+k_B T$. We therefore find that only a fraction $\sim k_B T/\epsilon_F = T/T_F$ of the electrons will contribute to the

---

[3]This expression for σ may be obtained by considering basic electromagnetism and by modifying the equation of motion of an electron subject to a DC field $\mathbf{E}$ by a phenomenological model of friction (due to collisions), as per

$$m^*\left(\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} + \frac{\mathbf{v}}{\tau}\right) = -e\mathbf{E} \,. \tag{8.22}$$

Conduction properties are always considered at steady state, after negligible transient times (on the order of τ), so that one can set $\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = 0$ and get $\mathbf{v} = -\frac{\mathbf{E}e\tau}{m^*}$. The electric current in then given simply by $-ne\mathbf{v} = n\mathrm{e}^2\tau\mathbf{E}/m^* = \sigma\mathbf{E}$.
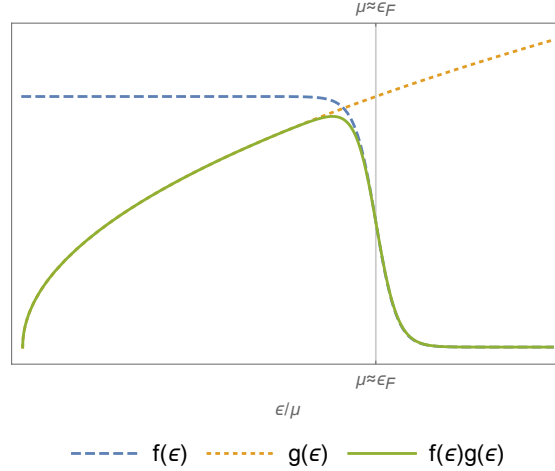
Figure 8.3: Plot of the Fermi-Dirac distribution $f(\epsilon)$, of the density of single-particle levels $g(\epsilon) \propto \sqrt{\epsilon}$, and of their products as functions of ϵ/μ, plotted at a temperature T defined by $\mu \approx \epsilon_F = k_B T_F \approx (10^4/300) k_B T \approx k_B T$, as applies for conduction electrons in a typical metals. The Fermi distribution approaches a step function, except for a small dent over an energy range $\epsilon_F \pm k_B T$.

heat capacity, and we would expect an electronic heat capacity $C_V \sim k_B N T / T_F$. A more accurate evaluation yields the value

$$C_V \approx \frac{\pi^2}{2} k_B N \frac{T}{T_F} \ . \tag{8.24}$$

Defining the heat conductivity α via the heat flux $\Phi = -\alpha \nabla T$ due to a temperature gradient ∇T, we expect α to scale with the capacity of the electrons to take up heat and next transport it. Based on a kinetic treatment of electrons as they carry heat through the metal, a more rigorous treatment — not discussed here — yields

$$\alpha = \frac{1}{3} \bar{v}^2 \tau \frac{C_V}{V} \ , \tag{8.25}$$

where $\bar{v}$ is the average velocity of the electrons, V is the volume of the sample and τ represents, in this case, the mean time between two electron-phonon collisions, which represent the dominant hurdle to heat conduction; electron-electron interactions turn out to be less significant and are effectively subsumed by the redefinition of the effective mass m_*, introduced above). Since we expect the typical kinetic energy $\frac{1}{2} m^* \bar{v}^2$ of these electrons to be of the order of the Fermi energy ϵ_F, we may approximate $\bar{v}^2 \approx 2\epsilon_F/m^* = 2k_B T_F/m^*$. Combining this with our result for the electronic heat capacity (equation 8.24), we then find the electronic heat conductivity

$$\alpha \approx \frac{1}{3} \frac{2 k_B T_F}{m^*} \tau \frac{\pi^2}{2} k_B \frac{N}{V} \frac{T}{T_F} = \frac{\pi^2}{3} \frac{\tau n k_B^2}{m_*} T \ . \tag{8.26}$$

These results lead to a rather remarkable observation if we divide the thermal conductivity (equation 8.26) by the electrical conductivity (equation 8.21):

$$\frac{\alpha}{\sigma} = \frac{\pi^2}{3} \frac{\tau n k_B^2 T}{m_*} \frac{m_*}{n e^2 \tau} = \frac{\pi^2}{3} \frac{k_B^2}{e^2} T = L\,T \ , \tag{8.27}$$

where L is the so-called "Lorentz number", $L \approx 2.45 \times 10^{-8}$ W Ω K^{-2}. The Lorentz number is a universal constant, which only depends on the Boltzmann constant and on the electron charge. This translates in the following notable statement:

Wiedemann-Franz law. "The ratio between thermal and electrical conductivities in metals is proportional to the temperature through a constant L that does not depend on any microscopic or thermodynamic variable of the metal."

This law is a very useful rule of thumb that finds good empirical confirmation in certain regimes, but does not always holds. In particular, by assuming the same τ in determining the thermal and electric conductivities, we have in fact assumed collisions hampering thermal and electrical conduction are the same, which is not always true. It turns out that, whilst all collisions hinder thermal conduction (which originates from a smudging of the Fermi surface due to thermal excitations), only collisions with relatively high momentum transfer effectively hinder electric currents. As already stated, the here dominant collision processes are those between the conduction electrons and the lattice, in which electron energy is converted into lattice vibrations (phonons) of the type discussed in section 7.3. The typical energy scale of the latter is given by the Debye frequency ω_D, which must be compared with the thermal energy $k_B T$. One can thus identify three regimes, well-confirmed by laboratory observations:

$k_B T \ll \hbar \omega_D$ all collisions imply a large momentum transfer, and thus affect equally thermal and electric conduction $\Rightarrow \tau$ is the same for both processes $\Rightarrow$ Wiedemann-Franz holds;

$k_B T \sim \hbar \omega_D$ some collisions are relevant hurdles to both electric and thermal conductivity while others only affect thermal conductivity $\Rightarrow \tau$ is different for either process, Wiedemann-Franz fails (typically, the ratio α/σ will be lower than LT);

$k_B T \gg \hbar \omega_D$ phonons become scant, large-momentum-change elastic scattering with impurities (vacancies or intruder atoms/ions) dominate here, affecting equally thermal and electric conduction $\Rightarrow \tau$ is the same for both processes $\Rightarrow$ Wiedemann-Franz holds.

As an aside, note that for the *total* heat capacity, we would need to take into account the contribution of conduction electrons, as calculated in equation 8.24, as well as the contribution of phonons as approximated by the Debye heat capacity (see equation 7.33).

8.4 Semiconductors

As discussed in the previous section, the free electron model presumes that conduction electrons can freely move through a metal. They are therefore considered as a gas of non-interacting particles in a box, with an energy $\epsilon = \hbar^2 k^2 / 2m^*$ and corresponding density of states $g(\epsilon)$. However, we may expect their behaviour to be affected by the lattice of positive ions (*i.e.*, the atoms stripped of the conduction electrons). This leads to a more complex dispersion relation between the electron energy ϵ and the wave number k (or, in 3D, the wave vector $\mathbf{k}$), generally denoted as the band structure of a material. Specifically, if such interactions are sufficiently strong, we might expect the electron energies to show features with the same periodicity as the atomic lattice.

In terms of wave numbers $k = 2\pi/\lambda$, we could expect maxima or minima in the energy when the electron wavelength — and hence k — matches the periodicity of the lattice. For such maxima/minima in energy, $d\epsilon(k)/dk = 0$ and the lowest-order expansion will be quadratic in k (or in $k - k_0$, with k_0 a constant).
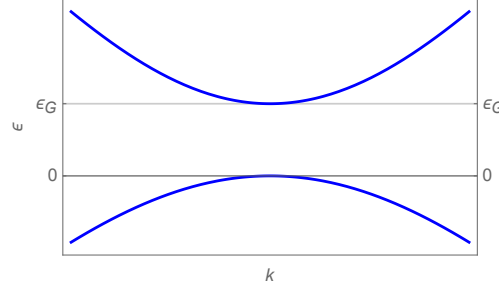
Figure 8.4: Simplified two-band structure of a semiconductor, showing the energy ϵ as a function of the wave number k.

In semiconductors and insulators, these effects result in a gap in the allowed energies at the Fermi level. This energy gap is denoted as the 'band gap'. If the band gap ϵ_G is large, this hampers the excitation of electrons from their ground states below the Fermi level to higher energy levels: this results in electrical insulation. If the band gap is relatively small, however, electrons may still be promoted — by external electric fields or thermal fluctuations — from energy levels below the Fermi level to energy levels above the Fermi level. This is a the case for semiconductors. The ability of controlling the concentration of conduction electrons implies the possibility of controlling the conductivity of semiconductors: transistors and — ultimately — all modern electronics are based on this.

To describe electronic behaviour in semiconductors, we will here assume a simplified two-band model, as shown in Fig. 8.4, with a 'conduction band' above the Fermi level, with energies given by $\epsilon_G + \hbar^2 k^2/2m_e^*$ and with a 'valence band' below the Fermi level with energies $-\hbar^2 k^2/2m_h^*$, with respective effective masses m_e^* and m_h^* (the reason for the subscript h will become clearer shortly). In a semiconductor, the Fermi energy ϵ_F of the electrons lies inside the band gap.

At this point, it is important to re-emphasise that electric currents are carried by electrons in incompletely filled bands. Once some electrons have been excited from the valence band to the conduction band, leaving unoccupied states in the valence band, then electrons in both the conductance band and the valence band can contribute to electrical conductivity. In the conductance band, the electrons are the (negatively charged) carriers of electric currents. In the valence band, however, it turns out that the correct counting for the number of configurations (and the correct associated energy) may be more expediently obtained by disregarding all filled valence electron states and instead considering each unoccupied valence electron state as a fictitious particle, generally denotes as a 'hole'. Each such hole has a positive change $+e$, a positive energy $\hbar^2 k^2/2m_h^*$ (since energy is required to lift an electron from the valence to the conduction band), and an effective mass m_h^*, which in general is different from the effective mass of the electrons in the conduction bands: recall that the effective mass incorporates effects due to electron-electron interactions and due to interactions with the atomic lattice, which do not need to be the same in the two energy bands.

The spatial density of the (negatively charged) electrons in the conduction band is then found as usual from the Fermi-Dirac distribution and the density of states

$$n = \frac{1}{V} \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \, g_0(\epsilon) \, d\epsilon \,, \tag{8.28}$$

where $\epsilon = 0$ refers to the top of the valence band (see figure 8.4), where the chemical potential μ (and Fermi level) for a semiconductor lies within the band gap, and where the density of states is

given by

$$g_0(\epsilon) = \begin{cases} 0 & \text{for } 0 < \epsilon < \epsilon_G \\ \frac{V}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \sqrt{\epsilon - \epsilon_G} & \text{for } \epsilon \geq \epsilon_G , \end{cases} \tag{8.29}$$

which is the usual expression for the density of states of a quantum gas (equation 6.11) of particles with spin $s = \frac{1}{2}$ and mass m_e^*, except for the presence of the energy gap, which lifts the bottom of the band up to ϵ_G.

To find the spatial density p of the (positively charged) holes in the valence band, we first note that the formation a hole with positive energy requires the removal of an electron with energy $\epsilon < 0$ (from inside the valence band). Hence the probability of such a single-particle hole state to be occupied equals 1 minus the probability for the corresponding electron state at energy ϵ to be occupied, with the latter probability given by the Fermi-Dirac function for a chemical potential μ:

$$1 - \underbrace{\frac{1}{e^{\beta(\epsilon - \mu)} + 1}}_{\text{probability of electron state at } \epsilon < 0 \text{ to be occupied}} = \frac{1}{e^{\beta(-\epsilon + \mu)} + 1}$$

$$= \underbrace{\frac{1}{e^{\beta(\epsilon_h + \mu)} + 1}}_{\text{probability of hole state at } \epsilon_h \equiv -\epsilon > 0 \text{ to be occupied}} . \tag{8.30}$$

This probability (for a valence state to be occupied by a hole) is just the usual Fermi-Dirac distribution, except for the sign of the chemical potential: holes therefore behave as fermions with a chemical potential $-\mu$, opposite to the chemical potential for the electrons.

This allows us to write the spatial density of holes as

$$p = \frac{1}{V} \int_{-\infty}^{0} \frac{1}{e^{\beta(-\epsilon + \mu)} + 1} \, g_0(\epsilon) \, d\epsilon , \tag{8.31}$$

with

$$g_0(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} \sqrt{-\epsilon} \quad \text{for } \epsilon < 0 . \tag{8.32}$$

This density of states g_0 and the Fermi-Dirac distribution are illustrated in figure 8.5. In the limit of $T = 0$, the Fermi-Dirac distribution is a step function, such that the valence band is completely occupied by electrons (and devoid of holes) whilst the conduction band is empty. At higher temperatures, however, thermal fluctuations smoothen the Fermi-Dirac distribution and allow electrons to be excited from the valence to the conduction band, such that electric currents can be carried by both electrons and holes. This is the case for — and the density of states g_0 refers to — what is known as an *intrinsic semiconductor*.

As may be clear from figure 8.5, we can drastically modify the the number of available electrons in the conduction band and holes in the valence band by respectively, shifting the chemical potential up or down inside the band gap, and thus drastically modify the conductivity of a semiconductor. Technically, this can be achieved by substituting a small fraction of the semiconductor atoms (e.g., silicon, germanium) with elements that are more or less easily ionised, in a process that is known as doping. E.g., phosphorus relinquishes its electrons more easily than silicon or germanium and is therefore denoted as a 'donor'. By substituting a donor atom into the semiconductor lattice, an additional electron becomes available to the conduction band and creates a system of a conduction electron weakly bound — with binding energy ϵ_D as measured with respect to the bottom of the
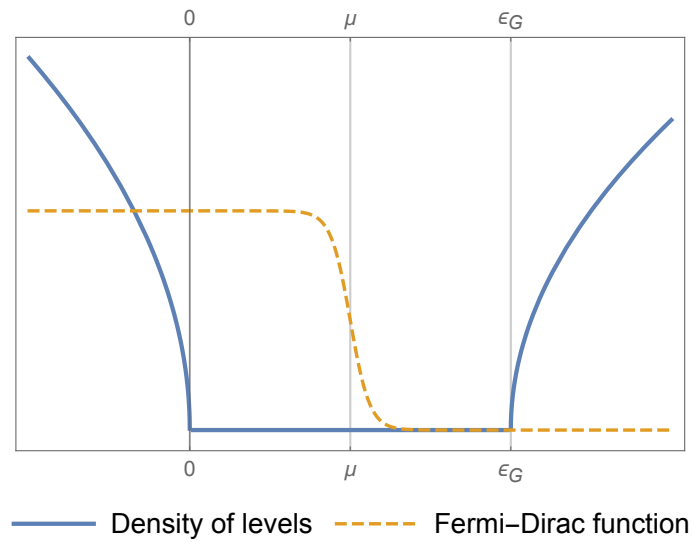
Figure 8.5: Density of levels and Fermi-Dirac distribution for an intrinsic, two-band semiconductor. The density of valence and conduction bands are portrayed with different concavities to emphasise that the effective masses m_h^* and m_e^* may be different from each other.

conduction band — to the positive donor ion. By contrast, boron is an example of an 'acceptor', as it binds electrons more tightly, such that its inclusion in the semiconductor lattice effectively amounts to capturing an electron from the valence band, thus creating a hole that is weakly bound — with binding energy ϵ_A — to the negative acceptor ion.

The inclusion of donor and acceptor impurities modifies the density of single-electron levels $g_0(\epsilon)$ by adding two allowed energies, which are usually taken to lie within the energy gap and may be represented by delta functions, to yield

$$g(\epsilon) = g_0(\epsilon) + n_A V \delta(\epsilon - \epsilon_A) + n_D V \delta(\epsilon - \epsilon_G + \epsilon_D) \,, \tag{8.33}$$

where n_D and n_A are the donor and acceptor concentrations, which are set during fabrication. Using this density of states, one can analyse in detail how finite temperatures and dopant concentrations affect the density of conduction electrons and holes — and hence electrical conductivity — in the two-band semiconductor. Here we will only consider some limiting cases that are arguably the most interesting for applications.

A rather common situation is that the donor energy level ϵ_D lies near the top of the band gap, well above the Fermi level of the intrinsic semiconductor $(0 < \epsilon_{F,intr} < (\epsilon_G - \epsilon_D) < \epsilon_G)$. If thermal fluctuations $k_B T \ll \epsilon_D$, this implies that pretty much all electrons in the conduction band are due to the donor impurities, i.e., $n \approx n_D^+$, where n_D^+ is the concentration of ionised donors. Alternatively, the acceptor energy level ϵ_A is commonly found at the bottom of the band gap, well below the Fermi level of the intrinsic semiconductor $(0 < \epsilon_A < \epsilon_{F,intr} < \epsilon_G)$. If thermal fluctuations $k_B T \ll \epsilon_A$, pretty much all holes in the valence band can then be attributed to the acceptor impurities, i.e., $p \approx n_A^-$, where n_A^- is the concentration of ionised acceptors. Such systems are denoted as *extrinsic semiconductors*.

Taking into account charge neutrality,

$$n + n_A^- = p + n_D^+ \,, \tag{8.34}$$

and assuming that the concentrations of ionised impurities saturate to $n_D^+ \approx n_D$ and $n_A^- \approx n_A$, these conditions lead to:

Extrinsic concentrations of holes and conduction electrons. Consider an extrinsic semiconductor with band gap ϵ_G, donor binding energy ϵ_D and acceptor binding energy ϵ_A, under the conditions for which thermal fluctuations may be ignored ($k_B T$ is small, the width of the Fermi-Dirac distribution is narrow compared to the differences between energy levels).
If $n_D > n_A$, the semiconductor is referred to as an 'n-type' semiconductor and has densities of holes and conduction electrons given by

$$p \approx 0 , \quad n \approx n_D - n_A \quad (n-\text{type}) . \tag{8.35}$$

If $n_A > n_D$, the semiconductor is referred to as a 'p-type' semiconductor and has densities of holes and conduction electrons given by

$$p \approx n_A - n_D , \quad n \approx 0 \quad (p-\text{type}) . \tag{8.36}$$

In general, doped semiconductors are extrinsic for $k_B T \ll \epsilon_D$ (or $k_B T \ll \epsilon_A$) and become intrinsic at sufficiently high temperatures.

At junctions between p- and n-type semiconductors, so-called pn-junctions, electrons from the n-type semiconductor locally recombine with the holes of the p-type semiconductor, creating a barrier that is depleted of charge carriers and that is therefore insulating. In transistors, additional charge carriers may be created and conductivity restored by applying a control current into or a control voltage to this barrier. This allows one to identify two distinct ("digital") states according to whether a current flows or not, which lies at the basis of all digital electronics.

8.5   Summary

In this chapter, we have discussed some thermodynamic properties of Fermi gases and the application of Fermi gas models in astrophysics and condensed matter physics. We have reiterated the notion that the quantum properties of half-integer spin particles prevent them from filling up different quantum states with more than one particle per state. This causes the fermions to occupy higher energy states up to a level that is known as the Fermi energy ϵ_F and that at zero temperature coincides with the chemical potential. Many useful properties can be derived if we assume that the $\epsilon_F \gg k_B T$, or — equivalently — that the Fermi temperature $T_F = \epsilon_F / k_B \gg T$: under such conditions, we can consider the Fermi-Dirac distribution as a step function, going from 1 to zero at ϵ_F (facilitating the evaluation of various integrals), and the speak of a degenerate Fermi gas.

The Fermi energy rises when we try to squeeze more particles in a smaller volume: it rises with the fermion density n; and so do the energy per particle $\langle E \rangle$ and the pressure of the Fermi gas, even at zero temperature. The latter may seem remarkable, since classical physics predicts zero pressure for zero temperature: under such conditions, the pressure of a Fermi gas is a purely quantum-mechanical effect, due to the exclusion principle that prevents more than one fermion to occupy the same quantum state.

Electrons, protons and neutrons in stars do have densities that are so high that $\epsilon_F \gg k_B T$, so we can consider them as degenerate Fermi gases, with corresponding pressure. This pressure can prevent a complete collapse of the star that would otherwise occur by the inward gravitational pull due to the big mass contained within the star.

The concept of a degenerate Fermi gas also applies to conduction electrons in metals, where the conductivity scales with the concentration of such electrons. Considering that only electrons within (roughly) $\epsilon_F \pm k_B T$ may contribute to the heat capacity, we find the electronic contribution to the heat capacity to scale with T/T_F, and that there is — with some caveats — a constant ratio between the thermal and electrical conductivity of a metal, known as the Wiedemann-Franz law.

In semiconductors, the picture of electrons as fermions in a box breaks down to some extent due to the interaction of electrons with the lattice of positive ions. This causes the emergence of a 'band structure'. In the simplest model of a semiconductor, we consider two bands of electronic states, one mostly filled 'valence' band below the Fermi level, and, separated by a band gap ϵ_G, another mostly empty 'conduction' band above the Fermi level. To describe electrical conduction, we refer to single-particle electron states in the conduction bands and to single-particle 'hole' states in the valence band (where electrons have been excited to the conduction band). Such states can arise at high enough temperature in an intrinsic semiconductor. For many technological applications, however, semiconductors are doped with electron donors and/or acceptors, which in an extrinsic semiconductor define the concentrations of electrons in the conduction band and of holes in the valence band. Combinations of electron-rich and hole-rich extrinsic semiconductors underpin the function of transistors, and therewith the technical feasibility of digital electronics.