

Thermal and Statistical Physics

Part II Michaelmas 2020

Supplementary Course Handout

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This handout goes back a long way:

- Initial version S. R. Julian around 1996.
- Revisions by R. J. Needs, E. M. Terentjev, W. Allison and F. M. Grosche 2001-2019.



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# Chapter 1

## The basics of thermodynamics

### 1.1 Introduction

The ideas and methods developed in this course find very broad application, not only within physics, but in biology, geology, chemistry, astronomy, engineering, computer science/artificial intelligence/information technology, finance, philosophy, etc. Indeed one of the central reasons why a physics degree is an ideal preparation for doing interdisciplinary research (not to mention investment banking, or theology) is that physicists are trained to quantitatively understand probability, entropy, equilibrium, fluctuations, irreversibility and chaos. Therefore, whether or not you end up with a career in physics, mastering the central ideas in this course will serve you well in the future.

The subject matter in this course divides into *Fundamental ideas* and *Methods of thermal physics*, which actually are not limited to this area and have very general relevance for the rest of physics. The topics are chosen to illustrate ideas and methods of thermal physics, but also because many important results about Nature will thus be obtained and discussed.

For the purposes of this course, the following “working definitions” might be helpful:

**Thermodynamics** is primarily concerned with *the flow of energy*: (a) from macroscopic to microscopic length scales, and vice-versa, and (b) between one kind of microscopic degree of freedom and another. Thermodynamics is a macroscopic ‘phenomenological’ theory which involves no assumptions about the microscopic nature of matter or radiation. Indeed much of the theory of thermodynamics was developed before accurate microscopic pictures were developed.

**Equilibrium statistical mechanics** is primarily concerned with the “storage” and balance between energy and entropy at the microscopic level, i.e. with the question of how energy is distributed among the many internal degrees of freedom of an object. Statistical mechanics involves a detailed microscopic theory and the use of probabilities to deduce macroscopic, observable characteristics.

These definitions are illustrated in the next section, which describes basic features of model systems which will be used throughout the course.

### 1.1.1 Ideal Gas

#### Energy storage:

The energy stored in a monatomic ideal gas is the sum of the kinetic energies of all the atoms in the gas:

$$U = \sum_{i=1}^N \frac{1}{2}mv_i^2, \quad (1.1)$$

where  $m$  is the atomic mass and  $\mathbf{v}_i$  is the velocity of the  $i^{th}$  atom in the gas. An external field such as gravity would give an additional term of potential energy  $\sum_{i=1}^N V(\mathbf{r}_i)$  in  $U$ . We know that the speeds of the atoms are randomly distributed according to the Maxwell distribution. You have seen it derived in previous years, and we shall also obtain it here as a classical limit of the general quantum-statistical description, as well as the steady-state limit of the probability of free Brownian motion:

$$P(v) dv = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} 4\pi v^2 dv. \quad (1.2)$$

This leads to the average total energy of mono-atomic ideal gas, in 3D:  $U = N\langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}Nk_B T$ , in agreement with the principle of equipartition of energy.

Other properties of the ideal gas with which you should be familiar are:

$$pV = Nk_B T \quad \text{Ideal gas law} \quad (1.3)$$

$$pV^\gamma = \text{a constant in an Adiabatic process} \quad (1.4)$$

where  $p$  is the pressure and  $\gamma$  is the ratio of the heat capacity at constant pressure,  $C_p$ , to that at constant volume,  $C_V$ . Note that we use  $Nk_B$ , where  $N$  is the number of molecules and  $k_B$  is the Boltzmann constant, rather than  $nR$ , where  $n$  is the number of mols and  $R$  is the molar gas constant. That is because we are developing the true microscopic theory where the ‘players’ are individual particles, and so we count them directly.

#### Energy flow in and out of an ideal gas:

##### **macroscopic ↔ microscopic energy flow:**

As illustrated in Fig. 1.1, energy can be transferred to the gas by macroscopic motion of a piston. Atoms colliding with an advancing piston gain kinetic energy (assuming for simplicity elastic collisions), and by this mechanism the gas as a whole gains energy as it is compressed. The change in the energy of the gas, assuming that no heat can flow into or out of it, is

$$dU = dW \quad (= -p dV \text{ if the compression is reversible}), \quad (1.5)$$

where we have used conservation of energy to state that the work done,  $dW$ , must be equal to the change in the internal energy of the gas.<sup>1</sup> The slash through the symbol  $d$  denotes that there is no actual function  $W$  of which we are taking the derivative; work is just one of a number of ways that energy can get into or out of the system, so it never makes sense to say that the system “contains” a given amount of work: it contains energy, in this case in the form of kinetic energy of the atoms in the gas. In other words,  $dW$  is a short-hand notation which means “a change in the internal energy  $U$  which occurs as a result of work being done on the system.”

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<sup>1</sup>The sign of  $dW$  can be confusing, because sometimes we talk about the system doing work on the outside world, and at other times we talk about the outside world doing work on the system. There should be no issues if you remember how  $dW$  relates to  $dU$ , where  $U$  is the system energy. Positive work means that the system energy goes up, and vice-versa.

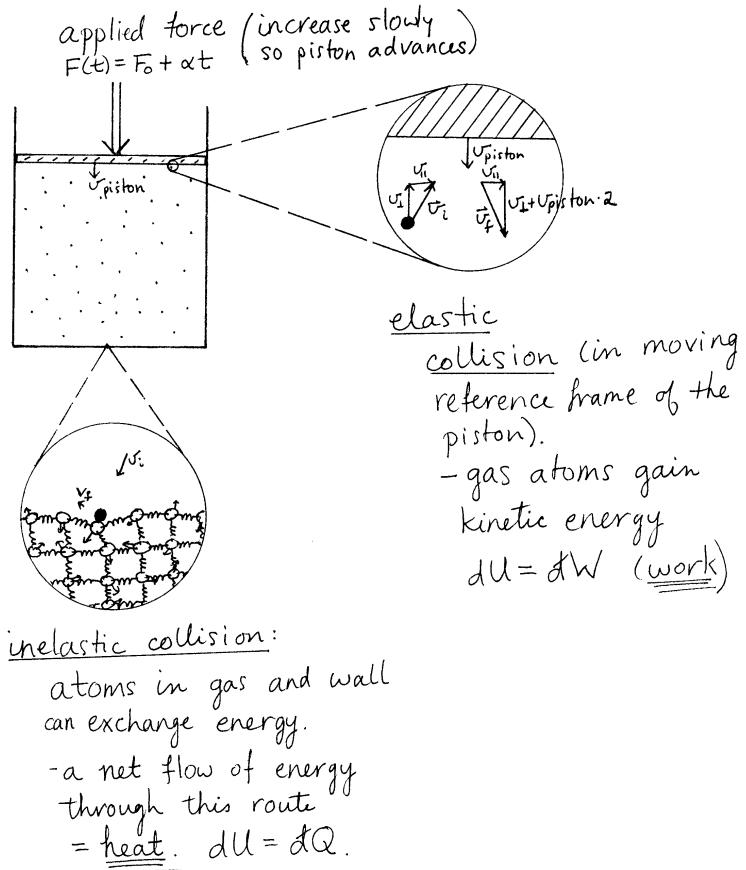


Figure 1.1: Microscopic model of heat and work for an ideal gas. The collisions with the moving piston are mostly inelastic, but *upon averaging over a large number of collisions* there will be a net gain or loss of energy which can be traced to the advance or retreat of the piston. The arrows in the ball and spring model of the wall denote random thermal motion.

#### microscopic $\leftrightarrow$ microscopic energy flow:

(1) **heat:** Energy can also leave or enter the gas as *heat*. For example, collisions between a molecule in the gas and the atoms in the wall will in general be inelastic, i.e., energy will be exchanged (see Fig. 1.1). The walls and the gas will be said to be in thermal equilibrium when, if we *average over an enormous number of such collisions*, there is no net flow of energy through this route. To get energy into the gas through this route we would first have to increase the average kinetic energy of the atoms in the wall (for example by frictional heating, a process which itself corresponds to an *irreversible* flow of energy from the macroscopic to the microscopic level).

Energy which enters or leaves the gas through inelastic collisions, or by net absorption of energy from radiation, or by other microscopic mechanisms, is called *heat*. In a heat flow process at constant volume the change in energy of the system is written as

$$dU = dQ \quad (= T dS \text{ if the heat flow is reversible}). \quad (1.6)$$

The requirement of reversibility may seem mysterious if we have fixed the volume of the system, but it rules out processes such as convection, in which the temperature  $T$  is not uniform and well defined throughout the system.

(2) **flow of particles:** Instead of changing the total energy of the gas by changing the energy of its molecules, we could change the *number* of molecules in the gas. If this is done in a reversible way, with the total entropy and volume of the system fixed, then the energy change is written as

$$dU \equiv \mu dN, \quad (1.7)$$

where  $\mu$  is called the “chemical potential”, defined as the change in energy when you bring an extra particle into the system:

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}. \quad (1.8)$$

Particle flows have important applications in phase transitions, chemical reactions, diffusion and in much of the quantum statistical mechanics, and the discussion of chemical potential  $\mu$  occupies a large part of this course. We will see later that there are a number of different but equivalent expressions for the chemical potential, but the one above is the definition.

The ideal gas will be used to illustrate methods and ideas of thermodynamics and statistical mechanics, but it has real applications: it accurately describes rarefied gases, and in quantum systems it is used to model Fermi gases (electrons in metals) and Bose gases (ultra-cold atoms) of particles, as well as statistics of quantum excitations: photons (black body radiation), or phonons in solids

### 1.1.2 Van der Waals gas and other systems

The van der Waals gas is a simple model system incorporating *interactions* between the particles. In this model the ideal gas law,  $pV = Nk_B T$ , is replaced by

$$\left( p + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T \quad \text{or} \quad p = \frac{Nk_B T}{V - Nb} - \left( \frac{N}{V} \right)^2 a \quad (1.9)$$

Inter-molecular interactions are represented by two new terms:  $Nb$  describes the volume from which a given molecule is excluded by the hard cores of all the other molecules, while  $-N^2 a/V^2$  arises from the pair inter-molecular attraction and acts to reduce the pressure at fixed  $V$  and  $T$ . The van der Waals equation of state has serious limitations as a model of matter – it doesn’t give a good quantitative account of the behaviour of real gases and liquids, and it doesn’t have a solid phase at all, but it does show a liquid-gas transition, which makes it an important model system.

#### Energy storage:

Energy is stored in the van der Waals gas in the form of kinetic energy, as in the ideal gas, but also in the inter-molecular *potential energy*. When the molecules are far apart, in a rarefied gas, the potential energy is small, but if they are condensed to form a liquid it becomes negative. If the system is strongly compressed so that the hard core repulsion is important, the potential energy becomes large and positive. These regimes are reflected in the *isotherms* of the van der Waals gas, which will be discussed in §1.3 (and which you have seen last year). Moreover, energy can be converted from kinetic to potential energy of the gas; this is the origin of the cooling seen upon Joule expansion of a van der Waals gas. The energy flow in/out of the system here is the same as in the ideal gas.

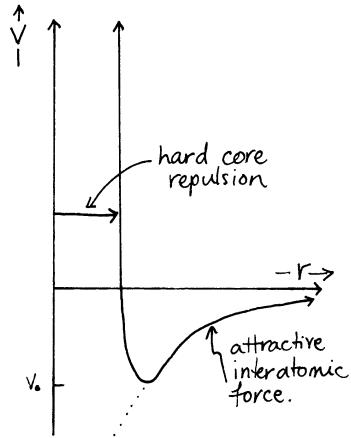


Figure 1.2: The inter-molecular potential for a van der Waals gas.

### 1.1.3 Paramagnetic salt in an applied magnetic field

The work required to change the magnetic moment of a substance from  $\mathbf{m}$  to  $\mathbf{m} + d\mathbf{m}$  in an applied external field  $\mathbf{H}$  depends on the precise definition of the process involved (let's not confuse the extensive total magnetic moment  $\mathbf{m}$  and the intensive local field of magnetisation  $\mathbf{M}$ ). The conventional definition regards only the work needed to change the state of the substance, returning any external sources of field back to zero. For example, a paramagnetic substance with magnetic moment  $\mathbf{m}(\mathbf{H})$  at some large distance from a permanent magnet will experience an attractive force  $(\mathbf{m} \cdot \nabla) \mathbf{H}$ . Letting the substance approach the magnet until it experiences a field  $\mathbf{H}_1$ , we can extract work, so that the work done *on* the substance is  $W' = -\mu_0 \int_0^{H_1} \mathbf{m}(\mathbf{H}) d\mathbf{H}$ . However, the magnet is still near the substance, so in order to calculate the work required to change the state of the substance alone, we need to pull the magnet away to the previous separation, while the magnetic moment of the substance is clamped at its final value  $\mathbf{m}_1$  (this is problematic in practice, but does not violate the laws of physics, so possible in a thought experiment). Pulling the magnet away requires a larger work, to be done on the system,  $W_1 = \mu_0 \int \mathbf{m}_1 d\mathbf{H} = \mu_0 \mathbf{m}_1 \mathbf{H}_1$ , giving a net work  $W = \mu_0 \int \mathbf{H} d\mathbf{m}$ . This argument produces the conventional expression for the work done on a magnetic substance, when its magnetisation is changed by first applying a field  $\mathbf{H}$  and then removing the source of the field again:

$$dW = \mu_0 \mathbf{H} d\mathbf{m}$$

This contrasts with the work done during the first part of the process only:  $dW' = -\mu_0 \mathbf{m} d\mathbf{H}$ . The difference between the two expressions is the change in the potential energy of the dipole moment in an applied field,  $-\mu_0 d(\mathbf{m}\mathbf{H})$ , which is conventionally not counted as part of the *internal* energy. A good discussion of this argument can be found in the book by Adkins.

In statistical mechanics, we study a simple model for a paramagnetic substance, the two-level system: the system is just one ionised atom with a spin equal to  $1/2$ , so it has only two quantum states: spin-up and spin-down. All  $N$  ions in the macroscopic body are assumed independent, so in effect we have a large statistical ensemble that probes what these spins do on average. However, in order to decide along which axis they are “up” or “down” we need an external field:

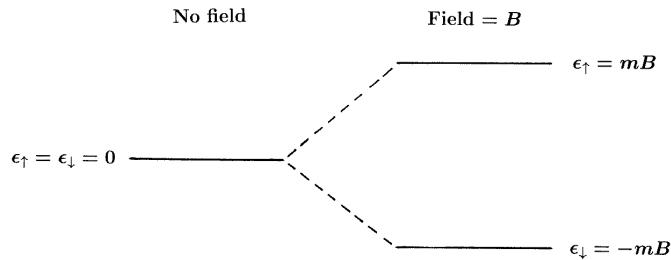


Figure 1.3: Without a magnetic field the up- and down-spin energy levels are degenerate, but the magnetic field splits the degeneracy.

**Energy storage:** How does the expression for the work on a macroscopic substance (above) relate to the microscopic degrees of freedom? We need to see how work can affect the potential energy of the microscopic dipoles in the paramagnetic substance. The potential energy of a dipole moment  $\mathbf{m}$  in a given magnetic field is  $-\mu_0 \mathbf{m} \cdot \mathbf{H}$ , so that the energy is minimal when  $\mathbf{m}$  is parallel to the external  $\mathbf{H}$  and maximal when it is anti-parallel. This energy can also be written as  $U_{pot} = \mu_0(N_\uparrow - N_\downarrow) \mathbf{m}_d \cdot \mathbf{H}$ , where  $\mathbf{m}_d$  is the magnetic moment of an ion and  $N_\uparrow$  and  $N_\downarrow$  are the numbers of up and down spins.

#### Energy flow in/out of the system:

(1) **macroscopic  $\leftrightarrow$  microscopic:** Let us again picture the situation described above, in which a paramagnetic substance approaches a permanent magnet. Now, consider the change of the internal energy, i.e. the energy stored in internal degrees of freedom. First, we apply a magnetic field, for instance as outlined above, by moving the substance infinitesimally closer to a permanent magnet. The energy levels of each microscopic moment split, and the lower energy level is more likely to be occupied than the higher one, so overall the overall energy – in this case made up from the potential energy contributions from all of the dipoles – changes as  $dU = -\mu_0 d(\mathbf{m} \cdot \mathbf{H})$ . This is only correct, if the dipoles do not interact, because otherwise there would be additional contributions to the overall energy from interactions. During this process the work done on the system – as explained in the preceding section – was  $dW' = -\mu_0 \mathbf{m} d\mathbf{H}$ . Setting  $dU = dQ + dW'$ , we find that heat is extracted during this process:

$$dQ = dU - dW' = -\mu_0 d(\mathbf{m} \cdot \mathbf{H}) + \mu_0 \mathbf{m} d\mathbf{H} = -\mu_0 \mathbf{H} d\mathbf{m}$$

How does this tally with the approach outlined earlier, which gave a work  $dW = \mu_0 \mathbf{H} d\mathbf{m}$ ? If potential energy is accounted for separately, not as part of the internal energy, then the change in internal energy would have been zero during this process, because all the energy is attributed to potential energy. On the other hand, the work done would be  $\mu_0 \mathbf{H} d\mathbf{m}$ . This still gives  $dQ = -\mu_0 \mathbf{H} d\mathbf{m}$ , so heat is extracted.

Even if no heat was exchanged between the surroundings and the sample, heat must have left the spin system, because  $dQ$  is negative: as the microscopic moments are aligned, their entropy is reduced, and a reduction in entropy corresponds to an equivalent loss of heat. Where does the heat go, if the sample was thermally isolated during this process?

(2) **microscopic  $\leftrightarrow$  microscopic:** In a solid containing paramagnetic ions the spins are normally in thermal equilibrium with the vibrations of the lattice (the phonons) and the electrons, so generally heat flow to/from the spins is from/to these other microscopic degrees of freedom

of the solid, not from/to an external reservoir. So as the substance is magnetised, energy will be transferred from the spin system to the lattice, which will heat up or pass the heat further onto the environment.

The paramagnetic salt will be used to illustrate methods and ideas of thermodynamics and statistical mechanics.

#### 1.1.4 Assembly of one-dimensional simple harmonic oscillators

The energy of a one-dimensional simple harmonic oscillator in its  $n^{th}$  excited state is

$$\epsilon_n = (n + 1/2)\hbar\omega_0 \quad (1.10)$$

##### **Energy storage:**

In an array of simple harmonic oscillators, energy is stored as the excitation energy of the individual oscillators. The total energy is  $U = \sum_i(n_i + 1/2)\hbar\omega_0$ , where the sum is over all the oscillators.

##### **Energy flow in/out of the system:**

Macroscopic to microscopic energy flow would be accomplished by changing  $\omega_0$ , which requires changing the shape of the potential wells of the oscillators (e.g., if you represent the phonons in a solid by simple harmonic oscillators, you can change the phonon frequencies by compressing the solid). Microscopic to microscopic energy flow requires for example a radiation bath (the walls of a black-body cavity might be modelled as an assembly of simple harmonic oscillators), or you could have energy exchanged via collisions with a surrounding gas.

This model system will be used to illustrate counting of states in statistical mechanics, and arises in the treatment of phonons and photons.

## 1.2 Thermodynamic variables

In thermodynamics, systems are characterised by the values of *thermodynamic variables*, which can be classified in various ways. For example as intensive or extensive:

**“Extensive”:** Extensive variables are proportional to the amount of stuff in the system and apply to the system as a whole. Examples are internal energy  $U$ , entropy  $S$ , volume  $V$ , particle number  $N$ , and heat capacity  $C$ . We can divide the heat capacity or energy by  $V$ , to get a quantity that is independent of the volume of the system.  $C/V$  is called the “specific” heat capacity. In physics, it is often more useful to divide by the number of molecules in the system, to obtain the energy, entropy, volume etc. *per molecule*; in these notes such variables will be written in lower case.

**“Intensive”:** Intensive variables are independent of the system size and measure a local quantity. Examples are  $p$ ,  $T$  and  $\mu$ , or an external magnetic field  $B$  in a system with magnetic interactions.

One can also classify thermodynamic variables as *conjugate pairs* of “thermodynamic force” and “thermodynamic variable”, in the sense that if one applies a constraint to the given system (an effective force), then the corresponding conjugate variable will change as a response. Many of these pairs are known to you, for instance, if the constraints are pressure  $p$ , linear force  $f$ , or magnetic field  $\mu_0\mathbf{H}$ , then the corresponding response variables are  $V$  (system volume), length  $l$  (in an elastic medium), or magnetisation  $\mathbf{M}$ .

The *thermodynamic state* of a system is defined by the values of its thermodynamic variables, which in turn depend on the contents of the system and its environment. If a macroscopic body is left undisturbed for a long time its thermodynamic variables attain constant values. This is the *equilibrium state* of the system in the given external conditions. Although in practice the state of a system can only be controlled by varying the *external* conditions, it is often useful, as a thought experiment, to place imaginary *internal* partitions in a thermodynamic system to establish *subsystems*. We then imagine we can vary the thermodynamic properties – energy, volume, or even particle number – of one subsystem, examining the overall effect on the total energy, entropy, etc. This conceptual trick is used in section §2 to study the meaning of thermodynamic equilibrium and it will also be central to our development of statistical mechanics.

Thermodynamic variables and potentials are special because they are *functions of state*, i.e., properties of a system which are completely determined by the contents and environment. That is, they don’t depend on what happened to the system in the past, only on the present conditions. For example, work and heat are *not* functions of state, but energy is; we can put energy into a system as work (e.g., by compressing a piston), and then remove it as heat (e.g., by putting the system in contact with a cold reservoir). Indeed, we can go around a loop in the  $(p, V)$  plane, doing net work and extracting net heat, but the system ends up with the same amount of energy at the end of each loop. Therefore the energy is a function of state, but work and heat are not.

An essential point about functions of state is that *we can find the magnitude of the change in a function of state in going between two equilibrium states, even if the path taken was irreversible, by choosing any convenient reversible path between the initial and final states and integrating along it.*

It was Clausius who identified the entropy as a “hidden” function of state, whose differential change is defined as

$$dS = \frac{dQ_{rev}}{T} \quad \text{or, for a finite change,} \quad \Delta S = \int_i^f \frac{dQ_{rev}}{T}. \quad (1.11)$$

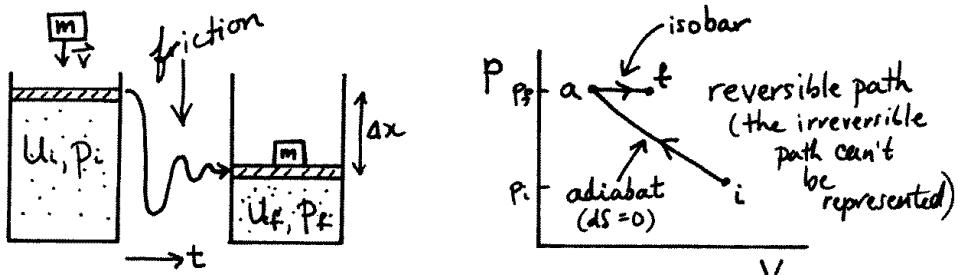
According to this equation, to find the difference in entropy between two states, we integrate along any *reversible* path connecting those states. See below for the arguments leading to this definition.

### 1.3 Equations of state; $p - V - T$ for a real substance

The equilibrium behaviour of a real substance can be expressed by equations of the form

$$\Phi(p, T, V, N_1, N_2, \dots) = 0. \quad (1.12)$$

(E.g., for an ideal gas,  $pV - Nk_B T = 0$ .) Analytic equations of state are never more than approximations, and the appropriate forms change radically depending on whether we are describing the solid, liquid or gaseous phases of a substance.



$$U_f = U_i + \frac{1}{2}mv^2 + mg\Delta x \quad P_f = P_i + \frac{mg}{\text{area}}$$

$$S_f = \int_a^f \left( \frac{\partial S}{\partial V} \right)_P dV + S_i$$

Figure 1.4: An irreversible process in which a mass  $m$  hits a piston at velocity  $v$  and compresses the gas.

Graphical representations are commonly used to illustrate equations of state. The most obvious example is the  $p - V - T$  surface, which makes it easier to grasp important features of the behaviour of materials. A typical example is shown in Fig. 1.5, along with the projections of the  $p - V - T$  surface into the  $(p, V)$  and  $(p, T)$  planes.

Fig. 1.6 shows a sequence of states numbered one to eight along an isotherm which passes through both the liquid-vapour and the solid-liquid phase equilibrium regions. As the system is compressed, energy in the form of work continually enters the system, and heat passes out into the reservoir. It is important to note that the phase transitions occur at constant pressure and, while the new phase condenses and grows, heat (called *latent* heat) is continuously evolved. In the liquid-vapour coexistence region on the  $(p, V)$  diagram, the latent heat associated with the transition is smaller for isotherms near the *critical isotherm*, and along the critical isotherm the latent heat vanishes. Phase transitions which have latent heat associated with them are called *first order* phase transitions.

### The equation of state of a van der Waals gas

The van der Waals equation (Eq. 1.9) is an example of an equation of state. Isotherms on its  $p-V-T$  surface, projected into the  $p-V$  plane, are shown in Fig. 1.7.

Starting at the low density side (i.e., high volume  $v$  per particle), we find behaviour approaching that of an ideal gas. As the density increases, the inter-molecular attraction term  $N^2a/V^2$  causes the isotherm to fall below the ideal gas pressure, until we start to approach the density of closest packing, at which point the hard core repulsion term  $Nb$  causes the pressure to skyrocket. On some isotherms there is a very odd region where  $\partial p/\partial V$  is positive, a situation which is mechanically unstable. This unphysical behaviour is a consequence of the tacit assumption that the density is uniform: in reality, in the region below the dashed line the system undergoes *phase separation* into a high density liquid phase and a low density vapour phase, following, in the case of the 80 K isotherm, the path A – E, rather than the path A – B – C – D – E.<sup>2</sup>

<sup>2</sup>Actually, the system can in some cases go along A – B and E – D, if the coexistence region is approached from outside. These correspond to “super-heating” and “super-cooling” respectively, and result from failure of the new phase to nucleate. The mechanically unstable region B – D is never observed.

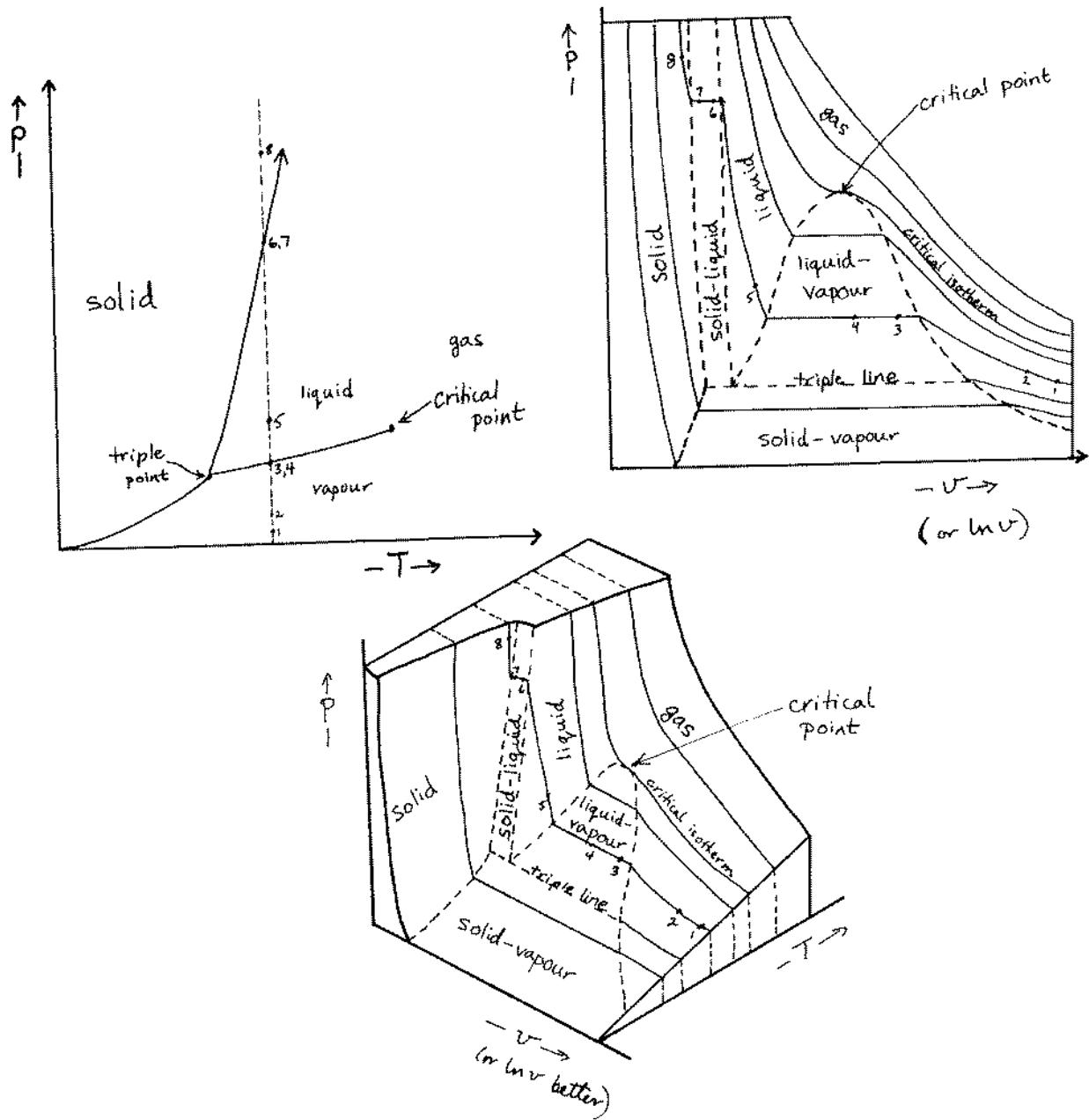


Figure 1.5: The  $p - V - T$  surface of a generic material, and its projections into the  $(p, V)$  and  $(p, T)$  planes. The isotherm with the numbers along it is illustrated in Fig. 1.6.

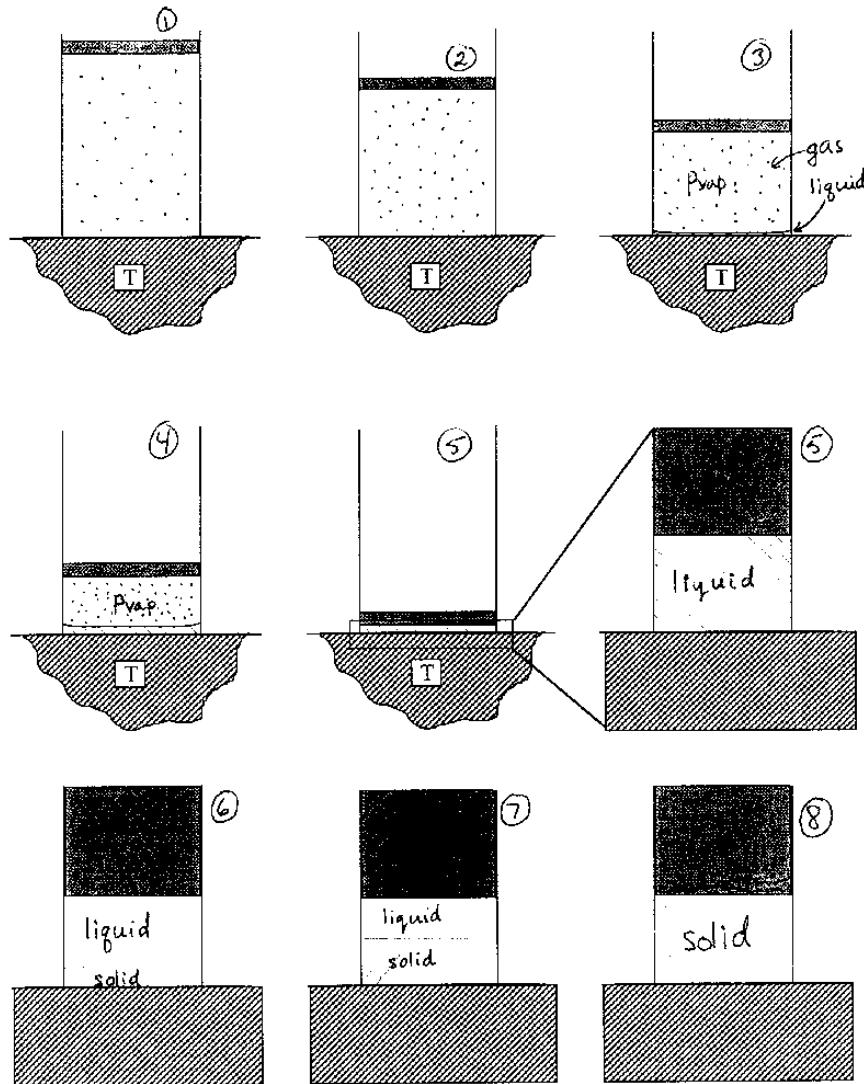


Figure 1.6: Illustration of the states of a system along an isotherm which passes through both the liquid-vapour and the solid-liquid phase equilibria regions. The numbers correspond to those on an isotherm of Fig. 1.5.

$$p = \frac{1.4 \times 10^{-23} T}{v - 5 \times 10^{-29}} - \frac{2.2 \times 10^{-49}}{v^2}$$

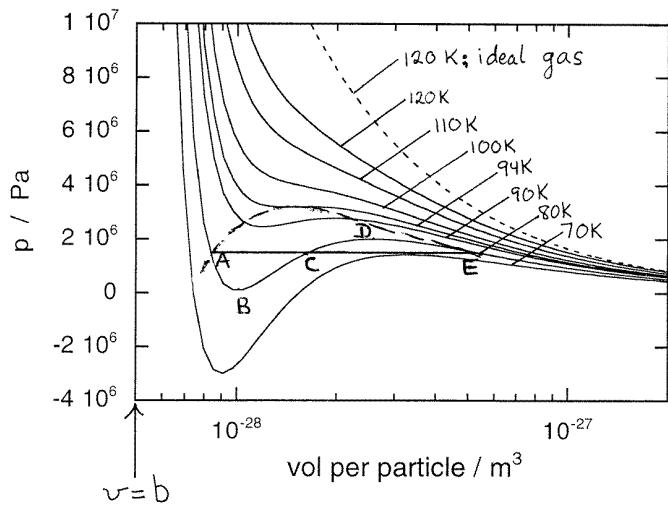


Figure 1.7: Isotherms of the van der Waals equation of state.

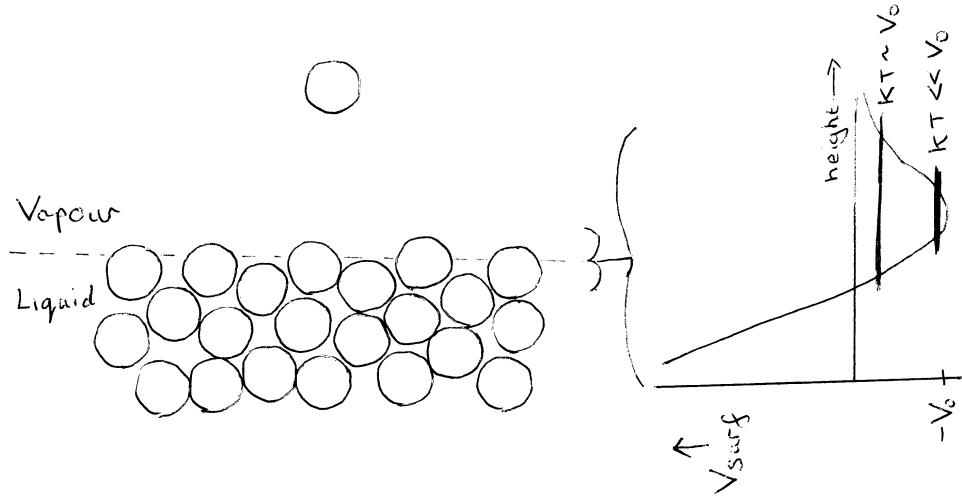


Figure 1.8: Toy model of the origin of latent heat.

As another example of using microscopic reasoning to understand macroscopic thermodynamics, a simple model of inter-molecular interaction explains what latent heat is, and why it is reduced for higher temperature isotherms in the coexistence region. Atoms are bound in the liquid by their attractive interaction with nearby atoms. Atoms at the surface are in a lopsided potential well, as shown in Fig. 1.8. The latent heat per particle is related to the amount of energy required for particles to escape into the gas from this potential well. As the temperature increases the atoms in the liquid move to higher energy states in the potential well, so less energy is required to liberate them, hence the latent heat decreases. A marginally deeper explanation comes from considering the distribution of energies of molecules in the potential well; it is the highest energy

atoms which escape from the liquid, so the mean of the distribution is shifted to lower energies by the escape of atoms into the gas. Skewing the energy distribution towards lower energies is equivalent to cooling the system. To keep the liquid at constant temperature as atoms evaporate, heat must be supplied to compensate this cooling effect.

## 1.4 The Laws of thermodynamics

**0<sup>th</sup> Law** The 0<sup>th</sup> Law says that if two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other. This can be used to show the existence of a quantity called *temperature*.

**1<sup>st</sup> Law** The First Law states that energy is conserved when heat is taken into account. This applies to the flow of energy from macroscopic to microscopic length scales and between microscopic length scales.

**2<sup>nd</sup> Law** There are many statements of the Second Law of thermodynamics, and here are three of the best known, which can be paraphrased as follows:

**Clausius** “*Heat does not flow, of itself, from a colder to a hotter body.*”

**Kelvin** “*You can't cool an object to below the temperature of its surroundings, and extract work in the process.*”

**Carathéodory** “*In the neighbourhood of any state there are states that cannot be reached from it by an adiabatic process.*”

The crowning glory of thermodynamics is that these statements (which are essentially all equivalent) imply that we can assign a value of a measurable quantity known as entropy to every equilibrium state of every system. Although it only holds on average, significant violations of it are incredibly unlikely. The Second Law of Thermodynamics is one of the most sacrosanct of all physical laws. This contrasts with Maxwell's equations (to which there are quantum corrections), Schrödinger's equation (relativistic corrections), and Newton's law of gravitation (general relativistic corrections).

The Clausius and Kelvin statements lend themselves to discussions involving heat engines, while the more mathematical Carathéodory statement has been the starting point for a number of modern attempts to formulate the Second Law. The Carathéodory statement uses the word “adiabatic”, a process in which no exchange of heat occurs. There is no implication that the process has to be slow or reversible. Examples of adiabatic processes are: expansion or compression of a gas, stirring a liquid, rubbing two objects together, smashing a plate with a hammer. Expansion or compression may be reversible, by which I mean that one can return to the original state by an adiabatic process, but rubbing, stirring and smashing are irreversible.

**3<sup>rd</sup> Law** The contribution to the entropy of a system from each aspect which is in internal thermodynamic equilibrium tends to zero as the temperature tends to zero.

Nernst introduced this law in 1906, which he inferred from the behaviour of chemical reactions at low temperatures. The third law implies the unattainability of absolute zero temperature and that all heat capacities must go to zero as the temperature approaches zero.

## 1.5 Entropy

In the Part 1B course, you have learned about the Carnot cycle. During a cycle, heat  $Q_1$  is taken from a hot reservoir at temperature  $T_1$  and less heat  $Q_2$  is deposited in a cold reservoir at temperature  $T_2$ . You find that if the cycle is operated reversibly (i.e. so slowly that the operating substance, the ideal gas, is in thermal equilibrium with the reservoirs when it is in contact with them),  $Q_1/T_1 = Q_2/T_2$ . The work that can be extracted is determined by the first law of thermodynamics as  $W = Q_1 - Q_2$  (see Fig. 1.9). The efficiency  $\eta = W/Q_1 = (Q_1 - Q_2)/Q_1 = (T_1 - T_2)/T_1$ , with which work can be extracted from the heat absorbed from the hot reservoir is the same no matter how the heat engine is actually implemented. This is the Carnot efficiency. If there was another reversible process between two reservoirs that could provide a higher efficiency, i.e. it extracts work  $W' > W$  for the same  $Q_1$ , then we could use some of that work to operate the Carnot cycle in reverse. This will pump the heat  $Q_1$  back and create a combined engine that would extract  $W' - W$  from a single reservoir, which violates Kelvin's statement of the second law. If there was another reversible process between two reservoirs that worked at a *lower* efficiency than we could again exploit the discrepancy in efficiencies by using the Carnot cycle as the heat engine and using the other cycle to pump the heat back. So all *reversibly* operated heat engines *between two reservoirs* must have the same efficiency.

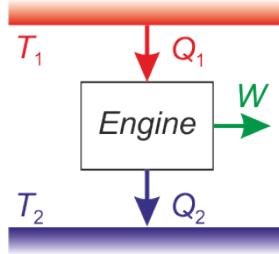


Figure 1.9: Schematic representation of a heat engine operating between a hot reservoir at temperature  $T_1$  and a cold reservoir at temperature  $T_2$ .

The finding that  $Q_1/T_1 = Q_2/T_2$  already suggests that summing the quantity  $\Delta Q/T$  over the cyclic process returns zero, so if we define a new variable  $S$  such that  $dS = dQ/T$ , we may arrive at a new function of state. Unfortunately, this argument so far only would hold for processes between two reservoirs. We can, however, generalise it to a system undergoing a cyclic process which involves any number of reservoirs (Fig. 1.10). If we hitch up such a cyclic process involving reservoirs at temperatures  $T_1, \dots, T_N$  to  $N$  heat pumps running just between a single reservoir  $T_0$  and each of the  $N$  reservoirs, then the work that could be extracted from this entire assembly would be  $W' = W - \sum W_n = \sum Q_n - \sum Q_n (T_n - T_0) / T_n = T_0 \sum Q_n / T_n$ .

But we cannot extract work from this assembly, otherwise it would violate Kelvin's statement of the second law. We must have  $W' \leq 0$ . Hence, we find

$$\sum \frac{Q_n}{T_n} \leq 0 \quad (1.13)$$

The best we can hope for is  $W' = 0$ , which would happen if all the processes are operated reversibly. So we learn that for *reversible* processes, the quantity obtained from summing up heat flow over temperature, which turns into an integral for continuous changes of temperature,  $\sum \Delta Q/T \rightarrow \int dQ/T$ , can be used to define a function of state (because when you do that integral

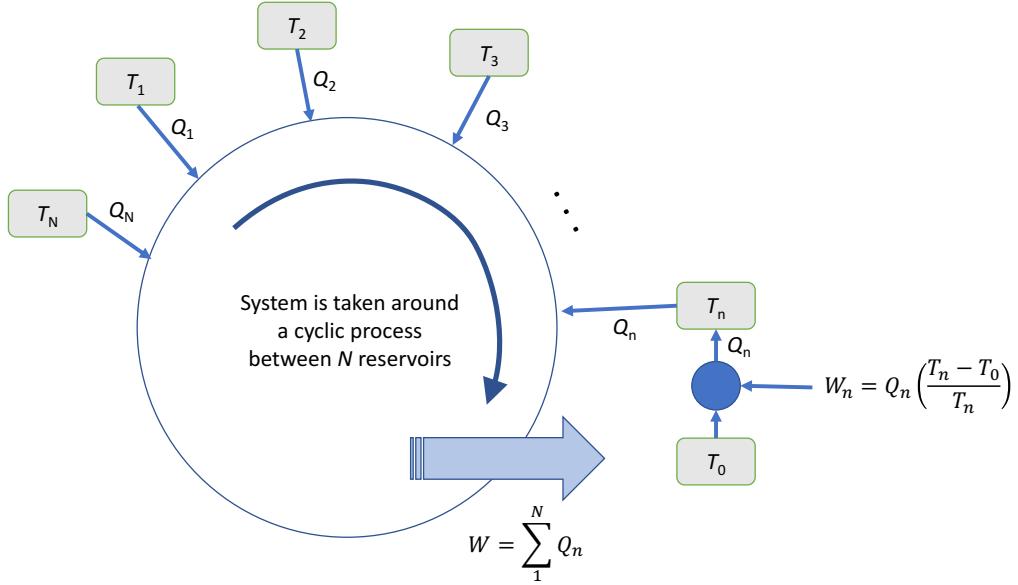


Figure 1.10: If we take a system around a cyclic process between reservoirs at temperatures  $T_1$  to  $T_N$ , we can extract a total amount of work  $W$  from the process. This work can be used to drive  $N$  heat pumps that will pump heat  $Q_1, \dots, Q_N$  back into the reservoirs, extracting heat from a single reservoir at temperature  $T_0$  in the process. The amount of work needed to drive all of these heat pumps must be at least as high as the work  $W$  we can extract from the cyclic process, otherwise we would be able to get work out of the entire arrangement, violating Kelvin's statement of the second law.

around a closed loop in parameter space, it gives zero). This leads to Clausius' definition of the entropy as a new function of state:

$$dS = dQ_{rev}/T , \quad (1.14)$$

$$S_B - S_A = \int_A^B dQ_{rev}/T \quad (1.15)$$

where  $dQ_{rev}$  denotes heat that flowed into the system in a reversible process and  $A, B$  denote two states of the system.

Somewhat surprisingly, maybe, the loop integral  $\oint dQ/T$  for irreversible processes is actually  $< 0$ . This can be understood by noting that the temperatures in the denominator are always the *reservoir* temperatures. These have to exceed the system temperatures when the system accepts heat irreversibly, or they are less than the system temperatures, when the system gives up heat, so compared to the contributions  $dQ/T$  for reversible processes, the contributions in the integral for irreversible processes are less.

If we now construct a process that runs from  $A$  to  $B$  and back again (Fig. 1.11), with the route

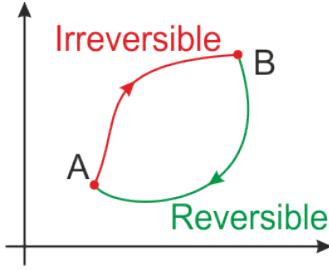


Figure 1.11: Considering the entropy change between two states  $A$  and  $B$ . Because the loop integral of  $dQ/T$  is  $\leq 0$ ,  $S_B - S_A \geq \int dQ/T$  along the irreversible path. If the system is actually isolated, then the r.h.s. is  $= 0$ , implying that the entropy will stay the same or increase, but cannot go down.

from  $A$  to  $B$  potentially irreversible, but the return reversible, we find for the entire loop:

$$\oint dQ/T \leq 0 \text{ and hence} \quad (1.16)$$

$$\int_A^B dQ/T \leq \int_A^B dQ_{rev}/T \text{ but the latter gives the entropy change; therefore:} \quad (1.17)$$

$$\Delta S = S(B) - S(A) \geq \int_A^B dQ/T \quad (1.18)$$

If, however, the outward route from  $A$  to  $B$  is taken without any heat flowing into the system or out of it, i.e. **if the system is thermally isolated, then the entropy change  $\Delta S$  must be zero or positive.**

This is a key result: an isolated system will evolve in such a way that its entropy increases. At some point, it will reach an equilibrium state, from which it cannot evolve further. In this equilibrium state, its entropy will have reached a maximum.

The Second Law has a very important implication for the behaviour of the entropy of the universe, which – as a whole – is an isolated system. These are encapsulated in the Law of Increase of Entropy, sometimes called the Entropy Statement of the Second Law:

$$\Delta S_{\text{total}} \geq 0. \quad (1.19)$$

That is, in any process, the entropy of the universe increases, or in the idealised limit of a reversible process, stays constant.

For example, (meant to be illustrative, not as a proof): consider a Carnot cycle, except make the thermally isolated processes irreversible (e.g., when the piston is compressed adiabatically, friction generates heat which goes into the system, see Fig. 1.12). Over one cycle the system (consisting of the piston and the gas inside it) comes back to the same point, so  $\Delta S_{\text{system}} = 0$  (one more time ...  $S$  is a function of state, so if the system comes back to the same state, the entropy returns to the same value). Because of the internal friction within the system, the reservoir sends in less heat during the warm expansion phase,  $Q_h < Q_h^{(\text{rev})}$ , and it absorbs more heat during the cold contraction phase,  $|Q_c| > |Q_c^{(\text{rev})}|$ . Note that  $Q_c < 0$ . Therefore, the change

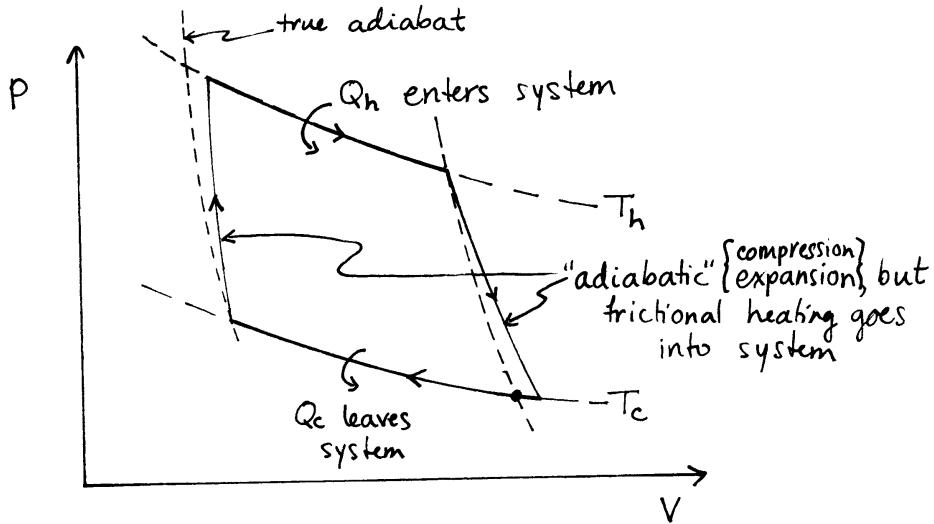


Figure 1.12: A Carnot cycle and an irreversible cycle.

in the total entropy of system plus reservoir is positive:

$$\Delta S_{\text{total}} = \underbrace{\Delta S_{\text{reservoir}}}_{-(Q_h/T_h + Q_c/T_c)} + \underbrace{\Delta S_{\text{system}}}_{=0} > 0. \quad (1.20)$$

As mentioned above, the first term on the right hand side represents the heat leaving the reservoir, which is smaller in magnitude than in the reversible case. The second term represents the heat entering the reservoir, which is larger than in the reversible case. In the reversible case the two terms add to zero, but in the irreversible case they do not cancel and  $\Delta S_{\text{total}} > 0$ .

### Some consequences of the First and Second Laws

The First Law essentially expresses the fact that energy is conserved if we take heat into account. That is, for *any* process we can write

$$dU = dQ + dW, \quad (1.21)$$

where the work term  $dW$  can in general account for not just the 'volume work'  $-pdV$ , but also other forms of work such as the magnetic work  $\mu_0 H dm$ , the electrical work  $VdQ$  and the 'particle work', or 'chemical work'  $\mu dN$ , where  $\mu$  is the chemical potential and  $N$  is particle number. Note that in principle we could include not just irreversible changes between equilibrium states but also changes between non-equilibrium states. All we are saying is that the energy can only change by a flow of heat in or out, or by work being done. If the change takes place between two adjacent *equilibrium* states, then (ignoring other forms of work than volume work and chemical work)

$$dW = -p dV + \mu dN \quad \text{for reversible changes only.} \quad (1.22)$$

$$dQ = T dS \quad \text{for reversible changes only,} \quad (1.23)$$

$$\text{so } dU = T dS - p dV + \mu dN \quad \text{for reversible changes only.} \quad (1.24)$$

But  $dS$ ,  $dV$  and  $dN$  are differentials of functions of state, so *provided that we are talking about a change between two equilibrium states,*

$$dU = T dS - p dV + \mu dN \quad \text{ALWAYS,} \quad (1.25)$$

even if the process connecting the equilibrium states is *irreversible*.

This equation shows that  $U$  is a function of the three independent variables  $S, V, N$  – these are the “natural variables of  $U$ ”; while  $T, p, \mu$  are “derived quantities”:

$$p = - \left( \frac{\partial U}{\partial V} \right)_{S,N}, \quad T = \left( \frac{\partial U}{\partial S} \right)_{V,N}, \quad \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}. \quad (1.26)$$

## 1.6 The Gibbs-Duhem equation

Although there are a number of ways in which changes between equilibrium states can be expressed mathematically, that based on Eq. 1.25 has a very special place. It expresses changes in the energy, which is itself an extensive quantity, in terms of changes in the other extensive quantities. We know that the energy is a homogeneous first order function of the extensive variables, or in plain English, if we simultaneously double the volume, number of particles and entropy of a system, while holding the temperature, pressure and chemical potential constant, then its energy also doubles. Therefore, generalising to an increase by a factor of  $\lambda$  we can write  $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$ , so that

$$U(S, V, N) = \frac{\partial(\lambda U(S, V, N))}{\partial \lambda} \quad (1.27)$$

$$= \left( \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \right)_{\lambda V, \lambda N} \frac{\partial(\lambda S)}{\partial \lambda} + \left( \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \right)_{\lambda S, \lambda N} \frac{\partial(\lambda V)}{\partial \lambda} + \\ \left( \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \right)_{\lambda S, \lambda V} \frac{\partial(\lambda N)}{\partial \lambda} \quad (1.28)$$

$$= \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} S + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} V + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} N. \quad (1.29)$$

This must be true for *any*  $\lambda$ , so we can set  $\lambda = 1$  to get

$$U(S, V, N) = \left( \frac{\partial U}{\partial S} \right)_{V,N} S + \left( \frac{\partial U}{\partial V} \right)_{S,N} V + \left( \frac{\partial U}{\partial N} \right)_{S,V} N. \quad (1.30)$$

But we know from Eq. 1.25 that

$$\left( \frac{\partial U}{\partial S} \right)_{V,N} = T, \quad \left( \frac{\partial U}{\partial V} \right)_{S,N} = -p, \quad \left( \frac{\partial U}{\partial N} \right)_{S,V} = \mu, \quad (1.31)$$

hence it must be true that

$$U = TS - pV + \mu N. \quad (1.32)$$

Again, this only worked for  $U(S, V, N)$ , uniquely, because of the extensive nature of all entries. You can never write this as  $U = TS - pV$ , even if the particle number is fixed. The  $\mu N$  term

is essential! This equation can be generalised to the case where several species of particle are present by replacing  $\mu N$  by  $\sum_i \mu_i N_i$ . Note that there was nothing special about starting from  $U(S, V, N)$ , we could just as well have derived Eq. 1.32 starting from, for example,  $S(U, V, N)$ , as it also has all entries extensive.

One can derive useful results directly from the Eq. 1.32. We know that  $dU = T dS - p dV + \mu dN$ , but Eq. 1.32 gives  $dU = T dS + S dT - p dV - V dp + \mu dN + N d\mu$ . Both of these equations can only be true at the same time if

$$Nd\mu = -S dT + V dp , \quad \text{or} \quad d\mu = -s dT + v dp, \quad (1.33)$$

where  $s$  and  $v$  are the entropy and volume per particle (now intensive, as is the chemical potential  $\mu$ ). This important result is known as the Gibbs-Duhem equation.



# Chapter 2

## Thermodynamic equilibrium

### 2.1 Internal equilibrium of closed systems

The method we adopt for studying the internal equilibrium of closed systems, which will be used repeatedly throughout the course, is to place imaginary partitions into a large system to partition it into two or more subsystems. This is illustrated in Fig. 2.1, which shows what happens if we partition a large volume of gas into two parts, and then independently vary their temperature.

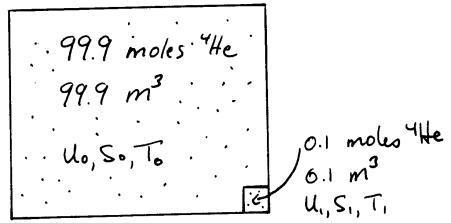
We know from the entropy statement of the Second Law,  $dS \geq 0$ , that the equilibrium state is characterised by maximum entropy of the universe. In this figure, if we close the system so that its total energy is fixed, then it constitutes the universe, so maximum  $S$  at fixed  $U$  is the equilibrium condition. From the figure we can observe that the state of maximum entropy at fixed total energy is also the state of minimum energy at fixed total entropy, a curious but not-very-useful condition in real systems. In the next section we explore the mathematical meaning of equilibrium using the *entropy representation*.

#### Maximum entropy principle

As discussed above, the actual equilibrium states we observe are the ones which maximise the entropy of the universe; in the *approach* to equilibrium, the entropy of the universe increases. We will illustrate this with two examples.

Example 1: Two systems with constant volumes and numbers of particles are allowed to exchange heat.

We bring two otherwise isolated, or “closed”, systems at temperatures  $T_1$  and  $T_2$  into thermal contact, holding their volumes and particle numbers constant. The entropy statement of the



$$U = U_0 + U_1$$

$$S = S_0 + S_1$$

assume ideal gas, so  $U_i = \frac{3}{2} N_i k_B T_i \rightarrow$

$$S_i = N_i k_B \ln \left( \exp \left( \sum \right) \frac{V_i}{N_i} \left( \frac{m k_B T_i}{2\pi \hbar^2} \right)^{3/2} \right)$$

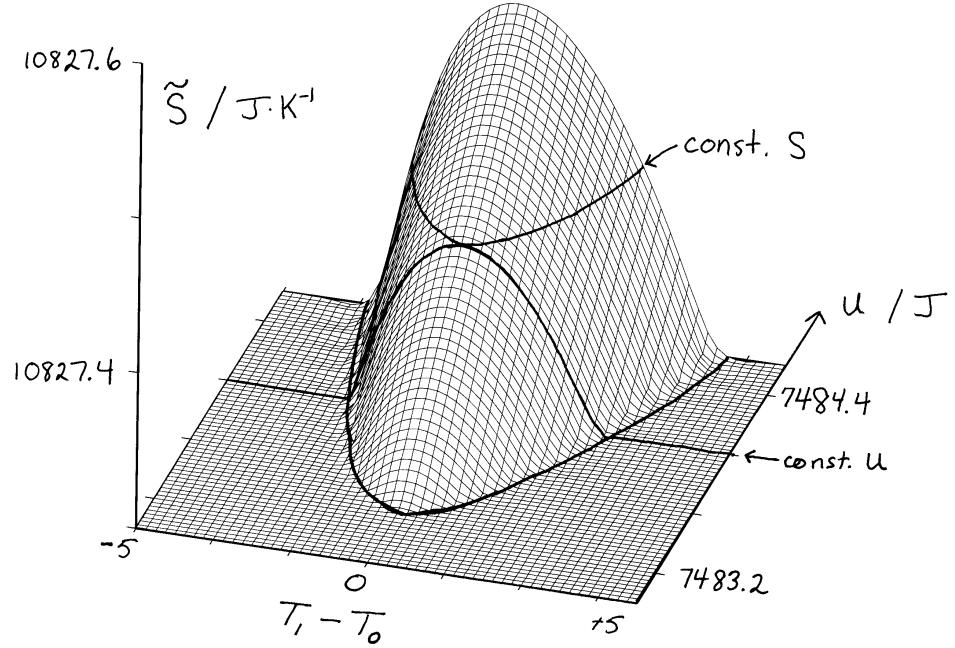


Figure 2.1: A small section of the  $(S - U - (T_1 - T_0))$  surface for a volume of ideal gas partitioned by an adiathermal wall. We imagine that we can transfer energy across the partition (using external heat engines for example) and then we calculate the total entropy, using the Sackur-Tetrode expression (to be rederived later). Equilibrium of the unpartitioned system at fixed total energy occurs when the entropy is a maximum. We see that this equilibrium corresponds, at fixed total entropy, to a minimum of the energy. They both occur when  $T_1 = T_0$ . Because the volumes chosen are arbitrary, this tells us that in equilibrium the temperature is uniform.

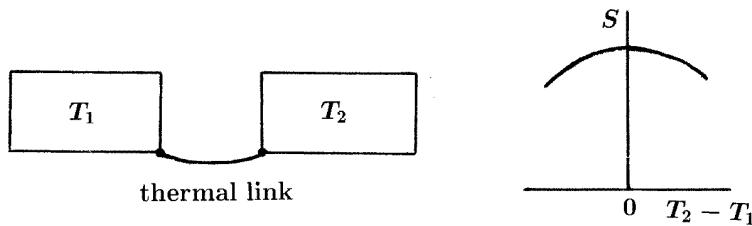


Figure 2.2: Two systems connected by a thermal link. The heat flows from the hotter to the colder body and at equilibrium  $T_1 = T_2$ .

Second Law is

$$\begin{aligned} dS_{\text{tot}} &= dS_1 + dS_2 \\ &= \frac{dU_1 + p_1 dV_1 - \mu_1 dN_1}{T_1} + \frac{dU_2 + p_2 dV_2 - \mu_2 dN_2}{T_2} \\ &= \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 \geq 0, \end{aligned} \quad (2.1)$$

where we have used  $dV_i = 0$  (constant volume),  $dN_i = 0$  (constant particle number), and  $dU_2 = -dU_1$  (energy conservation). This equation means that if  $T_1$  is greater than  $T_2$ ,  $dU_1$  is negative and heat flows from 1 to 2, but if  $T_1$  is less than  $T_2$ ,  $dU_1$  is positive and heat flows from 2 to 1. So heat flows from hot to cold. In equilibrium, the entropy is an extremum, and small displacements of  $U_1$  must not increase the entropy or we can't be at equilibrium. This requires  $T_1 = T_2$  at equilibrium.

Example 2: Similarly, from  $dS \geq 0$  we can show that particles flow from higher to lower chemical potential. Consider two systems with fixed volumes  $V_1$  and  $V_2$ , held at the same temperature  $T$ , but arranged so that their chemical potentials differ (for example we might add a small amount of salt on one side of a semi-permeable barrier separating the two volumes of water shown).

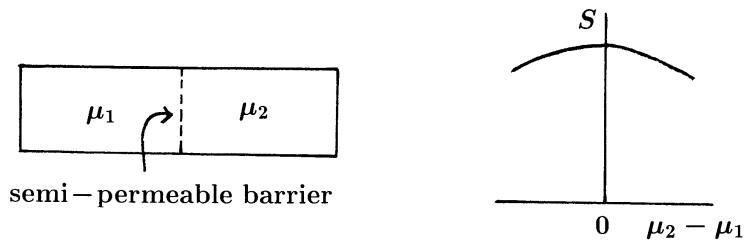


Figure 2.3: A container is divided into two parts by a membrane which is permeable to salt but not to water. On the left of the semi-permeable membrane the water contains some salt, and on the right is pure water. The entropy is maximised when  $\mu_1 = \mu_2$ , i.e., the salt concentrations are equal.

The entropy statement of the Second Law of thermodynamics gives

$$dS = dS_1 + dS_2 = \frac{dU_1 + p_1 dV_1 - \mu_1 dN_1}{T} + \frac{dU_2 + p_2 dV_2 - \mu_2 dN_2}{T} \geq 0. \quad (2.2)$$

The total energy is fixed, so  $dU_1 + dU_2 = 0$ , and the volumes are fixed so that  $dV_1 = dV_2 = 0$ . Particle number is also conserved, so  $dN_1 = -dN_2$ , and the law of increase of entropy reduces

to

$$(\mu_2 - \mu_1) dN_1 \geq 0. \quad (2.3)$$

Therefore if  $\mu_2 > \mu_1$  then  $dN_1 > 0$ , and particles flow from 2 to 1, whereas if  $\mu_2 < \mu_1$ , then  $dN_1 < 0$  and particles flow from 1 to 2. Hence

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V} \quad (2.4)$$

is a good definition of the chemical potential, because it makes explicit the dependence of particle flow on the law of increase of entropy.

## 2.2 Thermodynamic equilibrium in open systems

### 2.2.1 The Availability

For thermally isolated systems, as we have seen, thermodynamic equilibrium can be defined as the state of maximum entropy for a given total energy, or we can define it as the state of minimum energy for a given total entropy. However, for a system in contact with a reservoir – and most thermodynamic systems are in thermal and/or mechanical contact with the rest of the universe – it turns out that there is a very useful alternative to maximising the total entropy of the system *and* the reservoir with respect to the state of the system: there is a property of the *system*, called the *availability*, which is minimised when the entropy of the *universe* (system + reservoir) is maximised with respect to the state of the system.

To see this, consider a system (denoted by quantities without subscripts) and reservoir (labelled “R”), which can exchange energy in the form of heat and/or work, and particles. The Entropy Statement of the Second Law is

$$dS_{\text{tot}} = dS + dS_R \geq 0 \quad (2.5)$$

$$= dS + \frac{dU_R + p_R dV_R - \mu_R dN_R}{T_R} \quad (2.6)$$

$$= \frac{T_R dS - dU - p_R dV + \mu_R dN}{T_R}, \quad (2.7)$$

where we have used conservation of energy, volume and particle number, which give  $dU_R = -dU$ ,  $dV_R = -dV$  and  $dN_R = -dN$ .

The present situation is rather special, because it involves exchange of all possible quantities with the reservoir: there are many cases (discussed in more detail below, when thermodynamic potentials are introduced), in which the contact with the reservoir is only partial. For instance, the reservoir may receive volume from the system, but not particles. In such a case,  $dV_R = -dV$ , still, but  $dN_R = 0$ . You could rederive what follows below for such special cases, and this would lead to the definitions of the various potentials, or you can take the general route (now following) and then formally – as a shortcut – set certain terms to 0. For instance, the effect of having no particle exchange,  $dN_R = 0$ , on the reservoir entropy in Eq. 2.6 above can be achieved in Eq. 2.7 by simply setting  $\mu_R = 0$ .

So far we haven't used the assumption that the reservoir is large compared with the system, but if we now do so we have that for any change the system can undergo,  $dT_R = 0$ ,  $dp_R = 0$  and  $d\mu_R = 0$ . We can therefore bring all of the differentials to the front, i.e.,  $p_R dV = d(p_R V)$ . We now define the new object, called *availability A*, as  $dA = -T_R dS_{\text{tot}}$  which means:

$$\begin{aligned} dA &= dU - T_R dS + p_R dV - \mu_R dN \\ &= (T - T_R) dS - (p - p_R) dV + (\mu - \mu_R) dN \end{aligned} \quad (2.8)$$

The first of these differential equations tells us that availability is the function of *system variables*  $U, S, V$  and  $N$ , while the (constant) reservoir variables  $T_R, p_R$  and  $\mu_R$  act as the corresponding "forces". Since they are constant, we can integrate and obtain:

$$A = U - T_R S + p_R V - \mu_R N. \quad (2.9)$$

Since we have  $dS_{\text{tot}} \geq 0$  and  $T_R$  is assumed constant, we must conclude that

$$dA \leq 0. \quad (2.10)$$

We have developed a new statement for a system in contact with a reservoir which is equivalent to the Law of Increase of Entropy. In the approach to equilibrium the *entropy of the universe must increase* or, equivalently, the *availability of the system must decrease*. A stable equilibrium is stable with respect to perturbations, so  $dA = 0$  in equilibrium: the *availability of a system is a minimum in equilibrium*.

Because the availability is directly related to the overall entropy, Boltzmann's expression for entropy:  $S_{Boltz} = k_B \ln \Omega$ , where  $\Omega$  is the statistical weight or degeneracy, can be used to motivate an important aspect of this analysis, namely the relationship for the *probability* for the system (in contact with the reservoir) to have a certain set of values for its variable, e.g.  $X$ :

$$P(X) \propto e^{-\frac{A(X)}{k_B T}}. \quad (2.11)$$

### 2.2.2 Availability = useful work

The availability function in Eq. 2.9 has some subtleties: its natural variables are  $S, V, N$  (because these are the natural variables of  $U$ ), as well as  $T_R, p_R, \mu_R$ . So, in general, the system can be at temperature  $T = (\frac{\partial A}{\partial S})_{V,N} \neq T_R$ , pressure  $p = -(\frac{\partial A}{\partial V})_{S,N} \neq p_R$  and chemical potential  $\mu = (\frac{\partial A}{\partial N})_{S,V} \neq \mu_R$ . It would then not be in equilibrium with the reservoir. How much work could be extracted by bringing the system in contact with the reservoir? It turns out that the availability, which is also called *exergy*, directly gives the maximum useful work possible during a process that brings the system into equilibrium with a reservoir. This can be shown by revisiting the derivation of Eq. 2.9 and allowing for  $dU_R$  not to be  $= -dU$ , but rather putting  $dU_R + dU = -dW_{\text{extr}}$ , the amount of work extracted in the process. Alternatively, we can go directly for  $-dW_{\text{extr}} = dU + dU_R$  and replace  $U$  by  $A + T_R S - p_R V + \mu_R N$ :

$$\begin{aligned} -dW_{\text{extr}} = dU + dU_R &= d(A + T_R S - p_R V + \mu_R N) + T_R dS_R - p_R \underbrace{dV_R}_{=-dV} + \mu_R \underbrace{dN_R}_{=-dN} = \\ &= dA + T_R \underbrace{d(S + S_R)}_{\geq 0} \end{aligned}$$

The best we can do in extracting work by bringing the system in contact with the reservoir is to do this reversibly, so that the overall entropy  $S + S_R$  stays constant. In this case, the extracted work  $W_{\text{extr}}$  matches the reduction in the availability, or exergy:

$$\Delta W_{\text{extr}} = -\Delta A \quad (2.12)$$

### 2.2.3 Legendre transformations

The natural variables of  $A$  as in eqn. 2.9 are  $S, V, N$  (because these are the natural variables of  $U$ ), as well as  $T_R, p_R, \mu_R$ . In equilibrium, the condition  $dA = 0$  for all variations of  $S, V, N$  then produces  $(\frac{\partial A}{\partial S})_{V,N} = (\frac{\partial U}{\partial S})_{V,N} - T_R = T - T_R = 0 \implies T = T_R$ , and likewise  $p = p_R$  and  $\mu = \mu_R$ . Moreover, the requirement that the gradient of  $U$  w.r.t.  $S$  is equal to the fixed reservoir temperature  $T_R$ , is only fulfilled for one value of the entropy  $S = S_{\text{eq}}$ , the entropy in equilibrium. Likewise for  $V$  and  $N$ . So when the system is in equilibrium with the reservoir, the system variables  $S, V, N$  assume values  $S_{\text{eq}}, V_{\text{eq}}, N_{\text{eq}}$ , which are dictated by the reservoir temperature, pressure and chemical potential. As a consequence, the availability **in equilibrium** has as its natural values  $T_R, p_R, \mu_R$ , which are equal to  $T, p, \mu$  in equilibrium.

This is an application of *Legendre transformations*. If we have a function  $f(x)$  so that  $df = f'dx$ , we can use this to create a new variable  $y$  and a new function  $g(x, y) = f(x) - yx$ . The differential of  $g$  will now be

$$dg = f'dx - ydx - xdy$$

If we further look for the minimum of  $g$  w.r.t.  $x$ , we find it for  $f' = \left(\frac{\partial f}{\partial x}\right)_{x=x_0} = y$ . We can now define a function  $g_0$  as the value of  $g$  at its minimum w.r.t.  $x$  for a given value of  $y$ :  $g_0(y) = \min_x g(x, y) = g(x_0, y)$ , where  $x_0$  is the value of  $x$  at the minimum. We find that this minimum value changes with  $y$  as  $dg_0 = (f' - y)dx - x_0 dy = -x_0 dy$ . So the natural variable of  $g_0$  is  $y$ , when the natural value of  $f$  was  $x$ .

As an example, consider the potential energy of a spring,  $U(x) = \frac{1}{2}kx^2$ . Now, the spring is hanging from a ceiling, with a weight  $W$  on it. The potential energy becomes  $V(x, W) = \frac{1}{2}kx^2 - Wx$ . The minimum of  $V$  w.r.t.  $x$ , which gives the equilibrium position of the stretched spring for a given weight, occurs for  $x = x_0$  such that  $(\frac{\partial V}{\partial x})_{x=x_0, W} = 0$ , i.e.  $kx_0 = W$ . This fixes the *equilibrium potential energy* for a given  $W$  as  $V_0(W) = \frac{1}{2}kx_0^2 - Wx_0 = -\frac{1}{2}W^2/k$ , and  $dV_0 = -x_0 dW$ .

Applying this further, for instance, to the entropy dependence of  $U(S, V, N)$ , we can define a new variable  $T_R$  and a new function  $F(S, V, N, p_R) = U(S, V, N) - T_R S$ . This function has the differential

$$dF = \left[ \left( \frac{\partial U}{\partial S} \right)_{V,N} - T_R \right] dS - SdT_R - pdV + \mu dN ,$$

which for constant  $T_R$  is zero, when  $(\frac{\partial U}{\partial S})_{V,N,S=S_{\text{eq}}} = T = T_R$ , fixing the equilibrium entropy  $S_{\text{eq}}$  at a given temperature  $T = T_R$ . We now find that the value of  $F$  at equilibrium, when the change w.r.t.  $S$  is zero, depends on  $T_R, V$  and  $N$  as

$$dF_{\text{eq}} = -S_{\text{eq}}dT_R - pdV + \mu dN$$

Focusing solely on the equilibrium properties and replacing  $T_R$  by  $T$  and  $S_{\text{eq}}$  by  $S$ , this can be written as  $dF = -SdT - pdV + \mu dN$ , the well-known expression for the Helmholtz free energy,

on which more below. Carrying out Legendre transforms on all the variables of the system,  $S, V, N$ , leads to the availability  $A = U - T_R S + p_R V - \mu_R N$ , which – when equilibrium has been reached – would have the differential

$$dA_{\text{eq}} = -S_{\text{eq}}dT_R + V_{\text{eq}}dp_R - N_{\text{eq}}d\mu_R$$

and  $T = T_R$ ,  $p = p_R$  and  $\mu = \mu_R$  as the natural variables. Actually, the availability of a system in equilibrium with a reservoir is always simply zero! This follows from the realisation, mentioned above (Section 2.2.2), that the availability gives the extractable work on attaining equilibrium: if the system is already in equilibrium, then the availability must have reached zero. It also follows from Eq. 1.32,  $U - TS + pV - \mu N = 0$ .

Whereas the minimum in the availability when all variables  $T, p, \mu$  are constrained is zero, for more specific constraints, when the link to the reservoir is only partial, the minimum availability produces the various *thermodynamic potentials*. We will now look at the important cases.

## 2.3 Overview of the thermodynamic potentials

The *thermodynamic potentials* play a central role in thermal physics. They play a role analogous to energy. Why isn't energy conservation alone sufficient to determine the equilibrium state? Consider the following:

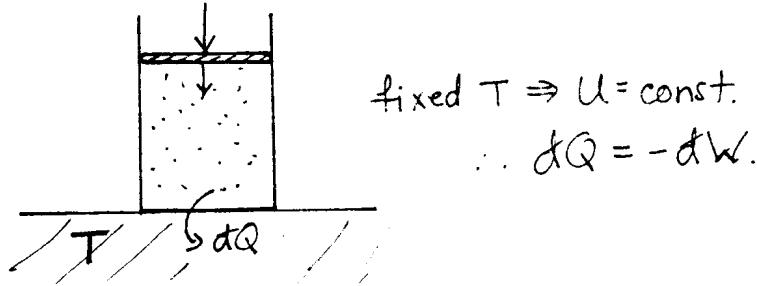


Figure 2.4: Reversible compression of a monatomic ideal gas connected to a reservoir at constant temperature.

Reversibly compress a monatomic ideal gas that is connected to a reservoir so that its temperature is constant. Energy is being put into the system in the form of work, but because the temperature of the (ideal) gas is constant its internal energy,  $U = \frac{3}{2}Nk_B T$ , is constant. So where does the energy that we put in as work go? It flows directly out of the system and into the reservoir as heat:

$$dU = 0 \quad \Rightarrow \quad dQ = -dW. \quad (2.13)$$

If we re-expand the piston reversibly, we get the energy back again; it flows back across the boundary from the reservoir into the system, and appears as work done by the system on the surroundings. The energy put into an isothermal ideal gas as work is therefore “stored” in the reservoir, *not* in the system, and if we want to consider energy conservation we have to keep in mind the energy of both the system and the reservoir. In general this might be quite a problem,

and it is certainly inconvenient, so it would be nice if there were *a property of the system alone, that corresponds to conservation of energy for the system plus the reservoir*, a property that in this case would act like a potential energy. In fact such a function exists; we can write for *any* system, not just ideal gases,

$$dW = dU - TdS \quad (2.14)$$

$$= d(U - TS)_T \quad \text{if } T \text{ is constant} \quad (2.15)$$

$$\equiv (dF)_T, \quad (2.16)$$

where  $F = (U - TS)$  is the Helmholtz free energy. We have assumed that the particle number is fixed. The free energy of an isothermal system is the quantity which corresponds to energy conservation in the system plus the reservoir.

The thermodynamic potentials are generated by adding terms like  $-TS$ ,  $pV$ ,  $-\mu N$ ,  $\mathbf{M} \cdot \mathbf{B}$ , etc. to the energy (corresponding to *Legendre transformation*, see Adkins). For a gas the most commonly encountered potentials are:

internal energy	$U = TS - pV + \mu N$	$dU = TdS - pdV + \mu dN$
enthalpy	$H = U + pV$	$dH = TdS + Vdp + \mu dN$
Helmholtz free energy	$F = U - TS$	$dF = -SdT - pdV + \mu dN$
Gibbs free energy	$G = U - TS + pV$	$dG = -SdT + Vdp + \mu dN$
grand potential	$\Phi = F - \mu N$	$d\Phi = -SdT - pdV - Ndu$

The variables which are differentiated in the above table are the “natural variables” of the corresponding thermodynamic potential, for example, the natural variables of  $F$  are  $(T, V, N)$ . It follows that a thermodynamic potential takes its minimum value in equilibrium under the conditions that its natural variables are held fixed. Another important result, which is not proved here, is that, if one knows any of the thermodynamic potentials as a function of its natural variables, one has complete thermodynamic information about the equilibrium state. For example if one knows  $F(T, V, N)$  one can work out any of the other thermodynamic potentials, but if one only has  $F(T, V, p)$  one cannot.

As we have now seen, the thermodynamic potentials play two distinct roles in thermal systems:

- 1) The appropriate thermodynamic potential is the property of the *system* that reflects *global* energy conservation.
- 2) For given external conditions, the appropriate thermodynamic potential is a *minimum* in equilibrium: the minimisation of this thermodynamic potential of the *system* is a direct consequence of the maximisation of *global* entropy.

It is very important that you learn which thermodynamic potential to consider in a given circumstance. The tables which follow are intended to help with this. As well as the tables, there follows a brief discussion of the uses of each potential.

### 2.3.1 Energy $U$ : Equilibrium at constant volume, entropy and particle number

The minimum energy state describes the equilibrium of a completely closed system (i.e.,  $dQ = 0$ ,  $dW = 0$ ,  $dN = 0$ ). Moreover, if you do work on a thermally isolated system then the energy of the system increases by the amount required to conserve energy (provided all irreversible processes are confined to the system, not the external mechanism). As well, because it is more fundamental, we often want to calculate the energy change in a system even when it isn't thermally isolated, so the energy arises in a number of contexts.

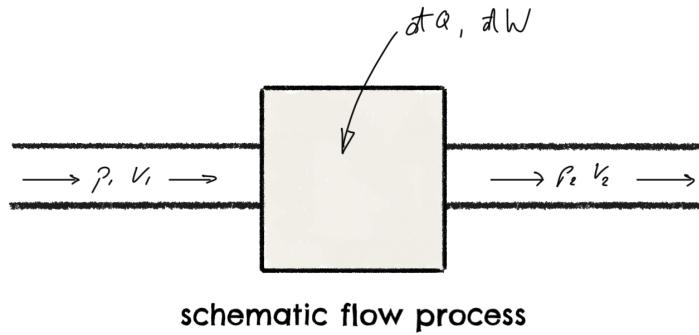


Figure 2.5: A schematic flow process.

### 2.3.2 Enthalpy $H$ : Equilibrium at constant pressure, entropy and particle number

This condition is called isobaric and isentropic. Because we have constant pressure,  $dp = 0$ , constant entropy means that  $dS = 0$ , while constant particle number means that  $dN = 0$ . Therefore

$$(dA)_{p,S,N} = (dU - T_R dS + p_R dV - \mu_R dN)_{p,S,N} \quad (2.17)$$

$$= d(U + pV)_{p,S,N} \quad (\text{used } dS = 0, dN = 0, p = p_R) \quad (2.18)$$

$$\equiv d(H)_{p,S,N}, \quad (2.19)$$

where  $H$  is the *enthalpy*. Hence in the condition of constant pressure, with no heat flow and no flow of particles, the minimum availability condition is equivalent to minimum enthalpy.

The minimum enthalpy state describes the equilibrium of a system at fixed pressure and constant entropy and particle number. As an example, the enthalpy is unchanged in a Joule-Kelvin expansion. In general the change in the enthalpy at constant pressure is equal to the heat entering or leaving the system. Therefore at a first order phase transition the amount of latent heat which enters or leaves the system is equal to the change in the enthalpy.

Its “conservation of energy role” arises in flow processes and is illustrated in figure 2.5.

### 2.3.3 Helmholtz free energy $F$ : Equilibrium at constant temperature, volume and particle number

This condition is referred to as isothermal and isochoric. The effects of these constraints are:  $dT = 0$  because the temperature is fixed;  $dV = 0$  because the volume is fixed; and  $dN = 0$ . We can then write

$$(dA)_{T,V,N} = (dU - T_R dS + p_R dV - \mu_R dN)_{T,V,N} \quad (2.20)$$

$$= d(U - TS)_{T,V,N} \quad (\text{used } T = T_R, dT = 0) \quad (2.21)$$

$$\equiv d(F)_{T,V,N}, \quad (2.22)$$

where  $F$  is the *Helmholtz free energy*. Hence minimisation of the availability is equivalent, for an isothermal isochoric system, to minimisation of the Helmholtz free energy.

A simple application of this principle is to find the mechanical equilibrium of an isothermal, isochoric system consisting of two gases “1” and “2”, as illustrated in Fig. 2.6. The total Helmholtz free energy is

$$F = F_1 + F_2 \quad (2.23)$$

$$= (U_1 - T_1 S_1) + (U_2 - T_2 S_2). \quad (2.24)$$

Using  $T_1 = T_2 = T$  and  $dU = TdS - pdV$  we have

$$dF = -p_1 dV_1 - p_2 dV_2. \quad (2.25)$$

Since  $dV_2 = -dV_1$  the equilibrium condition becomes

$$dF = 0 = -(p_1 - p_2)dV_1 \Rightarrow p_1 = p_2. \quad (2.26)$$

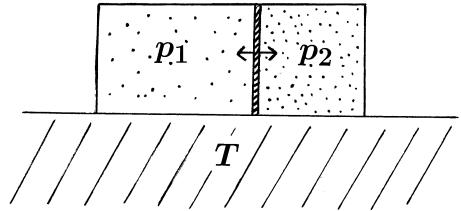


Figure 2.6: Two gases initially at pressures  $p_1$  and  $p_2$  are separated by a movable barrier. The temperature is fixed and equal to  $T$ . The barrier moves under the pressure forces until the Helmholtz free energy reaches its minimum value, which occurs when  $p_1 = p_2$ .

The change in  $F$  is the work done in a reversible process at constant temperature (see discussion above). As well, the Helmholtz free energy is a minimum at equilibrium for an isothermal, isochoric (constant volume) system.

### 2.3.4 Gibbs free energy $G$ : Equilibrium at constant temperature, pressure and particle number

If  $p$ ,  $N$  and  $T$  are constant then

$$(dA)_{T,p,N} = d(U - TS + pV)_{T,p,N} \quad (2.27)$$

$$\equiv d(G)_{T,p,N}, \quad (2.28)$$

where  $G$  is the *Gibbs Free energy*. On the approach to equilibrium the Gibbs free energy decreases, and in equilibrium it must be a minimum. This has very important applications in phase equilibria and chemical equilibria, which we will return to later. The Gibbs free energy is a minimum at fixed temperature, pressure and particle number, a situation that is naturally encountered in experiments, so it plays an important role in phase and chemical equilibria. It will therefore come up a lot in this course. From  $G = U - TS + pV$  we find

$$G = \mu N \quad (2.29)$$

for a pure substance; that is, the chemical potential is the Gibbs free energy per particle. This can be understood intuitively if we imagine a process whereby the system is built up by adding particles at constant  $T$  and  $p$ . Then  $dG = -S dT + V dp + \mu dN = \mu dN$ . This means in effect

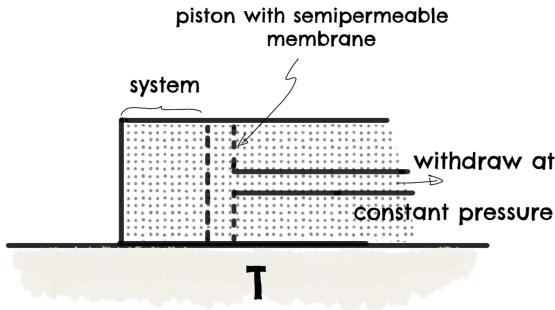


Figure 2.7: Adding particles at constant  $T$  and  $p$ .

that the chemical potential in a pure phase is the Gibbs free energy per particle. Moreover, from  $G = \mu N$  we find  $dG = \mu dN + N d\mu = -S dT + V dp + \mu dN$ . Therefore we can write

$$d\mu = -s dT + v dp \quad (2.30)$$

which is the *Gibbs-Duhem relation* again (derived in §1.6). This is a useful expression when analysing phase and chemical equilibria.

### 2.3.5 Grand Potential $\Phi$ : Equilibrium at constant temperature, volume and chemical potential

Under these conditions we have

$$(dA)_{T,V,\mu} = (dU - T_R dS + p_R dV - \mu_R dN)_{T,V,\mu} \quad (2.31)$$

$$= d(U - TS - \mu N)_{T,V,\mu} \quad (2.32)$$

$$\equiv d(\Phi)_{T,V,\mu}, \quad (2.33)$$

where  $\Phi$  is the *grand potential*. Minimum availability in this case corresponds to minimum grand potential.

Table 2.1: Potentials important for systems held at fixed temperature.

Name	Helmholtz Free En.	Gibbs Free En.	Grand Potential	
Differential	$F = U - TS$ $-SdT - pdV + \mu dN$	$G = U - TS + pV = \mu N$ $-SdT + Vdp + \mu dN$	$\Phi = F - \mu N = -pV$ $-SdT - pdV - Nd\mu$	$\Phi_2 = G - \mu N = 0$ $-SdT + Vdp - Nd\mu = 0$
Minimised when constraints are	$T, V, N$	$T, p, N$	$T, V, \mu$	Cannot be varied: $T, p, \mu$ are intensive and so not independent
Probability of fluctuation proportional to	$e^{-F/kT}$	$e^{-G/kT}$	$e^{-\Phi/kT}$	
Statistical formula	$-kT \ln Z$	$-kT \ln Z_p$	$-kT \ln \Xi$	
Important in	Mechanical equilibrium	Phase equilibrium	Fermions and Bosons	

Table 2.2: Potentials important for thermally isolated systems.

Name	Internal energy	Enthalpy		
Differential	$U$ $TdS - pdV + \mu dN$	$H = U + pV$ $TdS + Vdp + \mu dN$	$\Phi_3 = U - \mu N$ $TdS - pdV - Nd\mu$	$\Phi_4 = H - \mu N = TS$ $TdS + Vdp - Nd\mu$
Constant for isolated system when constraints are	$V, N$	$p, N$	$V, \mu$	$p, \mu$
Fluctuation probability proportional to	$e^{S/k}$	$e^{S/k}$	$e^{S/k}$	$e^{S/k}$
Important in	Isolated systems on which no work is done	Constant flow processes. $\Delta H$ is the heat energy in phase and chemical changes	Unimportant, not realised in practice	

## 2.4 Phase equilibria

We turn now to a thermodynamic analysis of a central feature of the  $p - V - T$  surfaces of real materials (see §1.3), enquiring into the stability of different phases and the nature of phase equilibrium. Consider a one component system at constant temperature, pressure and particle number, so that the equilibrium condition is that the Gibbs free energy is minimised. If we consider, for the sake of concreteness, the liquid-vapour transition, we hypothesise that we can calculate separate Gibbs free energies  $G_l(T, p)$  and  $G_v(T, p)$  for the liquid and vapour phases. At a given temperature and pressure, the stable phase will be the one with the lower Gibbs free energy. As illustrated in Fig. 2.8, if we imagine very slowly increasing the temperature of the reservoir at constant pressure, the phase transition will occur when the two functions cross.

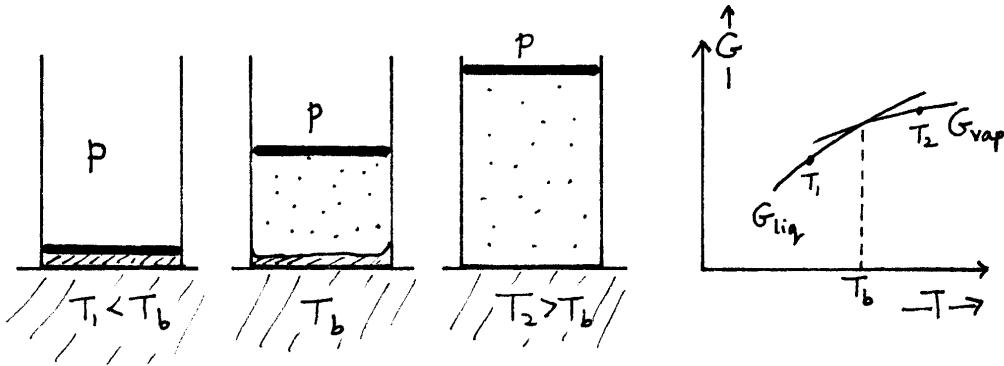


Figure 2.8: The condition for a phase transition is that the Gibbs free energies of competing phases cross. The extrapolation of the Gibbs free energy of a phase to beyond the region in which that phase is stable is justified, for a short distance at least, by the metastability of supercooled and superheated phases.

During the actual phase transition both phases are present, and we can express the total Gibbs free energy as the sum of  $G_l$  and  $G_v$ :

$$G = G_l + G_v \quad (2.34)$$

$$dG = 0 \Rightarrow dG_l = -dG_v \quad (2.35)$$

$$\Rightarrow -S_l dT + V_l dp + \mu_l dN_l = S_v dT - V_v dp - \mu_v dN_v \quad (2.36)$$

$$\Rightarrow \mu_l dN_l = -\mu_v dN_v \quad (T, p \text{ are constant}). \quad (2.37)$$

Matter conservation requires  $dN_l = -dN_v$ , so that

$$\mu_l = \mu_v. \quad (2.38)$$

The condition for phase equilibrium is that the chemical potentials of the two phases are equal.<sup>1</sup> It is quite clear that if you, instead, keep  $p$  and  $N$  constant, then the argument above gives you

$$T_l = T_v, \text{ or, similarly, } p_l = p_v, \quad (2.39)$$

when  $T$  and  $N$  are constant. The equality of  $T, p, \mu$  between any two subsystems is the condition for equilibrium.

### Application to the van der Waals gas

We can also understand the general structure of  $p - V - T$  diagrams via the chemical potential (although this is even easier to understand from microscopic considerations). Recall the Gibbs-Duhem relation (1.33),  $d\mu = -s dT + v dp$ , where  $s$  and  $v$  are the entropy and volume per

<sup>1</sup> Anyone trying to follow this discussion in *Adkins* may easily get confused by terminology and notation here. *Adkins* discusses phase equilibria using a quantity  $g$  which relates to the transport of mass from one phase to the other, whereas we are using transport of particles (because this allows consistent notation throughout the course). To convert between notations,  $g dm = \mu dN$ . To further confuse things for you, *Adkins* calls  $g$  the “chemical potential”, and he defines a quantity  $\mu$  as the molar partial potential which refers to transfer of moles of material from one component or phase to the other. I.e. to convert from his  $\mu$  to my  $\mu$ , use  $\mu_{Adkins} dn = \mu dN$ . Where  $n$  is the number of moles, and  $N$  is the number of molecules.

particle.<sup>2</sup> This equation tells us that at high temperatures the phase with the highest entropy per particle will have the smallest chemical potential (and will therefore be stable), while at high pressures the phase with the smallest volume per particle will be stable.

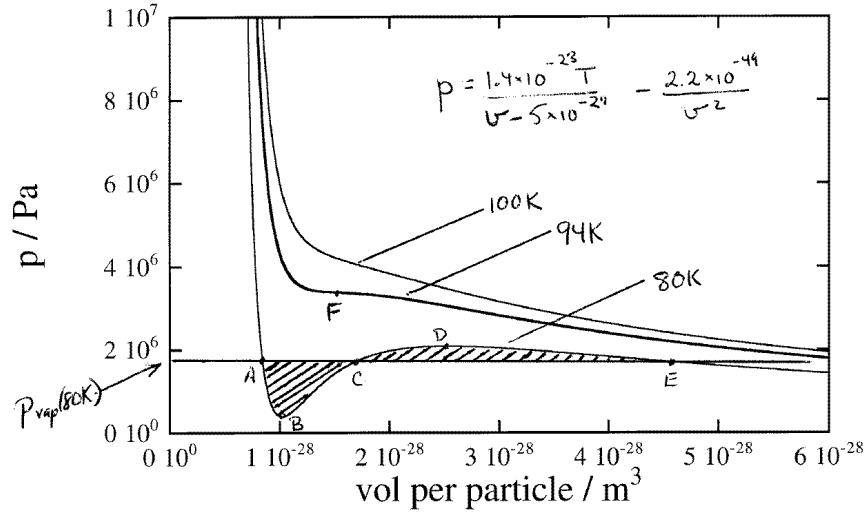


Figure 2.9: Isotherms of the van der Waals gas (see also §1.3). As shown in the text, the vapour pressure is fixed by the requirement that the two shaded regions have equal areas if the chemical potentials of the two phases are equal.

The condition for phase equilibrium is

$$\mu_v(E) = \mu_l(A) \quad (2.40)$$

$$\text{but } \mu_v(E) = \mu_l(A) + \int_A^E \left( \frac{\partial \mu}{\partial p} \right)_T dp \quad (2.41)$$

$$= \mu_l(A) + \int_A^E v dp. \quad (2.42)$$

The first and last lines are true provided that

$$\int_A^E v dp = 0, \quad (2.43)$$

i.e., the shaded regions in Fig. 2.9 must have equal areas. This allows us to calculate the vapour pressure,  $p_{vap}(T)$ , which is the pressure at which the phase transition takes place along the isotherm.

### Clausius-Clapeyron Equation

You have seen this derived last year, but perhaps not in the same way. To calculate the latent heat is more difficult; it is equal to the difference in the enthalpies of the two phases at the transition temperature, and such calculations are well beyond the scope of this course. However applying thermodynamic arguments to the latent heat we will show that it can be related to the pressure dependence of the transition temperature.

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<sup>2</sup>This equation can only be applied to a pure phase, mixtures are more complicated.

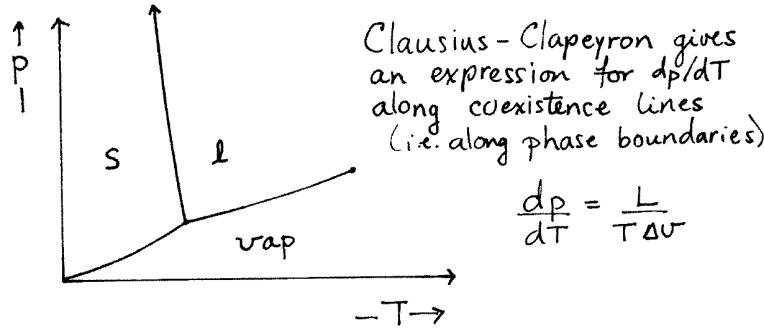


Figure 2.10: Phase coexistence lines in the  $(p, T)$  plane.

Starting from the Gibbs-Duhem equation (Eq. 1.33)

$$d\mu_1 = v_1 dp - s_1 dT, \quad (2.44)$$

where  $v_1$  and  $s_1$  are the volume and entropy per particle in phase 1, and using the fact that on the coexistence line  $\mu_1 = \mu_2$ , so that if we move along it  $d\mu_1 = d\mu_2$ , we have

$$v_1 dp - s_1 dT = v_2 dp - s_2 dT \quad (2.45)$$

$$\Rightarrow \frac{dp}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{T \Delta s}{T \Delta v} \equiv \frac{L}{T \Delta v}, \quad (2.46)$$

where  $L$  is the latent heat per particle. This result is more commonly quoted in units of  $L_m$  and  $v_m$ , the latent heat and volume per mol, and is called the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{L_m}{T \Delta v_m}. \quad (2.47)$$

This applies to first order phase transitions and, at the time it was invented, it led to predictions of unexpected effects, and played a role in demonstrating the validity of the Second Law of Thermodynamics. It predicts the pressure dependence of the transition temperature in terms of the latent heat and the change in the molar volume. The best known application is the lowering of the freezing point of water by pressure, a consequence of the expansion of water upon freezing (i.e.,  $\Delta v_m$  has an unusual sign for the water-ice transition).

The liquid-solid coexistence curve can have either negative or positive slope, depending on the sign of  $\Delta v$  (consider water, which expands on freezing), but we expect the liquid-vapour curve to always have a positive slope and to be much flatter than the liquid-solid line, because in the liquid-vapour case the change in volume per particle is positive and large.

## 2.5 Mixtures of ideal gases

The molecules of an ideal gas by definition do not interact with each other, or with the molecules of other ideal gases. Hence the molecules in a mixture of ideal gases move independently, regardless of how many different species are present, and the thermodynamic properties of the mixture are just the sum of the independent contributions of each species of “component” of gas, so these contributions can be calculated as if each component was present on its own.

(*Adkins* gives a derivation of this using purely thermodynamic arguments, but we will accept the microscopic argument).

Therefore, for example, the total pressure is the sum of the *partial pressures* (Dalton's Law)

$$p = \sum_i p_i \quad \text{where} \quad p_i = \frac{N_i k_B T}{V}. \quad (2.48)$$

Similarly for the entropy. If you recall, in 1B Thermodynamics we have derived the phenomenological Sackur-Tetrode formula via the following simple steps (starting from the definition of  $dU$ ):

$$\begin{aligned} \text{integrate } dS &= \frac{dU}{T} + \frac{pdV}{T} = \frac{C_v dT}{T} + \frac{Nk_B dV}{V} \\ \text{obtain } S &= C_v \ln T + Nk_B \ln V + S_0. \end{aligned} \quad (2.49)$$

Here we need to connect with the partial pressures (intensive variables) rather than volume (which is the same for the mixture components), so you should either repeat the above derivation in the  $(p, T)$  variables (i.e. starting from the definition of  $dH$  instead of  $dU$ ), or simply replace  $V = Nk_B T/p$  in Eq. 2.49 and then collect  $\ln T$  terms into  $C_p = C_v + Nk_B$ . This gives for the entropy of a pure (single component) gas at pressure  $p$ :

$$S = C_p \ln T - Nk_B \ln p + S_0, \quad (2.50)$$

where the integration constant  $S_0$  is not the same as in Eq. 2.49.

Starting with a collection of vessels all at the same pressure  $p$  and containing numbers of particles  $N_i$  of gas component  $i$ , we could achieve the mixing process by first, an isothermal expansion of each component  $i$  to the desired final partial pressure  $p_i$ , followed by joining together all the containers, then isothermally compressing again to the same pressure  $p$  as we had to start with. As a particular component  $i$  is diluted from initial pressure  $p$  to partial pressure  $p_i$ , its entropy changes by  $\Delta S_i = -N_i k_B \ln(p_i/p)$ , because both  $C_p$  and  $S_0$  do not depend on pressure.

Therefore the entropy of the mixture differs from the entropy of a separated out assembly of pure gases each at pressure  $p$  by

$$\begin{aligned} \Delta S &= S - S_{\text{pure}} = -k_B \sum_i N_i \ln(p_i/p) \\ &= -k_B \sum_i N_i \ln c_i = -Nk_B \sum_i c_i \ln c_i, \end{aligned} \quad (2.51)$$

where  $c_i = N_i/N = p_i/p$  is the concentration of the  $i^{\text{th}}$  component, directly related to the volume fraction. This is called the *entropy of mixing*.

To obtain the Gibbs free energy and thereby the chemical potential  $\mu$ , we could make use of this expression for the mixing entropy and use  $G = U - TS + pV$ . Because  $U$  and the product  $pV$  are the same for the components, whether in pure form or mixed, the change in  $G$  on mixing is entirely due to  $TS_i$ :  $G_i(p_i, T) = G_i(p, T) + N_i k_B T \ln c_i$ . However, we can also get  $G$  for the mixture directly from  $dG = -SdT + Vdp$ , and considering a process at constant  $T$  we have

$$\left( \frac{\partial G}{\partial p} \right)_T = V = \frac{Nk_B T}{p}, \quad (2.52)$$

and noting that  $\mu = G/N$  we have

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{k_B T}{p}. \quad (2.53)$$

Integrating from some reference pressure  $p_0$  to pressure  $p$  at constant  $T$  we obtain

$$\mu(T, p) = \mu(T, p_0) + k_B T \ln \frac{p}{p_0}. \quad (2.54)$$

We now apply this formula to each species,  $i$ . The Gibbs free energy of the mixture is

$$G = \sum_i G_i. \quad (2.55)$$

Using  $\left(\frac{\partial G_i}{\partial p_i}\right)_{T, N_i} = V$  we can relate the Gibbs free energy at partial pressure  $p_i$  to that at the total pressure  $p$  (which would be the Gibbs free energy if the system were composed of  $N_i$  atoms of pure component  $i$  at pressure  $p$ ):

$$G_i(p_i, T) = G_i(p, T) + \int_p^{p_i} V dp \quad (2.56)$$

$$= G_i(p, T) + N_i k_B T \int_p^{p_i} \frac{dp}{p} \quad (2.57)$$

$$= G_i(p, T) + N_i k_B T \ln(p_i/p) \quad (2.58)$$

$$= G_i(p, T) + N_i k_B T \ln c_i. \quad (2.59)$$

Using  $G_i = \mu_i N_i$  we obtain, similarly,

$$\boxed{\mu_i(p_i, T) = \mu_{0i}(p, T) + k_B T \ln c_i. \quad (2.60)}$$

That is, the chemical potential of the  $i^{th}$  component, which is present with concentration  $c_i$  in a mixture of ideal gases, differs from the chemical potential for the pure gas at the same total pressure by  $k_B T \ln c_i$ .

The chemical potentials of the different components are related. Since

$$dG = -S dT + V dp + \sum_i \mu_i dN_i \quad \text{we have} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, p, N_{l \neq i}}. \quad (2.61)$$

So for two components  $i$  and  $j$

$$\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T, p, N_{l \neq j}} = \frac{\partial^2 G}{\partial N_i \partial N_j} = \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T, p, N_{l \neq i}}. \quad (2.62)$$

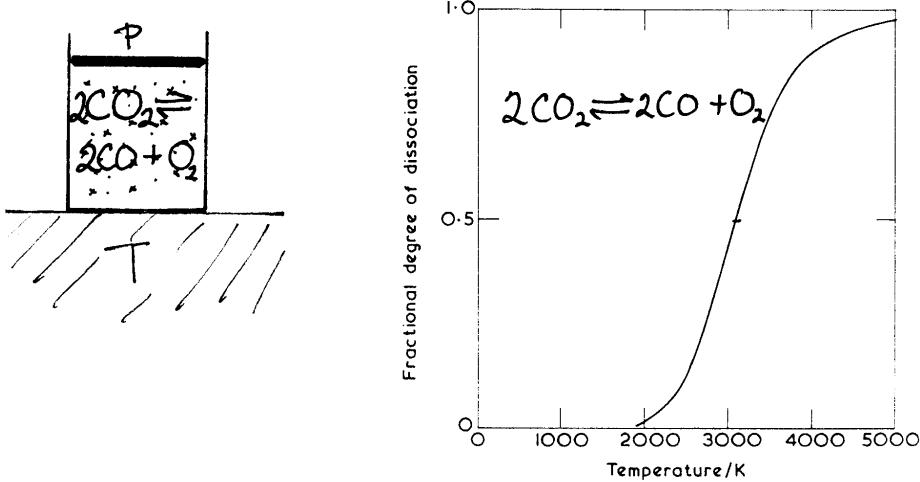


Figure 2.11: Chemical reaction at constant temperature and pressure. At a given temperature and pressure the relative amounts of the chemical components are functions of state. In our example, at high temperatures  $\text{CO}_2$  breaks down into  $\text{CO}$  and  $\text{O}_2$ .

### Chemical equilibrium

We will illustrate the equations with the equilibrium of carbon dioxide with carbon monoxide and oxygen, for which at high temperatures there is significant dissociation of  $\text{CO}_2$  (see Fig. 2.11).



As was the case for phase equilibrium, in chemical equilibrium we start from the condition that the availability must be a minimum:

$$(dA)_{T,p} = dU - TdS + pdV \quad (2.64)$$

$$= d(U - TS + pV) \quad \text{constant temperature and pressure} \quad (2.65)$$

$$= dG = 0 \quad \text{where} \quad (2.66)$$

$$G = \sum_i G_i = \sum_i \mu_i N_i. \quad (2.67)$$

Because  $d\mu_i = -s_i dT + v_i dp$  (Gibbs-Duhem) is zero at constant  $T$  and  $p$ , a variation of  $G$  about the equilibrium ratio of chemical components satisfies

$$dG = \sum_i \mu_i dN_i = 0 \quad (2.68)$$

$$(\text{i.e., } \mu_{\text{CO}_2} dN_{\text{CO}_2} + \mu_{\text{CO}} dN_{\text{CO}} + \mu_{\text{O}_2} dN_{\text{O}_2} = 0). \quad (2.69)$$

But the  $dN_i$ 's are related by matter conservation, which can be expressed as  $2\text{CO}_2 - 2\text{CO} - \text{O}_2 = 0$ , so that  $dN_i/\nu_i = \text{const}$ , i.e.,  $dN_{\text{CO}_2}/2 = -dN_{\text{CO}}/2 = -dN_{\text{O}_2}$ , which gives

$$\sum_i \nu_i \mu_i = 0, \quad (2.70)$$

i.e.,  $2\mu_{\text{CO}_2} - 2\mu_{\text{CO}} - \mu_{\text{O}_2} = 0$ .

## The equilibrium constant

Combining  $\sum_i \nu_i \mu_i = 0$  and Eq. 2.60 gives

$$\sum_i \nu_i \mu_{0i} + k_B T \sum_i \nu_i \ln c_i = 0 \quad (2.71)$$

$$\Rightarrow \sum_i \nu_i \mu_{0i} + k_B T \ln \left( \prod_i c_i^{\nu_i} \right) = 0. \quad (2.72)$$

This allows us to compute the “equilibrium constant for concentration”,  $K_c(T)$ , defined as

$$K_c(T) = \prod_i c_i^{\nu_i}, \quad (2.73)$$

where

$$\ln K_c(T) = -\frac{1}{k_B T} \sum_i \nu_i \mu_{0i}(T, p). \quad (2.74)$$

For the particular case of chemical decomposition of  $CO_2$  the equilibrium constant is the ratio of concentrations of three ingredients, raised to the power corresponding to each reaction coefficient:

$$K_c = \frac{c_{CO_2}^2}{c_{CO}^2 c_{O_2}}$$

But how can we regard a particular chemical reaction as an ideal-gas situation when many of them take place in the liquid or even solid state? It is in fact correct: even though there may be many (even densely packed) molecules in the system – every individual group, such as in (2.63), reacts on its own, independently of its neighbours. In order to calculate the equilibrium constant for an ideal gas reaction we need to calculate  $\mu_{0i}(T, p)$  for each component as a function of temperature. We will do this much later, in section §5.6.

Chemists commonly use a version of the equilibrium constant  $K_p$  that relates the partial pressures of the reactants, rather than their concentrations; moreover they give the partial pressures in atmospheres, assuming that the total pressure of the mixture is 1 atmosphere. In this case,  $c_i = p_i/p = p_i$ , so  $\ln K_p$ , shown in Fig. 2.12, has the same form as  $\ln K_c$ . From microscopic theory we will later derive yet another, related, equilibrium constant,  $K_N(T) = \prod_i N_i^{\nu_i}$ , from which  $K_c$  can be obtained by recognising that  $c_i = N_i/N$ , where  $N = \sum_i N_i$ . We will use the results of this section later.

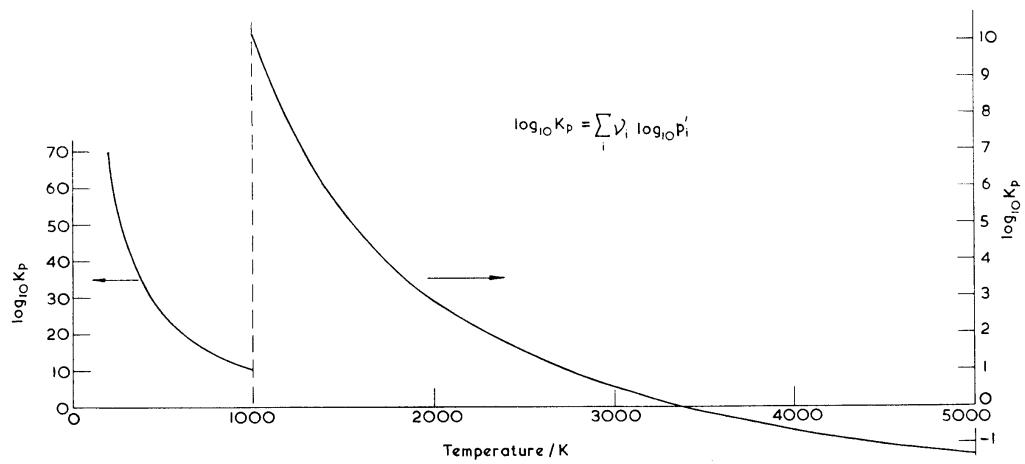


Figure 2.12: Equilibrium constant for the  $2\text{CO}_2 \leftrightarrow 2\text{CO} + \text{O}_2$  reaction (following Hayward, *Equilibrium Thermodynamics*).

# Chapter 3

## The basics of statistical mechanics

### 3.1 Microstates and Macrostates

In a quantum mechanical system the *microstates* (or microcanonical states) can be identified with the set of solutions of the Schrödinger equation with fixed energies  $E_i$ . There could be many such states, which gives rise to the ‘degeneracy of a microstate’  $\Omega(E_i)$ . In a system such as a gas of classical point-like non-interacting particles, each microstate corresponds to a particular set of positions and momenta of the particles. Normally a system will have other constraints, for example fixed volume, in which case we will only be interested in the microstates with that volume.

A *macrostate* is the most-probably, equilibrium, observable microstate. In a large system, where due to the Central Limit Theorem the mean of the probability distribution coincides with its median, the energy of the macrostate is  $\langle E \rangle = U$ , which satisfies the other imposed constraints, for example, fixed volume  $V$  and particle number  $N$ . Of course it may be a difficult task to find the macrostate among the microcanonical states available to the system, but if one can, then statistical mechanics will yield all equilibrium thermodynamic information about the system.

### 3.2 Principle of Equal Equilibrium Probability (PEEP)

Suppose we have a gas of energy  $E$  which consists of  $N$  classical particles in an isolated container of volume  $V$ . Due to the motion of the particles, and the collisions between them and with the walls, the system continually moves between different microstates. We would like to find a condition which determines the equilibrium of this system. In equilibrium, the macrostate must be completely specified by the thermodynamic set of extensive parameters  $(U, V, N)$ .

We now introduce the Postulate of Equal Equilibrium Probability (PEEP), which is also sometimes called the principle of equal *a priori* probability:

For an isolated system, all states within the microstate of a given energy  $E$ , compatible with the given constraints, are equally likely to occur.

The main justification for the PEEP is the enormous success of the resulting theory, although it can also be proved to hold in some cases. A philosophical argument may be advanced as “there is no reason to think otherwise”, but this is hardly a sufficient basis for a physical theory! A proper derivation of statistical mechanics should start from the laws of quantum or classical mechanics which govern the microscopic behaviour. This problem has not been solved in a satisfactory manner, but see Appendix 1 for more discussion of this point.

There are some subtleties involved in thinking about and applying the PEEP. In experiments we normally measure *time* averages of quantities, but we will use the PEEP to calculate averages over the *ensemble* of all accessible states, asserting that these are equivalent to time averages. An “accessible” state is one that is compatible with the given constraints, while an “inaccessible” one is not. The idea that, in the course of a sufficiently long period, an isolated system will pass through all of its accessible states is known as the “ergodic hypothesis”. Measurements are sometimes made over some fairly short time-scale and the system will not go through *all* of its states in the time-scale of the measurement. However, for the theory to work one only requires the system to go through a large number of states during the times-scale of the measurement which are “representative” of all the accessible ones.

All of this has to be consistent with quantum mechanics. Are the microstates the same as the energy eigenstates, with their own degeneracy, discussed in quantum mechanics courses? We will assume this to be the case and will obtain physically correct results by doing so. However, the energy levels of a macroscopic system are extremely close in energy and such systems are never sufficiently well isolated from the surroundings for the energy to be well defined to within the energy level spacing. In the cases of interest to us (i.e. in statistical thermodynamics) this doesn’t matter, but for future reference it turns out that one can formulate the problem in terms of “density matrices” which incorporate the idea that the system is not in a eigenstate of energy.

### 3.3 The Boltzmann entropy

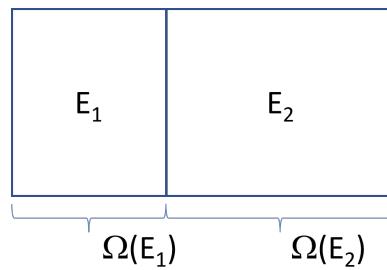


Figure 3.1: A partition of the total energy  $E$  between two subsystems.

Consider two systems with energies  $E_1$  and  $E_2$ , which are isolated from their surroundings. If we place them in thermal contact with one another we expect that eventually they will come into thermal equilibrium. The energy of the two systems must be

$$E = E_1 + E_2 , \quad (3.1)$$

where  $E_1$  and  $E_2$  may now vary with time, but their sum is constant.

At a particular time, subsystem 1 is equally likely to be in any of its microstates,  $\Omega_1(E_1)$ , while subsystem 2 is equally likely to be in any of its microstates,  $\Omega_2(E_2)$ . Therefore

$$\Omega(E; E_1) = \Omega_1(E_1)\Omega_2(E_2) , \quad (3.2)$$

where  $\Omega(E; E_1)$  is the number of microstates of the composite system with total energy  $E$ , such that there is energy  $E_1$  in subsystem 1 and energy  $E_2 = E - E_1$  subsystem 2.

For what value of  $E_1$  (and hence  $E_2$  since  $E$  is conserved) will the composite system be in equilibrium? The answer is the value of  $E_1$  which maximises  $\Omega(E; E_1)$ . The idea is that although the system passes through many macrostates denoted by  $E_1$  and  $E_2$ , on coming into equilibrium the PEEP implies that it will spend almost all its time in the macrostate for which  $\Omega(E; E_1)$  takes its maximum value. (The phrase “almost all its time” is true only if the equilibrium state is overwhelmingly more likely than ones which are close by in energy, but this is almost always the case.)

Let us denote the equilibrium value of  $E_1$  by  $U_1$ . Differentiating Eq. 3.2 with respect to  $E_1$  and evaluating at the macrostate  $U_1$  we have

$$\frac{\partial \Omega_1(E_1)}{\partial E_1} \Big|_{E_1=U_1} \Omega_2(U_2) + \Omega_1(U_1) \frac{\partial \Omega_2(E_2)}{\partial E_2} \Big|_{E_2=U_2} \frac{\partial E_2}{\partial E_1} = 0 . \quad (3.3)$$

Since  $\partial E_2 / \partial E_1 = -1$ , we have

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \Big|_{E_1=U_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \Big|_{E_2=U_2} . \quad (3.4)$$

The condition for equilibrium amounts to the equality of the parameters  $\beta_1 = \beta_2 = \beta$  for the two subsystems, where

$$\beta = \frac{\partial \ln \Omega(E)}{\partial E} \Big|_{E=U} . \quad (3.5)$$

It is natural to expect that  $\beta$  is related to the temperature. Recalling the relationship,

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,V} , \quad (3.6)$$

we can therefore make the identifications:

$$\frac{1}{k_B T} = \beta , \quad \text{and} \quad S = k_B \ln \Omega , \quad (3.7)$$

where the quantities on the left hand sides of Eqs. (3.7) refer to the thermodynamic quantities and those on the right hand side refer to the statistical mechanical quantities in equilibrium (macrostate). This is the definition of the statistical *Boltzmann entropy*. For our composite system we have

$$S = k_B \ln(\Omega_1 \Omega_2) = k_B [\ln \Omega_1(U_1) + \ln \Omega_2(U_2)] = S_1 + S_2 , \quad (3.8)$$

so the Boltzmann entropy is just the sum of the Boltzmann entropies of the two parts. The entropy is therefore extensive (and, of course, its conjugated thermodynamic variable – the temperature  $T$  is intensive).

The Boltzmann entropy is well defined for large systems, but not for small ones because the distinction between accessible and inaccessible states is not well defined in a small system, and also the identification of the highest-probability state with equilibrium is uncertain. We will come back to the problem of small systems later, but here I want to make a point about large systems. In practice systems are never isolated and their internal energy  $E$  fluctuates in some range, which may increase the number of accessible states. Suppose the number is increased by a factor of 2, is the entropy significantly altered? The new entropy is

$$S = k_B \ln 2\Omega = k_B \ln 2 + k_B \ln \Omega. \quad (3.9)$$

However,  $\Omega$  is typically of order  $10^N$ , where  $N$  is the number of atoms (note that  $\ln \Omega$  is proportional to the size of the system). If  $N = 10^{23}$  atoms, then increasing  $\Omega$  by a factor of two only increases  $S$  by roughly one part in  $10^{-23}!$

### 3.4 The Gibbs entropy

Consider a small system in contact with a reservoir with which it can exchange energy. The fluctuations in the energy of the system will be an appreciable fraction of the mean energy. The states of the system cannot simply be labelled as “accessible” or inaccessible”, we have to think about the *probabilities* that the system will be in each of its possible states.

Gibbs introduced a form of the entropy which is valid for both large and small systems,

$$S = -k_B \sum_i P_i \ln P_i, \quad (3.10)$$

where  $P_i$  is the probability of finding the system in state  $i$ . This is a function of the *probabilities* rather than the microstates themselves. You will, of course, see the connection between this expression and the expression (2.51) where  $c_i = N_i/N$  is essentially the probability to find a particle of species ‘ $i$ ’ in the mixture.

It is very important to note that for a large system in equilibrium the Gibbs and Boltzmann entropies are equal. This is easily seen because in a large system the probability distribution is very sharply peaked in energy, so that  $P_i \simeq 1/\Omega$  for all accessible states, and

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i 1/\Omega \ln 1/\Omega = k_B \ln \Omega = S_B, \quad (3.11)$$

where we have used  $\sum_i P_i = 1 = \sum_i 1/\Omega$ . For very small non-isolated systems or for systems away from equilibrium, the Gibbs and Boltzmann entropies may not be equal.

When it comes to answering problems in equilibrium statistical mechanics I want you to use the Gibbs entropy. Unlike the Boltzmann entropy, the Gibbs entropy can be used at the microscopic level, which is a very significant advantage. Also, the Gibbs entropy is precisely defined and is much the simplest entropy to use for problems in equilibrium statistical mechanics.

Gibbs used the idea of *ensembles* to think about problems in statistical physics. An ensemble is a very large number of imaginary replicas of the system of interest all prepared in the same way. The ensemble gives a concrete meaning to probabilities. For example, the probability of finding the system in a particular microstate or macrostate is equal to the fraction of members of the

ensemble in that state. Consider an ensemble of  $N$  replicas of a system in thermal contact with one another. For a particular member of the ensemble, the other  $N - 1$  replicas act as a heat reservoir. The ensemble of replicas is isolated from the surroundings and therefore its internal energy,  $E$ , is constant. Because all of the accessible states of the microcanonical ensemble have internal energy  $E$ , according to the PEEP they are all equally likely.

Each of the replicas has identical contents, but they are distinguishable from one another by their position within the ensemble. Let the number of replicas in microstate  $i$  be  $N_i$ , and the total number of states of each system be  $m$ , so that  $\sum_i^m N_i = N$ . The total number of distinct configurations of the ensemble is then

$$\Omega = \frac{N!}{N_1!N_2!\dots N_m!}. \quad (3.12)$$

The entropy of the entire ensemble is given by the Boltzmann formula

$$S = k_B \ln \Omega, \quad (3.13)$$

and using Stirling's approximation we obtain

$$\begin{aligned} S &= k_B \left[ N \ln N - \sum_i^m N_i \ln N_i \right] = k_B \left[ \sum_i^m N_i \ln N - \sum_i^m N_i \ln N_i \right] \\ &= -k_B N \sum_i^m \frac{N_i}{N} \ln \frac{N_i}{N}. \end{aligned} \quad (3.14)$$

The entropy per system is therefore given by the Gibbs formula (3.10), where  $P_i = N_i/N$  is the probability of finding the system in state  $i$ . Now the connection with the phenomenological expression (2.51) is even more transparent.

The entropy should take its maximum value in equilibrium. This leads naturally to the idea of maximising  $S$  with respect to the distribution of the probabilities,  $P_i$ , with the constraint that  $\sum_i P_i = 1$  and any other constraints which apply (constant energy or whatever). This is sometimes called the "method of most probable distributions", which is a very satisfying way to proceed <sup>1</sup>. Here, we will take another route which is less mathematical.

One of the strange features of the Gibbs entropy is that it depends on probabilities of the system being in particular configurations. But surely at any one time the system can only be in one configuration, so how can the other configurations, in which it is not, affect a physical variable such as the entropy or pressure? One important point to make is that if the system obeys the PEEP then an average over the probabilities of the system being in a particular configuration is the same as an average over time. One can object that we can measure some quantities over rather short times, such as the pressure of a gas, and it is not clear that an average over the probabilities of all configurations is relevant on short time-scales. To answer this we appeal to one of Boltzmann's ideas - with an overwhelmingly high probability the system will be in one of the microstates corresponding to the equilibrium macrostate, and all such microstates "look the same" so the value of *all* thermodynamic quantities is much the same for *all* the accessible microstates.

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<sup>1</sup>The method may be discussed in the lectures. It produces probabilities of the form  $\exp(-E_n\beta)/Z$  by maximising the Shannon information entropy  $-k \sum p_n \ln p_n$  subject to constraints such as  $\langle E \rangle = \sum p_n E_n = U$ . This approach, which makes the link between entropy and lack of information explicit, is first presented in detail in a paper by Jaynes: Phys. Rev. **106**, 620 (1957).

### 3.5 Statistical ensembles

Gibbs defined three kinds of ensembles, the microcanonical, the canonical, and the grand canonical. Microcanonical is the ensemble of all states that have the same energy  $E$ . Essentially “canonical” means “standard”; Gibbs wrote: “This distribution, on account of its unique importance in the theory of statistical equilibrium, I have ventured to call *canonical*”. The canonical and grand canonical ensembles represent what actually takes place in most thermodynamic systems. When we make a measurement with a physical device such as a thermometer, the device takes an average over a large number of quasi-independent regions of the system (assuming a macroscopically sized thermometer), each of which sees the rest of the system as a reservoir. Therefore most measurement systems do ensemble averaging in some sense.

#### Canonical ensemble: Boltzmann distribution and partition function

The *canonical* ensemble is an infinite collection of subsystems each connected to a large reservoir with which they can exchange energy (alternatively the subsystems can be connected to each other). If we wish to calculate average values of thermodynamic quantities we need to calculate the probability distribution for the microstates. Unlike the microcanonical ensemble, different microstates of a subsystem have different probabilities of occurring, because each is weighted by the number of compatible microstates of the reservoir.

We ask for the probability of finding the  $i^{th}$  subsystem (e.g. a particle) in energy eigenstate  $E_i$ , if the total energy of a closed system is  $U$ . This is an awkward moment, as we use the letter  $U$  normally reserved for the ‘average energy’ (thermodynamic potential), but since the big system is isolated – its energy  $E$  is not conserved, and so no different from  $U$ . This probability is proportional to the number of accessible states corresponding to this partition of the energy, which is 1 for the subsystem and  $\Omega_R(U - E_i)$  for the reservoir, by which here we simply mean the whole system minus the particle  $i$ . Since in a large system  $E_i$  is much less than  $U$  we expand in a Taylor series:

$$\begin{aligned} P_i \propto 1 \times \Omega_R(U - E_i) &= e^{\ln \Omega_R(U - E_i)} \\ &= \exp \left\{ \ln \Omega_R(U) - E_i \left( \frac{\partial \ln \Omega_R(U)}{\partial U} \right) + \dots \right\} \\ &\simeq e^{\ln \Omega_R(U)} e^{-\beta E_i}, \end{aligned}$$

where we have used  $S = k_B \ln \Omega_R(U)$  for the entropy of the reservoir, and have also used  $\partial S / \partial U = 1/T$ , and  $\beta = 1/k_B T$  as usual. Note that we are assuming that  $U$ ,  $S$  and  $T$  are thermodynamic (average) quantities in order for these last relations to hold. This is valid for a large closed system, where the total energy is constant and so is  $\Omega_R(U)$ . Therefore, for an individual system:  $P_i(E_i) \propto e^{-\beta E_i}$ . Now we need to find the normalisation constant for  $P_i$ , which we denote by  $Z$ ,

$$Z = \sum_{\text{all states } i} e^{-\beta E_i}. \quad (3.15)$$

This is called the *partition function*, and it turns out to be the single most important object in statistical mechanics! We can now write the normalised Boltzmann distribution:

$$P_i = \frac{1}{Z} e^{-\beta E_i}. \quad (3.16)$$

Now step back and look at a system that could have different ways to achieve its total energy, and now we really need to distinguish between the value of energy  $E_i$  and the average energy  $U$ . The probability,  $P(E_i)$ , that the system has an energy value  $E_i$  is increased by the number of distinct configurations of the system with energy  $E_i$ , and proportional to the Boltzmann factor itself:

$$P(E_i) \propto \Omega(E_i) e^{-\beta E_i}. \quad (3.17)$$

This is the probability of microcanonical state with its constant energy  $E_i$ . The most-probably microstate, or the maximum in  $P(E_i)$  can be determined by setting  $dP/dE_i = 0$ . Since in the large system the mean of the distribution  $P(E_i)$  is equal to the median, at the maximum of probability one is in equilibrium (which is what we call the macrostate). Also, in a large system, with many equivalent configurations,  $\Omega(E_i)$  increases very rapidly with  $E_i$  and therefore  $P(E_i)$  is sharply peaked at the mean value  $U = \langle E_i \rangle$ , as illustrated in Fig. 3.2. The energy distribution for a large system is regarded as Gaussian (according to the Central Limit Theorem of stochastic physics). A short algebra gives the expression for the probability of the microstate with energy  $E$  in the following form:

$$P(E) \propto e^{-\beta[E - k_B T \ln \Omega(E)]}. \quad (3.18)$$

Now you see that the maximum-probability microstate (which we also treat as equilibrium, in a large system) is obtained when the expression  $E - TS(E)$  is minimal. This macrostate is where we can replace  $E$  with its average, and take the equilibrium thermodynamic entropy  $S(U)$  to recognise the thermodynamic potential free energy  $F = U - TS$ . Do not mix  $F(E) = E - TS(E)$  with the equilibrium thermodynamic potential  $F = U - TS$ : it could be called the free energy of the microstate  $E$ , but it does not have to be in equilibrium (maximum-probability) state, not until its minimisation.

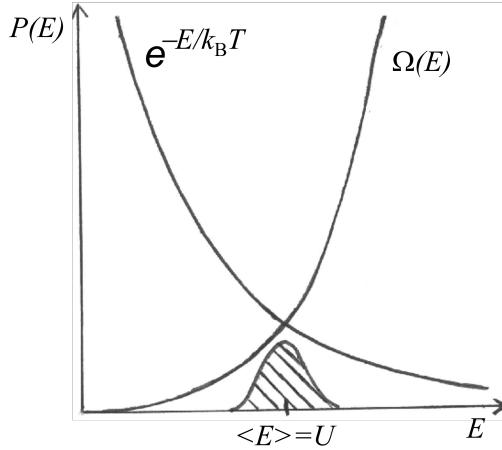


Figure 3.2: The probability,  $P(E)$ , that a system has energy  $E$  is proportional to the product of the statistical weight,  $\Omega(E)$ , and the Boltzmann factor.  $P(E)$  is sharply peaked around the mean value of  $U$ , the shaded area regarded as a Gaussian.

## Grand canonical ensemble: Gibbs distribution and grand partition function

We are now going to obtain an expression which parallels the Boltzmann distribution, but for Gibbs' *grand canonical ensemble*, which consists of an infinite number of subsystems each coupled to an identical reservoir with which it can exchange particles as well as energy. We consider a subsystem plus reservoir to have the total (constant) energy  $U$ , and the total particle number  $N$ . The probability of a given partition of the energy  $(E_i, U - E_i)$ , and particle number  $(N_i, N - N_i)$ , such that the system is in a definite energy eigenstate  $E_i$  with particle number  $N_i$ , is proportional to the number of microstates of the reservoir that are consistent with this partitioning. Again we take  $E_i$  and  $N_i$  to be small compared with  $U$  and  $N$ , and expand the logarithm of the accessible states function:

$$\begin{aligned} P_i(E_i, N_i) &\propto e^{\ln \Omega_R(U-E_i, N-N_i)} \\ &\sim \exp \left\{ \ln \Omega_R(U, N) - E_i \left( \frac{\partial \ln \Omega_R(U, N)}{\partial U} \right)_N - N_i \left( \frac{\partial \ln \Omega_R(U, N)}{\partial N} \right)_U + \dots \right\} \\ &\sim e^{\ln \Omega_R(U, N)} e^{-\beta(E_i - \mu N_i)}, \end{aligned}$$

where, in addition to the entropy  $S = k_B \ln \Omega$  and temperature, we have made the identification of the chemical potential using

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_U = -k_B T \left( \frac{\partial \ln \Omega}{\partial N} \right)_U. \quad (3.19)$$

Normalising, we obtain the Gibbs probability distribution:

$$P_i(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i - \mu N_i)}, \quad (3.20)$$

where the new normalisation factor  $\Xi$  is called the *Grand partition function*. To obtain it we need to sum over all energy states for each number of particles, as we did in the canonical partition function (3.15), but also over all possible number of particles the system might have (ultimately,  $N_i \in 0 \div N$ , where  $N$  might be infinity):

$$\Xi = \sum_{N_i} \sum_i e^{-\beta(E_i[N_i] - \mu N_i)}. \quad (3.21)$$

The exponential term,  $e^{-\beta(E_i - \mu N_i)}$  is called the *Gibbs factor*. The energy eigenstates are in general different for different particle numbers in the system, so this can be a complicated object.

## 3.6 Solving problems in statistical mechanics

The most general way to approach problems in statistical mechanics is to calculate the partition function,  $Z$ , or the grand partition function  $\Xi$ . All the thermodynamic potentials can then be obtained from  $Z$  or  $\Xi$ , as shown below. In problems for large systems one can normally use any of the microcanonical, canonical or grand canonical ensembles, obtaining identical values for the thermodynamic average values. A number of different approaches are often possible, and you should develop experience in choosing a convenient method by tackling problems.

## Canonical ensemble

In the canonical ensemble the probability of a particular microstate is given by the Boltzmann distribution,

$$P_i = \frac{e^{-\beta E_i}}{Z}, \quad (3.22)$$

where the partition function is

$$Z = \sum_{\text{all states } i} e^{-\beta E_i} = \sum_{\text{microstates } E} \Omega(E) e^{-\beta E_i} = \sum_{\text{microstates } E} e^{-\beta [E_i - TS(E_i)]}, \quad (3.23)$$

where, as before,  $S(E) = k_B \ln \Omega(E)$ . To find the equilibrium, we minimise  $[E_i - TS(E_i)]$ , and in a very large system the partition function sum will be dominated by the exponentially large factor describing the macrostate:

$$Z \approx e^{-\beta[U - TS(U)]}, \quad \text{hence } F = -k_B T \ln Z \quad (3.24)$$

Or look at it from the equilibrium Gibbs entropy angle:

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i P_i \left( -\frac{E_i}{k_B T} - \ln Z \right) \equiv \frac{U}{T} + k_B \ln Z, \quad (3.25)$$

where we used  $U = \langle E \rangle = \sum_i P_i E_i$  and  $\sum_i P_i = 1$ . From  $F = U - TS$  we can make the identification:  $F = -k_B T \ln Z$ . Once the minimisation of the free energy  $F(E)$  of macrostate is done, and we found the equilibrium macrostate, we may treat  $F$  as a thermodynamic potential: a function of  $T$  and  $V$ , and get the entropy from  $S = -(\partial F / \partial T)_V$  and the pressure as  $p = -(\partial F / \partial V)_T$ , and hence  $U, H$  and  $G$  from analytical thermodynamics.

Another useful formula connecting the partition function to a thermodynamic potential is

$$U = \sum_i E_i P_i(E_i) = -\frac{\partial}{\partial \beta} \ln Z. \quad (3.26)$$

## Grand canonical ensemble

Here the microstate probabilities are given by

$$P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi}, \quad (3.27)$$

where the grand partition function is

$$\Xi = \sum_{N_i} \sum_i e^{-\beta(E_i - \mu N_i)}.$$

As in the canonical ensemble, the key is to look at the microstate – a collection of states with the same energy  $E_i$ , and count them to  $\Omega(E_i)$ , the only difference is a now added summation over the variable number of particles in this microstate,  $N_i$ . The probability of such a microstate is

$$P_i = \frac{1}{\Xi} \Omega(E_i, N_i) e^{-\beta(E_i - \mu N_i)} = \frac{1}{\Xi} e^{-\beta[E_i - TS(E_i, N_i) - \mu N_i]}, \quad (3.28)$$

and to find the most-probably = equilibrium macrostate we need to minimise the exponent  $E - TS(E, N) - \mu N$ , which in equilibrium will become the grand thermodynamic potential  $\Phi = U - TS - \mu N$ , and  $\Xi \approx e^{-\beta\Phi}$ .

Or starting from the Gibbs entropy,  $S = -k_B \sum_i P_i \ln P_i$ , we have

$$TS = -k_B T \sum_i P_i \ln P_i = -k_B T \sum_i P_i \{-(E_i - \mu N_i)/k_B T - \ln \Xi\} \quad (3.29)$$

$$= U - \mu N + k_B T \ln \Xi, \quad (3.30)$$

where we used the definitions of averages, e.g.  $U = \sum_i P_i E_i$ . Recalling that the grand potential is given by  $\Phi = U - TS - \mu N$ , we have  $\Phi = -k_B T \ln \Xi$ .

From  $d\Phi = -S dT - p dV - N d\mu$  we then obtain the entropy, pressure and average particle number from

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{V,\mu} \quad p = - \left( \frac{\partial \Phi}{\partial V} \right)_{T,\mu} \quad N = - \left( \frac{\partial \Phi}{\partial \mu} \right)_{T,V}. \quad (3.31)$$

From these quantities we can construct all the other thermodynamic potentials.

### Example: defects in a solid

Point defects are present in a crystal in thermal equilibrium at finite temperatures. One of the simplest kinds of point defect is the vacancy in which an atom is missing from one of the lattice sites. Suppose that the increase in internal energy on introduction of a vacancy is  $\epsilon$ . This corresponds to the energy to take an atom from a lattice site and place it at the surface (called a *Schottky defect*). We can calculate the average number of vacancies,  $n$ , present in a crystal containing  $N$  atoms as follows.

Strictly speaking the system is not at constant volume, because the volume increases with the number of defects, but if the pressure is zero the work term  $pV = 0$ , and we can find the equilibrium state by minimising the Helmholtz free energy of the microstate with  $n$  defects,  $F$  rather than  $G$ . There are two contributions to  $F$  from the vacancies, the internal energy term and the configurational entropy term from the number of ways of choosing  $n$  vacant sites out of a total of  $N + n$  sites. Therefore

$$F(n) = E(n) - TS(n) = n\epsilon - k_B T \ln \frac{(N+n)!}{N!n!}. \quad (3.32)$$

Using the Stirling approximation for the factorials we obtain the free energy of the microstate with energy  $E = n\epsilon$ :

$$F = n\epsilon - k_B T [(N+n) \ln(N+n) - N \ln N - n \ln n]. \quad (3.33)$$

Minimising with respect to  $n$  gives

$$\frac{\partial F}{\partial n} = \epsilon - k_B T \ln \left( \frac{N+n}{n} \right) = 0, \quad (3.34)$$

and therefore the equilibrium (most probable) value of  $n$  is given by

$$n_{eq} = \frac{N}{e^{\epsilon/k_B T} - 1} \simeq N e^{-\epsilon/k_B T}. \quad (3.35)$$

Typically  $\epsilon$  might be about 1 eV, so that at room temperature  $n/N \simeq 10^{-17}$ , which is very small, but in ionic crystals such as NaCl the vacancies are responsible for the observed electrical conductivity and the colour of the crystals.

The equilibrium thermodynamic free energy is obtained by substitution of the maximum-probability value,  $F = F(n_{eq})$ , and after some algebra we can obtain:

$$F_{eq}(T, N) = Nk_B T \ln \left( 1 - e^{-\epsilon/k_B T} \right). \quad (3.36)$$

### Example: paramagnetic salt

Consider a paramagnetic salt in which magnetic ions with spin 1/2 and magnetic moment  $m_0$  are arranged on  $N$  sites. There is an external magnetic field  $B$ , and we assume that the moments do not interact with one another. Calculate the mean magnetic moment per spin,  $m$ , and the heat capacity per spin,  $c$ .

Note that each spin makes the same contribution to extensive parameters of the system, and therefore we need consider only quantities per spin, which will be denoted by lower case letters. We have  $dU_1 = TdS_1 + Bdm$  (see §1.1.3), from which we can obtain the relevant free energy  $F_1$ , which incorporates the constraints  $(T, B)$ , by a Legendre transformation:  $F_1 = U_1 - TS_1 - mB$ :

$$dF_1 = -S_1 dT - m dB. \quad (3.37)$$

A spin can either point up or down and therefore the partition function for a single spin is

$$Z_1 = \sum_i e^{-\beta E_i} = e^{+\beta m_0 B} + e^{-\beta m_0 B} = 2 \cosh \left[ \frac{m_0 B}{k_B T} \right]. \quad (3.38)$$

We have

$$F_1 = -k_B T \ln Z_1 = -k_B T \ln \left( e^{+\beta m_0 B} + e^{-\beta m_0 B} \right), \quad (3.39)$$

and from Eq. (3.37) we obtain

$$m = - \left( \frac{\partial F_1}{\partial B} \right)_T = m_0 \tanh \left( \frac{m_0 B}{k_B T} \right), \quad (3.40)$$

which is the average magnetic moment of a site. We now calculate  $s$ . From Eq. (3.37) we have

$$S_1 = - \left( \frac{\partial F_1}{\partial T} \right)_B = k_B \ln \left( 1 + e^{-2\beta m_0 B} \right) + \frac{1}{T} \frac{2m_0 B}{e^{2\beta m_0 B} + 1}, \quad (3.41)$$

and we obtain the heat capacity  $C_1$  from

$$C_1 = T \left( \frac{\partial S_1}{\partial T} \right)_B = \frac{(m_0 B)^2}{k_B T^2 \cosh^2(\beta m_0 B)}. \quad (3.42)$$

This form of the heat capacity, called a *Schottky anomaly*, is plotted in Fig. 3.3 along with the average magnetic moment per spin,  $m$  and the entropy per spin,  $s$ . Note that we did not have to minimise any free energy of a microstate here, since the analysis was done for just one spin: there is no statistics here (except for the two levels).

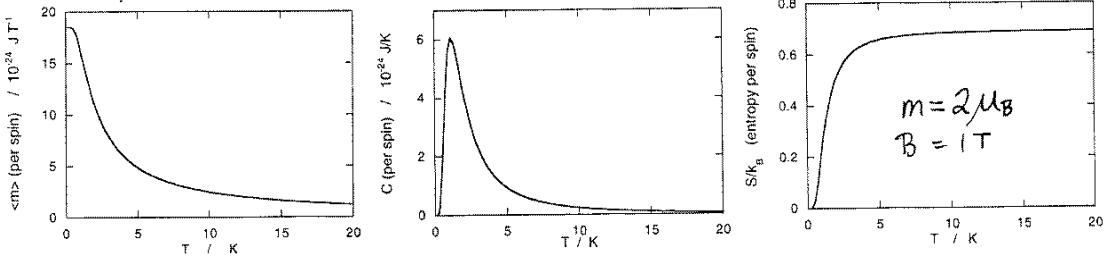


Figure 3.3: The mean magnetisation,  $m$ , per spin, the heat capacity per spin,  $C$ , and the entropy per spin,  $S/k_B$ , for a two-level system.

We could have treated the problem in a different way, to expose the microstates and the maximum-probability condition. We have a lattice of  $N$  sites, of which  $r$  are up (along the external field  $B$ ) and  $(N - r)$  are down. In the external field  $B$ , the energy is  $E(r) = -rm_0B + (N - r)m_0B = Nm_0B - 2rm_0B$ , where the first term is an additive constant. This is the microstate, with the large number of ways to achieve  $R$  out of  $N$ :  $\Omega(r) = N!/r!(N - r)!$ . We now have the free energy of the microstate (which is the exponent of its probability  $P(r)$  given by

$$F(r) = -2rm_0B - k_B T \ln \Omega(r) = -2rm_0B - k_B T[N \ln N - r \ln r - (N - r) \ln(N - r)] . \quad (3.43)$$

The most probable microstate (that is, the equilibrium macrostate) is obtained by minimisation of this free energy, in the way you are familiar with. The solution is

$$r_{eq} = \frac{N}{1 + e^{-2m_0B/k_B T}} \quad (3.44)$$

and the average magnetic moment, per spin, takes the form:

$$m_{eq} = \frac{1}{N} \cdot \frac{1}{2} m_0(2r - N) = m_0 \tanh\left(\frac{m_0B}{k_B T}\right) , \quad (3.45)$$

i.e. identical to the single-spin treatment. By substituting  $r_{eq}$  into  $F(r)$  we should obtain the same expression for the equilibrium thermodynamic potential  $F_{eq}(T, B)$  as in Eq. (3.39).

### Example: the Planck distribution

Consider a single simple harmonic oscillator. The partition function sum has every microstate with just one state. so it's just the geometric series:

$$Z = \sum_i \exp\left\{-\frac{E_i}{k_B T}\right\} = \sum_{n=0}^{\infty} \exp\left\{-\left(n + \frac{1}{2}\right) \frac{\hbar\omega_0}{k_B T}\right\} = \frac{e^{-\frac{1}{2}\hbar\omega_0/k_B T}}{1 - e^{-\hbar\omega_0/k_B T}} \quad (3.46)$$

$$\Rightarrow F_{eq} = -k_B T \ln Z = \frac{\hbar\omega_0}{2} + k_B T \ln\left(1 - e^{-\hbar\omega_0/k_B T}\right) \quad (3.47)$$

$$\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V = -k_B \ln\left(1 - e^{-\hbar\omega_0/k_B T}\right) + \frac{\hbar\omega_0}{T} \frac{e^{-\hbar\omega_0/k_B T}}{1 - e^{-\hbar\omega_0/k_B T}} \quad (3.48)$$

$$\Rightarrow U = F + TS = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1} . \quad (3.49)$$

This is Planck's formula for the energy of black-body radiation in a mode of frequency  $\omega_0$ . The mean number of photons with energy  $\hbar\omega_0$  is directly related to the energy;  $\langle n_{\hbar\omega_0} \rangle = (U - \frac{1}{2}\hbar\omega_0)/\hbar\omega_0 = 1/(e^{\hbar\omega_0/k_B T} - 1)$ .

### The microscopic meaning of heat and work

We can also use the Boltzmann distribution to gain insight into the meaning of heat and work. Start from the Gibbs entropy, and again substitute the Boltzmann distribution,

$$dS = -k_B \sum_i (dP_i \ln P_i + dP_i) \quad (3.50)$$

$$= -k_B \sum_i \left( dP_i \left( -\frac{E_i}{k_B T} - \ln Z \right) + 0 \right) = k_B \sum_i \frac{E_i dP_i}{k_B T}, \quad (3.51)$$

where we have twice used  $\sum_i dP_i = 0$  (from  $\sum_i P_i = 1$ ). Cancelling the  $k_B$ 's and multiplying by  $T$ , we have

$$T dS = \sum_i E_i dP_i. \quad (3.52)$$

This is the reversible heat flow  $dQ_{\text{rev}}$ . But in general  $U = \sum_i E_i P_i$ , so from  $dU = T dS + dW$  we conclude that the reversible work is

$$dW_{\text{rev}} = \sum_i P_i dE_i. \quad (3.53)$$

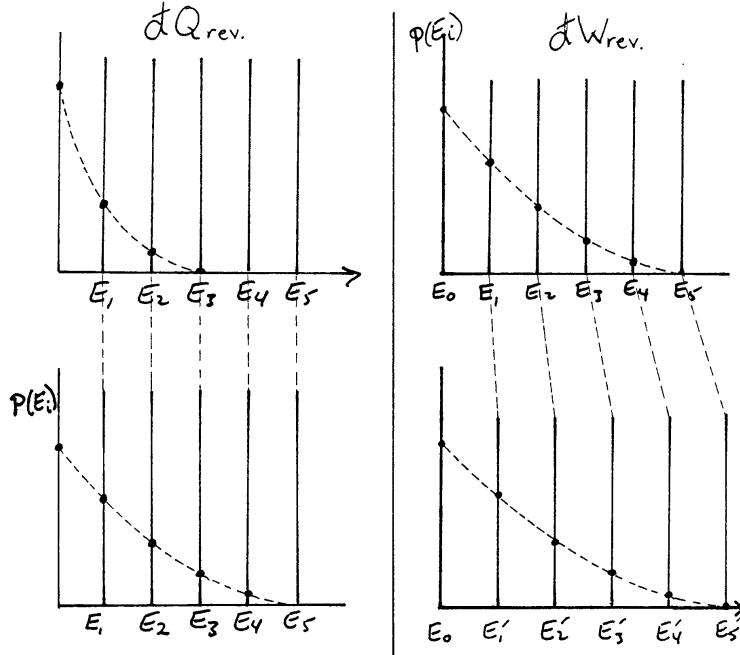


Figure 3.4: The reversible heat flow,  $dQ_{\text{rev}}$ , comes from the change in the probability distribution while the reversible work,  $dW_{\text{rev}}$ , comes from the change in the energy levels.

In other words, heat corresponds to a change in the probability distribution with the underlying energy levels unchanged, while work corresponds to shifts in the energy levels with the probability distribution unchanged. Note that the probability distribution may, however, change in a  $dW$  process, because energy levels may cross and while they are degenerate their occupancy may shift.

This realisation provides a justification for identifying statistical and thermodynamic entropy, as it leads to a very plausible microscopic interpretation of heat and work. We could also, with hindsight, launch into statistical thermodynamics differently: if we were to start by postulating that heat flow and work must correspond to changes in the probability distribution and in the energy level scheme, respectively, we would find that the Boltzmann probability distribution is the only one consistent with the postulate, and we would arrive, via a back route, at the Gibbs expression for entropy.

# Chapter 4

## Classical Ideal Gas

### 4.1 Phase space

Many problems may be addressed satisfactorily using classical mechanics rather than quantum mechanics, and of course Boltzmann and Gibbs developed statistical mechanics before the advent of quantum mechanics. Here we develop statistical mechanics for use with classical mechanics.

The meaning of the number of states  $\Omega$  in an expression such as  $S = k_B \ln \Omega$  is often clear, e.g., when you have a discrete system where states can be enumerated, as in several examples in §3.6. It is often easy to enumerate the states for a quantum system – when the number of microstates corresponding to the macrostate: quantised states are discrete, so we can count them and then calculate the entropy or the partition function. In classical mechanics on the other hand, variables such as the energy, or coordinate-velocity of a particle, are continuous so it isn't immediately clear how to count the states.

In order to think about this issue it will be useful to introduce the notion of the *phase space*. Those of you familiar with Lagrangian and Hamiltonian dynamics would be familiar with this concept: in a normal space, in order to describe the continuous motion we characterise a particle by its coordinate,  $\mathbf{r}(t)$ . However, just knowing the function  $\mathbf{r}(t)$  is not sufficient to fully describe the evolution of the system: you need to simultaneously know the particle velocity  $\dot{\mathbf{r}}(t)$  (or, equivalently, its momentum  $\mathbf{p} = m\mathbf{v}$ ) to be able to predict where it will end up at  $t + dt$ . The phase space is double in dimensions and represents the particle by a representative point  $(\mathbf{r}(t), \mathbf{p}(t))$ . In a classical system of  $N$  point particles the precise *microstate* of the system is specified by the position of a representative point in the  $6N$ -dimensional phase space,  $X = (\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{p}_1, \dots, \mathbf{p}_N)$ , where  $\mathbf{r}_i$  is the position of the  $i^{th}$  particle and  $\mathbf{p}_i$  is its momentum. The positions and momenta of the particles change with time, and therefore the representative point moves along a trajectory in the phase space, as determined by the classical laws of Newtonian mechanics. This is easy to see if we consider a one-dimensional simple harmonic oscillator, whose “system point” is defined by the position,  $x = u \sin \omega t$ , and momentum,  $p = m\omega u \cos \omega t$ , in the two-dimensional phase space. The trajectory in phase space is an ellipse.

To do statistical mechanics, we imagine that we have an ensemble of identical classical systems, which allows us to define a *probability density*,  $\varrho(\{\mathbf{r}_i, \mathbf{p}_i\})$ , in phase space, which is equal to the fraction of systems located within an infinitesimal volume  $d\Gamma$  surrounding the point  $\{\mathbf{r}_i, \mathbf{p}_i\}$ . The infinitesimal volume is given by

$$d\Gamma \equiv \prod_{i=1}^N \frac{d^3 r_i d^3 p_i}{(2\pi\hbar)^3}. \quad (4.1)$$

Note the appearance of a factor of Planck's constant  $\hbar$  for each momentum component,  $p_i$ . Clearly this factor could not have arisen from a classical argument! Indeed, there are several ways to demonstrate that the particle position in the phase space is in fact quantised, with the discretisation  $\Delta x \Delta p \sim 2\pi\hbar$  for each degree of freedom, and so this factor is necessary when one converts from the (non-dimensional) sum over discrete states to the continuous integral over  $dx dp$ . Remarkably, the value of this factor (and thus the “memory” about the underlying quantum nature of the phase space) *cancels* in the differences between thermodynamic functions for different states of a system.

In Appendix 2 it is shown that  $\varrho$  is constant along system trajectories in phase space. This is a very important result, because the trajectories in phase space are lines of constant internal energy of the system, so it tells us that in equilibrium the probability density depends only on the energy, so that states with the same energy have the same probability, i.e., the PEEP.

### Classical partition function

The definition of quantities in classical statistical mechanics follows in a fashion analogous to the development of quantum statistical mechanics. If we are dealing with a closed system, whose energy is confined to a narrow region between energy  $E$  and  $E + dE$ , then all states with energy in this interval are equally likely, while those outside have probability zero. The number of states in this energy shell is proportional to  $(d\Gamma/dE) dE$ , so we define the microcanonical entropy  $S(E)$  as

$$S = k_B \ln \left( \frac{d\Gamma(E)}{dE} dE \right). \quad (4.2)$$

Moreover we can define the Gibbs entropy as  $S = -k_B \int \varrho \ln \varrho d\Gamma$ , where we interpret the continuous integration over the phase space as the ‘sum over all configurations’ or all states. The most important consequence is that if we consider a ‘subsystem’ plus a ‘reservoir’ as a larger closed system then, as before, we can derive the Boltzmann distribution for the probability density  $\varrho(E)$  and the associated partition function for the subsystem:

$$\varrho = \frac{e^{-\beta E(\{\mathbf{p}_i, \mathbf{q}_i\})}}{Z_{cl}} \quad (4.3)$$

$$Z_{cl} = \int e^{-\beta E(\{\mathbf{p}_i, \mathbf{q}_i\})} d\Gamma. \quad (4.4)$$

We mentioned earlier that the factor of  $2\pi\hbar$  in the definition of  $\Gamma$  was not important. From Eqs. (4.3) and (4.4) it is clear that if we multiply  $\Gamma$  by a constant factor  $A$ , then  $S \Rightarrow S + k_B \ln A$ , just a constant added.

Consider a single classical particle in a box of volume  $V$ . The classical partition function is

$$Z_1 = \int e^{-\beta E(\mathbf{p}, \mathbf{r})} d\Gamma = \int e^{-p^2/2mk_B T} \frac{d^3 r d^3 p}{(2\pi\hbar)^3} \quad (4.5)$$

$$= \frac{V}{(2\pi\hbar)^3} \int_0^\infty e^{-p^2/2mk_B T} 4\pi p^2 dp = \left( \frac{k_B T m}{2\pi\hbar^2} \right)^{3/2} V. \quad (4.6)$$

Actually, this is not the smartest way to do this integration (twice by parts), given that the Boltzmann exponential factorises in each of the dimensions:  $p^2 = p_x^2 + p_y^2 + p_z^2$  if all three are involved. So in 3D

$$Z_1 = \int d^3 r \left( \int_{-\infty}^\infty e^{-p_x^2/2mk_B T} \frac{dp_x}{2\pi\hbar} \right)^3 = V \left( \sqrt{\frac{k_B T m}{2\pi\hbar^2}} \right)^3 \quad (4.7)$$

... and equally easy to consider 2D or 1D cases. In essence, you only ever need to do one 1D-momentum integral, which is a simple Gaussian, and then take it to the appropriate power.

Let us stop for a second and examine what we have just obtained. Strictly, the free particle in a box has no potential energy and so the standard Boltzmann factor (statistical weight of a given microstate) should be equal to  $e^0 = 1$ . Hence, by evaluating the partition function according to its definition,  $Z = \sum_i \exp[-\beta E_i]$ , we should have obtained just the number of states this particle can have in this box,  $\Omega = \sum_i$  (the “phase space” arguments are just to help us to count the states in this sum). And we see that this number is:

$$\Omega = V/\lambda^3, \text{ where the length scale } \lambda \text{ is: } \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad (4.8)$$

You may recognise this length scale as the *thermal* de Broglie wavelength of this particle, as you have studied in foundations of quantum physics! By ‘thermal’ we mean that the mean momentum of the particle is due to the thermal motion ( $m\bar{v} = \sqrt{mk_B T}$ ). So the partition function, or the number of states a free classical particle can take inside the box is just the number of ways you can place the “packet” of size  $\lambda^3$  inside a fixed  $V$ . It’s not that surprising, if you look at this result in such a way.

**Average energy:** The average energy of the particle is

$$U_1 = -\frac{\partial}{\partial \beta} \ln Z_1 = \frac{3}{2} k_B T. \quad (4.9)$$

**Entropy:** The entropy of this single free particle in the box is given by

$$S_1 = -\left( \frac{\partial F_1}{\partial T} \right)_V = -\frac{\partial}{\partial T} (-k_B T \ln Z_1) = k_B \ln Z_1 + \frac{3}{2} k_B = k_B \ln \left( \frac{V}{\lambda^3} e^{3/2} \right). \quad (4.10)$$

## 4.2 Ideal gas of $N$ particles

Having derived the partition function for a single particle in a box, which resulted in the expression for its entropy, Eq. (4.10), we now ask about  $N$  identical particles in the box. Our initial inclination is to say that the particles of ideal gas can be treated as independent thermodynamic

systems, because they don't interact with one another. In that case their entropies would just add, to give

$$S_N^{\text{wrong}} = NS_1 = Nk_B \ln \left\{ V e^{3/2} \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \right\}, \quad (4.11)$$

which is equivalent to saying that the partition function for  $N$  particles is the product of the partition functions for the individual particles,

$$Z_N^{\text{wrong}} = Z_1^N. \quad (4.12)$$

Unfortunately Eq. (4.11) suffers from the major problem that it is not *extensive*: if we double  $V$  and  $N$ , then  $S_N$  should double, but it doesn't! Note that our thermodynamic derivation (see Eq. 2.50) led to the extensive Sackur-Tetrode formula for the entropy of an ideal gas.

The lack of extensivity of Eq. (4.11) leads to what is known as the “Gibbs paradox”. If we allow two gases of identical molecules at the same pressure to mix then Eq. (4.11) predicts that the total entropy changes, which cannot be correct, while Eq. (2.50) predicts that it is unchanged.

All the thermodynamic potentials depend on  $\ln Z$ , e.g.,  $U = -\frac{\partial}{\partial\beta} \ln Z$ ,  $F = -k_B T \ln Z$ ,  $S = \frac{\partial}{\partial T} (k_B T \ln Z)$ , etc. To make the thermodynamic potentials extensive we therefore need

$$Z_N = \frac{1}{N!} Z_1^N, \quad (4.13)$$

so that, for large systems, the free energy is

$$F = -k_B T \ln Z_N = -Nk_B T(\ln Z_1 - \ln N + 1). \quad (4.14)$$

In particular, the entropy now becomes

$$S = -\frac{\partial F}{\partial T} = Nk_B \ln \left\{ \frac{V}{N} \exp \left( \frac{5}{2} \right) \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \right\}, \quad (4.15)$$

which is extensive and is exactly the Sackur-Tetrode formula (2.49) for the entropy of an ideal gas, with all the constants now properly defined.

It was Gibbs who realised that, for the entropy to be extensive, we should only count microstates which are *distinguishable* from one another. Swapping the positions and momenta of two particles amounts merely to relabelling the two particles, and the microstate is indistinguishable from the original one. Removing all such indistinguishable permutation configurations from the sum over states amounts to dividing  $Z_N^{\text{wrong}}$  by  $N!$

Eq. (4.15) is consistent with Eq. (2.49), but now we have an explicit formula for the unknown integration constant  $S_0$  which appeared in the earlier derivation. We will derive the Sackur-Tetrode entropy again later using the grand partition function, which automatically takes indistinguishability into account. All this is correct for an ideal classical gas but it is still wrong for the fully quantum regime: you can note that Eq. (4.15) does not satisfy the Third Law of Thermodynamics, as the entropy does not go to zero as  $T \rightarrow 0$  (when quantum effects would take over).

## Thermodynamic properties of ideal gas

Once the partition function of a system is found, in effect, you know everything about your system! We just need to learn the route to find these answers. In the case of ideal gas, the Eq. (4.13) provides:

$$Z = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N. \quad (4.16)$$

We have obtained the entropy, which was essential for the discussion of proper accounting for particle degeneracy. However, the primary aim should always be the appropriate thermodynamic potential. One is the mean energy  $U$ , the other is the free energy  $F$ :

$$U = -\frac{\partial}{\partial \beta} \ln Z; \quad F = -k_B T \ln Z. \quad (4.17)$$

To find  $U$  you need to differentiate  $Z$  with respect to temperature (or its inverse,  $\beta$ ) and that is “hiding” under the square-root in the de Broglie wavelength  $\lambda = \sqrt{2\pi\hbar^2/mk_B T}$ . The logarithm allows factorisation of all other terms in  $Z$ , for us not to worry about anything except the proportionality  $Z \propto \beta^{-3/2}$ , so that  $U = \frac{3}{2}Nk_B T$ . This is great, but only useful for one thing: to evaluate the heat capacity

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2}Nk_B. \quad (4.18)$$

In all other senses the mean energy expressed as a function of temperature is not a good object to work with, because  $T$  is not the natural variable of  $U = U(S, V)$ .

Since by its construction, via the integration of the statistical weight  $e^{-\beta E}$  over the phase space, the partition function depends on  $T$  and  $V$ , the more natural route is to evaluate the free energy  $F = F(T, V, N)$ :

$$F = -Nk_B T \ln \left( \frac{V}{\lambda^3} \right) + Nk_B T \ln N - Nk_B T = Nk_B T \ln \left( \frac{N\lambda^3}{V e} \right), \quad (4.19)$$

the last term on the first line arising from the Stirling approximation of the factorial, and part of it contributes to the factor of  $e$  in the denominator of (4.19). The dependence of this thermodynamic potential on its natural variables is explicit and we can reap the benefits. The entropy,  $S = -(\partial F / \partial T)_{V,N}$  is already obtained in its Sackur-Tetrode form. The other two conjugate variables are the pressure  $p$  and the chemical potential  $\mu$ :

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = \frac{Nk_B T}{V} \quad (4.20)$$

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} = k_B T \ln \left( \frac{N\lambda^3}{V} \right). \quad (4.21)$$

In both cases we benefited from the very convenient property of logarithm factorisation, which allows one to only look at the relevant variable in its argument. The equation of state of the ideal gas is a pleasing, and inevitable result; the expression (4.21) for the chemical potential of classical ideal gas is very important and will be required several times below. Please compare it with the expression in Eq. (2.60) obtained from entirely thermodynamic arguments: the two are clearly the same, if you think of the ratio  $N\lambda^3/V$  as an effective volume fraction of particles (see §4.5). This resonates with our old  $\mu = k_B T \ln c$  with ‘concentration’.

### 4.3 Equipartition theorem

The equipartition theorem is an extremely important result from classical statistical mechanics. It applies to terms in the Hamiltonian which are *separable* and *quadratic* in one of the generalised coordinates or momenta, meaning that they can be written as

$$\mathcal{H} = Aq^2 + \Delta\mathcal{H}(Q), \quad (4.22)$$

where  $Q$  represents all of the other  $6N - 1$  coordinates of the phase space.

We first examine the consequences of separability. In the canonical ensemble we have

$$\varrho(q) dq = \frac{e^{-\beta Aq^2} dq \int e^{-\beta \Delta\mathcal{H}} dQ}{\int e^{-\beta Aq^2} dq \int e^{-\beta \Delta\mathcal{H}} dQ} = \frac{e^{-\beta Aq^2} dq}{\int e^{-\beta Aq^2} dq} = \frac{e^{-\beta Aq^2} dq}{\sqrt{\pi k_B T / A}}. \quad (4.23)$$

The meaning of this result is that if a coordinate is separable in the Hamiltonian then its probability distribution is independent of all of the other coordinates. So it has its own “private” Boltzmann distribution.

The average internal energy of the system is

$$U = \langle Aq^2 \rangle + \langle \Delta\mathcal{H}(Q) \rangle, \quad (4.24)$$

and, using Eq. 4.23, we obtain

$$\langle Aq^2 \rangle = \frac{\int Aq^2 e^{-\beta Aq^2} dq}{\int e^{-\beta Aq^2} dq} = \frac{\frac{\sqrt{\pi}}{2\beta^{3/2}}}{\frac{\sqrt{\pi}}{\beta^{1/2}}} = \frac{1}{2} k_B T. \quad (4.25)$$

Hence the average energy for the  $q$  degree of freedom is  $\frac{1}{2}k_B T$ . This is the equipartition theorem: each squared, separable degree of freedom in the Hamiltonian has a mean energy of  $\frac{1}{2}k_B T$ . This law allows us to write down the internal energy result of Eq. (4.9) without explicit calculation: single free particle in 3-dimensions has three components of its kinetic energy,  $(1/2m)(p_x^2 + p_y^2 + p_z^2)$ , each averaging to  $\frac{1}{2}k_B T$ .

Equipartition holds for any term in the Hamiltonian which is separable and squared, but *only in the classical limit*. The precise definition of the classical limit will be left until later, but for a simple harmonic oscillator the condition is  $k_B T \gg \hbar\omega_0$ .

#### Kinetic energy of particles in classical interacting systems

The kinetic energy degrees of freedom are generally separable and squared. So even when the interaction term is present in the Hamiltonian,

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + V(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (4.26)$$

in some form of complicated potential energy, our discussion immediately above shows that the probability distribution for the  $x$ ,  $y$  and  $z$  components of the velocity of the  $i^{th}$  particle in the system still follows the Maxwell-Boltzmann distribution. In each dimension:

$$\varrho(v_{x,i}) dv = \sqrt{\frac{m}{2\pi k_B T}} e^{-\beta \frac{1}{2} m v_{x,i}^2} dv_{x,i}, \quad (4.27)$$

the corresponding factor in the partition function is  $1/\lambda$ , and the mean energy is still  $\frac{1}{2}k_B T$  per kinetic degree of freedom. These statements are completely independent of the interactions between the particles; they are equally true in gases, liquids and solids, as long as the system is in the classical limit.

## 4.4 Gas of diatomic molecules

In this example we bring together the ideas of quantum statistical mechanics and classical statistical mechanics and the equipartition theorem, and also examine the role of additional degrees of freedom each particle might possess. Consider a diatomic molecule consisting of two different atoms bonded together. As well as the translational motion the molecule can rotate in space and also vibrate along its bond. These internal degrees of freedom contribute to the internal energy and hence the heat capacity of the molecule.

The vibrations can be approximated by those of a harmonic oscillator of frequency  $\omega_0$ . Following Eqs. (3.46) and (3.48) we have

$$S = -k_B \ln \left( 1 - e^{-\hbar\omega_0/k_B T} \right) + \frac{\hbar\omega_0}{T} \frac{e^{-\hbar\omega_0/k_B T}}{1 - e^{-\hbar\omega_0/k_B T}}. \quad (4.28)$$

Or simply calculate the partition function:

$$Z = \sum_i \exp \left\{ -\frac{E_i}{k_B T} \right\} = \sum_{n=0}^{\infty} \exp \left\{ -(n + 1/2)\hbar\omega_0/k_B T \right\} = \frac{e^{-\frac{1}{2}\hbar\omega_0/k_B T}}{1 - e^{-\hbar\omega_0/k_B T}}, \quad (4.29)$$

and then find  $S = -dF/dT$ , or  $U = -d \ln Z/d\beta$ .

The vibrational contribution to the heat capacity from  $N$  diatomic molecules is given by:

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_V = N \frac{\hbar^2 \omega_0^2}{k_B T^2} \frac{e^{\hbar\omega_0/k_B T}}{(e^{\hbar\omega_0/k_B T} - 1)^2} = N k_B \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}, \quad (4.30)$$

where we used a shorthand notation for the effective temperature,  $k_B \Theta_v = \hbar\omega_0$ . This relation is plotted in Fig. 4.1.

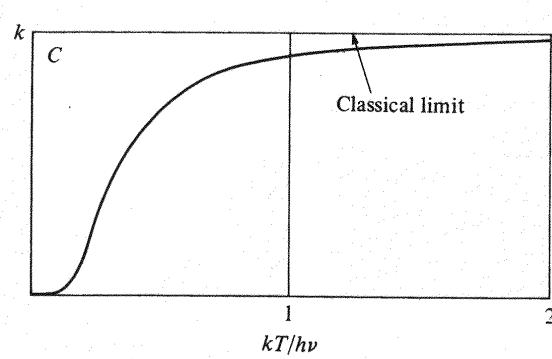


Figure 4.1: The heat capacity of a harmonic oscillator as a function of temperature.

The molecule can also exist in different orbital angular momentum states. The energies of the rotational states are given by

$$\epsilon_J = \frac{\hbar^2 J(J+1)}{2I}, \quad J = 0, 1, 2 \dots, \quad (4.31)$$

where  $I$  is the moment of inertia of the molecule about an axis through its centre of mass, and the degeneracy of each state is  $\Omega_J = 2J + 1$ . These again are discrete states, easy to enumerate, and the corresponding partition function is

$$Z = \sum_{J=0}^{\infty} (2J+1) \exp\left(-\frac{\hbar^2 J(J+1)}{2Ik_B T}\right).$$

The full sum is tedious, but at low temperatures we need only consider the low-energy terms  $J = 0$  and  $J = 1$ , which gives

$$Z \simeq 1 + 3 \exp\left(-\frac{\hbar^2}{Ik_B T}\right) \dots$$

The Helmholtz free energy at low temperatures is given by

$$F = -k_B T \ln Z \simeq -3k_B T \exp\left(-\frac{\hbar^2}{Ik_B T}\right).$$

The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 3k_B \exp\left(-\frac{\hbar^2}{Ik_B T}\right) + \frac{3\hbar^2}{IT} \exp\left(-\frac{\hbar^2}{Ik_B T}\right),$$

from which we can obtain the rotational contribution to the heat capacity from  $N$  diatomic molecules at low temperatures:

$$C_r = T \left(\frac{\partial S}{\partial T}\right)_V = 12Nk_B \left(\frac{\Theta_r}{T}\right)^2 \exp\left(-\frac{2\Theta_r}{T}\right), \quad (4.32)$$

where  $k_B \Theta_r = \hbar^2 / (2I)$ , a different effective temperature corresponding to the rotational motion. At high temperatures we get the equipartition result,

$$C_r \simeq Nk_B. \quad (4.33)$$

The full result is shown in Fig. 4.2.

Normally  $\Theta_r \ll \Theta_v$ . Experimental results for the heat capacity at constant pressure,  $C_p$ , are shown in Fig. 4.3 as a function of temperature for the diatomic gases DT, HT, and HD, where D≡deuterium, H≡hydrogen, T≡tritium. At low  $T$  there is only translational motion, then rotational motion is excited, and finally vibrational motion is excited, so the heat capacity should follow:

0 << T << $\Theta_r$ translational motion :		$C_v = \frac{3}{2}Nk_B, \quad C_p = \frac{5}{2}Nk_B$
$\Theta_r << T << \Theta_v$ translational, rotational motion :		$C_v = \frac{5}{2}Nk_B, \quad C_p = \frac{7}{2}Nk_B$
$T >> \Theta_v$ translational, rotational, vibrational motion :		$C_v = \frac{7}{2}Nk_B, \quad C_p = \frac{9}{2}Nk_B.$

Note that in the flat part of the curves, where  $\Theta_r << T << \Theta_v$ , the masses of the atoms are irrelevant - this is when the translational and rotational degrees of freedom can be approximated by their high temperature limits (classical limits) and the vibrations are not excited significantly. Homonuclear molecules, such as  $H_2$ , are a bit different at low temperatures - quantum effects due to indistinguishable nuclei!

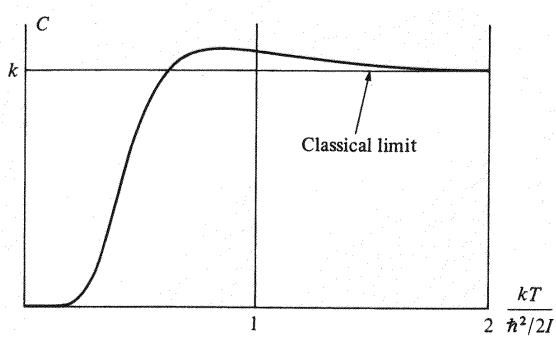


Figure 4.2: The rotational heat capacity as a function of temperature.

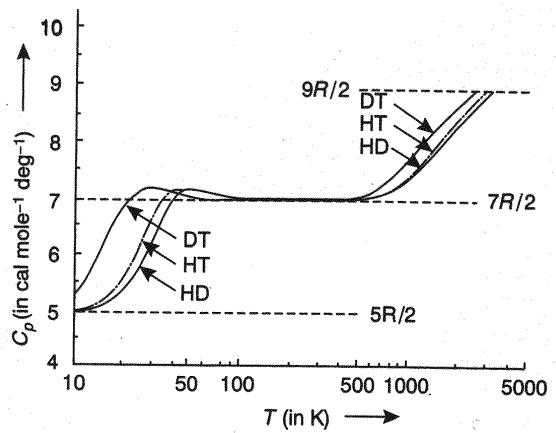


Figure 4.3: The rotational-vibrational heat capacities at constant pressure,  $C_p$ , for the diatomic gases DT, HT, and HD, as a function of temperature.

## 4.5 Classical to quantum crossover

Let us explore the conditions under which quantum nature of the system (ideal gas in this chapter) becomes important, as opposed to the classical regime where we have just obtained, e.g., Eqs. (4.19) and (4.21) for the free energy and chemical potential. Please note how both these expressions, as in fact the entropy (4.15), depend on the combination of parameters (in a 3-dimensional system):

$$\frac{N\lambda^3}{V} = \frac{N}{V} \left( \frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}. \quad (4.34)$$

You can look at this expression and have a scheme illustrated in Fig. 4.4 in mind. Clearly, the ratio in Eq. (4.34) is related to the effective volume fraction of particles in the box – and the limit when the thermal de Broglie volumes associated with the particles do not clash is when  $N\lambda^3/V \ll 1$ . This is the limit of classical ideal gas. We can depart from this limit in several ways: by increasing the density of particles ( $N/V$ ) or by increasing  $\lambda = \sqrt{2\pi\hbar^2/mk_B T}$  which, in turn, can be achieved by lowering the temperature ( $T \rightarrow 0$ ), or by considering lighter particles

$m \rightarrow 0$ ). Evidently, when  $N\lambda^3/V \geq 1$ , we can no longer talk about a classical gas: their wave packets (of the size  $\sim \lambda$ ) will start interfering with each other and we drop into the quantum limit of statistical mechanics.

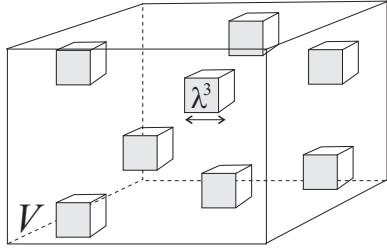


Figure 4.4: Particles of “size”  $\lambda^3$  filling the box of volume  $V$ .

The same conclusion can be reached from the “quantum side”. Quantum effects become unimportant when the occupancy of each of the energy levels becomes small and therefore the discreteness (quantisation) relevant. This is the reciprocal  $k$ -space condition, but there is a corresponding real space condition. The maximum energy of a particle in the gas is around  $k_B T$  (ignoring ‘rare’ fluctuations). From  $\varepsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$  the wavevector for which the kinetic energy of our classical particles matches  $k_B T$  is, therefore:

$$k_{\max} \sim \sqrt{\frac{2mk_B T}{\hbar^2}}. \quad (4.35)$$

This would correspond to a wavelength  $\lambda_{\max} = \frac{2\pi}{k_{\max}} = \frac{2\pi\sqrt{\hbar^2}}{\sqrt{2mk_B T}}$ , which is close to the *thermal de Broglie wavelength* introduced earlier (Eqn. 4.8), up to a factor of order one. In different textbooks the thermal de Broglie wavelength is given with various factors of  $\pi$  floating around, but the most systematic approach for calculating this important quantity, based on the single-particle partition function  $Z_1 = V/\lambda^3$  gives, as shown earlier (Eqn. 4.8):

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \quad (4.36)$$

The wave-packets of the particles will cease to overlap in *real* space when the number of particles per unit volume  $N/V$  is less than  $n_Q = 1/\lambda^3$ , which is sometimes called the quantum concentration. That is, the wave-packets cease to overlap in real space when the inter-particle separation becomes greater than the thermal de Broglie wavelength. How does this correspond to the  $k$ -space condition? The average occupation of an accessible energy level is

$$\langle n \rangle = \frac{\text{number of particles}}{\text{number of accessible energy levels}} = \frac{N}{4/3 \pi k_{\max}^3} \frac{(2\pi)^3}{V}, \quad (4.37)$$

and the behaviour is classical when  $\langle n \rangle \ll 1$ . From Eq. 4.37 we see that the crossover occurs at roughly  $N\lambda^3/V \sim 1$ , so the  $k$ -space and real-space criteria agree.

Air at room temperature and pressure is in the classical regime while electrons in a solid are in the quantum regime. A system of Fermions or Bosons is sometimes referred to as *degenerate* if it is within the quantum regime and *non-degenerate* if it is within the classical regime.

# Chapter 5

## The grand canonical ensemble

### 5.1 Quantum mechanics and indistinguishability

In our discussion of the classical partition function of  $N$  particles in §4.2 we used the idea that we should only count indistinguishable microstates. Ultimately this arises from the underlying quantum mechanical nature of matter. In quantum mechanics particles are either indistinguishable (identical) or distinguishable (different). In addition, particles come in two types - Fermi particles or fermions which have half-integer spins ( $\frac{1}{2}, \frac{3}{2}, \dots$ ) and Bose particles or bosons which have integer spins (0, 1, 2, ...). Examples of fermions include protons, neutrons, electrons, muons, neutrinos, quarks, and the  ${}^3\text{He}$  atom. Examples of bosons include photons, pions, mesons, gluons, and the  ${}^4\text{He}$  atom. The quantum mechanical wave function of a system of identical fermions is *antisymmetric* under the interchange of two particles, while the wave function of a system of identical bosons is *symmetric* under exchange of two particles, that is,

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2) = \pm \Psi(\mathbf{r}_2 s_2, \mathbf{r}_1 s_1), \quad (5.1)$$

where  $\mathbf{r}$  is the position of a particle and  $s$  is its spin, while the plus sign refers to bosons and the minus to fermions.

To understand the problem more deeply consider two non-interacting quantum particles in a box, in states  $|\mathbf{k}_1\rangle$  and  $|\mathbf{k}_2\rangle$ . If the two particles are distinguishable (say a helium atom and an argon atom), then the state  $\Psi_{\mathbf{k}_1, \mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}_2}$  is different from  $\Psi_{\mathbf{k}_2, \mathbf{k}_1}(\mathbf{r}_1, \mathbf{r}_2) = e^{i\mathbf{k}_2 \cdot \mathbf{r}_1} e^{i\mathbf{k}_1 \cdot \mathbf{r}_2}$ , where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  label the positions of the two particles. But if the particles are indistinguishable then, according to Eq. 5.1, the wave function must be

$$\Psi_{\mathbf{k}_1, \mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left( e^{i\mathbf{k}_1 \cdot \mathbf{r}_1} e^{i\mathbf{k}_2 \cdot \mathbf{r}_2} |s_1; s_2\rangle \pm e^{i\mathbf{k}_2 \cdot \mathbf{r}_1} e^{i\mathbf{k}_1 \cdot \mathbf{r}_2} |s_2; s_1\rangle \right), \quad (5.2)$$

where the plus sign refers to bosons, and the minus to fermions.

So we *don't* have two different states, there is only one state. Also, if  $\mathbf{k}_1 = \mathbf{k}_2$ , the same-spin fermion wave-function is zero; this state is forbidden by the Pauli exclusion principle, as shown by Eq. 5.1. When we do statistical mechanics of quantum mechanical particles we must count the states correctly.<sup>1</sup>

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<sup>1</sup>It is worth noting as an aside that identical particles with different spin states behave like distinguishable particles, i.e., the spin state is a ‘label’ that lets us distinguish particles. Therefore we only have to worry about the effect of wave-function symmetrisation for same-spin particles, and the system can be broken down into same-spin subsystems, whose thermodynamic potentials will add.

As an interesting aside, the plus or minus sign in the wave function leads to profound differences in the physics of fermions and bosons. The particle densities from the wave functions of Eq. 5.2 are uniform. However, consider the joint probability density for the state  $\Psi_{\mathbf{k}_1, \mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2)$  of finding one particle at  $\mathbf{r}_1$  and the other at  $\mathbf{r}_2$ ,

$$P_{\mathbf{k}_1, \mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{\mathbf{k}_1, \mathbf{k}_2}^*(\mathbf{r}_1, \mathbf{r}_2) \Psi_{\mathbf{k}_1, \mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) \quad (5.3)$$

$$= \frac{1}{2} \left( 1 + 1 \pm \delta_{s_1, s_2} \left\{ e^{-i\mathbf{k}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)} e^{-i\mathbf{k}_2 \cdot (\mathbf{r}_2 - \mathbf{r}_1)} + e^{-i\mathbf{k}_2 \cdot (\mathbf{r}_1 - \mathbf{r}_2)} e^{-i\mathbf{k}_1 \cdot (\mathbf{r}_2 - \mathbf{r}_1)} \right\} \right) \\ = (1 \pm \delta_{s_1, s_2} \cos\{(\mathbf{k}_1 - \mathbf{k}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2)\}). \quad (5.4)$$

This is called the pair-correlation function, and it is sketched in Fig. 5.1. Note that for same-spin bosons there is an increased probability of finding them close together, while for same-spin fermions this probability is reduced.

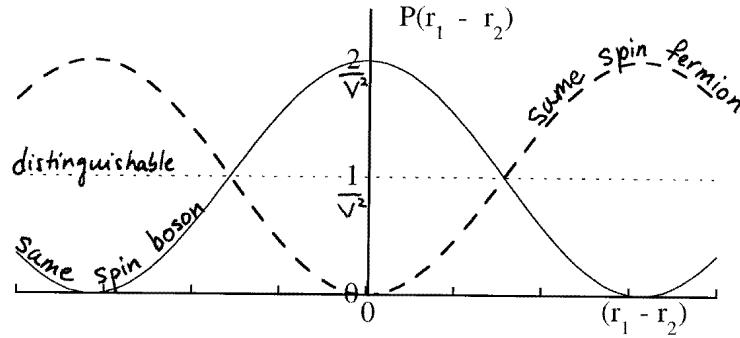


Figure 5.1: The pair-correlation functions for two fermions of the same spin and for two bosons of the same spin.

To evaluate the partition function correctly we should count only microstates corresponding to wave functions of the correct symmetry. It would be a major difficulty if we had to discuss the many-body wave functions of a system every time we wanted to do statistical mechanics. Fortunately it turns out that there is an easy way around this for non-interacting systems; *we stop treating the particles as independent thermodynamic systems, and instead treat the energy levels as independent thermodynamic systems, which contain particles and energy.* The best method for dealing with systems with variable particle number and energy is to use the grand partition function and the grand potential. In the next section we will see how to do this.

## 5.2 Using the grand canonical ensemble

For a large system we get the same values of quantities such as the mean energy or the entropy whichever ensemble we use. We will of course choose the most convenient ensemble. Within the canonical ensemble we will want to evaluate the partition function,  $Z$ , for a set of  $N$  particles. Suppose the particles occupy a set of energy levels  $\varepsilon_1, \varepsilon_2, \dots$ , whose occupation numbers we denote by  $n_1, n_2, \dots$ . The partition function is then

$$Z(T, V, N) = \sum_{n_1, n_2, \dots}^N e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots)}, \quad (5.5)$$

where the sum is over all sets of occupation numbers,  $n_1, n_2, \dots$ , which satisfy  $n_1 + n_2 + \dots = N$ . The  $N$  above the summation sign reminds us that only sets of occupation numbers obeying this constraint are included. For fermions the occupation numbers of each level can be 0 or 1, and for bosons they can take the values 0, 1, 2, .... The condition  $n_1 + n_2 + \dots = N$  leads to considerable mathematical difficulties, because it means that the sums over  $n_1, n_2, \dots$  in Eq. 5.5 are not independent.

Suppose we multiply Eq. (5.5) by  $e^{\beta\mu N}$ , where  $\beta = 1/k_B T$  and  $\mu$  is the chemical potential, and then sum over  $N$ ,

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} Z(T, V, N) e^{\beta\mu N} = \sum_{N=0}^{\infty} \sum_{n_1, n_2, \dots}^N e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots - \mu N)}. \quad (5.6)$$

We recognise  $\Xi$  as being the grand partition function, first defined in Eq. (3.21). Noting that  $N = n_1 + n_2 + \dots$ , we write

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} \sum_{n_1, n_2, \dots}^N e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots - \mu(n_1 + n_2 + \dots))}. \quad (5.7)$$

The sums are over all sets of the  $n_i$  such that  $n_1 + n_2 + \dots = N$ , and over all  $N$ . This is equivalent to summing over all  $n_1, n_2, \dots$  *without* the constraint that  $n_1 + n_2 + \dots = N$ , because any set of the  $n_i$  corresponds to some value of  $N$ . We can therefore remove the sum over  $N$  if we also remove the constraint that  $n_1 + n_2 + \dots = N$ , and write

$$\Xi(T, V, \mu) = \sum_{n_1, n_2, \dots} e^{-\beta(\varepsilon_1 n_1 + \varepsilon_2 n_2 + \dots - \mu(n_1 + n_2 + \dots))} \quad (5.8)$$

$$\begin{aligned} &= \sum_{n_1, n_2, \dots} e^{-\beta(\varepsilon_1 - \mu)n_1} e^{-\beta(\varepsilon_2 - \mu)n_2} \dots \\ &= \left[ \sum_{n_1} e^{-\beta(\varepsilon_1 - \mu)n_1} \right] \left[ \sum_{n_2} e^{-\beta(\varepsilon_2 - \mu)n_2} \right] \dots \\ &= \Pi_i \Xi_i. \end{aligned} \quad (5.9)$$

The last line, Eq. (5.9), shows that the grand partition function is just the product of the grand partition functions  $\Xi_i$  of the individual energy levels, which is what we would get if we treated the energy levels as independent and distinguishable, each in contact with a reservoir at temperature  $T$  and chemical potential  $\mu$ . All we need to do is work out the grand partition function for each energy level and multiply them together! Although it is difficult to evaluate the partition function it is much simpler to evaluate the grand partition function! We can obtain all of the required thermodynamic information from the grand partition function. We will see over the coming lectures that the grand partition function leads to a very powerful and elegant approach.

### 5.3 The classical limit

Consider a single energy level, of energy  $\varepsilon_{\mathbf{k}}$ , in contact with a reservoir with which it can exchange both energy and particles. The grand partition function of the level is

$$\Xi_{\mathbf{k}} = \sum_n e^{-\beta(n\varepsilon_{\mathbf{k}} - n\mu)} = \sum_n \left( e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right)^n. \quad (5.10)$$

If the particles are bosons (i.e., have integer spin) the occupancy of the level is not restricted, so the sum runs from  $n = 0$  to  $\infty$ . If the particles are fermions (i.e., have half-integer spin), the Pauli exclusion principle dictates that there are only two terms in the sum,  $n = 0$  and  $n = 1$ . We shall turn to these cases soon. If, however, for either fermions or bosons, a limit when the exponent is small is observed,

$$\beta(\varepsilon_{\mathbf{k}} - \mu) \gg 1, \quad (5.11)$$

then the contribution from  $n > 1$  is negligible. Note that this is not trivially the “high-temperature limit” where we often expect a relationship like  $\beta\varepsilon \ll 1$ . Now we have to a good approximation

$$\Xi_{\mathbf{k}}^{\text{cl}} \approx 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} + \dots \quad (5.12)$$

If the Eq. (5.11) is valid for all energy levels then we have an *ideal classical gas* where the distinction between bosons and fermions is irrelevant to the thermodynamics. Examining the ratio  $(\varepsilon_{\mathbf{k}} - \mu)/k_B T$  for an arbitrary value of energy, we can see that this can only be large if the chemical potential is large and negative, as we know is indeed the case in the classical ideal gas where  $\beta\mu = \ln(N\lambda^3/v)$ .

From Eq. (5.12) we obtain the grand potential for a given level of energy of an ideal classical gas:

$$\Phi_{\mathbf{k}} = -k_B T \ln \Xi_{\mathbf{k}}^{\text{cl}} = -k_B T \ln(1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}) \simeq -k_B T e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \quad (5.13)$$

where in the last step the logarithm has been expanded to lowest order. The average occupancy of an energy level  $\mathbf{k}$  is

$$\langle n_{\mathbf{k}} \rangle = - \left( \frac{\partial \Phi_{\mathbf{k}}}{\partial \mu} \right)_{T,V} \simeq e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \quad (5.14)$$

which is the *Maxwell-Boltzmann distribution*. From Eq. (5.11) we see that the classical gas corresponds to  $\langle n_{\mathbf{k}} \rangle$  being small for all  $\mathbf{k}$  including  $\mathbf{k} = 0$ .

## 5.4 Grand thermodynamic potential

We now calculate the full thermodynamic grand potential  $\Phi = -k_B T \ln \Xi$  using Eq. (5.13) and carrying out the summation over all energy states,  $\Phi = \sum_{\mathbf{k}} \Phi_{\mathbf{k}}$ . We must appreciate that this is exactly the same summation over the microstates, as in the definition of the canonical partition function  $Z$  in (3.15), because the other aspect of grand statistical summation (over the number of particles) is effectively done for each microstate in Eq. (5.12). So for a continuous classical gas in 3-dimension this summation over the available phase space is the same as in Eq. (4.6):

$$\Phi = \sum_{\mathbf{k}} \Phi_{\mathbf{k}} = \int \Phi(\varepsilon) \frac{d^3x d^3p}{(2\pi\hbar)^3} = -k_B T \int_0^\infty e^{-\beta(\varepsilon - \mu)} g(\varepsilon) d\varepsilon, \quad (5.15)$$

where, after a change of variables, we write the measure of integration as  $g(\varepsilon) d\varepsilon$  which is the number of eigenstates with energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ . This function is called the density of states. Note that this density of states refers to states of individual particles, not to states of the system as the whole, so that  $g(\varepsilon)$  is very different from the function  $\Omega(U)$  we used earlier.

To transform the integral over  $p$  ( $= \hbar k$ ) into one over  $\varepsilon$  we differentiate  $\varepsilon = p^2/2m$ , which gives

$$dp = \sqrt{\frac{m}{2\varepsilon}} d\varepsilon . \quad (5.16)$$

The density of states depends on the dimensionality of space, and in the case of 3-dimensions the integral the 6-component phase space becomes

$$\int \frac{\sigma d^3x d^3p}{(2\pi\hbar)^3} = 4\pi \int_0^\infty \frac{\sigma V}{(2\pi\hbar)^3} p^2 dp = \frac{\sigma V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \sqrt{\varepsilon} d\varepsilon . \quad (5.17)$$

where we have also included the spin degeneracy factor  $\sigma = 2s + 1$  (the number of spin states per  $p$ -state). Now we conclude:

$$\Phi = -k_B T \frac{\sigma V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} e^{\beta\mu} \int_0^\infty \sqrt{\varepsilon} e^{-\beta\varepsilon} d\varepsilon \quad (5.18)$$

$$= -k_B T \frac{\sigma V}{4\pi^2} \left(\frac{2mk_B T}{\hbar^2}\right)^{3/2} e^{\beta\mu} 2 \int_0^\infty x^2 e^{-x^2} dx \quad (5.19)$$

$$= -k_B T \sigma V \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu} = -k_B T \frac{\sigma V}{\lambda^3} e^{\beta\mu} \quad (5.20)$$

for the classical ideal gas. From the constraint on the total (constant) number of classical particles in the ideal gas we have

$$N = - \left( \frac{\partial \Phi}{\partial \mu} \right)_{T,V} = \frac{\sigma V}{\lambda^3} e^{\beta\mu}, \quad (5.21)$$

where you can note that  $Z_1 = \sigma V / \lambda^3$  is the single-particle canonical partition function of this gas. We can invert this equation to obtain the chemical potential:

$$\mu = k_B T \ln \left\{ \frac{N\lambda^3}{\sigma V} \right\} . \quad (5.22)$$

This is, of course, the same as the result obtained from the canonical ensemble and differentiating the free energy, Eq. (4.21), apart from the extra spin-degeneracy factor  $\sigma$  accounted for here.

**The Maxwell distribution:** If we substitute this expression for  $\mu$  into Eq. (5.14) and multiply by the density of states,  $g(\varepsilon)$ , we obtain the Maxwell-Boltzmann probability distribution. The probability,  $p(\varepsilon)$ , that a particular particle has energy  $\varepsilon$  is given by

$$P(\varepsilon) d\varepsilon = \frac{1}{N} \langle n_k \rangle g(\varepsilon) d\varepsilon = \frac{1}{N} e^{-\beta(\varepsilon-\mu)} g(\varepsilon) d\varepsilon = \frac{1}{N} \frac{\sigma V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{N\lambda^3}{\sigma V} e^{-\beta\varepsilon} \sqrt{\varepsilon} d\varepsilon, \quad (5.23)$$

where we have substituted for  $g(\varepsilon)$ , from (5.17), and  $e^{\beta\mu}$  from (5.22). Substituting the classical expression for the kinetic energy,  $\varepsilon = \frac{1}{2}mv^2$ , and rearranging we obtain

$$P(v) dv = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta mv^2/2} 4\pi v^2 dv, \quad (5.24)$$

which is the Maxwell distribution of speeds. There are obviously more direct ways of getting this, but it is reassuring that our more formal approach works.

**The pressure of an ideal gas:** Our expression for  $\Phi(T)$  gives the pressure as the usual thermodynamic derivative:

$$p = - \left( \frac{\partial \Phi}{\partial V} \right)_{T,\mu} = k_B T \frac{\sigma}{\lambda^3} e^{\beta\mu} = \frac{Nk_B T}{V}, \quad (5.25)$$

which is the usual ideal gas law. We got the last equality by substituting for  $\mu$  from Eq. (5.22).

**The entropy of an ideal gas:** Finally, let us obtain the entropy from

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\mu,V} = k_B \frac{\sigma V}{\lambda^3} e^{\mu/k_B T} \left\{ \frac{5}{2} - \frac{\mu}{k_B T} \right\}. \quad (5.26)$$

Substituting for  $\mu$  gives

$$S = k_B N \ln \left( \exp \left( \frac{5}{2} \right) \frac{\sigma V}{N \lambda^3} \right) = k_B N \ln \left( e^{5/2} \frac{\sigma V}{N} \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \right). \quad (5.27)$$

This is the Sackur-Tetrode expression for the entropy of an ideal classical gas yet again; we derived it in §4.2 using the canonical partition function and the principle of indistinguishability.

**Grand partition function of an ideal gas via  $Z$ .** Or we could have done it in a different way, directly from  $Z(T, V, N)$  using the definition (5.6). We have already calculated and discussed the canonical partition function

$$Z = \frac{1}{N!} Z_1^N, \quad \text{therefore} \quad \Xi = \sum_{N=0}^{\infty} \frac{1}{N!} (Z_1 e^{\beta\mu})^N = \exp(Z_1 e^{\beta\mu}) \quad (5.28)$$

the sum is evaluated assuming the number of particles in the gas is ‘capable’ to be very large. Now we recall what  $Z_1$  is, e.g. in 3D:

$$\Xi = \exp \left( \frac{V}{\lambda^3} e^{\beta\mu} \right) = \exp \left( V \left[ \frac{mk_B T}{2\pi\hbar^2} \right]^3 e^{\beta\mu} \right), \quad (5.29)$$

$$\text{hence } \Phi = -k_B T Z_1 e^{\beta\mu} = -k_B T V \left[ \frac{mk_B T}{2\pi\hbar^2} \right]^3 e^{\beta\mu}, \quad (5.30)$$

which is the expression (5.20), with all that followed it.

## 5.5 Internal degrees of freedom and external potentials:

One of the principal results of the previous section was the derivation of the chemical potential of a monatomic ideal gas. It is a simple matter to extend this expression to an ideal gas where there are internal degrees of freedom (for example vibrational and rotational degrees of freedom), or where there is an external potential.

Let’s assume that we can write the energy of a molecule in the form  $\varepsilon = \varepsilon_{\mathbf{k}} + \varepsilon_{\text{int}} + \varepsilon_{\text{ext}}$ , where for a diatomic molecule  $\varepsilon_{\text{int}}$  is (see §4.4),

$$\varepsilon_{\text{int}} = \left( n + \frac{1}{2} \right) \hbar\omega_0 + \frac{\hbar^2 J(J+1)}{2I}, \quad (5.31)$$

the first term being the vibrational energy and the second term being the rotational energy ( $I$  is the moment of inertia of the molecule). The rotational states have a degeneracy of  $(2J+1)$ . An example of an external potential is gravity, for which  $\varepsilon_{\text{ext}} = mgh$ , where  $m$  is the mass of the molecule,  $g$  is the acceleration due to gravity, and  $h$  is the height of the molecule in the gas. A gravitational field does not affect the internal degrees of freedom because the gravitational potential does not vary significantly over the size of the molecule, so the separation of internal and external degrees of freedom is clean. In other cases, such as for an applied magnetic field, the separation is artificial, because the external field changes the sum over the internal degrees of freedom by interacting with the rotational states (via their magnetic moment), lifting their degeneracy, so although the field is external, the energy would be included in  $\varepsilon_{\text{int}}$ . In a given case it should be clear what is meant.

If we consider, for the sake of concreteness, a small volume of gas at height  $h$ , then the grand partition function for energy level  $\varepsilon_{\mathbf{k}}$  is (in the classical limit)

$$\Xi_{\mathbf{k}}(h) = 1 + \sum_{\text{int}} e^{-\beta(\varepsilon_{\mathbf{k}} + \varepsilon_{\text{int}} + \varepsilon_{\text{ext}} - \mu)} = 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} e^{-\beta\varepsilon_{\text{ext}}} \sum_{\text{int}} e^{-\beta\varepsilon_{\text{int}}} \equiv 1 + Z_{\text{int}} Z_{\text{ext}}(h) e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \quad (5.32)$$

where we have defined the partition functions for the internal and external degrees of freedom in the obvious way.

The grand potential of the level is then

$$\Phi_{\mathbf{k}}(h) = -k_B T \ln \Xi_{\mathbf{k}}(h) \simeq -k_B T Z_{\text{int}} Z_{\text{ext}}(h) e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \quad (5.33)$$

where the last equivalence holds in the classical limit only. We have seen this form in equations (5.20) and (5.30) just above. Carrying through the same calculation as in Eq. 5.20 etc., we find the chemical potential for fixed particle number  $N$ ,

$$\mu = k_B T \left\{ \ln \left( \frac{N(h)\lambda^3}{\sigma V} \right) - \ln Z_{\text{int}} - \ln Z_{\text{ext}}(h) \right\}, \quad (5.34)$$

where the possible dependence of particle number on the height  $h$  is also emphasized. With  $\varepsilon_{\text{ext}} = mgh$  we have  $-k_B T \ln Z_{\text{ext}}(h) = mgh$ , and we see that this contribution to the chemical potential is a real potential energy.

As a very simple example of the use of these formulae, consider the variation of particle number with height in an ideal classical gas in a gravitational field. In equilibrium the temperature must be independent of height, so that  $Z_{\text{int}}$  is independent of height. In equilibrium  $\mu$  must also be independent of height, and from Eq. 5.34 we can see that  $N(h)$  must therefore be of the form

$$N(h) = N(0) e^{-mgh/k_B T}. \quad (5.35)$$

The density therefore drops exponentially with height.

## 5.6 Equilibrium constant for chemical reactions

In §2.4 we derived an expression for the so-called equilibrium constant,  $K_c(T)$ , for the concentrations of molecules involved in a chemical reaction between ideal gases. Here we derive an expression for the related equilibrium constant  $K_N(T)$ , defined by

$$K_N(T) \equiv \prod_i N_i^{\nu_i}, \quad (5.36)$$

where  $\nu_i$  is the number associated with molecules of species  $i$  in the reaction equation, and  $N_i$  is the number of molecules of species  $i$  in the ideal gas.

First we write the chemical potential of Eq. (5.34) for each species as

$$\mu_i = k_B T (\ln N_i - \ln Z_1^i), \quad (5.37)$$

where  $Z_1^i$  is the partition function for a single molecule of species  $i$  confined to a volume  $V$ , including translational, internal, and external degrees of freedom. We now substitute for  $\mu_i$  in the condition for chemical equilibrium,  $\sum_i \nu_i \mu_i = 0$ , which gives

$$\sum_i \nu_i \mu_i = \sum_i \nu_i k_B T (\ln N_i - \ln Z_1^i) = 0, \quad (5.38)$$

and therefore

$$K_N(T) = \prod_i N_i^{\nu_i} = \prod_i (Z_1^i)^{\nu_i}. \quad (5.39)$$

We now have an expression for the equilibrium constant for chemical reactions which involves a quantity that we can calculate, the single-particle partition function which was extensively discussed in §4.1. This is called “The Law of Mass Action”.

## 5.7 Langmuir adsorption isotherm

Suppose a vapour is in thermal equilibrium with a surface, and that a molecule of the vapour may attach itself to the surface at one of  $N_s$  surface sites, which lowers its energy by an amount  $\epsilon$ . The internal degrees of freedom of the molecule can be neglected in the vapour phase, but when the molecule is attached to the surface it vibrates against it, and the partition function of a single adsorbed molecule is denoted by  $z_s(T)$ . Derive the relationship between the fraction of the surface sites occupied by molecules,  $\theta = N/N_s$ , and the vapour pressure,  $p$ .

We proceed by calculating the chemical potential of the adsorbed species,  $\mu_s$ , and equating it to that of the vapour,  $\mu_v$ . We can use either the canonical or grand canonical ensembles to calculate the chemical potential of the adsorbed species and here I give both derivations.

### (1) Canonical ensemble

The partition function for  $N$  adsorbed molecules is

$$Z_N = \frac{N_s!}{(N_s - N)!N!} z_s^N e^{-\beta(-N\epsilon)}. \quad (5.40)$$

Using Stirling’s approximation we obtain

$$F = -k_B T \ln Z_N = -N\epsilon - k_B T [N \ln z_s + N_s \ln N_s - (N_s - N) \ln(N_s - N) - N \ln N]. \quad (5.41)$$

The chemical potential is then

$$\begin{aligned} \mu_s &= \frac{\partial F}{\partial N} = -\epsilon - k_B T \left( \ln z_s + \ln \frac{N_s - N}{N} \right) \\ &= -\epsilon + k_B T \ln \frac{N}{(N_s - N)z_s} = -\epsilon + k_B T \ln \left( \frac{\theta}{(1 - \theta)z_s} \right). \end{aligned} \quad (5.42)$$

## (2) Grand canonical ensemble

The surface sites are independent and therefore we consider a single site. The grand partition function is

$$\Xi = \sum_i e^{-\beta(E_i - \mu_s N_i)} Z_{int}^{(i)}, \quad (5.43)$$

where each site has two states:  $i = 0$  (site is empty so that  $N_0 = 0$  and  $E_0 = 0$ ) and  $i = 1$  (site is full and  $N_1 = 1$  and  $E_1 = -\epsilon$ ).  $Z_{int}^{(i)}$  denotes the sum over internal degrees of freedom, in this case the vibrational motion, which for  $i = 1$  has the partition function  $z_s$ . This gives

$$\Xi = 1 + z_s e^{\beta(\epsilon + \mu_s)}. \quad (5.44)$$

The corresponding grand potential is  $\Phi = -k_B T \ln \Xi$  and the average occupation of the site is

$$\theta = \frac{N}{N_s} = - \left( \frac{\partial \Phi}{\partial \mu_s} \right)_{T,V} = \frac{z_s e^{\beta(\epsilon + \mu_s)}}{1 + z_s e^{\beta(\epsilon + \mu_s)}}$$

Rearranging we obtain

$$\mu_s = -\epsilon + k_B T \ln \left( \frac{\theta}{(1-\theta)z_s} \right), \quad (5.45)$$

which is, of course, the same as we obtained in the canonical ensemble.

The chemical potential of an ideal gas is given by Eq. (5.22):

$$\mu_v = k_B T \ln \left( \frac{N \lambda^3}{V} \right) = k_B T \ln \left( \frac{p}{k_B T} \lambda^3 \right). \quad (5.46)$$

Equating  $\mu_v$  and  $\mu_s$  we obtain the Langmuir adsorption isotherm,

$$p = \frac{\theta}{1-\theta} \frac{k_B T}{z_s \lambda^3} e^{-\beta \epsilon}. \quad (5.47)$$

One can also derive the Langmuir adsorption isotherm from a kinetic argument. The rate of change of  $\theta$  due to adsorption is

$$\frac{d\theta_a}{dt} = k_a p (1 - \theta), \quad (5.48)$$

where  $k_a$  is the rate constant for adsorption, defined in such a way that the increase of absorption rate with pressure is made explicit. The rate of change of  $\theta$  due to desorption is just a basic decay:

$$\frac{d\theta_d}{dt} = -k_d \theta, \quad (5.49)$$

where  $k_d$  is the rate constant for desorption (note that  $k_a$  and  $k_d$  have different dimensionality, obviously). In equilibrium

$$\frac{d\theta_a}{dt} + \frac{d\theta_d}{dt} = 0, \quad (5.50)$$

and therefore

$$p = \frac{\theta}{1-\theta} \frac{k_d}{k_a}, \quad (5.51)$$

which is illustrated in Fig. 5.2. Eq. (5.47) therefore gives an expression for the ratio of the rate constants in terms of microscopic variables. The Langmuir adsorption isotherm often works quite well as long as  $\theta$  is not too large.

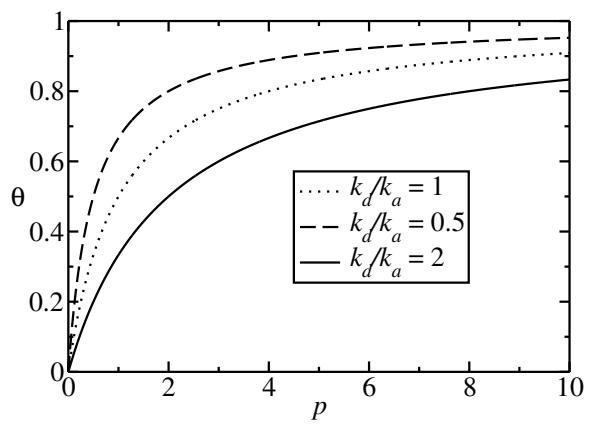


Figure 5.2: Langmuir isotherms for different ratios of the rate constants,  $k_d/k_a$ .

# Chapter 6

## Ideal Fermi gas

### 6.1 Fermi-Dirac statistics for the ideal quantum gas

The grand partition function for level  $\mathbf{k}$  of an ideal gas obeying Fermi-Dirac statistics is

$$\Xi_{\mathbf{k}} = \sum_{n=0}^1 \left( e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right)^n = 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \quad (6.1)$$

and the grand potential is

$$\Phi_{\mathbf{k}} = -k_B T \ln \left\{ 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right\}. \quad (6.2)$$

The average occupation of level  $\mathbf{k}$  is

$$\langle n_{\mathbf{k}} \rangle = - \left( \frac{\partial \Phi_{\mathbf{k}}}{\partial \mu} \right)_{T,V} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}} - \mu)} + 1}, \quad (6.3)$$

which is the *Fermi-Dirac distribution*, or the mean particle number for the given microstate in an ideal Fermi-Dirac gas.

In this grand canonical ensemble, the entropy of each level of a Fermi gas can be calculated as

$$S_{\mathbf{k}}(T, \mu) = - \left( \frac{\partial \Phi_{\mathbf{k}}}{\partial T} \right)_{V,\mu} \quad (6.4)$$

$$= k_B \ln \left( 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right) + \frac{k_B \beta (\varepsilon_{\mathbf{k}} - \mu)}{e^{\beta(\varepsilon_{\mathbf{k}} - \mu)} + 1} \quad (6.5)$$

$$= -k_B [\langle n_{\mathbf{k}} \rangle \ln \langle n_{\mathbf{k}} \rangle + (1 - \langle n_{\mathbf{k}} \rangle) \ln (1 - \langle n_{\mathbf{k}} \rangle)]. \quad (6.6)$$

The Fermi case is illustrated in Fig. 6.1. Excitations are only significant within roughly  $k_B T$  of the Fermi energy. The entropy comes only from those levels whose occupation differs significantly from 0 or 1.

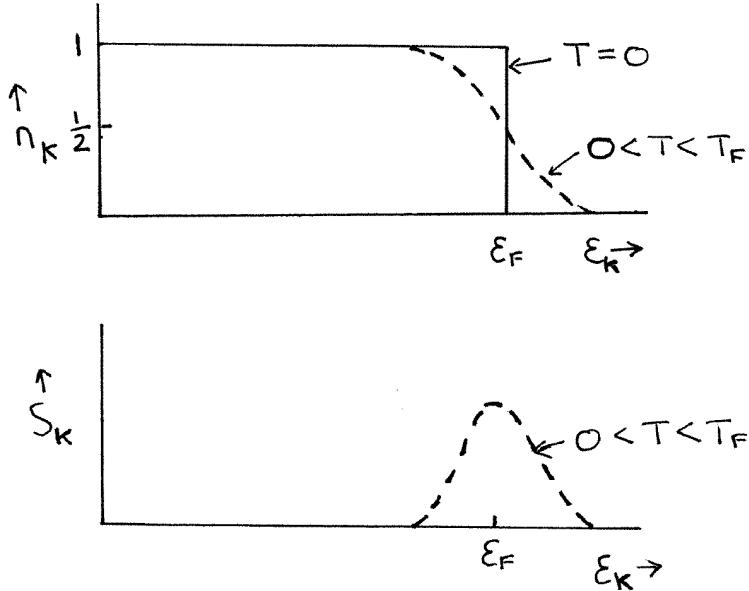


Figure 6.1: The average occupation and entropy of an energy level as a function of energy in a Fermi gas at zero temperature (solid line) and at a finite temperature  $T \ll T_F$  (dashed line).

## 6.2 Quantum states of an ideal gas

The quantum states of free particles are solutions of the Schrödinger equation with a constant potential, but they also depend on the boundary conditions. These must be irrelevant for a large system. We have two main choices for the boundary conditions:

### 6.2.1 Hard-wall boundary conditions

The more familiar choice of boundary conditions would “hard walls”, which means that the wave-function must vanish at the walls of a three-dimensional box. This produces standing waves. The eigenstates for such a box having dimensions  $L_x, L_y$  and  $L_z$  are

$$\psi = \left( \frac{2}{L_x} \frac{2}{L_y} \frac{2}{L_z} \right)^{1/2} \sin(k_x x) \sin(k_y y) \sin(k_z z). \quad (6.7)$$

The associated eigenenergies are

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2). \quad (6.8)$$

In order to satisfy the boundary conditions we need  $k_i = n\pi/L_i$ , where  $n$  is an integer, so that  $\psi(x_i = 0) = \psi(x_i = L_i) = 0$ . The allowed values of the  $\mathbf{k}$ -vector form a lattice in  $k$ -space, with volume per point

$$\Delta k_x \Delta k_y \Delta k_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}, \quad (6.9)$$

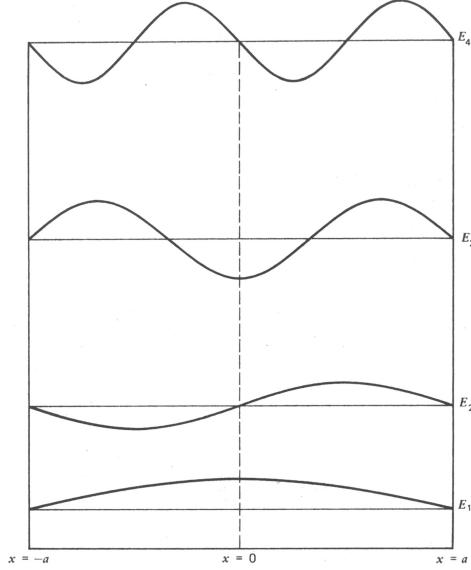


Figure 6.2: The four lowest-energy eigenfunctions for a particle in a box.

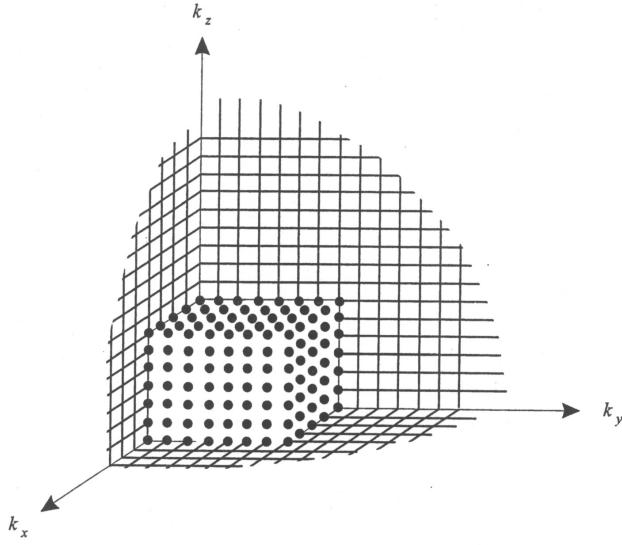


Figure 6.3: The allowed  $k$ -values for a box with hard walls.

where  $V$  is the volume of the box.

We will transform sums over quantum states into integrals over momentum or energy, in which case we need the density of allowed  $\mathbf{k}$ -vectors in  $k$ -space. This is the inverse of the volume per point, multiplied by the spin degeneracy factor  $\sigma = 2s + 1$  (the number of spin states per  $k$ -state):

$$\text{density} = \frac{\sigma}{\Delta k_x \Delta k_y \Delta k_z} = \frac{\sigma V}{\pi^3}. \quad (6.10)$$

### 6.2.2 Periodic boundary conditions

Less intuitive but more useful in the long term are periodic boundary conditions, by which the wavefunction must be invariant under translations along  $x$ ,  $y$  or  $z$  by the respective box sizes  $L_x$ ,  $L_y$ ,  $L_z$ :

$$\psi(x + L_x, y, z) = \psi(x) \quad (6.11)$$

and similarly for the other two coordinates. The eigenstates in this case are travelling waves

$$\psi = \frac{1}{\sqrt{L_x L_y L_z}} e^{i\mathbf{k}\mathbf{r}} \quad (6.12)$$

where  $\mathbf{r} = (x, y, z)$  and the allowed values of the wavevector  $\mathbf{k}$  again form a lattice, but now the spacing between lattice points is  $2\pi/L_x$  etc., giving a larger volume per lattice point and a lower density:

$$\Delta k_x \Delta k_y \Delta k_z = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V} \quad (6.13)$$

$$\text{density} = \frac{\sigma}{\Delta k_x \Delta k_y \Delta k_z} = \frac{\sigma V}{(2\pi)^3} \quad (6.14)$$

So, compared to the standing-wave, or hard-wall boundary conditions above, are there fewer  $k$ -points, as there is more volume per  $k$ -point? No, because we now count wavevectors  $\mathbf{k}$  from all eight octants of the three-dimensional wavevector space, whereas for standing wave boundary conditions, states with wavevector  $(\pm k_x, \pm k_y, \pm k_z)$  are actually the same, and so we have to limit our sums to one octant, as shown in Fig. 6.3. This compensates for the lower  $k$ -space density of allowed states. For this reason, all sums or integrals come out the same whichever of the two boundary conditions we choose.

The advantage in choosing travelling wave boundary conditions is two-fold. Firstly, it is simpler to work with exponentials than with sine and cosine functions. Secondly, and more importantly, transport processes require particles to move. We can picture a moving particle as a wavepacket constructed from travelling wave solutions, but it is much harder to do this in terms of standing wave solutions. So to model transport processes, it is natural to think in terms of travelling wave boundary conditions.

Of course, we could simply recall the integration over the phase space, done in two previous chapters and find it gives the identical result for the measure of integration:

$$\sum_{\text{states}} = \int d\Gamma = \int \frac{d^3x d^3k}{(2\pi)^3}. \quad (6.15)$$

. Suppose we wish to evaluate a sum over states of the form  $\sum_{\text{states}} f(\varepsilon_{\mathbf{k}})$ , where  $f(\varepsilon_{\mathbf{k}})$  is some function of the energies. Therefore to convert the sum over  $k$  into an integral over  $k$  or energy  $\varepsilon$  we use

$$\sum_{k_x, k_y, k_z} f(\varepsilon_{\mathbf{k}}) \rightarrow \frac{\sigma V}{8\pi^3} \int_0^\infty f(\varepsilon_{\mathbf{k}}) 4\pi k^2 dk = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon, \quad (6.16)$$

where  $g(\varepsilon) d\varepsilon$  is the density of states, which is given by Eq.(5.17) in 3-dimensions. However, the nice factorisation of the integrand that we saw in the classical case (with  $E = p^2/2m$ ) is no longer happening here, so it's necessary to switch to the scalar variable  $\varepsilon$  and face the consequences. We will use Eqs. (6.16) for both fermion and boson systems in forthcoming sections and you should familiarise yourself with the method of turning the sum over states into an integral over  $k$  or  $\varepsilon$  (e.g. make sure you have practiced obtaining the corresponding expressions for  $g(\varepsilon)$  in 2- and 1-dimensions.)

Consider the partition function of a single particle of mass  $m$  in a box of volume  $V$ , calculated in the way we develop here:

$$Z_1 = \sum_{k_x, k_y, k_z} e^{-\beta \varepsilon_k} = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty e^{-\beta \varepsilon} \sqrt{\varepsilon} d\varepsilon \quad (6.17)$$

$$= \frac{\sigma V}{4\pi^2} \left( \frac{2mk_B T}{\hbar^2} \right)^{3/2} 2 \int_0^\infty e^{-x^2} x^2 dx, \quad (6.18)$$

where the substitution  $x^2 = \varepsilon/k_B T$  has been made. The mon-dimensional integral in infinite limits is always equal to a number of order one... here it is equal to  $\sqrt{\pi}/4$ , giving

$$Z_1 = \sigma V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = \frac{\sigma V}{\lambda^3}, \quad (6.19)$$

where  $n_Q(T) = 1/\lambda^3$  could be interpreted as the quantum concentration, although we saw and worked with  $1/\lambda^3$  in the classical gas already.

Of course, you have noted that Eq. (6.19) is the same as we found earlier in Eq. (4.6), apart from the factor of  $\sigma$  which corresponds to an internal degree of freedom of the particle which we will neglect in this discussion. This means that it gives the classical equipartition result for the energy, i.e.,  $U_1 = 3/2k_B T$ . It is worth considering for a moment why this is so here in the case of quantum particle. The procedure we used for replacing the sum over states by an integral is valid when  $k_B T$  is much larger than the maximum separation of the energy levels,  $\Delta E$ , which have appreciable average occupation. This condition is satisfied if the box is large enough (because the separation of the energy levels gets smaller as the box size increases) and/or the temperature is high enough. It turns out that the condition  $k_B T \gg \Delta E$ , is the condition for the system to be in the classical regime, where it can be described as a classical gas. When this condition does not apply the system is in the *quantum regime*. For example, the entropy of the particle would also be given by Eq. (4.10), which does not obey the Third Law of Thermodynamics. To obtain the correct result at very low temperatures or very small box sizes one has to take into account the discrete nature of the energy levels. We will have more to say about this issue later.

### 6.3 Chemical potential of a Fermi gas

The total particle number is:

$$N = \int_0^\infty g(\varepsilon) n(\varepsilon) d\varepsilon = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1}. \quad (6.20)$$

As the temperature changes we have to adjust  $\mu$  so that the integral always gives  $N$ . Unfortunately the integral cannot be expressed in a closed form.

In the zero-temperature limit we note that the Fermi-Dirac distribution of Eq. (6.3) becomes a step function,

$$\langle n_{\mathbf{k}} \rangle = 1 \quad \text{for } \varepsilon_{\mathbf{k}} < \mu, \quad (6.21)$$

$$\langle n_{\mathbf{k}} \rangle = 0 \quad \text{for } \varepsilon_{\mathbf{k}} > \mu. \quad (6.22)$$

In this limit we can evaluate the integral in Eq. (6.20) analytically. The chemical potential at zero temperature is called the Fermi energy,  $\varepsilon_F$ , which is related to the Fermi wave-vector by  $\varepsilon_F = \hbar^2 k_F^2 / 2m$ . We have

$$N = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{2\varepsilon_F^{3/2}}{3}, \quad (6.23)$$

and therefore

$$\mu_F(T \rightarrow 0) \equiv \varepsilon_F = \frac{\hbar^2}{2m} \left( \frac{6\pi^2 N}{V\sigma} \right)^{2/3}. \quad (6.24)$$

As the temperature is increased the chemical potential shifts to lower values, and ultimately becomes negative. In the limit  $\beta(\varepsilon - \mu) \gg 1$ , which was the classical limit (5.11), we can expand

$$\frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \Rightarrow e^{-\beta(\varepsilon-\mu)}, \quad (6.25)$$

and the Fermi-Dirac distribution reduces to the classical (Maxwell-Boltzmann) result, where the chemical potential must be large and negative, see §5.3. The variation of the chemical potential with temperature is shown in Fig. 6.4.

## 6.4 Ideal Fermi gas at low temperatures

The full grand thermodynamic potential of the system is given by

$$\Phi = \sum_k \Phi_k = \int_0^\infty g(\varepsilon) \Phi(\varepsilon) d\varepsilon \quad (6.26)$$

$$= -k_B T \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \sqrt{\varepsilon} \ln(1 + e^{-\beta(\varepsilon-\mu)}) d\varepsilon \quad (6.27)$$

$$= -\frac{2}{3} \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon, \quad (6.28)$$

where we have integrated by parts to get the last line. The mean energy can be expressed as the average over all levels with the probability density, given by the product of the mean occupation number of each state  $\varepsilon$  and the density of these states:

$$U = \int_0^\infty \varepsilon n(\varepsilon) g(\varepsilon) d\varepsilon = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon. \quad (6.29)$$

Therefore  $\Phi = -\frac{2}{3}U$ , but please be mindful of what are the natural variables of these two thermodynamic potentials. From its derivation, we see that  $\Phi = \Phi(T, V, \mu)$ , that is, expressed

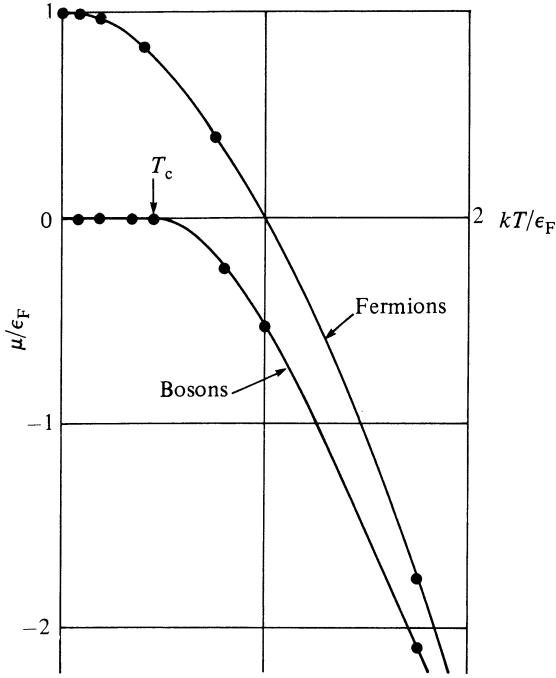


Figure 6.4: Variation of  $\mu$  with  $T$  for non-interacting fermions and bosons at fixed density. From Waldram *The theory of thermodynamics*.

in its proper variables (unlike  $U$ , which should be a function of  $N$  not  $\mu$ ). We also know that  $\Phi = -pV$ , so this gives us directly:

$$p = \frac{\sigma}{6\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1} d\varepsilon. \quad (6.30)$$

This is the equation of state of the ideal Fermi gas, expressed as  $p = p(T, V, \mu)$ .

### Zero temperature limit

It is interesting to look at these expressions in the zero-temperature limit. In this case we don't need to evaluate the complicated Fermi integral but simply use the "trick" employed in (6.23). That is,  $n(\varepsilon) = 0$  for all values of energy  $\varepsilon > \varepsilon_F$  and so

$$U_{T=0} = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{2}{5} \varepsilon_F^{5/2}. \quad (6.31)$$

Now, this expression no longer depends on  $T$  (because it is strictly at  $T = 0$ ), nor on  $\mu$  (because at  $T = 0$  we have  $\mu = \varepsilon_F$ ). Substituting (6.24) and cancelling many factors, we obtain

$$U_{T=0} = \frac{2}{5} \frac{(6\pi^2)^{5/2}}{4\pi^2} \frac{\hbar^2}{2m} \frac{N^{5/3}}{(\sigma V)^{2/3}} = U_0(V, N), \quad (6.32)$$

so now we can find the zero-temperature Fermi pressure in the usual way (ignoring the numerical factor of order one in front):

$$p_F = -\frac{\partial U}{\partial V} \approx \frac{\hbar^2}{2m} \left( \frac{N}{V} \right)^{5/3}. \quad (6.33)$$

## Low temperature limit of the grand potential

We now look at the low (but non-zero) temperature behaviour of the grand potential.

It is sometimes useful to expand the integrands in expressions such as Eq. (6.29) or (6.30) in a series valid at low temperatures,

$$\begin{aligned} I &= \int_0^\infty \frac{f(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1} \\ &\simeq \int_0^{\varepsilon_F} f(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 f'(\varepsilon_F) + \frac{7\pi^4}{360} (k_B T)^4 f'''(\varepsilon_F) + \dots \end{aligned} \quad (6.34)$$

To get the grand potential to second order in  $k_B T$  we substitute  $f(\varepsilon) = \varepsilon^{3/2}$ , to obtain

$$\Phi(T) = \Phi(0) - \frac{\sigma V k_B^2 T^2}{24} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{1/2}, \quad (6.35)$$

and the corresponding expression for the mean energy  $U = -(3/2)\Phi$ . The entropy and heat capacity can now be calculated directly. We deal with electrons, for which  $\sigma = 2$ , so that

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\mu, V} = \frac{k_B^2 T}{3} \frac{V}{2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon_F} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T. \quad (6.36)$$

$$C_V = T \left( \frac{\partial S}{\partial T} \right)_{V, \mu} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T. \quad (6.37)$$

This linear variation of the heat capacity with temperature is characteristic of the Fermi gas (and indeed of Fermi liquids at very low temperature), and it is often written as  $C = \gamma T$ , where  $\gamma$  is the linear temperature coefficient of the heat capacity.

Note that all the above expressions retain a symbolic form for the density of states  $g(\varepsilon)$ . Therefore the conclusions are general, valid for systems of all dimensions (3-d, as well as 2-d and 1-d) in spite of the explicit form of  $g(\varepsilon)$  differing in these cases.

## Application to metals

For temperatures much lower than the Fermi temperature,  $T_F = \varepsilon_F/k_B$ , we can use the low temperature theory described above. In a metal  $T_F$  is very large, typically 50,000 K, so the low temperature theory is extremely good under most conditions.

In a metal the electrons give a contribution to the heat capacity proportional to  $T$ , while the phonons (as zero-mass bosons) give a contribution to the heat capacity proportional to  $T^3$ , which we discuss below in §7.3. Remember the same result you have seen for the black-body radiation, since photons are also zero-mass bosons. The total heat capacity can be approximated by

$$C = \gamma T + \alpha T^3. \quad (6.38)$$

At room temperature the phonon contribution is dominant, but at low temperatures the electron contribution is significant. In Fig. 6.5  $C/T$  is plotted against  $T^2$  for gold, and the values of  $\gamma$  and  $\alpha$  may be extracted from the intercept and slope of the line.

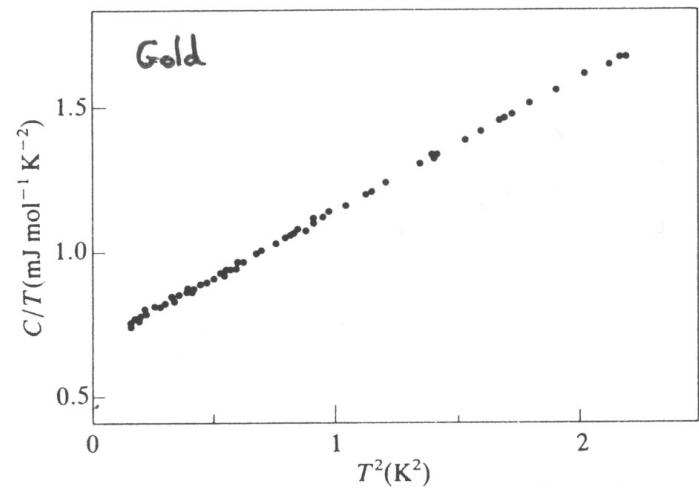


Figure 6.5:  $C/T$  versus  $T^2$  for gold.



# Chapter 7

## Ideal Bose gases

### 7.1 Bose-Einstein statistics for the ideal quantum gas

To obtain the grand partition function for the level of energy  $\varepsilon_{\mathbf{k}}$  for boson particles we use Bose-Einstein statistics,

$$\Xi_{\mathbf{k}} = \sum_{n=0}^{\infty} \left( e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right)^n = \frac{1}{1 - e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}}. \quad (7.1)$$

The grand partition function for the whole system is

$$\Xi = \prod_{\mathbf{k}} \Xi_{\mathbf{k}}, \quad (7.2)$$

and the grand potential is then

$$\Phi = -k_B T \ln \Xi = -k_B T \ln \prod_{\mathbf{k}} \Xi_{\mathbf{k}} = -k_B T \sum_{\mathbf{k}} \ln \Xi_{\mathbf{k}} = \sum_{\mathbf{k}} \Phi_{\mathbf{k}}. \quad (7.3)$$

Each of the energy levels contributes separately to the grand potential and hence separately to other quantities such as the energy and entropy. The mean particle number, entropy and pressure are given by derivatives of the grand potential. All the other thermodynamic potentials can be constructed from these.

For an ideal Bose-Einstein gas the grand potential for level  $\mathbf{k}$  is

$$\Phi_{\mathbf{k}} = -k_B T \ln \left\{ \frac{1}{1 - e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}} \right\} = k_B T \ln \left\{ 1 - e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right\}. \quad (7.4)$$

The average occupation of level  $\mathbf{k}$  is, therefore,

$$\langle n_{\mathbf{k}} \rangle = - \left( \frac{\partial \Phi_{\mathbf{k}}}{\partial \mu} \right)_{T,V} = \frac{1}{e^{\beta(\varepsilon_{\mathbf{k}} - \mu)} - 1}, \quad (7.5)$$

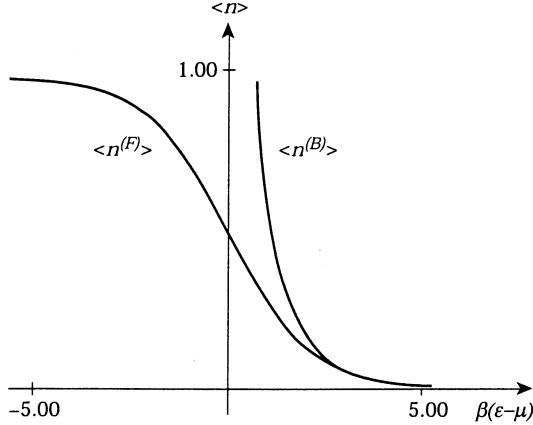


Figure 7.1: The Fermi-Dirac,  $\langle n^{(F)} \rangle$ , and Bose-Einstein,  $\langle n^{(B)} \rangle$ , distributions as a function of  $\beta(\varepsilon_{\mathbf{k}} - \mu)$ .

which is the *Bose-Einstein distribution*. The Fermi-Dirac and Bose-Einstein distributions are numerically plotted in Fig. 7.1.

The entropy from level  $\mathbf{k}$  is

$$S_{\mathbf{k}} = - \left( \frac{\partial \Phi_{\mathbf{k}}}{\partial T} \right)_{V,\mu} \quad (7.6)$$

$$= -k_B \ln \left( 1 - e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} \right) + \frac{k_B \beta (\varepsilon_{\mathbf{k}} - \mu)}{e^{\beta(\varepsilon_{\mathbf{k}} - \mu)} - 1} \quad (7.7)$$

$$= -k_B [\langle n_{\mathbf{k}} \rangle \ln \langle n_{\mathbf{k}} \rangle - (1 + \langle n_{\mathbf{k}} \rangle) \ln(1 + \langle n_{\mathbf{k}} \rangle)]. \quad (7.8)$$

## 7.2 Black-body radiation

Black-body radiation can be thought of as a gas of photons, and because the photons do not interact, it is an ideal gas. Moreover, photons have integer angular momentum, so photons obey Bose statistics.

Because photons are non-interacting, to come into equilibrium they have to interact with a reservoir, which is taken to be the walls of the black-body cavity. Thermal equilibrium is reached by absorption and emission of photons by the walls, so we cannot take  $N$ , the number of photons in the gas, to be constant. Rather, we take  $\mu$  to be constant, and find  $\mu$  from the condition (at constant temperature and volume) that the Helmholtz free energy  $F$  must be minimal with respect to variations in the average number of photons,

$$\left( \frac{\partial F}{\partial N} \right)_{T,V} = 0. \quad (7.9)$$

But  $(\partial F / \partial N)_{T,V} = \mu$ , therefore the chemical potential is zero for black-body radiation. In this case the grand potential and the free energy are the same (recall  $\Phi = F - \mu N$ ).

With  $\mu = 0$  the Bose-Einstein distribution becomes

$$\langle n_{\mathbf{k}} \rangle = \frac{1}{e^{\beta \hbar \omega_{\mathbf{k}}} - 1}, \quad (7.10)$$

which you recognise as the Planck distribution.

The phase space element for radiation is ( $\sigma = 2$ , because photons can have two polarisations)

$$g(\varepsilon) d\varepsilon = \frac{2V}{8\pi^3} 4\pi k^2 dk = \frac{V}{\pi^2 c^3} \omega^2 d\omega, \quad (7.11)$$

where we have used  $\omega = ck$ , and  $c$  is the speed of light. It is interesting to note how this differs from the density of states of real particles (with the rest mass  $m$  and  $\varepsilon = \hbar^2 k^2 / 2m$ ). Photons, as all other elementary excitations, do not have mass and their energy is  $\varepsilon = \hbar\omega$ . Also it is clear that such “quasiparticles” have no classical limit: you can never make  $N\lambda^3/V$  small with  $m \rightarrow 0$ .

From  $g(\varepsilon)$  and the Bose-Einstein distribution for photons, we immediately obtain the energy of black-body radiation in a frequency interval  $d\omega$  at energy  $\omega$ ,

$$E_{\omega} d\omega = \frac{V}{\pi^2 c^3} \frac{\hbar\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}. \quad (7.12)$$

This is the well known Planck radiation law, the result which most clearly marked the beginning of quantum theory. This distribution is shown in Fig. 7.2.

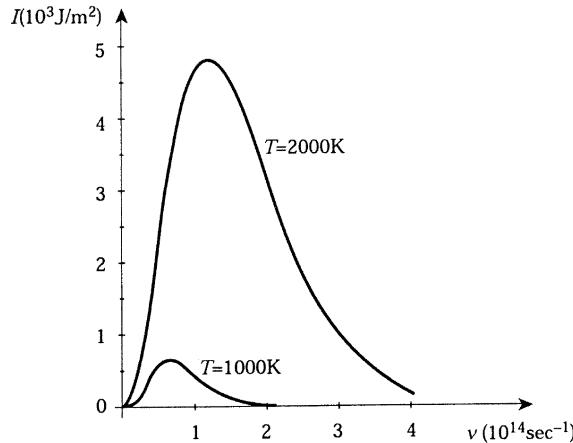


Figure 7.2: Energy density for black-body radiation at 1000 and 2000 K (represented here as proportional to the measurable intensity of light). The total energy densities correspond to the areas under the respective curves.

The total energy density is

$$u = \frac{U}{V} = \frac{1}{V} \int_0^\infty E_{\omega} d\omega = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} T^4. \quad (7.13)$$

This is the full form of the Stefan-Boltzmann law,  $u \propto T^4$ , which Stefan obtained experimentally in 1879 and Boltzmann derived in 1894 using thermodynamics. Obviously Boltzmann could not get the prefactor as it contains  $\hbar$ . The corresponding specific heat varies as  $T^3$ . Note that as

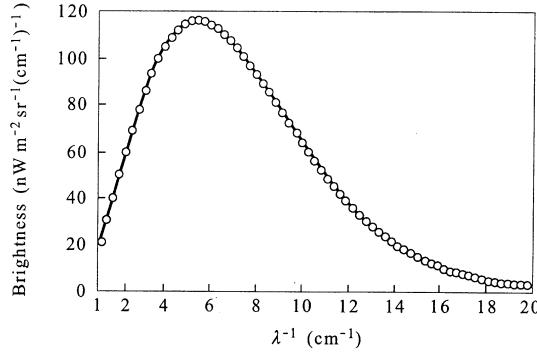


Figure 7.3: The cosmic background radiation as measured by the Cosmic Background Explorer (COBE), after Mather *et al.* (1990). The continuous curve is a fit to the data using the Planck distribution, which yields a temperature of  $T = 2.735 \pm 0.06$  K. Since the Big Bang the background radiation has undergone expansion, with its temperature gradually decreasing.

the temperature goes to zero the total energy density, and hence the total number of photons in the black-body cavity, goes to zero.

A quantity which could be useful in understanding how the particles with zero chemical potential behave is the mean number of photons in a frequency interval  $d\omega$  around  $\omega$ :

$$N(\omega) d\omega = \frac{V}{\pi^2 c^3} \frac{\omega^2 d\omega}{e^{\beta \hbar \omega} - 1}. \quad (7.14)$$

The mean number density,  $n_\omega = N(\omega)/V$ , can be plotted as a function of  $\omega$  at various temperatures, similar to the energy density  $E_\omega$ . Note that as the temperature goes to zero the number of photons in the black-body cavity also goes to zero.

### 7.3 Other elementary excitations

Many (most, in fact!) physical systems cannot be treated as ideal gas: a large number of particles are interacting with each other and the exact description is very difficult. A common approach in physics is to take a system which is close to its ground state and subject it to a weak external influence, for example we might heat it up a bit - or shine some light on it. In this case we would be interested in the small changes to the system caused the external influence. These can often be described in terms of the excited states or *excitations* of the system. Although the interactions between elements of the system may be strong, the excitations from the ground state often interact only weakly with one another. In this case we can treat the excitations as *non-interacting* and do the “ideal gas” statistical mechanics with them. We will briefly discuss such systems, interpreting their low temperature properties in terms of approximate normal modes, or “elementary excitations”. They are characterised by the zero rest mass (and, therefore, de Broglie wavelength  $\lambda \rightarrow \infty$ , i.e. always in the quantum regime), and they are always bosons (mostly with no spin at all).

## Phonons

The atoms of a solid interact very strongly with one another and to calculate the vibrational properties of a solid containing  $10^{23}$  strongly interacting atoms appears at first sight to be a hopeless task. The task is, however, greatly simplified if we note that as long as the magnitude of the vibrations is small, then the interaction potentials between the atoms can be approximated as harmonic. Writing down the equations of motion of the atoms for harmonic interactions, we find eigenstates (normal modes) which are plane waves with a linear dispersion relation at low frequency, flattening off near the Brillouin zone boundary. This is illustrated in Fig. 7.4. These eigenstates are interpreted in terms of a new kind of excitation, called *phonons*. These excitations are non-interacting, so we can use our ideal gas treatment to study their thermodynamics.

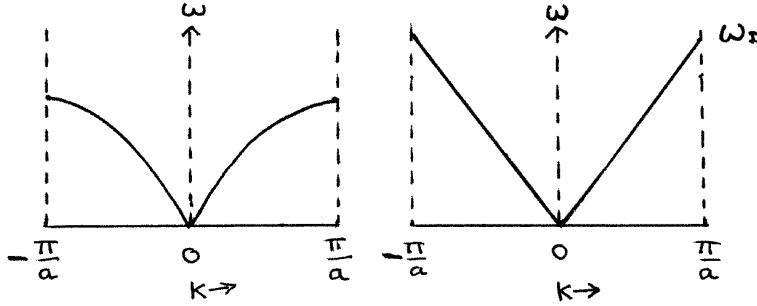


Figure 7.4: A realistic model (left) and the Debye model (right) of the phonon dispersion relation in a simple solid.

Debye developed a simple model of phonons in a solid. He approximated the dispersion relation as a linear function,  $\omega = ck$ , with a cutoff at the Debye frequency,  $\omega_D$ , such that the total number of vibrational modes is correct ( $3N$  modes for  $N$  atoms). The “effective velocity” parameter  $c$  is chosen so as to reproduce the experimental density of states at small  $\omega$ . This is done by choosing

$$\frac{3}{c^3} = \frac{1}{c_L^3} + \frac{2}{c_T^3}, \quad (7.15)$$

where  $c_L$  is the speed of longitudinal waves and  $c_T$  is the speed of transverse waves in the solid. There is one longitudinal mode and two transverse modes at each wave vector.

The condition that the number of vibrational modes is correct is very simple to apply in  $k$ -space, it just means that the volume of  $k$ -space for the modes should be correct. In frequency space we have

$$3N = \int_0^{\omega_D} g(\omega) d\omega = \int_0^{\omega_D} \frac{3V}{2\pi^2 c^3} \omega^2 d\omega = \frac{V \omega_D^3}{2\pi^2 c^3}, \quad (7.16)$$

where the Debye frequency,  $\omega_D$ , is given by

$$\omega_D^3 = \frac{6\pi^2 c^3 N}{V}. \quad (7.17)$$

The internal energy is

$$U = \int_0^{\omega_D} \hbar \omega \frac{3V \omega^2}{2\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1} d\omega. \quad (7.18)$$

At low  $T$  the occupation of the higher frequency modes is negligible so that the range of integration can be extended to infinity, giving

$$U \approx \int_0^\infty \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} d\omega = \frac{3\pi^4}{5} N k_B T \left( \frac{T}{\Theta_D} \right)^3 \quad (7.19)$$

$$C = \frac{dU}{dT} = \frac{12\pi^4}{5} N k_B \left( \frac{T}{\Theta_D} \right)^3, \quad (\text{Low T}) \quad (7.20)$$

where  $k_B\Theta_D = \hbar\omega_D$  defines the Debye temperature. Note that the low  $T$  theory is the same as for photons, except that  $c$  is now the speed of sound rather than the speed of light. In particular we find that the heat capacity is proportional to  $T^3$ .

At high  $T$  the cutoff is required but we can expand the denominator in Eq. (7.18) as follows

$$U = \int_0^{\omega_D} \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} d\omega \approx \int_0^{\omega_D} \hbar\omega \frac{3V\omega^2}{2\pi^2 c^3} \frac{1}{1 + \beta\hbar\omega + \dots - 1} d\omega = 3Nk_B T \quad (7.21)$$

so that

$$C = 3Nk_B, \quad (\text{High T}) \quad (7.22)$$

which is the equipartition result. In between things get a bit messy, but conceptually it is clear, we simply have to evaluate Eq. (7.18).

Fig. 7.5 shows that the Debye model works very well for Al, Cu, and Pb, even though the measured density of states is significantly different from the Debye  $\omega^2$  dependence (see Fig. 7.6). The Debye theory contains only a single parameter, the velocity  $c$ , and it predicts *universal* behaviour of the heat capacity as a function of  $T/\Theta_D$ .

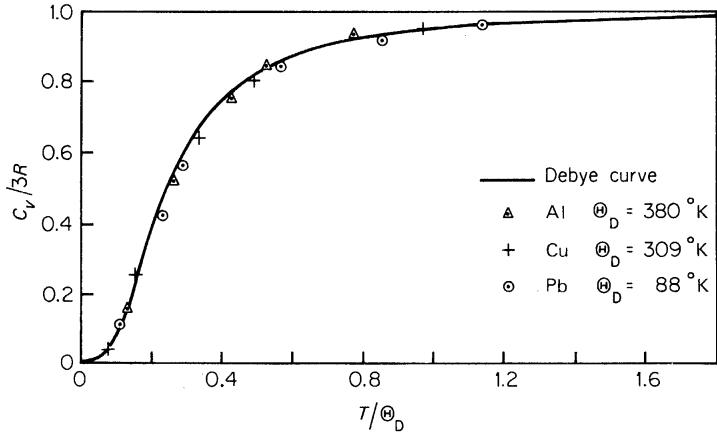


Figure 7.5: The specific heats of Al, Cu and Pb, from experiment and from the Debye model, plotted against  $T/\Theta_D$ .

Why is the Debye theory so good in spite of its obvious crudeness? The most important reason is that it is actually exact at both high and low temperatures. The high- $T$  behaviour is correctly reproduced because the number of modes is correct. At low frequencies the Debye model correctly reproduces the experimental density of states, which are the only modes excited at low

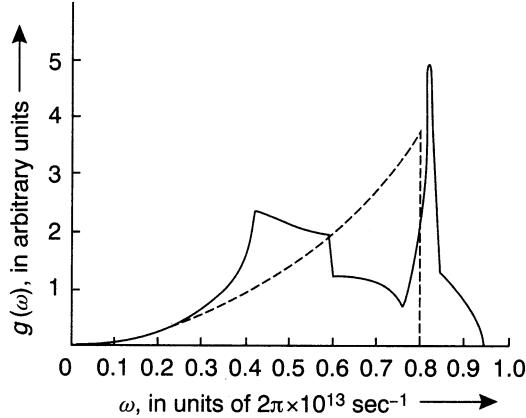


Figure 7.6: The phonon density of states of aluminium (solid line) and of the Debye model (dashed line).

$T$ . A theory which correctly reproduces both the high and low  $T$  behaviour and gives a smooth interpolation between them is likely to work at all  $T$  if the physics of the phenomenon is smooth (e.g., no phase transitions). The second reason why the Debye theory works so well is related to the Bose occupation factor. The Bose occupation factor is a rapidly decaying function of  $\omega$  at low  $T$ , but the Debye density of states is exact at small  $\omega$  so the heat capacity is given correctly. At high  $T$  the Bose factor is a smooth function of  $\omega$  and the large discrepancies between the Debye and experimental densities of states at large  $\omega$  are averaged out by integrating over the frequencies.

The main point is that the underlying dispersion relation, the dimensionality of the system, and Bose-Einstein statistics, completely define the thermodynamic behaviour. Even though we are dealing with very strongly interacting atoms we are able to apply our ideal gas theory by finding normal modes. If we look more deeply, we find that the phonons are only approximate normal modes (because the inter-atomic potential is only approximately harmonic), so our theory is not perfect. For example, in its simplest form it predicts zero thermal expansion, although this fault can be rectified very successfully using the “quasi-harmonic approximation” in which the vibrational frequencies are allowed to depend on the volume.

### Spin waves

A similar example is found in the elementary excitations of a ferromagnetic system in which the size of the moments is fixed. These excitations are called “spin waves”, and they obey Bose statistics. In the simplest case the dispersion relation is  $\varepsilon_{\mathbf{k}} = \alpha k^2$ , which is the same form as for ideal gas particles. The density of states is therefore proportional to  $\sqrt{\varepsilon}$ , and at low temperatures we have, from Eq. 6.16, (note that  $\sigma = 1$  for spin waves)

$$U = \frac{V}{4\pi^2\alpha^{3/2}} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\varepsilon/k_B T} - 1} = \frac{V}{4\pi^2\alpha^{3/2}} (k_B T)^{5/2} \int_0^\infty \frac{x^{3/2} dx}{e^x - 1}. \quad (7.23)$$

Using  $C = dU/dT$  we find that the spin wave heat capacity should be proportional to  $T^{3/2}$ , which is seen experimentally. Note that we have obtained this result purely from knowing the

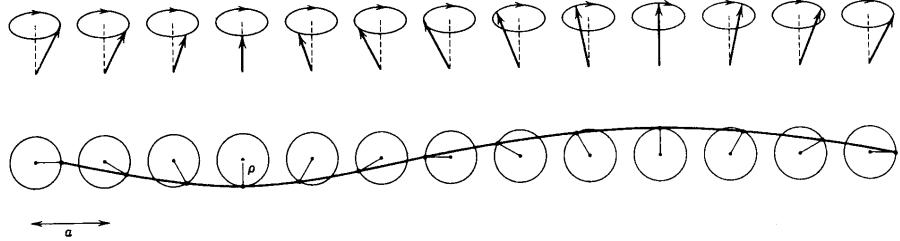


Figure 7.7: Classical picture of a spin wave in a ferromagnet. In the ground state all the spins are parallel, but when a spin-wave excitation is present the spin vectors precess, with successive spins being advanced by a constant phase angle. The line drawn through the ends of the spins in the lower picture shows the wavelength of the excitation.

dispersion relation and that spin waves obey Bose statistics.

Historically, most of these results went in the opposite direction, first a certain temperature dependence of the heat capacity was observed, which was interpreted in terms of some underlying “elementary excitation”, whose dispersion relation was inferred from  $C(T)$ . This was the case with phonons, the vanishing of the heat capacity at low temperatures led Einstein to try and interpret the thermal energy of vibration of a lattice in terms of quantised simple harmonic oscillators and, soon after, Debye produced a more accurate theory by finding the normal modes of the entire lattice.

In the case of electrons, the linear temperature dependence of the heat capacity was known long before an adequate theory was found, and both Einstein and Fermi attempted to apply their quantum gas theories to obtain a linear heat capacity (Fermi was successful). It is quite amazing, really, that you can treat electrons in a metal as being non-interacting particles, given the very strong Coulomb repulsion between them. Indeed, it is rather too good to be true! It turns out that it is often good enough to ignore the interactions between electrons (or include them in an approximate manner using simple concepts such as effective mass) when calculating excitations, but they can *never* be ignored when calculating ground state properties which depend on the chemical bonding between atoms (e.g., the frequencies of atomic vibrations).

### Quantum liquids $^4\text{He}$ and $^3\text{He}$

We will now apply these ideas to the behaviour of the quantum liquids  $^4\text{He}$  and  $^3\text{He}$ . The first somewhat surprising result is that neither isotope of helium has a solid phase at atmospheric pressure, they liquefy at 4.2 K and 3.2 K, respectively, and remain liquids down to absolute zero (or as close as anyone has been able to take them).

The reason that they remain liquid is that the energy of their zero point motion is comparable to the binding energy of their inter-atomic potential. The inter-atomic potential, which arises from the combination of a van der Waals attractive force and a hard core repulsion, has a depth of about  $\epsilon/k_B \sim 10$  K, with the minimum occurring at a separation of 2.9 Å. To understand this we have to calculate the kinetic energy of zero point motion. From the Heisenberg uncertainty principle, the kinetic energy of a particle of mass  $m$  confined within a box of volume  $\Delta x^3$  is

roughly

$$\Delta E \sim \frac{\Delta p^2}{2m} \sim \frac{\hbar^2}{2m\Delta x^2}. \quad (7.24)$$

In the liquid phase well below the boiling point and at atmospheric pressure, the average separation of the He atoms is about 3.73 Å. To calculate the kinetic energy we must take into account the hard core of the atom, which reduces the volume,  $\Delta x^3$ , available to the atom for kinetic motion. An appropriate value is  $\Delta x = 1.2$  Å, giving  $\Delta E/k_B \sim 4$  K, which is of the same order as the potential energy. Remaining in the liquid state allows the helium atoms to keep their kinetic energy down, because they are allowed to move around somewhat more. On the other hand, they would have even lower zero point energy at gaseous densities, but then their potential energy would be higher. The liquid represents a compromise between potential and kinetic energy.

The question which then arises is how the entropy of a liquid can go to zero at  $T \rightarrow 0$ . In fact we already know of one case where this happens, because the electrons in a metal are a kind of liquid at low temperature, and they lose their entropy by condensing into a Fermi gas in which all states below the Fermi energy are occupied.

Fig. 7.8 shows a comparison of the specific heat of pure  ${}^3\text{He}$  and  ${}^4\text{He}$  at low temperature, where both are in the liquid state. There is a very striking difference. Starting with  ${}^3\text{He}$ , we see that below about 0.15 K the specific heat is linear in  $T$ . This is the behaviour we derived for a Fermi gas. This shows us that the elementary excitations of  ${}^3\text{He}$  must correspond to excitations which are linear in  $k$  about some Fermi surface. The detailed theory of these excitations was worked out by Landau in his remarkable papers on “Fermi liquid theory” of 1957 and 1958.

Below 0.6 K,  ${}^4\text{He}$  shows a specific heat proportional to  $T^3$ , which is the same behaviour as we found for phonons. Moreover, as the temperature is increased there is an abrupt increase in the specific heat at about 0.6 K. Landau postulated that the lowest energy elementary excitations in  ${}^4\text{He}$  are phonons (i.e., sound waves in the liquid), while the upturn above 0.6 K he ascribed to a dip in the dispersion relation which in effect produces a large number of nearly degenerate states with energy  $\Delta$ , called rotons. Landau calculated  $\Delta$ , and his results were later confirmed by neutron scattering experiments (see Fig. 7.8).

## 7.4 Bose condensation at low temperatures

For black-body radiation and all quasiparticles (elementary excitations)  $\mu$  is fixed at zero and  $N$  varies, but in a gas of real atoms  $N$  is constant and  $\mu$  varies with temperature.  $N$  is calculated by integrating over the Bose-Einstein distribution,

$$N = \int_0^\infty n(\varepsilon)g(\varepsilon) d\varepsilon = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}. \quad (7.25)$$

This is a messy integral, but we can see what happens by looking at the integrand as a function of temperature (see Fig. 7.9). We expect the chemical potential to be large and negative at high temperatures, so that  $n \ll 1$  for all  $\varepsilon$ . As the temperature is reduced, in order to keep the area under the curve constant the chemical potential must become less negative. As a result the shape of  $n(\varepsilon)g(\varepsilon)$  changes. Note that the chemical potential cannot be zero or positive,

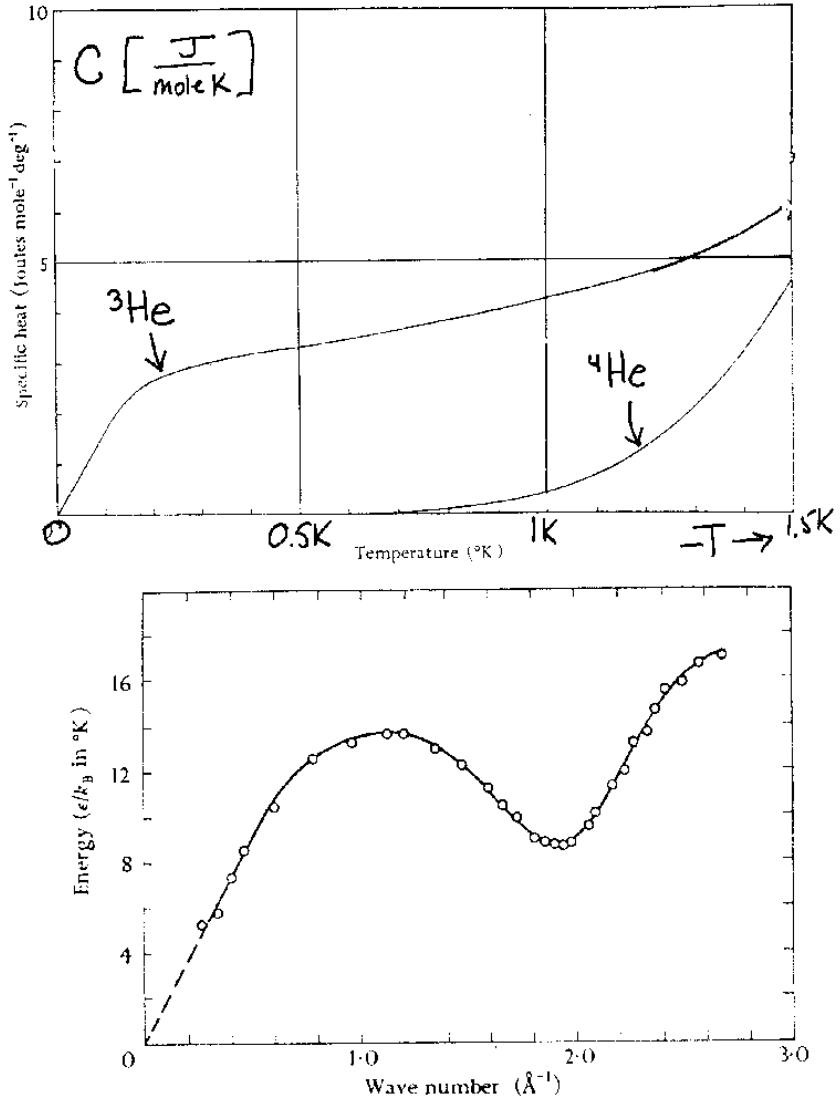


Figure 7.8: Comparison of the low temperature specific heats of <sup>4</sup>He and <sup>3</sup>He. This difference arises because <sup>3</sup>He is a fermion, while <sup>4</sup>He is a boson. The lower figure shows the measured dispersion curve for the elementary excitations in liquid <sup>4</sup>He.

because the occupation number at energy  $\varepsilon = \mu$  would become infinite, which conflicts with our assumption that  $N$  is finite. We see in Fig. 7.9 that below some temperature (between 5 and 10 K on the figure), even for  $\mu \rightarrow 0_-$  the area under the curve cannot be preserved, and at 1 K the area is very far from being equal to the area under the 20 K curve, even with  $\mu$  effectively zero. Einstein realised that the atoms which are ‘disappearing’ from the integrand are piling up in the ground state, and the occupation number of the ground state is proportional to the size of the system, which is known as ‘macroscopic occupation’. We have in effect made a mistake in assuming that we can always replace the sum over  $k$ -states with an integral over energy.

It is perhaps easiest to understand this situation starting from  $T = 0$ , where all  $N$  particles are in the ground state, that is,

$$\lim_{T \rightarrow 0} n_{\varepsilon=0} = \lim_{T \rightarrow 0} \frac{1}{e^{-\beta\mu} - 1} = N. \quad (7.26)$$

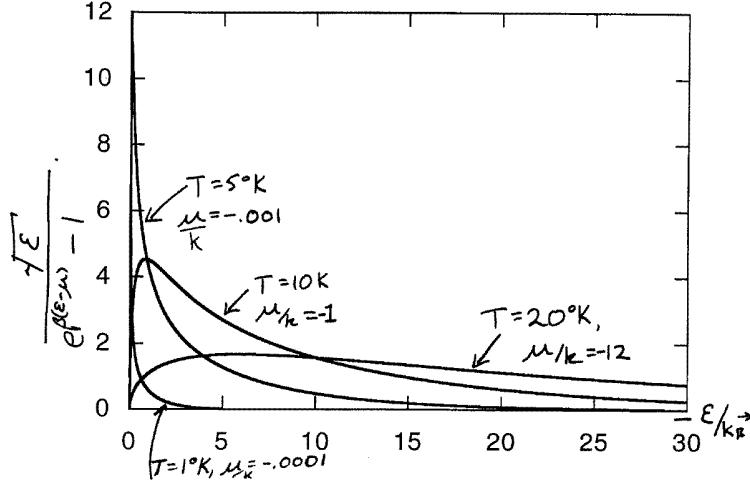


Figure 7.9: Integrand of Eq. 7.25. We try to change  $\mu$  as  $T$  changes, to keep the area under the curves constant. At low temperature this becomes impossible, without making  $\mu$  positive, which causes infinite occupation numbers in some levels (and is thus not allowed).

For  $N \sim 10^{23}$  this means that  $e^{-\beta\mu}$  is equal to 1 to within  $10^{23}$  decimal places (!), and we can Taylor expand to get

$$-\frac{\mu}{k_B T} \sim \frac{1}{N} \quad \text{or} \quad \mu \simeq -\frac{k_B T}{N}. \quad (7.27)$$

For  $T = 1$  K we have  $|\mu| \sim 10^{-46}$  J, which is much less than the energy of the lowest excited state of the system. Therefore at low temperatures  $\mu \simeq 0$ , while at high temperatures  $\mu$  becomes large and negative, see Fig. 7.10.

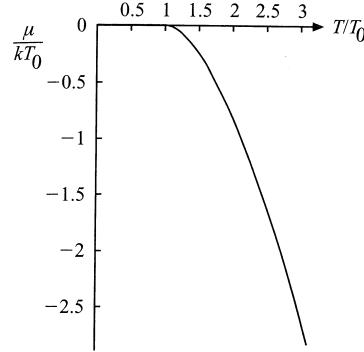


Figure 7.10: The chemical potential as a function of temperature in an ideal Bose gas.

At finite temperatures we treat the particles in the ground state differently from those in the excited states, calculating the number of particles in the excited states by setting  $\mu = 0$ ,

$$N(\varepsilon > 0) = \frac{\sigma V}{4\pi^2} \left( \frac{2mk_B T}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\sqrt{x} dx}{e^x - 1} = 2.612 \sigma V n_Q(T) \equiv N \left( \frac{T}{T_0} \right)^{3/2}, \quad (7.28)$$

where we have earlier called  $n_Q(T) = 1/\lambda^3$  the *quantum concentration*. Remember that  $\lambda = \sqrt{2\pi\hbar^2/(mk_B T)}$  is the thermal de Broglie wavelength. The number of particles in the ground

state (known as the “condensate”) is then

$$N_0 = N \left[ 1 - (T/T_0)^{3/2} \right]. \quad (7.29)$$

The temperature  $T_0$ , above which the ground state is no longer macroscopically occupied, is known as the *Bose condensation temperature*. The occupation numbers of the condensate and of the excited states are shown in Fig. 7.11.

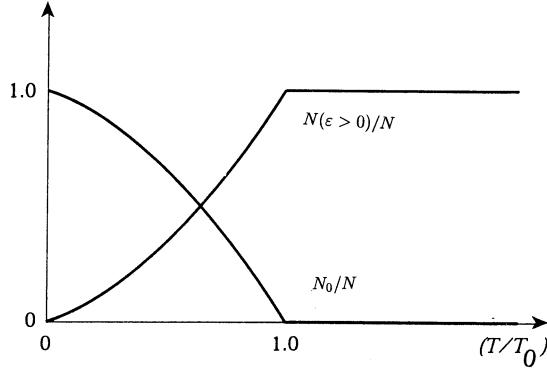


Figure 7.11: The fraction of the particles in the ground state,  $N_0/N$ , and in the excited states,  $N(\varepsilon > 0)/N$ , as a function of temperature.

### Energy and heat capacity for Bose-Einstein condensation

We can calculate the energy and heat capacity of a Bose-Einstein gas straightforwardly. Only the atoms not in the condensate contribute to the energy. Using the standard formula for evaluating sums over phase space, see Eq. (6.16), we have

$$U = \int_0^\infty \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} g(\varepsilon) d\varepsilon = \frac{\sigma V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} - 1} d\varepsilon. \quad (7.30)$$

Below  $T_0$  we can set  $\mu = 0$ , which gives

$$U = \frac{2\sigma V}{\sqrt{\pi}} n_Q(T) k_B T \int_0^\infty \frac{x^{3/2} dx}{e^x - 1}, \quad (7.31)$$

(remember  $n_Q(T) = 1/\lambda^3$  is the quantum concentration.) The integral is equal to  $1.005\sqrt{\pi}$ , and we obtain

$$U \approx 2\sigma V n_Q(T) k_B T \propto T^{5/2}. \quad (7.32)$$

The heat capacity is given by

$$C(T) = \left( \frac{\partial U}{\partial T} \right)_V = \frac{5}{2} \frac{\sigma k_B V}{\sqrt{2}} n_Q(T) \propto T^{3/2}. \quad (7.33)$$

Increasing the temperature to well above the Bose-Einstein condensation temperature we move into the classical regime, where the heat capacity is  $\frac{3}{2} N k_B$ .

The Bose-Einstein condensate was, for a long time, considered a theoretical oddity. With the discovery of superfluidity in liquid  ${}^4\text{He}$ , however, there was evidence that it is a real phenomenon.  ${}^4\text{He}$  shows a “ $\lambda$ ”-transition at  $T_0 = 2.17 \text{ K}$ , where the condensate is a superfluid (zero viscosity and entropy). In liquid helium, the atoms are so close to each other that inter-atomic forces are important. These interactions are not included in the calculations for the Bose-Einstein condensate so far, and they produce significant corrections to the theory, which are apparent from Fig. 7.12 (see also §7.3).

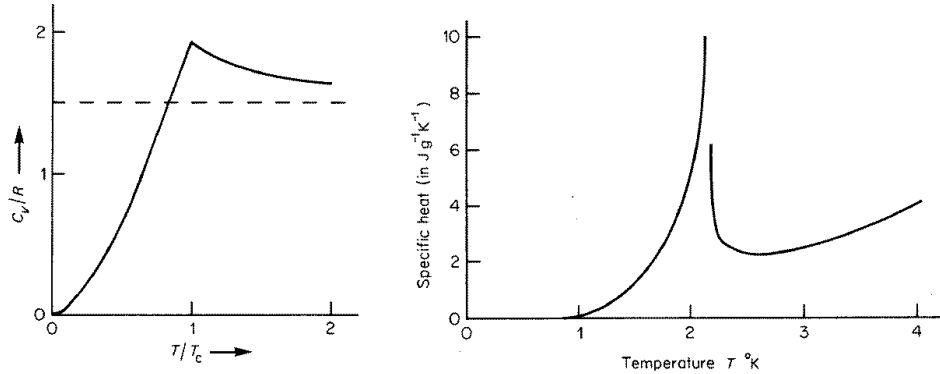


Figure 7.12: The specific heat in the ideal gas theory of Bose-Einstein particles and in  ${}^4\text{He}$ .

In 1995 Bose-Einstein condensation was discovered in a very nearly ideal gas, consisting of a dilute supersaturated vapour of rubidium-87 atoms with a density of  $2.5 \times 10^{12} \text{ atoms per cubic centimetre}$ , at a temperature below about 100 nanokelvin. The measurement is very elegant, and employs some interesting thermodynamic concepts. A simple description is given by C. J. Wieman, *Am. J. Phys.* 64 July 1996, p. 847. The atoms are trapped in a magneto-optic trap, and then cooled by a novel kind of evaporative cooling. The momentum distribution of the cooled gas is probed, again using a very elegant technique. The central finding is that the momentum distribution of the gas consists at “high” temperatures (above about 100 nK) of a Maxwell-Boltzmann distribution, while below about 100 nK a very sharp peak in the momentum distribution appears, centred on  $k = 0$  (the lowest energy eigenstate), which is what we would expect upon formation of a Bose condensate. The 2001 Nobel Prize for physics was awarded to Wolfgang Ketterle, Eric Cornell and Carl E. Wieman for this work.

### An exercise: Bose condensation in 2D

It is generally believed that Bose-Einstein condensation occurs only in dimensions  $d \geq 3$ . The argument below is based on number conservation and on peculiarities of the density of states  $g(\varepsilon)$  at the band edge ( $\varepsilon \rightarrow 0$ ). Specifically, in 2D, we have in the usual way

$$N = A \frac{m}{2\pi\hbar^2} \int_0^\infty \frac{d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}. \quad (7.34)$$

Note that we can define the interparticle separation distance  $r$  in terms of article density,  $N/A = 1/r^2$ . To obtain the critical temperature, set  $\mu = 0$ :

$$N = A \frac{m}{2\pi\hbar^2} k_B T_c \int_0^\infty \frac{dx}{e^x - 1}. \quad (7.35)$$

The integral clearly diverges as  $x \rightarrow 0$ , hence we must correctly conclude that  $T_c = 0$ . This effect, that we cannot have an “ordered phase” (in this case, the condensate into a special ground state) in the low-dimensional system (2D and 1D) is related to the so-called *Landau-Peierls instability* and you shall meet it a few more times, in this and other courses.

However, the very same feature that causes the integral above to diverge also makes the system unstable against arbitrary weak perturbations and promotes the appearance of bound states at  $\varepsilon \leq 0$ . This feature can be demonstrated by introducing a single weak, short-ranged potential well at some fixed (random) position on the plane. If sufficiently short-ranged, it will sustain only a single bound state with finite binding energy  $(-\Delta)$ . The modified density of states will then include this single bound state:

$$g(\varepsilon) = \frac{1}{A} \delta(\varepsilon + \Delta) + \frac{m}{2\pi\hbar^2} \Theta(\varepsilon) \quad (7.36)$$

(the step function  $\Theta(\varepsilon)$  is simply to reflect that only  $\varepsilon > 0$  states contribute to the normal phase space element). Now the lowest value that  $\mu$  can take is  $(-\Delta)$  and if there is a non-vanishing  $T_c$ , this has to be determined from the same particle conservation, but with the lowest  $\mu$  factored in:

$$N = A \frac{m}{2\pi\hbar^2} k_B T_c \int_0^\infty \frac{dx}{(e^{\Delta/kT_c}) e^x - 1}. \quad (7.37)$$

Now there is no zero in the denominator at  $x \rightarrow 0$  and the integral can be evaluated in closed form. The result is an explicit expression for  $T_c$ :

$$\frac{2\pi\hbar^2 N}{mA} \equiv \frac{2\pi\hbar^2}{r^2 m} = k_B T_c \ln \left( \frac{1}{1 - e^{-\Delta/kT_c}} \right). \quad (7.38)$$

For any  $\Delta > 0$  this equation always has a solution for  $T_c$ . The r.h.s. increases monotonically with  $T_c$  from 0 to  $\infty$ , allowing a unique value  $T_c(r)$  for any given particle separation  $r = \sqrt{A/N}$ . Below  $T_c$  the number of particles  $N_0$  condensed into the eigenstate at  $\varepsilon = -\Delta$  is found by the application of the particle-counting principle (7.28) to the present example of 2D and  $\mu = -\Delta$  (and using the same integral again):

$$\begin{aligned} N(\varepsilon > 0) &= A \frac{m}{2\pi\hbar^2} k_B T \int_0^\infty \frac{dx}{(e^{\Delta/kT}) e^x - 1}, \\ \text{so } N_0 &= N - N(\varepsilon > 0) = A \frac{m}{2\pi\hbar^2} k_B \cdot (T_c - T) \cdot \ln \left( \frac{1}{1 - e^{-\Delta/kT_c}} \right) \\ &= N \left( 1 - \frac{T \ln(1 - e^{-\Delta/kT})}{T_c \ln(1 - e^{-\Delta/kT_c})} \right). \end{aligned} \quad (7.39)$$

# Chapter 8

## Non-ideal Gases and Liquids

In the previous chapters we dealt with particles or excitations which were (approximately) non-interacting. This is a very useful approach, but if one wants to know the equation of state of a material there is no alternative to dealing with the interactions between the particles. In general a quantum mechanical approach is necessary to describe these interactions accurately. In this section we deal with liquids and imperfect gases, describing the interactions by a simple central inter-atomic potential. We can then use classical statistical mechanics to calculate the equation of state.

### 8.1 Virial theorem

This approach offers a neat way to arrive at an equation of state. The classical virial  $\mathcal{V}$ , introduced by Clausius in 1870, is defined as

$$\mathcal{V} = -\frac{1}{2} \sum_i \mathbf{r}_i \cdot \mathbf{f}_i, \quad (8.1)$$

where  $\mathbf{r}_i$  and  $\mathbf{f}_i$  are, respectively, the position of, and the force acting on, the  $i^{th}$  particle. From Newton's second law we find that

$$\mathcal{V} = -\frac{1}{2} \sum_i \mathbf{r}_i \cdot m_i \frac{d\mathbf{v}_i}{dt} = -\frac{1}{2} \sum_i m_i \frac{d}{dt}(\mathbf{r}_i \cdot \mathbf{v}_i) + \sum_i \frac{1}{2} m_i \mathbf{v}_i^2. \quad (8.2)$$

Consider a liquid consisting of  $N$  particles in a container of volume  $V$ . The value of  $\mathbf{r}_i \cdot \mathbf{v}_i$  can only fluctuate between finite limits. Over a long period, its time derivative must therefore average to zero, which leads to

$$\langle \mathcal{V} \rangle = \sum_i \frac{1}{2} m_i \langle v_i^2 \rangle = \langle K.E. \rangle = \frac{3}{2} N k_B T. \quad (8.3)$$

The mean virial is equal to the mean kinetic energy. This is Clausius' *virial theorem*.

For our system in its container the force on each particle, and hence the mean virial, is the sum of two parts, the external virial due to the pressure forces exerted on the particles by the walls, and the internal virial due to forces acting between particles, i.e.,

$$\langle \mathcal{V} \rangle = \langle \mathcal{V}_{\text{ext}} \rangle + \langle \mathcal{V}_{\text{int}} \rangle. \quad (8.4)$$

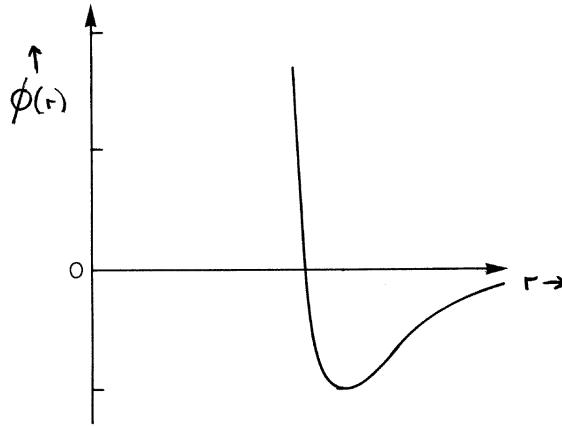


Figure 8.1: A Lennard-Jones potential.

We will calculate these two contributions separately. To calculate the external virial we note that the force on an element of the wall is  $p d\mathbf{A}$ . The force on the particles acts inwards and  $d\mathbf{A}$  is directed outwards, so that we have

$$\langle \mathcal{V}_{\text{ext}} \rangle = \left\langle -\frac{1}{2} \sum_i \mathbf{r}_i \cdot \mathbf{f}_{\text{ext},i} \right\rangle = \frac{1}{2} \int_A \mathbf{r} \cdot p d\mathbf{A} = \frac{p}{2} \int_A \mathbf{r} \cdot d\mathbf{A}, \quad (8.5)$$

where the integral is over the surface of the container. Using the divergence theorem we find

$$\langle \mathcal{V}_{\text{ext}} \rangle = \frac{p}{2} \int_A \mathbf{r} \cdot d\mathbf{A} = \frac{p}{2} \int_V \nabla \cdot \mathbf{r} dV = \frac{3}{2} p V. \quad (8.6)$$

As a quick “sanity check” we note that for an ideal gas this is the total virial, and combining Eqs. 8.3, 8.4 and 8.6 we obtain the ideal gas law,  $pV = Nk_B T$ .

To calculate the internal virial, we model the interactions between particles via a potential,  $\phi(r)$  (Fig. 8.1), which for simplicity we assume depends only on the separation of the point-like particles:  $\phi(r_{ij}) = \phi(|\mathbf{r}_i - \mathbf{r}_j|)$ . An example of an interaction potential is the Lennard-Jones 6-12 inter-atomic potential,

$$\phi(r) = 4\epsilon \left\{ \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right\}. \quad (8.7)$$

This potential consists of a short ranged hard-core repulsion and a long ranged van der Waals attraction, which decays as  $1/r^6$ . As an aside, consider an object moving in a potential of the form

$$\phi(r) = \frac{A}{r}. \quad (8.8)$$

In this case the contribution to the internal virial  $-(1/2)\mathbf{r} \cdot \mathbf{f}$  is

$$\frac{1}{2} r \frac{d\phi}{dr} = -\frac{1}{2} \phi, \quad (8.9)$$

and as there is no external virial and hence no pressure,

$$\langle \mathcal{V} \rangle = \langle K.E. \rangle = \langle \mathcal{V}_{\text{int}} \rangle = -\frac{1}{2} \langle P.E. \rangle. \quad (8.10)$$

This result often comes up in the context of orbits in classical dynamics. As a simple example of the quantum virial theorem you might like to verify for yourself that Eq. 8.10 also holds for the ground state of the hydrogen atom, when the proton mass is taken to be infinite.

Now back to our gas. We consider first just two molecules. The virial for such a pair is

$$\mathcal{V}_{ij} = -\frac{1}{2}(\mathbf{f}_{ij} \cdot \mathbf{r}_i + \mathbf{f}_{ji} \cdot \mathbf{r}_j) = \frac{d\phi}{dr_{ij}} \frac{r_{ij}}{2}, \quad (8.11)$$

because  $f_{ji} = -f_{ij}$ . We can then get the contribution to the virial from the forces between the single molecule at  $\mathbf{r}_i$  and all the other molecules  $j$  by integrating over all space:

$$\langle \mathcal{V}_i \rangle = \frac{1}{2} \sum_{j \neq i} \frac{d\phi}{dr_{ij}} r_{ij} = \frac{1}{2} \int_0^\infty n g(r) r \frac{d\phi}{dr} 4\pi r^2 dr, \quad (8.12)$$

where  $g(r)$  is the *radial distribution function* (Fig. 8.2). This function is dimensionless, and it goes to 1 for large  $r$  when no correlation between the particle at  $o$  and at  $r$  is expected (this needs to be revised in an ideal infinite crystalline lattice, where such correlation does persist). The probability density that given a particle at the origin you would find a second particle at distance  $r$  is given by  $ng(r)$ , i.e. the product of particle density  $n = N/V$  and radial distribution function  $g(r)$ .

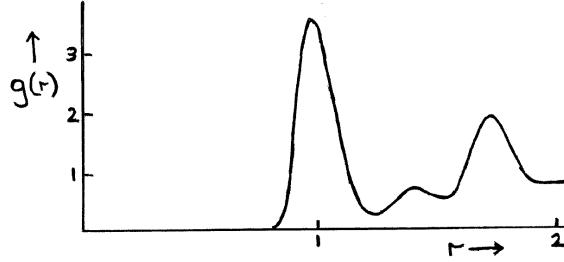


Figure 8.2: A typical radial distribution function for a liquid, calculated using Monte Carlo techniques with a Lennard-Jones 6-12 potential.

To get the total virial, we need to multiply by  $N$ , because each molecule in the gas makes the same contribution to the virial, and then divide by 2, because each contribution to the virial  $\mathcal{V}_{ij}$  is traced back to a pair of molecules. Thus

$$\langle \mathcal{V}_{\text{int}} \rangle = \frac{N}{2} \langle \mathcal{V}_i \rangle = \frac{N}{4} \int_0^\infty 4\pi r^2 n g(r) r \frac{d\phi}{dr} dr \quad (8.13)$$

Combining this expression for the internal virial with the virial theorem (Eq. 8.3) and with our earlier result for the external virial (Eq. 8.6),

$$\langle \mathcal{V} \rangle = \frac{3}{2} N k_B T = \langle \mathcal{V}_{\text{ext}} \rangle + \langle \mathcal{V}_{\text{int}} \rangle = \frac{3}{2} p V + \frac{N}{4} \int_0^\infty 4\pi r^2 n g(r) r \frac{d\phi}{dr} dr \quad (8.14)$$

we obtain the *virial equation of state*:

$$p = nk_B T - \frac{n^2}{6} \int_0^\infty r \frac{d\phi}{dr} g(r) 4\pi r^2 dr. \quad (8.15)$$

### 8.1.1 More on the pair distribution function

The Hamiltonian of the system is

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_{j>i} \phi(r_{ij}), \quad (8.16)$$

where  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ , and the symbol  $\sum_{j>i}$  denotes a sum over all pairs of particles.

The classical partition function is

$$Z = \sum_{\text{microstates}} e^{-\beta \mathcal{H}(\mathbf{r}, \mathbf{p})} = \frac{1}{N!} \int e^{-\beta \mathcal{H}} d^3 r_1 \cdots d^3 r_N \frac{d^3 p_1 \cdots d^3 p_N}{(2\pi\hbar)^{3N}}. \quad (8.17)$$

The momentum integrals can be done straight away, as always with the quadratic kinetic energy part, giving the  $3N$ -th power of quantum concentration

$$Z = \frac{1}{N!} \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3N/2} Z_\phi, \quad (8.18)$$

where the factor is our familiar ideal-gas partition function arising from the momentum integration, while the complicated sum over potential-energy terms gives

$$Z_\phi = \int e^{-\sum_{j>i} \beta \phi(r_{ij})} d^3 r_1 \cdots d^3 r_N, \quad (8.19)$$

which is called the configurational partition function. Unfortunately,  $Z_\phi$  involves very difficult integrals over the interaction potential.

One way to deal with averages involving the interaction energy is to use the two-particle distribution function,

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{Z_\phi} \int e^{-\sum_{j>i} \beta \phi(r_{ij})} d^3 r_3 \cdots d^3 r_N, \quad (8.20)$$

which is the probability density of finding a particle at  $\mathbf{r}_1$  and another particle at  $\mathbf{r}_2$ . For a liquid or gas (with no orientational symmetry breaking as in a crystalline lattice),  $P_2$  depends only on the distance  $|\mathbf{r}_1 - \mathbf{r}_2|$ . It has dimensions of density squared,  $n^2$ . We can divide through by  $n^2$  to obtain the *radial distribution function*, which is dimensionless:

$$g(r_{12}) = \frac{V^2}{N^2} P_2(\mathbf{r}_1, \mathbf{r}_2). \quad (8.21)$$

A typical  $g(r)$  for a liquid is shown in Fig. 8.2. The radial distribution function is small at short distances because of the hard-core repulsion between the atoms. It rises to a peak at the distance of the first shell of neighbours. There is a smaller peak at the second shell but at large

distances  $g(r)$  goes to unity, which is the value it would have in the absence of interactions (so that  $P_2(r) \rightarrow (N/V)^2$ ). We can understand roughly how  $g(r)$  will change when  $T$  and  $V$  are altered. If the system is compressed we expect the peaks of  $g(r)$  to move to smaller separations, and if  $T$  is increased we expect the peaks to become less pronounced as the thermal motion smears them out.

We can find a very useful approximation to the radial distribution function which is accurate at low densities. We rewrite the two-particle distribution function of Eq. (8.20) as

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) e^{-\beta\phi(r_{12})} \frac{\int e^{-\beta\sum'_{j>i}\phi(r_{ij})} d^3r_3 \cdots d^3r_N}{\int e^{-\beta\sum_{j>i}\phi(r_{ij})} d^3r_1 \cdots d^3r_N}, \quad (8.22)$$

where the primed summation indicates that we have removed the  $\phi(r_{12})$  term. At very low densities the integrals over particles 3, 4, ...,  $N$  in the numerator mostly involve configurations in which these particles are distant from each other and from particles 1 and 2, and therefore we can set all the  $\phi(r_{ij})$  inside the integral to zero. In the denominator particles 1 and 2 are also far apart for almost all configurations, so we can again set all the  $\phi(r_{ij})$  inside the integral to zero. Therefore

$$P_2(\mathbf{r}_1, \mathbf{r}_2) \simeq \frac{N(N-1)}{V^2} e^{-\beta\phi(r_{12})}, \quad (8.23)$$

and, as  $N$  is large,

$$g(r) \simeq g_0(r) = e^{-\beta\phi(r)}, \quad (8.24)$$

where we use the term  $g_0(r)$  to express the fact that in this approximation  $g(r)$  is explicitly independent of density – more on this in the section on the virial expansion, below. We can see that this form has the right sort of behaviour;  $\phi(r=0) = \infty$ , so that  $g_0(r=0) = 0$ , and  $\phi(r=\infty) = 0$ , so that  $g_0(r=\infty) = 1$ . Also  $g_0(r)$  takes its maximum value at the minimum in  $\phi(r)$ , which seems sensible.

The key quantities in the classical statistical mechanics of liquids are the inter-molecular potential and the radial distribution function. For simple liquids such as those of the noble gases Ne, Ar etc., the Lennard-Jones potential works very well. The Lennard-Jones potential also works well for He, but in this case the effects of quantum statistics are important. The Lennard-Jones potential normally gives a poor description of systems with strong ionic, covalent or metallic bonding. For ionic bonding one should include the long-range Coulomb forces, for covalent materials one needs directional bonding forces, and in metals the interaction energy is not well described by a sum of pairwise terms. Also, if the molecules are far from spherical or have significant dipole moments the inter-molecular potentials will depend on the relative orientation of the molecules.

Radial distribution functions can be measured using x-ray or neutron diffraction techniques. They can also be calculated using Monte Carlo or Molecular Dynamics methods. Monte Carlo methods are statistical techniques for generating ensembles of configurations,  $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ , distributed according to a known probability distribution. In classical Molecular Dynamics methods the molecules are moved according to Newton's laws in what amounts to a “computational experiment”. An important modern development is the use of computational quantum mechanical techniques to calculate the interaction energy, which can readily be combined with the classical theory of liquids developed here.

### 8.1.2 Internal energy

Calculating the internal energy, we find

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} N k_B T - \frac{\partial}{\partial \beta} \ln Z_\phi. \quad (8.25)$$

The  $Z_\phi$  term gives

$$-\frac{\partial}{\partial \beta} \ln Z_\phi = \frac{1}{Z_\phi} \int \sum_{j>i} \phi(r_{ij}) e^{-\sum_{j>i} \beta \phi(r_{ij})} d^3 r_1 \cdots d^3 r_N \quad (8.26)$$

$$= \frac{N(N-1)}{2Z_\phi} \int \phi(r_{12}) e^{-\sum_{j>i} \beta \phi(r_{ij})} d^3 r_1 \cdots d^3 r_N, \quad (8.27)$$

where the last line follows because there are  $N(N-1)/2$  terms in the sum. Substituting from Eqs. 8.19, 8.20 and 8.21 we find

$$U = \frac{3}{2} N k_B T + \frac{1}{2} \int \phi(r_{12}) P_2(\mathbf{r}_1, \mathbf{r}_2) d^3 r_1 d^3 r_2 = \frac{3}{2} N k_B T + \frac{N^2}{2V} \int_0^\infty \phi(r) g(r) 4\pi r^2 dr. \quad (8.28)$$

In retrospect this result is obvious; the internal energy is the sum of the kinetic energy, which follows from equipartition, and the potential energy that is evaluated here in some average manner.

Unfortunately, even if we knew  $\phi(r)$  and had  $g(r)$  as a function of  $T$ ,  $V$  and  $N$  we wouldn't have enough information to do the complete thermodynamics of liquids, because  $T$ ,  $V$  and  $N$  are not the natural variables of  $U$ . This is why we had to employ the virial theorem earlier on to arrive at the equation of state.

$$p = nk_B T - \frac{n^2}{6} \int_0^\infty r \frac{d\phi}{dr} g(r) 4\pi r^2 dr. \quad (8.29)$$

The expression for  $U(T, V, N)$  and the equation of state give a great deal of equilibrium thermodynamic information. For a complete description we also need a “non-mechanical” quantity such as the chemical potential. The chemical potential can also be written in terms of the radial distribution function, although the dependence is more complicated.

Although we now have nice expressions for the equation of state and for the internal energy, we would need to know the radial distribution function to calculate anything. We now turn to a series expansion of the equation of state, which enables us to go a bit further, still:

## 8.2 Virial expansion

If we start off with a very dilute gas, interactions are unimportant, and the equation of state will approach the ideal gas law. As density increases, we may expect increasing corrections to the ideal gas law. This is the motivation for the *virial expansion*, which expresses the equation of state in terms of increasing powers of density:

$$\frac{p}{k_B T} = n + B_2(T) n^2 + B_3(T) n^3 + \dots \quad (8.30)$$

The  $m^{th}$  virial coefficient,  $B_m(T)$ , reflects the  $m$ -body correlations in the equation of state. Mayer developed a diagrammatic recipe which (in principle) allows each coefficient to be calculated.

The radial distribution function  $g(r)$  likewise depends on the density. If we expand it in powers of  $n = N/V$ ,

$$g(r) = g_0(r) + g_1(r) n + g_2(r) n^2 + \dots, \quad (8.31)$$

and substitute into the virial equation of state of Eq. 8.29, we can link the coefficients  $B_m$  in the virial expansion to coefficients  $g_{m-2}$  in the expansion of the radial distribution function.

The virial expansion is not useful at liquid densities because it only converges when the distance between molecules is much greater than their size. However, the virial expansion gives an excellent description of imperfect gases at low densities, when only pair interactions between particles are relevant. To calculate  $B_2(T)$ , we can use our earlier approximate result for the leading order contribution to  $g(r)$  (Eq. 8.24):  $g_0(r) = e^{-\phi(r)}$ .

We substitute  $g_0(r)$  into Eq. 8.15, and integrate by parts:

$$\frac{p}{k_B T} = n - \frac{n^2}{6k_B T} \int_0^\infty 4\pi r^3 \frac{d\phi}{dr} e^{-\phi/k_B T} dr \quad (8.32)$$

$$= n + \frac{n^2}{6} \left\{ 4\pi r^3 e^{-\phi/k_B T} \Big|_0^\infty - \int_0^\infty 12\pi r^2 e^{-\phi/k_B T} dr \right\} \quad (8.33)$$

$$= n + \frac{n^2}{6} \left\{ \int_0^\infty 12\pi r^2 dr - \int_0^\infty 12\pi r^2 e^{-\phi/k_B T} dr \right\} \quad (8.34)$$

$$= n + n^2 \left\{ \int_0^\infty 2\pi r^2 \left( 1 - e^{-\phi/k_B T} \right) dr \right\}, \quad (8.35)$$

where to get Eq. (8.34) we have used the fact that  $e^{-\phi/k_B T}$  is equal to 1 at  $r = \infty$ . Comparing with Eq. (8.30) we see that the second virial coefficient is

$$B_2(T) = \int_0^\infty 2\pi r^2 \left( 1 - e^{-\phi/k_B T} \right) dr. \quad (8.36)$$

Fig. 8.3 shows the second virial coefficient for a gas of particles interacting via the Lennard-Jones 6-12 potential, compared with data for some real gases. At high temperatures the second virial coefficient is dominated by hard core repulsion, and is positive and roughly constant. At low temperatures it is dominated by the van der Waals attraction, and is negative and roughly proportional to  $1/T$ . Experimental values have been determined by careful measurements of  $p$  as a function of density, and the agreement with theory is excellent except where quantum effects are important, when more sophisticated calculations are necessary.

The **Boyle temperature** is defined as the temperature at which the second virial coefficient  $B_2(T)$  passes through zero, see Fig. 8.3. At this point, the gas is nearest to the ideal gas equation,

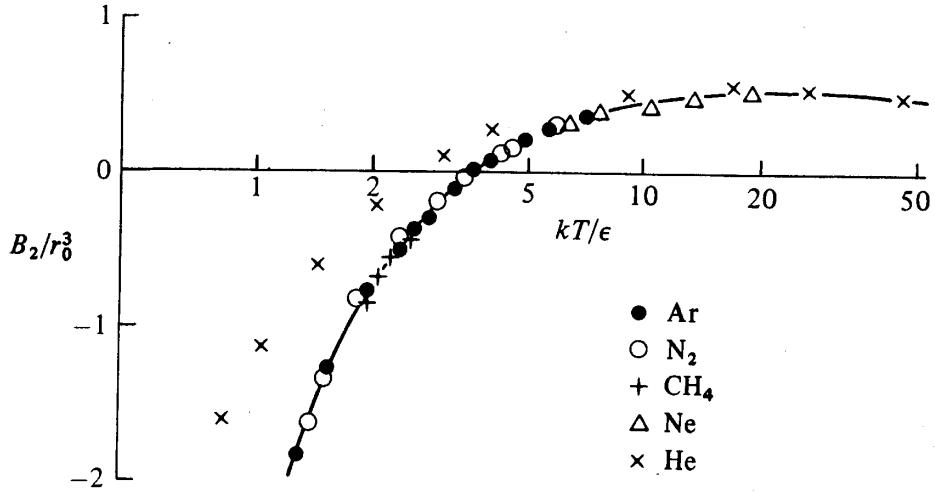


Figure 8.3: The second virial coefficient in reduced units for a Lennard-Jones gas (solid line) as a function of the reduced temperature,  $T^* = k_B T / \epsilon$ , compared with experimental data. Note that at low  $T^*$  the He data does not fit the classical result because of quantum effects.

$pV = Nk_B T$ , essentially because the contribution from the long-range particle attraction on average exactly compensates the short-range repulsion – leaving effectively “non-interacting” particles. At higher temperature the gas is *harder* to compress than an ideal gas (effect of the hard core repulsion), and at lower  $T$  it is *easier* (effect of long-range attraction, pulling the pairs of particles together).

We can motivate the general Eq. (8.36) by a simple argument, finding the mean potential energy of the  $N$ -particle system by counting the interacting pairs:

$$U_{\text{pair}} = \sum_{i>j} \phi(r_{ij}) \approx \frac{N^2}{2} \frac{1}{V} \int \phi(r) d^3r = \frac{N^2}{2} \bar{\phi} \quad (8.37)$$

where  $\frac{1}{2}N^2$  is the number of distinct pairs in the system and we have replaced the pair potential by its average over space,  $\bar{\phi}$ , which is obviously a very crude approximation. This is only meaningful if the potential is weak and slowly-varying, in which case the limit  $\beta \phi(r) \ll 1$  in Eq. (8.36) produces  $B_2 \approx \frac{1}{2} \int \beta \phi(r) d^3r$  and we can make the connection:

$$U_{\text{pair}} \approx \frac{N^2}{V} k_B T B_2(T) . \quad (8.38)$$

This is a “poor man’s” form of the second term in Eq. (8.28). It is also important to note that the average potential energy density of a system of particles with pair interactions,  $u = U/V$ , is proportional to the square of the particle density.

### 8.3 The van der Waals equation of state

Typical inter-atomic potentials can be written as the sum of a short-range repulsive part,  $\phi_r(r)$ , and an long range attractive part,  $\phi_a(r)$ ,

$$\phi(r) = \phi_r(r) + \phi_a(r) , \quad (8.39)$$

so that the partition function becomes

$$Z = \frac{1}{N!} \left( \frac{m}{2\pi\hbar^2\beta} \right)^{3N/2} \int e^{-\sum_{j>i} \beta[\phi_r(r_{ij}) + \phi_a(r_{ij})]} d^3r_1 \cdots d^3r_N. \quad (8.40)$$

Each particle will feel the long range attractive potential from many others and therefore we can write

$$\sum_{j>i} \phi_a(r_{ij}) = \frac{1}{2} \sum_{j \neq i} \sum_i \phi_a(r_{ij}) \simeq \frac{N(N-1)}{2} \frac{1}{V} \int \phi_a(r) d^3r \simeq -\frac{aN^2}{V}, \quad (8.41)$$

where

$$a = -\frac{1}{2} \int \phi_a(r) d^3r. \quad (8.42)$$

The effect of the short range repulsive part is to exclude the particles from a volume around each of them, and so we can write

$$\int e^{-\sum_{j>i} \beta \phi_r(r_{ij})} d^3r_1 \cdots d^3r_N \simeq (V - Nb)^N. \quad (8.43)$$

We now have

$$Z \simeq \frac{1}{N!} \left( \frac{m}{2\pi\hbar^2\beta} \right)^{3N/2} (V - Nb)^N e^{\beta a N^2 / V}. \quad (8.44)$$

Calculating the Helmholtz free energy we obtain

$$F = -k_B T \ln Z = -k_B T \ln \left[ \frac{1}{N!} \left( \frac{m}{2\pi\hbar^2\beta} \right)^{3N/2} \right] - k_B T N \ln(V - Nb) - \frac{aN^2}{V}. \quad (8.45)$$

The pressure is given by

$$p = - \left( \frac{\partial F}{\partial V} \right)_T = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}, \quad (8.46)$$

which is the van der Waals equation of state. The second virial coefficient of a van der Waals gas is  $B_2^{\text{vdW}} = b - a/k_B T$ , and the Boyle temperature is  $k_B T_B^{\text{vdW}} = a/b$ . One of the advantages of this derivation is that we have the full partition function, from which we can calculate all equilibrium thermodynamic information. As we know, the van der Waals equation of state contains a description of a liquid-vapour transition, although it is a rather poor one.



# Chapter 9

## Phase Equilibria and Transitions

A phase transition is the occurrence of an abrupt change in the physical properties of a system when a thermodynamic variable, such as the temperature or pressure, is changed by a small amount. In §2.4 we have examined the coexistence and transitions between the three basic phases of a pure substance: gas, liquid and solid. Fig. 2.10 gives an example of what is called the *phase diagram*, or a map that shows where the different phases occur. In that particular case, the map was drawn in the variables  $p, T$  where the transition between the gas and the liquid was a sharp line, in contrast with the same transition represented in  $p, V$  variables in Fig. 2.9 where we find a broad region of coexistence (along  $V$ ) for any fixed  $p$  and  $T$ .

### 9.1 Examples of phase transitions

Earlier we have already met another example of a phase transition, namely Bose-Einstein condensation. Further examples are the ferromagnetic/paramagnetic phase transition in magnetic materials and the separation of components from a homogeneous mixture. Both examples will be discussed below. A more subtle example is the superconducting phase transition in metals. Phases must be distinguished by an *order parameter*. The idea is to identify a macroscopic quantity which changes abruptly at the phase transition. Some examples of order parameters are given in Table 9.1.

System	Order Parameter
Fluid	Density difference $n_l - n_g$
Binary mixture	Concentration difference $\phi = c - c_X$
Nematic liquid crystal	Degree of alignment $\frac{1}{2}\langle 3\cos^2 \theta - 1 \rangle$
Ferromagnet	Magnetisation $\mathbf{M}$
Ferroelectric	Polarisation $\mathbf{P}$
Superconductor	Complex field $\psi$ , which relates to the density of super-electrons $n_s =  \psi ^2$

Table 9.1: Examples of systems with phase transitions and their order parameters.

### 9.1.1 Magnetism and the Ising model

Consider  $N$  spins,  $\sigma_i$ , which can either point up ( $\sigma = 1$ ) or down ( $\sigma = -1$ ), arranged on a one-, two-, or three-dimensional lattice. The energy (Hamiltonian) for this model is

$$H = -m_0 B \sum_i \sigma_i - J \sum_{ij,nn} \sigma_i \sigma_j, \quad (9.1)$$

where  $B$  is an external magnetic field,  $m_0$  is the magnetic moment of the spin,  $J$  is the interaction energy between nearest-neighbour spins, and  $\sum_{ij,nn}$  means the sum over all pairs of spins which are nearest neighbours.  $J > 0$  favours parallel spins and can lead to the phenomenon of *spontaneous magnetisation*, that is, a non-zero magnetisation,  $M$ , which occurs even when  $B = 0$ , due to the potential energy of interaction between the spins. At  $T = 0$  we expect all the spins to be aligned. If the temperature is increased we expect the spins to become progressively more disordered, so that  $M$  will decrease. At this stage one can raise the objection that if  $B = 0$  then for each configuration of the spins there is another configuration of equal energy in which the direction of every spin is reversed. These two states are of equal energy and have equal weight in the partition function, and therefore the average magnetisation must be zero. This is correct, but at low temperatures the system is likely to be stuck with a net magnetisation of either  $+M$  or  $-M$ , and it is extremely unlikely to jump between the two equivalent macrostates because of the high energy barrier between them. Spontaneous magnetisation is observed in real systems.

The Ising model of Eq. 9.1 has been solved analytically for spins in one-dimension (by Ernst Ising) and in two-dimensions (a mathematical *tour de force* by Lars Onsager). The three-dimensional model has not been solved analytically although accurate numerical results have been obtained.

#### Ising model in 1D

For a one-dimensional chain of interacting spins and with  $B = 0$  it is straightforward to evaluate the partition function. We do it here for the enthusiasts, but this indented section is not essential for the rest of the course and it is not examinable:

Using periodic boundary conditions (where the  $N + 1$  spin is the first spin), we have

$$Z = \sum_{\{\sigma_i\}} \exp \left[ \beta J \sum_{ij,nn} \sigma_i \sigma_j \right] = \sum_{\{\sigma_i\}} \exp \left[ \beta J \sum_{i=1}^N \sigma_i \sigma_{i+1} \right] \quad (9.2)$$

$$= \left( \sum_{X=\pm 1} \exp [\beta J X] \right)^N = [2 \cosh(\beta J)]^N. \quad (9.3)$$

This relies on the fact that the sum in the exponent can be reduced to a sum over a single index,  $X = \pm 1$  depending whether the two neighbours are parallel or antiparallel. Unfortunately this trick doesn't work in higher dimensions. In the presence of external field the calculation is a little more difficult, and we simply quote the result

originally obtained by Ernst Ising in 1925:

$$Z = \left[ e^{\beta J} \cosh(\beta m_0 B) + \sqrt{e^{-2\beta J} + e^{2\beta J} \sinh^2(\beta m_0 B)} \right]^N. \quad (9.4)$$

The free energy  $F(T, N, B) = -k_B T \ln Z$  and the macroscopic magnetisation is given by

$$M = - \left( \frac{\partial F}{\partial B} \right)_{T,N} = \frac{Nm_0 \sinh(m_0 B/k_B T)}{\sqrt{e^{-4J/k_B T} + \sinh^2(m_0 B/k_B T)}}. \quad (9.5)$$

For  $T = 0$ ,  $M = Nm_0$ , as expected, but as  $B \rightarrow 0$ , for any  $T > 0$ , Eq. (9.5) gives  $M = 0$ .

The one-dimensional Ising model shows a phase transition, but only at the exact  $T = 0$ . The reason for this is that it costs very little energy to reverse the direction of a large block of spins on a line. For dimensions greater than one, the Ising model shows a real phase transition as  $B \rightarrow 0$  at a temperature proportional to  $J$ , into a ferromagnetic phase with non-zero magnetisation, while the high-temperature disordered paramagnetic phase has  $M = 0$ . When  $B \neq 0$ , the equilibrium value of  $M$  is finite and varies smoothly with temperature, and therefore no phase transition occurs.

### The Ising model within mean field theory

We now solve the Ising model within a *mean field approximation* known in this case as the Weiss theory. The idea is to focus on a particular spin and assume that the interactions with the other spins can be represented by their average effect. This particular spin is then  $\sigma_i = \langle \sigma \rangle + \delta\sigma_i$  and we assume the fluctuation is small. Now let's replace the pair-interaction term in the Hamiltonian of Eq. (9.1):

$$\begin{aligned} H &= -m_0 B \sum_i \sigma_i - J \sum_{ij} (\langle \sigma \rangle + \delta\sigma_i)(\langle \sigma \rangle + \delta\sigma_j) \\ &= -m_0 B \sum_i \sigma_i - J \sum_{ij} (\langle \sigma \rangle^2 + \langle \sigma \rangle(\delta\sigma_i + \delta\sigma_j) + \delta\sigma_i \delta\sigma_j). \end{aligned} \quad (9.6)$$

Now drop the small term quadratic in fluctuations, and assume that fluctuations are site-independent:

$$\begin{aligned} H &= -m_0 B \sum_i \sigma_i - J \sum_{ij} (\langle \sigma \rangle^2 + 2\langle \sigma \rangle \delta\sigma_i) \\ &= -m_0 B \sum_i \sigma_i - \frac{1}{2} z J \sum_i (\langle \sigma \rangle^2 + 2\langle \sigma \rangle [\sigma_i - \langle \sigma \rangle]), \end{aligned} \quad (9.7)$$

where  $z$ , the coordination number, is the number of nearest neighbours and the  $1/2$  prefactor avoids double-counting, since each bond participates in two spins. Thus we now have an *effective Hamiltonian* which is linear in the variable  $\sigma_i$ , that is, a single-particle two-state system which we certainly know how to solve!

$$H_{\text{eff}} = \frac{1}{2} z J N \langle \sigma \rangle^2 - (m_0 B + z J \langle \sigma \rangle) \sum_i \sigma_i. \quad (9.8)$$

The partition function for a spin is easily evaluated, just like in the case of paramagnetic salt, Eq. (3.38). The only difference is that the external field value is “shifted” by the term representing the mean effect of pair interactions.

$$Z_1 = \sum_{\sigma=\pm 1} \exp \left[ -\frac{zJ\langle\sigma\rangle^2}{2k_B T} - \frac{m_0 B \sigma + J z \sigma \langle\sigma\rangle}{k_B T} \right] \quad (9.9)$$

$$= 2 \cosh \left[ \frac{m_0 B + J z \langle\sigma\rangle}{k_B T} \right] \cdot e^{-\frac{1}{2}\beta z J \langle\sigma\rangle^2}. \quad (9.10)$$

Note that we carry through the constant term in Eq.(9.8); this is not needed for now, but will play a role in the next section. The Helmholtz free energy per spin is

$$F_1 = -k_B T \ln \left( 2 \cosh \left[ \frac{m_0 B + J z \langle\sigma\rangle}{k_B T} \right] \right) + \frac{1}{2} z J \langle\sigma\rangle^2. \quad (9.11)$$

The mean magnetic moment per spin (which is related to the mean value of spin) we obtain in the usual way:

$$m = m_0 \langle\sigma\rangle = - \left( \frac{\partial F_1}{\partial B} \right)_T = m_0 \tanh \left( \frac{m_0 B + J z \langle\sigma\rangle}{k_B T} \right). \quad (9.12)$$

To obtain the spontaneous magnetisation we set  $B = 0$ , which gives

$$\langle\sigma\rangle = \tanh \left( \frac{J z \langle\sigma\rangle}{k_B T} \right), \quad (9.13)$$

and rearranging the exponentials we obtain

$$\frac{T_c}{T} = \frac{1}{2\langle\sigma\rangle} \ln \left( \frac{1 + \langle\sigma\rangle}{1 - \langle\sigma\rangle} \right), \quad (9.14)$$

where the shorthand notation  $T_c = z J / k_B$ . To find  $\langle\sigma\rangle$  as a function of temperature we can substitute values of  $\langle\sigma\rangle$  in the right hand side ( $0 \leq \langle\sigma\rangle \leq 1$ ). A plot of  $\langle\sigma\rangle$  against  $T/T_c$  is given in Fig. 9.1, showing that all the spins are aligned at  $T = 0$  but, as the temperature is increased,  $\langle\sigma\rangle$  decreases and goes to zero at  $T = T_c$ , which is the critical temperature.

The exact and mean field results for  $T_c$  are compared in Table 9.2. Note that the mean field value depends on the number of nearest neighbours, but is otherwise independent of the dimensionality, which is incorrect. The mean field theory is qualitatively incorrect in one dimension because, as we have seen, there is no transition in this case for  $T > 0$ . Note, however, that the mean field theory becomes more accurate as the dimensionality increases. In spite of its many limitations, the mean field approach has one great advantage: the physical problem can usually be solved, while the exact solution is often impossibly difficult.

Lattice	Mean field $k_B T_c$	Exact $k_B T_c$
One-dimensional line	$2J$	No transition for $T > 0$
Two-dimensional square lattice	$4J$	$0.567 \times 4J$
Three-dimensional simple cubic lattice	$6J$	$0.752 \times 6J$

Table 9.2: Critical temperatures for the Ising model in one, two, and three dimensions.

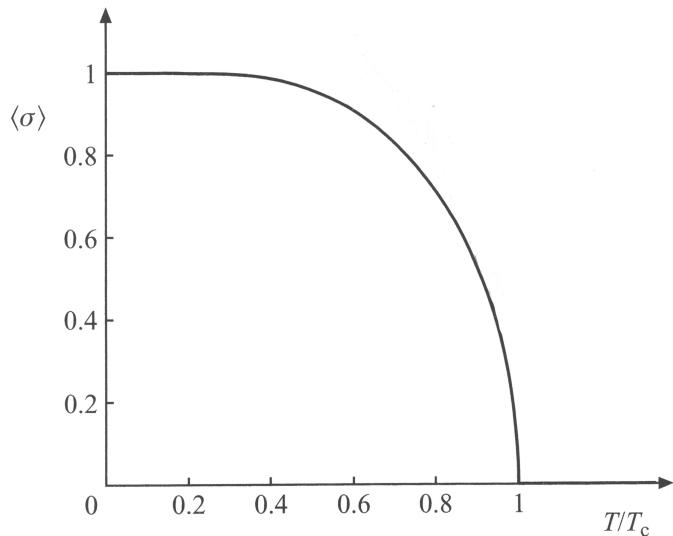


Figure 9.1: The average value of the spin on a site,  $\langle \sigma \rangle$ , as a function of  $T/T_c$  within the Weiss theory.

### 9.1.2 Mixing and phase separation

An important and generic situation of phase coexistence and separation occurs in the problem of mixing. Let us consider a mixture of just two species, so that the total number of particles is  $N = N_A + N_B$ . The entropy of mixing (2.51) has been derived for an arbitrary number of species, now we just have

$$S_{\text{mix}} = -k_B N \sum_i c_i \ln c_i = -k_B N [c_A \ln c_A + (1 - c_A) \ln(1 - c_A)], \quad (9.15)$$

where the concentration (fraction) of species is  $c_i = N_i/N = p_i/p$ , and for just two components  $c_B = 1 - c_A$ . If the system is a non-interacting ideal gas, then the discussion of the earlier §2.5 applies. An ideal gas of different species will always remain homogeneously mixed, because this maximises the entropy and there is no potential energy to benefit from. When particles of our system interact, then – at least for low particle densities – we can estimate the mean energy in terms of the virial expansion. Limiting ourselves to the pair interactions only, the second virial coefficient contribution to the average potential energy of the system (8.38) now gives for each combination of species:

$$U_{AA} \approx \frac{N_A^2}{V} k_B T B_2(AA) \quad (9.16)$$

$$U_{AB} \approx 2 \frac{N_A N_B}{V} k_B T B_2(AB) \quad (9.17)$$

$$U_{BB} \approx \frac{N_B^2}{V} k_B T B_2(BB), \quad (9.18)$$

where each of the  $B_2$  coefficients corresponds to the interaction of the given pair of species, and the factor of 2 in Eqn. 9.17 arises from the distinguishability of species A and B: there is only one way to have an A, A or B, B pair, but there are two A, B pairs, namely A-B and B-A.

Using the species concentrations  $c_A$  and  $c_B = 1 - c_A$ , Eqns. 9.16-9.18 can be recast as:

$$U_{AA} \approx N\epsilon_{AAC_A^2} \quad (9.19)$$

$$U_{AB} \approx 2N\epsilon_{ABC_A}(1 - c_A) \quad (9.20)$$

$$U_{BB} \approx N\epsilon_{BB}(1 - c_A)^2, \quad (9.21)$$

where each energy coefficient  $\epsilon_{ij}$  is related to the corresponding virial coefficient by  $\epsilon_{ij} = k_B T B_2(ij)/v_0$  for a molecular volume  $v_0$ . The  $\epsilon_{ij}$  are more straightforwardly interpreted in terms of a bond energy  $E_{ij}$  and coordination number  $z$ , so that  $\epsilon_{ij} = \frac{z}{2} E_{ij}$ . In this picture,  $Nc_A$  A-particles now each have  $zc_A$  A-type neighbours. We therefore have in total  $Nzc_A^2/2$  A-A bonds (divide by two to avoid double-counting), each with energy  $E_{AA}$ , leading to Eqn. 9.19 and, likewise, the other two internal energy expressions above. We find for the internal energy of the mixture:

$$U_{\text{int}} = U_{AA} + U_{AB} + U_{BB} = N [\epsilon_{AAC_A^2} + 2\epsilon_{ABC_A}(1 - c_A) + \epsilon_{BB}(1 - c_A)^2] \quad (9.22)$$

A negative  $\epsilon_{ij}$  means an effective attraction between molecules of species “i” and “j”, so that the corresponding contribution to the overall potential energy is less than the non-interacting ideal-gas value of zero; positive  $\epsilon_{ij}$  means an effective repulsion and the increase in energy. What is being done here is a “mean field” approximation, that is, the average field (concentration of monomers in this case) is being used instead of the spatially dependent value of concentration.

The energy of the un-mixed (or phase-separated) state is also non-zero. Putting all the species “A” to one side, each A-particle now has  $z$  A-neighbours, giving in total  $zNc_A/2$  A-A bonds and an interaction energy  $U_{AA} = N\epsilon_{AAC_A}$ , and similar for the species “B”. Neglecting the energy of the interface between separated species, we have:

$$U_{\text{unmixed}} = N [\epsilon_{AAC_A} + \epsilon_{BB}(1 - c_A)] \quad (9.23)$$

If we subtract the energy of the unmixed state from Eq. (9.22), and pull out the common concentration-dependent factor, we get the average internal energy of mixing:

$$\begin{aligned} U_{\text{mix}} &= U_{\text{int}} - U_{\text{unmixed}} = N [2\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})] c_A(1 - c_A) \\ &\equiv Nk_B T \chi c_A(1 - c_A), \end{aligned} \quad (9.24)$$

where the shorthand non-dimensional parameter  $\chi$  is defined as a measure of the average interaction energy,  $k_B T \chi = [2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}]$ , or

$$\chi = \frac{1}{k_B T} [2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}]. \quad (9.25)$$

A positive  $\epsilon_{AB}$  (i.e. species “A” and “B” repelling each other) and negative  $\epsilon_{AA}, \epsilon_{BB}$  (each species attracting their like) would result in a large and positive parameter  $\chi$ , leading to the trend for the two species to separate from each other. Evidently, the opposite case of small, or even negative  $\chi$  would promote mixing of species. Combining the mixing entropy and energy terms leads to the free energy for the mixture (or solution of concentration  $c_A = N_A/N \equiv c$ ), expressed in its proper variables  $T, V, N$  (Fig. 9.2):

$$F_{\text{mix}} = Nk_B T \left[ c \ln c + (1 - c) \ln(1 - c) + \chi c(1 - c) \right]. \quad (9.26)$$

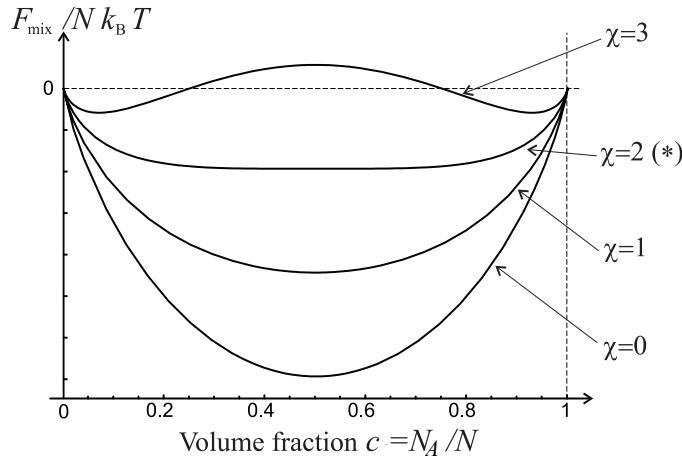


Figure 9.2: Plots of the free energy of mixing (9.26) for different values of the  $\chi$ -parameter. The figure illustrates that the mixture for  $\chi = 3$  is energetically unfavourable compared to the fully phase separated arrangement, whereas for small  $\chi$  values (higher temperatures), it is favourable for the two species to remain fully mixed.

### Spinodal and binodal lines

Fig. 9.2 tells us the answer to an attempt to find a minimum of the free energy of mixing. Differentiating w.r.t. concentration gives

$$\frac{\partial F_{\text{mix}}}{\partial c} = \chi(1 - 2c) - \ln\left(\frac{1-c}{c}\right) = 0 . \quad (9.27)$$

This equation is difficult to solve analytically, but we can see from the plot of free energy that it should have one solution, at  $c = 1/2$  for small and negative  $\chi$  (when we expect the good mixing of species), and three roots at large and positive  $\chi$  (when we might expect demixing to occur), one of which (at  $c = 1/2$ ) is now the maximum. The line of solutions for the minimum of the mixing free energy,  $c^*(\chi)$ , is called the binodal line and is plotted in Fig. 9.3 as the function  $\chi(c^*)$ .

The stability of the mixture at concentration  $c$  against small fluctuations is given by the sign of second derivative:

$$\frac{\partial^2 F_{\text{mix}}}{\partial c^2} = \frac{1}{(1-c)c} - 2\chi . \quad (9.28)$$

The set of inflection points given by the solution of  $\partial^2 F_{\text{mix}}/\partial c^2 = 0$  is called the spinodal line,  $c_s(\chi)$ . It represents the boundary of stability and is plotted in Fig. 9.3 as a dashed line for  $\chi(c_s)$ .

The plot of  $\chi(c)$  in Fig. 9.3 is the phase diagram that maps the regions of different behaviour. Below the binodal line, at any concentration the mixture is stable: the mixing free energy is convex at any value of  $c$ . Above the spinodal line, the values of  $c$  and  $\chi$  are such that the mixture is absolutely unstable and its components separate immediately. The region between the two lines is more complicated, it is the region of *metastability* where one of the phases (mixed or separated) may have a higher free energy than the other, but is prevented from reaching the ground state by an energy barrier; we shall discuss this feature of *first order* phase transitions shortly. Fig. 9.3 also highlights the *critical point* where the region of metastability shrinks to

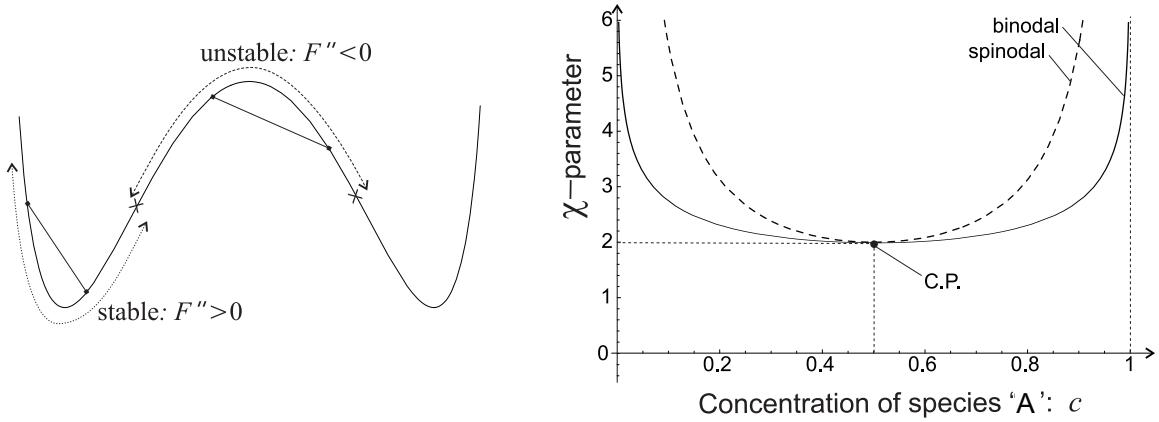


Figure 9.3: [Left] The sketch of  $F_{\text{mix}}(c)$  illustrating stability of the mixture against separation of species. In the convex ( $F'' > 0$ ) region, at any concentration  $c$ , any small fluctuation leading to two nearby regions  $c \pm \Delta c$  leads to the overall free energy increase. A similar fluctuation in the concave ( $F'' < 0$ ) region leads to the decrease of free energy on any small fluctuation and, therefore, instability of the mixture against macroscopic separation. The boundary of stability (labelled by X on this sketch) gives the spinodal line on the phase diagram. — [Right] Plots of the binodal and spinodal lines, as  $\chi(c)$  variation.

zero as its two boundaries coincide. It is easy to find the coordinates of this critical point, from Eq. (9.28) we can find the minimum of the spinodal line:

$$\chi_s = \frac{1}{2c(1-c)} \quad \text{hence} \quad \frac{\partial \chi_s}{\partial c} = \frac{2c-1}{2c^2(1-c)^2} = 0. \quad (9.29)$$

This gives the critical point at  $c_0 = 1/2$  and  $\chi_0 = 2$ , as seen on the plot.

The conclusion is that the least stable mixture is at concentration  $c = 1/2$  (this is obtained assuming that the molecular size of both species was approximately the same,  $v_0$ , otherwise there would be corrections to the above analysis). This mixture has to separate at the lowest value of the effective (repulsive) interaction  $\chi$ .

Since  $\chi$  is inversely proportional to temperature, the phase diagram can be re-plotted in more accessible coordinates  $T, c$  – see Fig. 9.4. Suppose we prepare a good mixture, at some concentration  $c_A$  and temperature  $T_A$  (in the stable region of phase diagram). The easiest way to change the balance between the mixing entropy and potential energy is by reducing the temperature: this corresponds to the point  $A'$  on the phase diagram in Fig. 9.4. This is the absolutely unstable region, corresponding to the convex region on the corresponding high- $\chi$  curve for  $F_{\text{mix}}(c)$  in Fig. 9.2, so the mixture will separate (at constant temperature) into the two regions, each rich in one of the two species. The final state will be given by the minima of the free energy for the value  $\chi$  that corresponds to this temperature  $T_{A'}$ .

## 9.2 First order phase transition

Let us consider the process of quenching and demixing analytically. We start with a system at equilibrium at concentration  $c_X$  (see Fig. 9.4) and allow the concentration to fluctuate, so

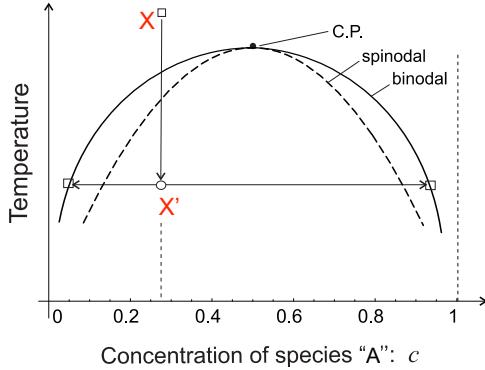


Figure 9.4: The phase diagram of a mixture plotted in  $T, c$  coordinates, with the binodal, spinodal and critical point labelled. An initial mixture, prepared at concentration  $c_A$  at temperature  $T_A$ , after cooling to a temperature inside the demixing region (point  $A'$  on the diagram) will phase separate into the fractions, one rich in “1” (high  $c$ ) and one rich in “2” (low  $c$ ) minima of the mixing free energy.

that a value  $c = c_X + \phi$  is reached. Before going further, we need to consider a subtlety about the free energy of the mixture. It would seem at first that an arbitrary concentration away from  $c = 0.5$  could never be present in equilibrium, because the slope of the free energy versus concentration in Fig. 9.2 is nonzero for most values of  $c$ . In contrast to, for instance, the case of ferromagnetism, in which magnetic moments can flip and thereby convert from one type to another, the total number of A and B particles is still conserved as the system finds stable equilibrium. To consider the practically relevant case when in the mixture the concentration of species A is fixed at some value  $c_X \neq 0.5$ , we need to implement a constraint on  $c$  by using a Lagrange multiplier  $\alpha$ , defining a modified free energy  $F_\alpha(c, T) = F_{\text{mix}}(c, T) - \alpha c$  such that  $\partial F_\alpha / \partial c|_{c_X} = 0$ , i.e.  $\alpha = \partial F_{\text{mix}} / \partial c|_{c_X}$  and the free energy, thus transformed, becomes  $F_{c_X}(c, T) = F_{\text{mix}}(c, T) - \partial F_{\text{mix}} / \partial c|_{c_X} c$ . This means that a straight line is subtracted from the mixing free energy shown in Fig. 9.2 to produce zero slope at the concentration dictated by the external constraint, namely by the amount of the species actually put into the mixture. This is the free energy we would need to consider when analysing phase separation in a mixture with arbitrary starting concentrations.

Assuming  $\phi$  is small we can expand Eq. (9.26) and obtain

$$\frac{F_{c_X}(c) - F_{c_X}(c_X)}{Nk_B T} = -\frac{1 - 2\chi c_X(1 - c_X)}{2c_X(1 - c_X)} \phi^2 - \frac{1 - 2c_X}{6c_X^2(1 - c_X)^2} \phi^3 + \frac{1 - 3c_X + 3c_X^2}{12c_X^3(1 - c_X)^3} \phi^4 + \dots \quad (9.30)$$

Note that the linear term  $\propto \phi = c - c_X$  has disappeared due to the equilibrium condition mentioned above. Fig. 9.5 plots this free energy difference as function of  $\phi$  for an arbitrary  $c_X = 0.4$  and several values of  $\chi$ -parameter, starting from the critical point value  $\chi = 2$  upwards. You can see how on increasing  $\chi$  (or equivalently – decreasing temperature) we pass through the region of metastability. At first, it is clear that any fluctuation  $\phi \neq 0$  increases the free energy and is therefore unfavourable. Starting from  $\chi \geq 2.02$  we see a new minimum developing; this corresponds to crossing the binodal line on the phase diagram. Eventually there is a point ( $\chi \approx 2.035$  for the chosen  $c_X$  value) when there is a new free energy minimum at a finite  $\phi^*$ ; this curve is highlighted. However, there is an energy barrier separating this new state of increased  $c$  from the original  $c_X$ . The barrier persists even when the new “A”-rich state has a significant preference in free energy, preventing the actual separation. Only at a substantially

higher  $\chi$  the barrier finally disappears and the state  $\phi = 0$  (or the initial  $c_X$ ) becomes absolutely unstable: this corresponds to crossing the spinodal line. At higher  $\chi$  (or lower  $T$ ) the mixture immediately separates into the “A”-rich state (and the associated “A” poor state, to conserve the total number of particles). When this happens, the concentration changes discontinuously, with a jump from  $\phi = 0$  to  $\phi = \phi^*$ . This scenario is the essence of the *First order phase transitions*, the other example familiar to you is the liquid-gas transformation.

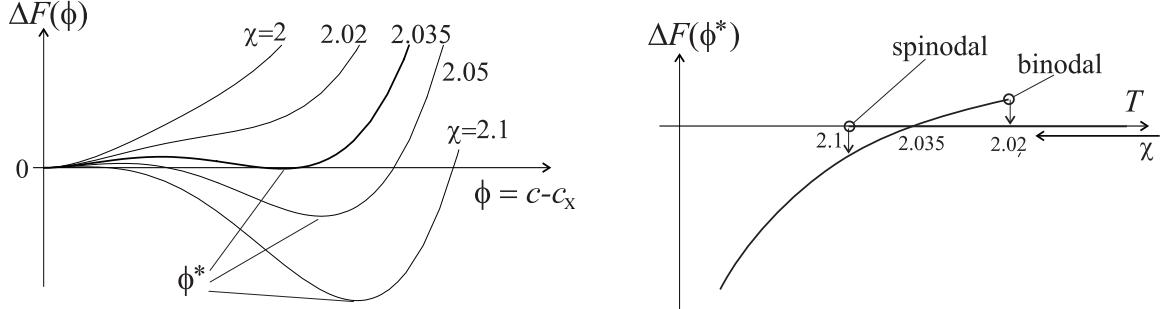


Figure 9.5: [Left] The change in the free energy,  $\Delta F = F_{\text{mix}}(c) - F_{\text{mix}}(c_X)$  plotted against the fluctuation amplitude  $\phi = c - c_X$  for several values of  $\chi$ -parameter above the critical point. — [Right] The values of  $\Delta F(\phi)$  at the point of minimum  $\phi = \phi^*$ , as function of  $\chi$  or  $T$ , showing the region of coexistence with the mixed state  $\phi = 0$ ,  $\Delta F = 0$ .

What happens at the critical point? If the starting concentration  $c_X$  was chosen at the exact value  $c_X = c_0 = 1/2$ , then on cooling the mixture (or on increasing  $\chi$ ) we will cross the critical point on the phase diagram. In that case Eq. (9.30) takes the form which looks much simpler:

$$\frac{F_{\text{mix}}(c) - F_{\text{mix}}(c_X)}{Nk_B T} = (2 - \chi)\phi^2 + \frac{4}{3}\phi^4 + \dots \quad (9.31)$$

The new, phase-separated value  $\phi^*$  now emerges in a continuous manner, which is easy to obtain by minimisation,  $\partial\Delta F/\partial\phi = 0$  gives

$$\phi^* = \sqrt{\frac{3}{8}(\chi - 2)} . \quad (9.32)$$

### General classification of phase transitions

Fig. 2.8 shows the Gibbs free energies of liquid and vapour phases, same as Fig. 9.5 showed the free energies of the mixed and phase-separating states. At the transition the free energy of the equilibrium (that is, lowest in energy) phase has a discontinuity in its first derivative. From the thermodynamic relation, e.g. for the Gibbs free energy,

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad (9.33)$$

we see that the entropy is discontinuous at the transition, and there is a latent heat,  $L = T\Delta S$ . In Ehrenfest’s classification scheme, phase transitions were labelled by the lowest derivative of the free energy which is discontinuous at the transition. Under this classification scheme the transitions shown in Figs. 2.8 and 9.5 are *first order* transitions. A second order transition has a discontinuity in the second derivative of the free energy, for example, the liquid/vapour

transition or demixing phase separation at the critical point. Third and higher order transitions could be similarly defined. However, in a ferromagnet the heat capacity (proportional to the second derivative of the free energy) diverges as  $|T_c - T|^{-\alpha}$  at the critical temperature  $T_c$ , which means that there are no discontinuities in any of the derivatives of the Gibbs free energy. Unfortunately, this case cannot be classified satisfactorily within Ehrenfest's scheme. In the modern classification phase transitions are divided into just two categories: First-order or *discontinuous* transitions are those which involve a latent heat, while all other transitions are referred to as second order or *continuous* phase transitions. Critical behaviour and *continuous*, or *second order*, phase transitions are the subject of the rest of this chapter.

### 9.3 Landau theory of phase transitions

We illustrate the ideas of Landau theory using a simple magnetic system which is essentially equivalent to the Ising model discussed above. In this case the order parameter is the magnetisation  $M$ . Near the phase transition the order parameter is small and the idea is to expand the free energy as a power series in the order parameter. Remember, we have done something similar in the problem of mixing, see Eqs. (9.30) and (9.31). Expanding  $F(T, M)$  in a Taylor series about  $M = 0$ , and truncating after a few terms, we have

$$F(T, M) = F_0(T) + \mathcal{A}(T)M + \mathcal{B}(T)M^2 + \mathcal{C}(T)M^3 + \mathcal{D}(T)M^4 + \dots \quad (9.34)$$

At this stage we use the symmetry of the system and note that, in the absence of an applied magnetic field,  $F$  must be unchanged if we reverse the magnetisation,  $M \rightarrow -M$ . Therefore the coefficients of the odd powers of  $M$  must be zero and the free energy reduces to

$$F(T, M) = F_0(T) + \mathcal{B}(T)M^2 + \mathcal{D}(T)M^4. \quad (9.35)$$

This expression, similar to (9.31), determines the thermodynamics of the second-order phase transition within the Landau theory.

The Landau theory is in fact equivalent to the mean field theory in the vicinity of the transition. To demonstrate this we expand the Helmholtz free energy of Eq. (9.11) in powers of  $m$  around  $m = 0$ . If you do this algebra yourself, you will see that the constant term that we kept in that expression now plays an important role in determining the transition point (the change of sign of the Landau coefficient  $\mathcal{B}$ ). We obtain the series expansion:

$$F_1 \simeq -k_B T \ln 2 + \frac{zJ}{2k_B T m_0^2} [k_B T - zJ] m^2 + \frac{1}{12} \frac{(zJ)^4}{(k_B T)^3 m_0^4} m^4, \quad (9.36)$$

which is exactly the form obtained in the Landau theory. To see this, we must realise that in the vicinity of  $T = T_c$  only the term in square brackets has any relevant temperature dependence: in all other instances we can reliably replace  $k_B T$  with  $k_B T_c = zJ$ . Then the Landau coefficient  $\mathcal{B}(T)$  takes the form  $\mathcal{B} = (k_B/2m_0^2)[T - T_c]$ , while  $\mathcal{D} = k_B T_c / 12m_0^4 \approx \text{const}$ . Note that the only ingredients required to obtain Eq. (9.35) were a suitable order parameter and the symmetry of the system.

## Magnetic phase transition within Landau theory

The equilibrium state of the system described by Eq. (9.35) is found by minimising  $F(M)$ ,

$$\left(\frac{\partial F}{\partial M}\right)_T = 2\mathcal{B}(T)M + 4\mathcal{D}(T)M^3 = 0, \quad (9.37)$$

which has three solutions,

$$M_0 = 0, \text{ or } M_0 = \pm \sqrt{\frac{-\mathcal{B}}{2\mathcal{D}}}. \quad (9.38)$$

Suppose that  $\mathcal{D} > 0$  so that  $F$  increases at large  $M$ . The behaviour depends on the sign of  $\mathcal{B}$ , if  $\mathcal{B} > 0$  the only solution is  $M = 0$ , which corresponds to a minimum in  $F$ , but if  $\mathcal{B} < 0$  there are three solutions, although only the two with  $M = \pm\sqrt{-\mathcal{B}/(2\mathcal{D})}$  are minima in  $F$ . The phase transition must therefore occur at  $\mathcal{B} = 0$ .

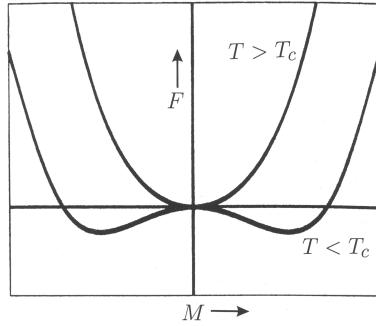


Figure 9.6: The free energy  $F$  of a simple magnetic system as a function of magnetisation  $M$  when no magnetic field is present, for a value of  $T > T_c$  and a value of  $T < T_c$ .

Expanding  $\mathcal{B}(T)$  and  $\mathcal{D}(T)$  in powers of  $T - T_c$  and truncating after the first term we obtain

$$\mathcal{B}(T) = b(T - T_c) \quad (9.39)$$

$$\mathcal{D}(T) = d, \quad (9.40)$$

where  $b$  and  $d$  are positive constants. The free energy becomes

$$F(T, M) = F_0(T) + b(T - T_c)M^2 + dM^4, \quad (9.41)$$

which is plotted in Fig. 9.6 for  $T < T_c$  and  $T > T_c$ . The order parameter is continuous at  $T_c$  and therefore this is a second order or continuous phase transition. The equilibrium values of  $M$  and  $T$  are related by

$$M_0(T) = \begin{cases} \pm \sqrt{\frac{b}{2d}(T_c - T)} & T < T_c \\ 0 & T > T_c. \end{cases} \quad (9.42)$$

To complete the thermodynamic description, let us find the entropy from the equilibrium free energy  $F_{\text{eq}}(T) = F(T, M_0(T))$ . Assuming  $\mathcal{D}(T)$  is temperature independent, at least near the transition, we have:

$$S = - \left( \frac{\partial F(M_0, T)}{\partial T} \right) = S_0(T) - bM_0(T)^2. \quad (9.43)$$

Using Eq. (9.42) for equilibrium magnetisation we obtain

$$S = \begin{cases} S_0(T) - \frac{b^2}{2d}(T_c - T) & T < T_c \\ S_0(T) & T > T_c. \end{cases} \quad (9.44)$$

The entropy is continuous at  $T_c$ , but the heat capacity is not; there is a finite jump in heat capacity at  $T_c$ :

$$C = T \left( \frac{\partial S}{\partial T} \right)_{B=0} = \begin{cases} C_0(T) + \frac{b^2}{2d}T & T < T_c \\ C_0(T) & T > T_c \end{cases} \quad (9.45)$$

With an applied magnetic field,  $B$ , the free energy becomes

$$F(T, M, B) = F_0(T) + b(T - T_c)M^2 + dM^4 - BM. \quad (9.46)$$

The  $-BM$  term breaks the symmetry between the states with  $+M$  and  $-M$ . The equilibrium state at temperature  $T$  is found by minimising  $F(T, M, B)$  with respect to  $M$ ,

$$\left( \frac{\partial F}{\partial M} \right)_{T,B} = 2b(T - T_c)M + 4dM^3 - B = 0. \quad (9.47)$$

Plots of  $F$  as a function of  $M$  are shown in Fig. 9.7, at fixed  $T$ , with a symmetry-breaking magnetic field  $B > 0$ . For  $T > T_c$  a single minimum exists with small positive  $M$ , while for  $T < T_c$  there are two unequal minima, a deeper one at a positive value of  $M$  and a shallower one at a negative value. There is an analytic expression for the roots of a cubic equation such

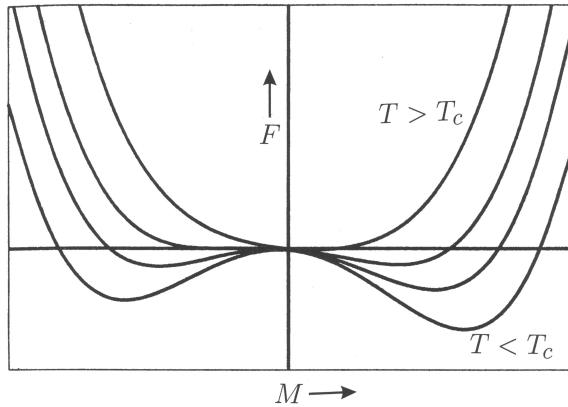


Figure 9.7: The free energy  $F$  as a function of magnetisation  $M$  with a symmetry-breaking magnetic field  $B > 0$ , for one value of  $T > T_c$ , and three values of  $T < T_c$ .

as Eq. (9.47), but it is a bit messy. However, if we restrict ourselves to the region close to  $T_c$  with  $B$  extremely small we can neglect the  $M^3$  term, so that

$$M = \frac{B}{2b(T - T_c)}. \quad (9.48)$$

The phase diagram is shown in Fig. 9.8. If we start with a magnetic field  $B < 0$  and follow the path labelled 1 where  $T < T_c$  then, as the system passes through  $B = 0$ , the equilibrium value of the magnetisation flips from a negative value to an equal and opposite positive value. At this

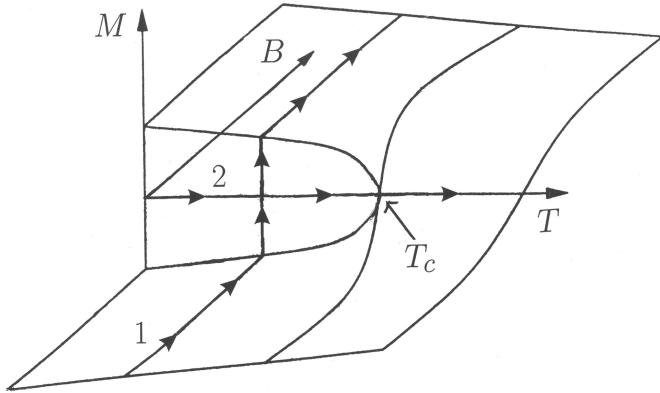


Figure 9.8: Phase diagram for a simple magnetic system.

phase transition the order parameter changes discontinuously and, although there is no latent heat, we classify it as a first order phase transition. Landau conceived his theory for continuous phase transitions, but it can also be applied to many discontinuous ones. If we set  $B = 0$  and increase the temperature from below  $T_c$ , following path 2, then a second order continuous phase transition occurs at the critical point where  $T = T_c$ .

Landau conceived his theory for continuous phase transitions, but it can also be applied to many discontinuous, first-order transitions – the example of such analysis was shown in the problem of mixing and phase separation. In general, the Landau expansion of the free energy in powers of the appropriate order parameter, such as (9.34), can always be done (although its accuracy depends on how small the order parameter is near the transition: that's why Landau has originally developed this approach for the continuous transitions). In ferromagnetic system, with the order parameter being a vector  $\mathbf{M}$ , the symmetry has excluded odd-power terms in the expansion, leading to Eq. (9.35). However, in a different system symmetry this might not be the case, e.g. the concentration difference  $\phi$  is a scalar and we had a cubic term present in Eq. (9.30), except at an isolated critical point. The same would apply to the (scalar) density in a liquid-gas transition, or a degree of alignment in a nematic liquid crystal. All these are first-order transition systems, which could be generically described by the Landau expansion

$$F(T, \phi) = F_0(T) + b(T - T_c)\phi^2 - c\phi^3 + d\phi^4, \quad (9.49)$$

where  $\phi$  is the order parameter corresponding in a given system ( $\phi = 0$  in the high-temperature phase), and we followed the assumption (9.39) that only the leading square-power term has a relevant temperature dependence. The discussion of the resulting transition is essentially that we have already had at the end of §9.1.2.

## 9.4 Critical exponents and universality

Continuous phase transitions are easier to study than first-order transitions due to the absence of latent heat, and they have been discovered to have many interesting properties. The phenomena associated with continuous phase transitions are called critical phenomena, due to their association with critical points. Returning back to the case of ferromagnetic transition, let us

define the magnetic susceptibility:

$$\chi = \left( \frac{\partial M}{\partial B} \right)_{B \rightarrow 0}. \quad (9.50)$$

We can calculate  $\chi$  from differentiating Eq. (9.47), which gives

$$\chi = \frac{1}{2b(T - T_c) + 12dM^2}. \quad (9.51)$$

We should treat the cases  $T > T_c$  and  $T < T_c$  separately because  $M$ , which is given by Eq. (9.42), is different in the two cases. For  $B \rightarrow 0$  and  $T > T_c$ , we obtain

$$\chi_+ = \frac{1}{2b(T - T_c)}, \quad (9.52)$$

which is the Curie-Weiss law, while for  $B \rightarrow 0$  and  $T < T_c$ ,

$$\chi_- = \frac{1}{4b(T_c - T)}. \quad (9.53)$$

Also, if we set  $T = T_c$  in Eq. (9.47), we obtain at the critical point:

$$B = 4dM^3. \quad (9.54)$$

Let us write

$$M \propto (T_c - T)^\beta \quad T < T_c, B = 0 \quad (9.55)$$

$$\chi \propto |T - T_c|^{-\gamma} \quad B \rightarrow 0 \quad (9.56)$$

$$B \propto M^\delta \quad T = T_c. \quad (9.57)$$

The numbers  $\beta$ ,  $\gamma$ , and  $\delta$  are examples of *critical exponents* where, for the simple magnetic system, Landau theory predicts

$$\beta = 1/2; \quad \gamma = 1; \quad \delta = 3. \quad (9.58)$$

It turns out that Landau theory predicts these values to be *universal*, that is, the same for all phase transitions, irrespective of underlying physical interactions. Unfortunately the critical exponents for real systems don't always take these values! Some values of critical exponents are given in Table 9.3.

	$\beta$	$\gamma$	$\delta$
Landau theory	1/2	1	3
Two-dimensional Ising model	1/8	7/4	15
Three-dimensional Ising model	0.33	1.24	4.77
Three-dimensional ferromagnets	0.30-0.36	1.2-1.4	4.2-4.8

Table 9.3: Values of critical exponents within mean field theory, for the two- and three-dimensional Ising model, and experimental values for three-dimensional ferromagnets.

Experimental and theoretical investigations have led to the idea that very different physical systems show precisely the same values of the critical exponents, in which case they are said to belong to the same *universality class*. Three factors determine the universality class:

- (1) the dimensionality of the physical space;
- (2) the number of components in the order parameter;
- (3) whether the interaction is short ranged or long ranged.

For example, in the Ising model, the order parameter has one component and the interaction is short ranged.

Landau theory is not adequate for describing the precise detail of critical behaviour that occurs close to a continuous phase transition. Landau theory assumes that the free energy can be expanded about the transition point in a power series in the order parameter, but this assumption is actually invalid at  $T = T_c$  because the free energy is *singular* at a continuous phase transition. Crucially, Landau theory ignores *fluctuations in the order parameter*. To understand what this means, think about the Weiss theory in which each spin feels the average effect of the others. This cannot be correct because in reality the partition function includes contributions from different arrangements of the nearest neighbour spins. As shown by the example of critical opalescence, very large fluctuations occur near a critical point, which can be thought of as strong correlations between the behaviour at distant points in space. Landau theory neglects these correlations.

We have examined failures of mean field theories at some length. One must not conclude that mean field theories are useless. In fact they are *very useful* for describing and understanding phase transitions. They give the wrong critical behaviour, but can still give useful insights into the nature of the phases involved and reasonable numerical estimates of when a phase transition will occur.

What is the origin of this universality? To give a crude answer we return to the example of critical opalescence. In a fluid the long ranged correlations produce variations in the density on length scales many times larger than the molecular dimensions. This suggests that the details of what happens on the molecular length scale should be irrelevant to the critical behaviour.

# Chapter 10

## Fluctuations in equilibrium

So far we have mostly been concerned with the average values of thermodynamic quantities, such as the internal energy  $U$  or magnetisation  $M$ . Even in equilibrium the actual value of the internal energy of a system in contact with a heat reservoir fluctuates in time around the average value.

### 10.1 Fluctuations

Although they are an inherent part of the equilibrium state, under normal conditions fluctuations of macroscopic thermodynamic quantities are unmeasurably small. There are, however, situations in which fluctuations are important. At second-order phase transitions fluctuations in some thermodynamic quantities diverge, and in that case fluctuations *dominate* the physics. Even far from critical points, spatial fluctuations in the density (e.g., number density, magnetisation density) scatter particles such as photons or neutrons, although it is again at critical points that these effects become most spectacular. Another important example is the scattering of conduction electrons in metals from density fluctuations of the positively charged ions on the lattice (electron-phonon scattering). At normal temperatures in reasonably pure metals such scattering is usually the main source of electrical resistivity. We won't treat scattering from fluctuations here. We will, however, look at some general properties of fluctuations, calculating the fluctuations in the magnetisation of a paramagnet, and generic fluctuations in energy, particle number and volume.

#### Fluctuations and the Boltzmann-Gibbs distribution

We can, if we know the energy eigenstates of a system, directly obtain from the Boltzmann or Gibbs distributions not only the average value of a quantity  $x$  but also its variance, a measure of the magnitude of fluctuations of  $x$ :

$$\langle \Delta x^2 \rangle \equiv \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{Z} \sum_i x_i^2 e^{-E_i/k_B T} - \left( \frac{1}{Z} \sum_i x_i e^{-E_i/k_B T} \right)^2, \quad (10.1)$$

where  $x_i$  is the value of variable  $x$  when the system is in state  $i$ . This is a useful method of calculating fluctuation magnitude, which becomes even more attractive if there is a simple

dependence of the microstate energy on the variable. E.g. if such dependence is linear,  $E_i = -f x_i$ , then a generic trick applies:

$$\langle x \rangle = \frac{1}{Z} \sum_i x_i e^{fx_i\beta} = \frac{1}{\beta Z} \left( \frac{\partial Z}{\partial f} \right) = k_B T \frac{\partial}{\partial f} \ln Z \quad (10.2)$$

$$\langle x^2 \rangle = \frac{1}{Z} \sum_i x_i^2 e^{fx_i\beta} = \frac{1}{Z\beta^2} \frac{\partial^2 Z}{\partial f^2}. \quad (10.3)$$

But if we take one more derivative of  $\langle x \rangle$ , we note:

$$k_B T \left( \frac{\partial \langle x \rangle}{\partial f} \right) = (k_B T)^2 \left[ -\frac{1}{Z^2} \left( \frac{\partial Z}{\partial f} \right)^2 + \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial f^2} \right) \right] \equiv -\langle x \rangle^2 + \langle x^2 \rangle, \quad (10.4)$$

which is exactly the same as  $\langle \Delta x^2 \rangle$ . For example, consider the fluctuations in the magnetisation of a subsystem consisting of a paramagnet in an external field  $B$ , and in contact with a reservoir at temperature  $T$ .

Applying the Boltzmann distribution with  $E_i = -M_i B$  we have

$$\langle M \rangle = \frac{1}{Z} \sum_i M_i e^{M_i B / k_B T} = \frac{k_B T}{Z} \left( \frac{\partial Z}{\partial B} \right)_T \quad (10.5)$$

Following the method above, the mean square fluctuation in  $M$  is (NB. change of sign)

$$\langle \Delta M^2 \rangle = \langle M^2 \rangle - \langle M \rangle^2 = k_B T \left( \frac{\partial \langle M \rangle}{\partial B} \right)_T. \quad (10.6)$$

We showed earlier (see §3.6) that for a system of non-interacting spins

$$\langle M \rangle = N m_0 \tanh \left( \frac{m_0 B}{k_B T} \right). \quad (10.7)$$

Substituting this into our expression for the mean square fluctuation in  $M$  we obtain

$$\langle \Delta M^2 \rangle = \frac{N m_0^2}{\cosh^2(m_0 B / k_B T)}. \quad (10.8)$$

This is an interesting result, because it shows that the root mean square fractional fluctuation is proportional to the square-root of the number of particles,  $\sqrt{\langle \Delta M^2 \rangle} \propto N^{1/2}$ , so the relative size of the fluctuation to the magnetisation value is:

$$\frac{\sqrt{\langle \Delta M^2 \rangle}}{\langle M \rangle} \propto \frac{1}{\sqrt{N}}. \quad (10.9)$$

The dependence on  $1/\sqrt{N}$  is a characteristic that will emerge repeatedly.

Another useful example using the same approach involves asking about the fluctuations of mean energy of the system. Although  $U$  is not a thermodynamic variable, we can still write the same sequence of steps:

$$U = \langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-E_i/k_B T} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right); \quad \langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad (10.10)$$

and the mean square fluctuation in  $U$  is

$$\langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial}{\partial \beta} \left[ \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right] = k_B T^2 \left( \frac{\partial U}{\partial T} \right). \quad (10.11)$$

## 10.2 Connection with thermodynamics

In our discussion of availability theory in §2.2 it may have occurred to you as odd that we only ever used the condition  $dA = 0$ . This enabled us to locate the equilibrium conditions for thermodynamic systems in contact with various kinds of reservoirs. But we might ask if there isn't some meaning to the entire availability function, not just its extremal value. The answer is that for finite systems, the *curvature* of the availability function is related to the size of the fluctuations. We now proceed to find out what this relationship is.

Consider a system that can exchange energy and particles with a large reservoir. We wish to calculate the probability distribution,  $P(x)$ , for variable  $x$  of the system, when the total internal energy of the system+reservoir is  $U_{\text{tot}}$ . It is easy to see that

$$P(x) \propto \Omega_{\text{tot}}(x, U_{\text{tot}}), \quad (10.12)$$

where  $\Omega_{\text{tot}}(x, U_{\text{tot}})$  is the number of microstates of the system+reservoir in which the variable of the system is equal to  $x$ . The entropy of the system+reservoir is given by

$$S_{\text{tot}}(x, U_{\text{tot}}) = k_B \ln \Omega_{\text{tot}}(x, U_{\text{tot}}), \quad (10.13)$$

so that

$$P(x) \propto e^{S_{\text{tot}}(x, U_{\text{tot}})/k_B}. \quad (10.14)$$

This formula is inconvenient as it contains the entropy of the system+reservoir. However, we found out how to get around this in §2.2 by using the availability,

$$A = U - T_R S + p_R V - \mu_R N, \quad (10.15)$$

where the subscript  $R$  refers to the reservoir, and the other variables are for the system. Because the reservoir is large  $T_R$ ,  $p_R$ , and  $\mu_R$  are constant. A change in the total entropy of the system+reservoir is related to a change in the availability by

$$dS_{\text{tot}} = -\frac{dA(x)}{T_R}, \quad (10.16)$$

where  $T_R$  is the temperature of the reservoir. Therefore

$$P(x) = \aleph e^{-A(x)/k_B T_R}, \quad (10.17)$$

where  $\aleph$  is a normalisation constant. In this formula the availability is calculated in equilibrium with the system variable of interest constrained to take the value  $x$ .

As discussed in §2.3.3, for an isothermal, constant volume system,  $dA$  reduces to  $dF$ , so  $P(x) \propto e^{-F(x)/k_B T_R}$ , while for constant  $T$  and  $p$ ,  $dA = dG$ , and the fluctuation probability is  $P(x) \propto e^{-G(x)/k_B T_R}$ , and for  $dQ = 0$  and  $dp = 0$  the fluctuation probability is  $P(x) \propto e^{-H(x)/k_B T_R}$ .

Eq. 10.17 is the general formula, but for a large system the probability distribution is almost Gaussian and one can extract the mean square fluctuation by simply expanding about the equilibrium value of  $x$ , which we denote by  $x_0$ ,

$$A(x) = A(x_0) + (x - x_0) \left( \frac{\partial A}{\partial x} \right)_{x=x_0} + \frac{1}{2} (x - x_0)^2 \left( \frac{\partial^2 A}{\partial x^2} \right)_{x=x_0} + \dots \quad (10.18)$$

The second term on the right hand side is zero because we are expanding about a minimum. Combining Eqs. 10.17 and 10.18 we obtain the probability distribution within the Gaussian approximation

$$P(x) = \frac{1}{\sqrt{2\pi\langle\Delta x^2\rangle}} \exp\left[-\frac{\Delta x^2}{2\langle\Delta x^2\rangle}\right], \quad (10.19)$$

where

$$\langle\Delta x^2\rangle = \langle(x - x_0)^2\rangle = \frac{k_B T_R}{(\partial^2 A / \partial x^2)_{x=x_0}}. \quad (10.20)$$

There is an important and simple message emerging from this discussion. You may recall (from §2.2) that the small increment of availability, such as  $\Delta A(x) = A(x) - A(x_0)$  here, is actually equal to a corresponding thermodynamic potential (in which  $x$  is the proper variable). Therefore the first derivative  $(\partial A / \partial x)$ , evaluated in equilibrium, is in fact equal to the thermodynamic force  $f$  conjugate to the variable  $x$ . Let's say that the corresponding thermodynamic potential (not specifying its name to any of the familiar ones) is  $\Pi(x)$ , so that  $d\Pi = f dx + \dots$  Then we see from Eq. (10.20) that

$$\langle\Delta x^2\rangle = k_B T \frac{1}{(\partial f / \partial x)_{x=x_0}} = k_B T \left( \frac{\partial x}{\partial f} \right)_{x=x_0}. \quad (10.21)$$

If you think of the arbitrary conjugate pair of thermodynamic variables  $(x, f)$  as a force and the corresponding displacement which are related by the *linear response* relation  $x = \alpha f$ , then we conclude that the mean square fluctuation of a thermodynamic variable is given by  $k_B T$  times the linear response coefficient:  $\langle\Delta x^2\rangle = k_B T \alpha$  in our notations. This is the first example of *Fluctuation Dissipation Theorem* we discover in this course.

Let us now derive the probability distribution for fluctuations in the internal energy  $U$  of a system held at constant volume and particle number but thermally coupled to a reservoir. This is an example when the fluctuating object is not the basic thermodynamic variable, and so we have to be cautious with the conclusions reached above. We will use the thermodynamic approach, although if the eigenstates were known we could use statistical mechanics.

A change in the availability (Eq. 10.15) is given by

$$dA = dU - T_R dS + p_R dV - \mu_R dN, \quad (10.22)$$

which for constant  $V$  and  $N$  reduces to

$$dA = dU - T_R dS = dF. \quad (10.23)$$

Therefore

$$\left( \frac{\partial F}{\partial U} \right)_V = 1 - T_R \left( \frac{\partial S}{\partial U} \right)_V, \quad (10.24)$$

and using  $\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T}$  we obtain

$$\left( \frac{\partial F}{\partial U} \right)_V = 1 - \frac{T_R}{T}, \quad (10.25)$$

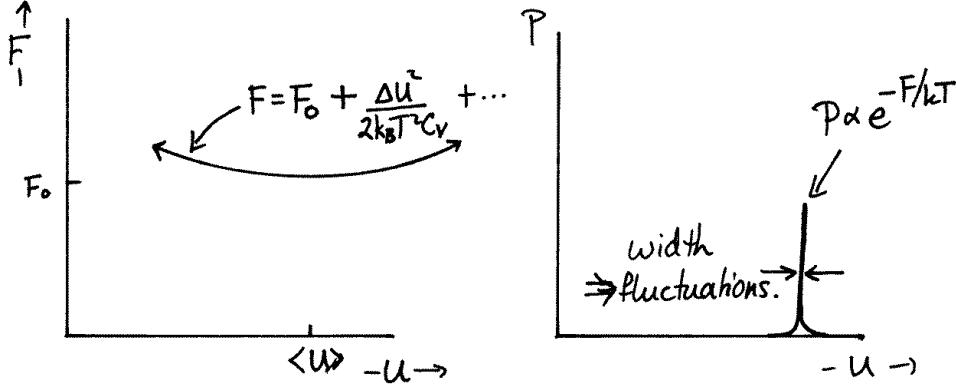


Figure 10.1: The Helmholtz free energy is a minimum at the mean value of  $U$ , and the probability distribution for  $U$  is a sharply peaked Gaussian centred on the mean value.

which must be zero in equilibrium so that, as expected,  $T = T_R$  is the equilibrium condition. Differentiating again we obtain

$$\left( \frac{\partial^2 F}{\partial U^2} \right)_V = \frac{T_R}{T^2} \left( \frac{\partial T}{\partial U} \right)_V. \quad (10.26)$$

Using  $(\frac{\partial U}{\partial T})_V = C_v$  and setting  $T_R = T$  we obtain

$$\left( \frac{\partial^2 F}{\partial U^2} \right)_V = \frac{1}{TC_V}, \quad (10.27)$$

so that using Eq. (10.20) we obtain the same expression as we have seen earlier, in Eq. (10.11),

$$\langle \Delta E^2 \rangle = \frac{k_B T}{\left( \frac{\partial^2 F}{\partial U^2} \right)_V} = k_B T^2 C_V, \quad \text{for } \langle E \rangle = U, \quad (10.28)$$

and

$$P(E) = \frac{1}{\sqrt{2\pi k_B T^2 C_V}} \exp \left[ - \frac{[E - \langle E \rangle]^2}{2k_B T^2 C_V} \right]. \quad (10.29)$$

Let's consider, for example, 1 cm<sup>3</sup> of monatomic ideal gas:

$$N = \frac{pV}{k_B T} \sim 2.5 \times 10^{19} \quad \text{atoms.} \quad (10.30)$$

Equipartition gives  $U = 3/2Nk_B T = 0.15$  J, and the heat capacity at constant volume is  $C_V = 3/2Nk_B = 5.2 \times 10^{-4}$  J/K, so the root mean square fluctuation is

$$\langle \Delta E^2 \rangle^{1/2} \sim T \sqrt{k_B C_V} \sim 2.5 \times 10^{-11} \text{ J.} \quad (10.31)$$

The fractional fluctuation is

$$\frac{\langle \Delta E^2 \rangle^{1/2}}{U} \sim 1.6 \times 10^{-10}. \quad (10.32)$$

Thus the fluctuations in energy would be unmeasurably small. Note from the formulae that the fractional fluctuation is again proportional to  $1/\sqrt{N}$ .

Before considering other examples of fluctuations we should think a little more carefully about what is going on.

(1) Some variables, for example  $T, S, \mu$ , are not well defined for each microstate, they are only defined as averages over them. Can such variables be considered to fluctuate at all? This is related to the discussion of the law of increase of entropy in Appendix 1, which implies that the answer is “yes”. However this is a subtle question which I will not address further.

(2) Some variables cannot be fixed in practical situations, such as the pressure of a gas, or the magnetisation of a paramagnet. However, this does not prevent us from calculating the fluctuations in the pressure or magnetisation. You can read about this on pages 207-208 of Waldram, but this issue is not examinable.

(3) You should beware that in general it is *incorrect* to take the formula for the probability distribution of one variable and substitute for another one. As a trivial example, consider an isolated cylinder of ideal monatomic gas held at constant volume. As the system is isolated  $U$  is constant, and in equilibrium  $U = 3/2 pV$ . If  $V$  is constant one might conclude that because  $U$  does not fluctuate neither can  $p$ . This is nonsense because the usual equilibrium relations between functions of state do not hold during the course of fluctuations.

### 10.3 Fluctuations near critical points

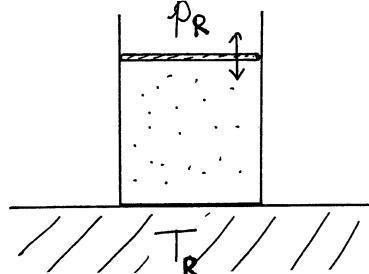


Figure 10.2: Volume fluctuations at constant  $T$  and  $N$ .

The first example of critical point we have encountered, back in Fig. 1.5, was for the van der Waals gas. In  $p - V$  coordinates the critical isotherm has a single point where  $dp/dV = 0$  (at lower temperatures there are two such points on each isotherm, but the liquid-gas transition occurs outside their range).

Let us calculate the fluctuation of thermodynamic variable  $V$  in the vessel shown in Fig. 10.2, at constant  $T$  and  $N$ . This is similar to what we have done for  $U$ , but requires a little more thought about which variables are fixed and which ones fluctuate. In this problem  $U$  is free to fluctuate but  $T$  is fixed and equal to its equilibrium value of  $T_R$ . Applying the first law to the system we have

$$dU = T_R dS - pdV, \text{ so that } dA = (p_R - p) dV. \quad (10.33)$$

Differentiating w.r.t.  $dV$  and taking  $T$  to be constant we have

$$\left( \frac{\partial A}{\partial V} \right)_T = p_R - p, \quad (10.34)$$

which must be zero in equilibrium so that, as expected,  $p = p_R$  is the equilibrium condition. Differentiating again we obtain

$$\left( \frac{\partial^2 A}{\partial V^2} \right)_T = - \left( \frac{\partial p}{\partial V} \right)_T \equiv \frac{1}{\kappa_T V}, \quad (10.35)$$

where we have defined the parameter  $\kappa_T$  – the isothermal compressibility, which is effectively the linear response coefficient for the conjugate pair of thermodynamic variables  $p, V$ . Therefore

$$\langle \Delta V^2 \rangle = k_B T V \kappa_T, \quad \text{and} \quad P(V) = \frac{1}{\sqrt{2\pi k_B T V \kappa_T}} \exp \left[ -\frac{\Delta V^2}{2k_B T V \kappa_T} \right]. \quad (10.36)$$

The fractional volume fluctuation is

$$\frac{\sqrt{\langle \Delta V^2 \rangle}}{V} = \sqrt{\frac{k_B T \kappa_T}{V}} \quad (10.37)$$

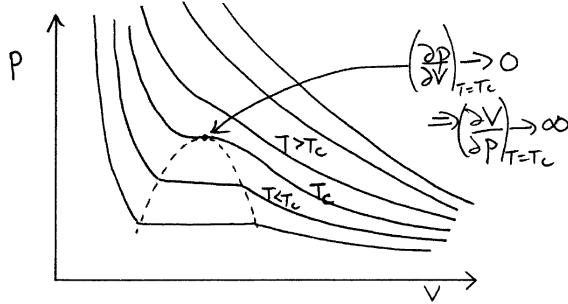


Figure 10.3: The fluctuations grow as one approaches the critical point, where they diverge.

In line with our other findings, the fractional fluctuation is proportional to  $1/\sqrt{V}$ . Note that  $\kappa_T \propto (dV/dp)$  diverges at the liquid-vapour critical point (see Fig. 10.3), and hence the magnitude of the volume fluctuations. This effect has the name of ‘critical opalescence’ and you can see it every time when slowly boiling water in a pan: as the critical point is approached, the volume of density fluctuations (microscopic bubbles of vapour in the liquid) increases so that they start scattering light.

Two other examples of critical points we examined in *phase transitions* were the isolated C.P. at the end of the demixing region of a phase-separating mixture, and the continuous second order phase transition in ferromagnets at zero external  $B$ -field. The first C.P. is fully analogous to the van der Waals critical point, only represented in variables  $T, c$ . It is convenient to look at both these transition with the help of Landau expansion(s) of the corresponding thermodynamic potential, Eq. (9.31) for the critical mixture and Eq. (9.41) for the magnet. For instance, taking the magnetic case at  $T_c$ , we can write the mean square fluctuation of magnetisation as

$$\langle \Delta M^2 \rangle = k_B T \left( \frac{\partial M}{\partial B} \right). \quad (10.38)$$

Evaluated at  $B \rightarrow 0$  and in equilibrium  $M_0 = 0$  at  $T > T_c$ , the derivative is equal to the susceptibility  $\chi$ , that is, the corresponding linear response coefficient of the  $M, B$  pair. As we have seen in Eq. (9.52), this susceptibility diverges at the critical point and so must the magnitude of fluctuation in magnetisation. Note that this divergence occurs on both sides of the critical point.



# Chapter 11

## Elements of stochastic physics

### 11.1 Brownian motion

The origin of all thermodynamic fluctuations is, of course, the underlying thermal motion of particles in matter. It is most explicitly represented in the phenomenon of *Brownian motion*: the perpetual irregular motions exhibited by small grains or particles of colloid size immersed in a liquid. A botanist Robert Brown is credited with the formal discovery of this effect in 1827, when he observed in the microscope tiny particles within the vacuoles of the pollen grains executing a jittery motion. By repeating the experiment with particles of dust, he was able to rule out that the motion was due to pollen particles being 'alive'.

Brownian motion is one of the simplest phenomena where we need the new approach – called the *stochastic physics*. As in the equilibrium statistical physics, one cannot predict the outcome on the basis of solving the dynamic (Newton) equations, and yet a lot of knowledge about the system can be acquired via the probability distributions and average properties. It is a common case when the characteristic length scales of the problem are well separated, as it is with a relatively large Brownian particle experiencing collisions and exchanging the momentum with very small molecules of liquid. Under normal conditions, in a liquid, a particle will suffer about  $10^{21}$  collisions per second. So we cannot – and really should not speak of separate events, or attempt to follow the particle trajectory in any detail.

The theory of the Brownian motion of a free particle (i.e. Brownian motion in the absence of external field or force) starts with the *Langevin equation* for the particle dynamics:

$$m \frac{d\mathbf{u}}{dt} = -\gamma \mathbf{u} + \xi(t) \quad (11.1)$$

where  $\mathbf{u}$  denotes the vector of particle velocity. According to this equation, the influence of the surrounding medium on the motion of the particle can be split up into two parts: first, a systematic part  $-\gamma \mathbf{u}$  representing the kinetic friction experienced by the particle (with  $\gamma$  the corresponding friction coefficient). It is assumed that this is governed by fluid dynamics, e.g., the Stokes law which states that the frictional force decelerating a spherical particle of radius  $a$  and mass  $m$  in a liquid with a viscous coefficient  $\eta$  is given by  $\gamma = 6\pi a \eta$ .

The second contribution to the force acting on the Brownian particle in Eq. (11.1) is fluctuating part  $\xi(t)$ , which is the force provided by collisions with molecules of surrounding liquid, which

are in thermal motion. If we had a purely 1-dimensional motion, then an example of such a force might be seen in Fig. 11.1. This type of force is called the *stochastic force* and it is clear that any solution  $\mathbf{u}(t)$  of the Langevin equation would also have the same unpredictable nature at any instance of time.

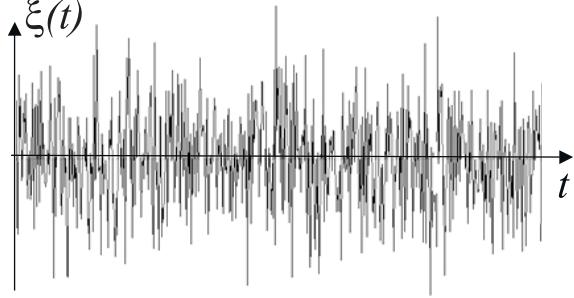


Figure 11.1: An example of stochastic force acting on the Brownian particle from the surrounding medium in thermal motion.

This problem is, in fact, very general. For instance in an electric ( $L, R$ ) circuit,  $L(dI/dt) + RI = V(t)$ , the thermal noise acting on electrons generates the stochastic contribution to the voltage; using the charge as variable:  $L\ddot{q} = -R\dot{q} + V_\xi(t)$  we reproduce Eq. (11.1). In general, the Langevin equation for any given system is the corresponding classical dynamical equation (2nd Newton law, if we talk about moving particles) with the stochastic force added to any other forces present.

What can we say about the properties of stochastic force  $\xi(t)$ ? The simplest approach would be to consider the 1-dimensional motion and assume the “white noise” properties, that is

$$\langle \xi(t) \rangle = 0; \quad \text{but} \quad \langle \xi(t)^2 \rangle \neq 0 \quad \text{and} \quad \langle \xi(t_1)\xi(t_2) \rangle = 0 \quad \text{if } t_1 \neq t_2 \quad (11.2)$$

The complete lack of correlations between its pulses can be described by the shorthand notation  $\langle \xi(t)\xi(t') \rangle = \Gamma \delta(t - t')$ , although one can show that a little spreading of the delta-function will not change the properties of Brownian motion on long time scales. Here the parameter  $\Gamma$  is the measure of intensity of the stochastic force.

### Fluctuation-dissipation relation

The homogeneous dynamical equation  $m\dot{u} = -\gamma u$  has the obvious solution,  $u = u_0 \exp[-(\gamma/m)t]$ , which represents the decay of the initial condition: the particle having velocity  $u_0$  at  $t = 0$ . With the added stochastic force, the formal solution of Eq. (11.1) is

$$u(t) = u_0 e^{-(\gamma/m)t} + \int_0^t e^{-(\gamma/m)[t-t']} \frac{\xi(t')}{m} dt' \quad (11.3)$$

which you can readily verify by evaluating the derivative  $m(du/dt)$ . The instantaneous value of  $u(t)$  cannot be predicted, but its mean square value is easy to determine:

$$\begin{aligned}\langle u^2 \rangle &= \left\langle u_0^2 e^{-2(\gamma/m)t} + 2u_0 e^{-(\gamma/m)t} \int_0^t e^{-(\gamma/m)[t-t']} \frac{\xi(t')}{m} dt' + \int_0^t \int_0^t e^{-(\gamma/m)[2t-t_1-t_2]} \frac{\xi(t_1)\xi(t_2)}{m^2} dt_1 dt_2 \right\rangle \\ &= u_0^2 e^{-2(\gamma/m)t} + \frac{1}{m^2} \int_0^t \int_0^t e^{-(\gamma/m)[2t-t_1-t_2]} \langle \xi(t_1)\xi(t_2) \rangle dt_1 dt_2\end{aligned}\quad (11.4)$$

$$\begin{aligned}&= u_0^2 e^{-2(\gamma/m)t} + \frac{\Gamma}{m^2} e^{-2(\gamma/m)t} \int_0^t e^{2(\gamma/m)t_1} dt_1 \\ &= u_0^2 e^{-2(\gamma/m)t} + \frac{\Gamma}{2m\gamma} \left(1 - e^{-2(\gamma/m)t}\right)\end{aligned}\quad (11.5)$$

The cross term, linear in  $\langle \xi \rangle$  dropped out in writing the second line (11.4). In the long-time limit<sup>1</sup> the decaying exponential disappears,  $e^{-2t/\tau} \rightarrow 0$ , and we are left with the value of the mean kinetic energy of the particle:

$$\left\langle \frac{mu^2}{2} \right\rangle = \frac{\Gamma}{4\gamma} = \frac{1}{2}k_B T, \quad (11.6)$$

where the equipartition was used for this 1-dimensional free motion. The important conclusion we have now reached is that the intensity of stochastic force is proportional to temperature (which is expected, in retrospect), but also to the friction constant of the particle in this medium:  $\Gamma = 2k_B T \gamma$ ; the two effects initially might have appeared independent. This is a representation of the fluctuation-dissipation theorem, relating the fluctuation of the energy input,  $\langle \xi^2 \rangle$ , to the linear response coefficient of energy dissipation (friction constant) via  $k_B T$ .

## 11.2 Diffusion of free and confined particles

If we persist with the notion that, after a long time of observation,  $t \gg m/\gamma$ , no memory of the initial particle velocity  $u_0$  must remain and the current velocity must be distributed according to the Maxwell distribution (Eq. 1.2 gave its 3-dimensional form), the next step of the coarse-graining would be to say that the inertial effects are irrelevant on long time scales of interest and the particle acceleration  $\dot{u}$  must average out of Eq. (11.1). We have to maintain the balance of forces:

$$0 = -\gamma u + \xi(t), \quad \text{or} \quad \frac{dx}{dt} = \frac{1}{\gamma} \xi(t).$$

Continuing our example of the simplest 1-dimensional example, the current position of the Brownian particle is evolving according to

$$x(t) = \frac{1}{\gamma} \int_0^t \xi(t') dt' \quad (11.7)$$

$$\begin{aligned}\text{hence } \langle x^2 \rangle &= \frac{1}{\gamma^2} \int_0^t \int_0^t \langle \xi(t_1)\xi(t_2) \rangle dt_1 dt_2 \\ \text{i.e. } \langle x^2 \rangle &= \frac{\Gamma}{\gamma^2} t \equiv 2D t \quad \text{with } D = \frac{k_B T}{\gamma}.\end{aligned}\quad (11.8)$$

This is the famous law of diffusion (Einstein 1905), meaning that the r.m.s. displacement of the free particle from its position at  $t = 0$  increases  $\propto t^{0.5}$ , that is, slower than for the free

---

<sup>1</sup>E.g. for small ( $1\mu\text{m}$  size) organic particles in water the time scale of this decay,  $\tau = m/\gamma \sim 10^{-8}\text{s}$ .

motion with constant velocity. The fact that  $\langle x^2 \rangle = 2Dt$  is a very basic property of any Gaussian stochastic process and you have no doubt seen this before. In 3-dimensions, without any constraints, we only need to repeat the same analysis in all directions to end up with

$$\langle \mathbf{r}^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 6Dt \quad (11.9)$$

In 1909, Jean Perrin has completed quantitative microscopic observations of Brownian diffusion, which confirmed the Einstein's theory and earned him the 1926 Nobel prize. The theory based on the Langevin equation has been applied to many diffusion phenomena: mixing of gases or liquids, atom motion in solids, spread of the black plague, spread of agriculture in Neolithic times, spread of clothing fashions, spread of africanized-bees, etc.

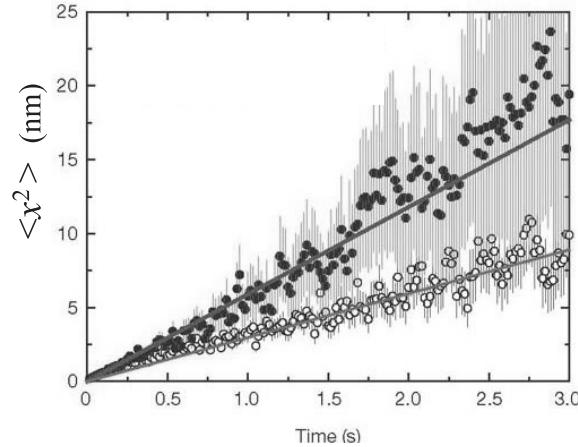


Figure 11.2: Mean square displacement of labelled impurities, diffusing in pure and distorted crystalline lattices.

### Brownian particle in a potential well

What is the effect of stochastic (thermal) noise on a system that is not free, but is confined by a potential energy to be near its equilibrium. A mechanical analogy of this is the Brownian particle that is moving in a quadratic potential  $V = \frac{1}{2}kx^2$  – essentially, the particle tied to an origin by an elastic spring exerting a force  $f = -kx$ .

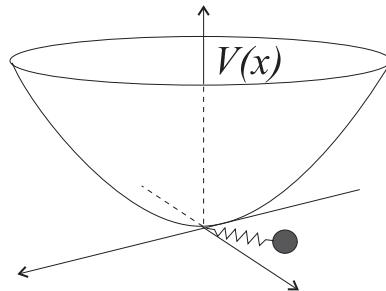


Figure 11.3: Particle moving under thermal noise in a potential well.

At time scales of observation which are much longer than the velocity relaxation time  $\tau = m/\gamma$ , inertial effects are again irrelevant and the acceleration averages to zero in the equation of motion

for the average position. In this limit, the Langevin equation takes the *overdamped* form:

$$\gamma \frac{d\mathbf{x}}{dt} = -k \mathbf{x} + \xi(t) \quad (11.10)$$

which is exactly the same as the equation for the free particle with the inertial term present, Eq. (11.1). Therefore the algebra of solving this problem of confined Brownian particle is exactly the same as what led us to the expression (11.5) for the mean square velocity. Once again, assuming 1-dimensional motion, for simplicity of argument, the stochastic solution for  $x(t)$  is

$$x(t) = x_0 e^{-(k/\gamma)t} + \int_0^t e^{-(k/\gamma)[t-t']} \frac{\xi(t')}{\gamma} dt' \quad (11.11)$$

The instantaneous value of  $x(t)$  cannot be predicted, but its mean square value is easy to determine:

$$\langle x^2 \rangle = x_0^2 e^{-2(k/\gamma)t} + \frac{1}{\gamma^2} \int_0^t \int_0^t e^{-(k/\gamma)[2t-t_1-t_2]} \langle \xi(t_1) \xi(t_2) \rangle dt_1 dt_2 \quad (11.12)$$

$$\begin{aligned} &= x_0^2 e^{-2(k/\gamma)t} + \frac{\Gamma}{\gamma^2} e^{-2(k/\gamma)t} \int_0^t e^{2(k/\gamma)t_1} dt_1 \\ &= x_0^2 e^{-2(k/\gamma)t} + \frac{\Gamma}{2k\gamma} (1 - e^{-2(k/\gamma)t}) \end{aligned} \quad (11.13)$$

There is a new time scale emerging,  $\tau_x = k/\gamma$ , which essentially determines how long does the memory of the initial condition  $x_0$  persists in such a system. Without thermal noise  $\xi(t)$ , the particle released at  $x = x_0$  would come to a rest at the point of its equilibrium  $x = 0$  in approximately this length of time.

In the long time limit, at  $t \gg \tau_x$  we obtain the result, that the mean square displacement of the particle from its equilibrium is constant:

$$\langle x^2 \rangle = \frac{\Gamma}{2k\gamma} = \frac{k_B T}{k} \quad (11.14)$$

if we recall the value for the intensity of the stochastic force,  $\Gamma = 2k_B T \gamma$ . This conclusion is interesting for two reasons. First of all, this is yet another example of the formula for general thermodynamic fluctuations in equilibrium, Eq.(10.21): the conjugate variable to the particle displacement is force,  $f = k x$ , and what we see above is just  $\langle x^2 \rangle = k_B T (\partial x / \partial f)$ . Secondly, this expression has a wide significance in a variety of real physical systems (well outside Brownian motion). For instance, consider atoms experiencing thermal motion in a crystalline lattice: their mean square displacement is proportional to  $k_B T$  – and inversely proportional to the strength of their confining lattice potential.

### 11.3 Damped harmonic oscillator

So far, we have started with a white-noise (uncorrelated) Langevin force and deduced the properties of Brownian motion in certain scenarios from it. But how do we know that the Langevin force has the form which has been postulated? We will investigate the properties of the Langevin force in detail by considering the more general example of a damped harmonic oscillator: a mass on a spring surrounded by a fluid at temperature  $T$ . We have seen that the position of the mass fluctuates, so as a function of time it follows some random curve. We know that

if we push down on the mass and then release it, its position will oscillate, but the oscillations decay with some time constant  $m/\gamma$ , where friction against the fluid is given by  $\gamma v$ , and the mass will eventually return to its original behaviour of fluctuation around its average position. If we imagine that we had an *ensemble* of identical mass-spring systems, and we displaced each mass by an amount  $x$ , and then released it, the *average* displacement would obey a damped harmonic oscillator equation:

$$m\ddot{x} + \gamma\dot{x} + kx = 0 \quad (11.15)$$

We call  $\gamma$  the damping constant.

More generally, if we apply a time dependent sinusoidal force  $f(t) = f_\omega e^{-i\omega t}$  to the system, and observe the displacement it observes,  $x(t) = x_\omega e^{-i\omega t}$ , then we define the response function as

$$\alpha_\omega = \langle x_\omega / f_\omega \rangle = \frac{1}{-m\omega^2 - i\gamma\omega + k} \quad (11.16)$$

$$= \frac{m(\omega_0^2 - \omega^2) + i\gamma\omega}{m^2(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \quad (11.17)$$

$$\equiv \alpha'_\omega + i\alpha''_\omega , \quad (11.18)$$

where  $\omega_0^2 = k/m$  and  $\alpha'$ ,  $\alpha''$  are the real and imaginary part of  $\alpha$ . Because the mass behaves like a damped simple harmonic oscillator, it must be possible to write down a potential energy  $\frac{1}{2}kx^2$  associated with displacement  $x$ . The principle of equipartition of energy tells us that this must have an average energy of  $\frac{1}{2}k_B T$ . We immediately deduce that the mean square displacement of the mass must be

$$\langle x^2 \rangle = k_B T / k = k_B T \alpha'_{\omega=0}. \quad (11.19)$$

## Langevin equation

Using Langevin's idea that the fluctuating system obeys the damped simple harmonic oscillator equation but on top of the applied force  $f(t)$  also has a *random force*  $\xi(t)$  acting on it, we formulate the equation

$$m\ddot{x} + \gamma\dot{x} + kx = \xi(t) , \quad (11.20)$$

which is what we already saw in (11.1) and (11.10).

Within the Langevin equation, we see that there must be some connection between the random force and the damping term  $\gamma$ , because the mean square displacement in Eq. 11.19 is independent of  $\gamma$ , whereas the response to the force which causes the displacement gets smaller as the damping gets stronger: *as the damping gets larger, the random force must also get stronger*. To calculate the properties of the Langevin force, we can use the form of classical fluctuation dissipation theorem (FDT), explored in the appendix, section 12.3:

$$\langle \delta x_\omega^2 \rangle = \frac{2k_B T}{\omega} \alpha''_\omega \quad (11.21)$$

Here,  $\delta x = x - \bar{x} = x$ , as  $\bar{x} = 0$  for our damped oscillator, and the difference with the earlier constant forms of FDT is that here we retain the time/frequency dependence of retarded parameters.

We can now apply this powerful relation to our damped oscillator, taking the Langevin force as an applied force  $f(t)$ :

$$x_\omega = f_\omega \alpha_\omega = \frac{f_\omega}{-m\omega^2 - i\gamma\omega + k} \quad (11.22)$$

$$\langle x_\omega^2 \rangle = \langle |x_\omega|^2 \rangle = \langle |\xi_\omega|^2 \rangle |\alpha_\omega|^2 = \frac{2k_B T}{\omega} \alpha_\omega'' \quad (11.23)$$

$$\Rightarrow \langle |\xi_\omega|^2 \rangle = \frac{2k_B T}{\omega} \frac{\alpha_\omega''}{|\alpha_\omega|^2} = 2k_B T \gamma \quad (11.24)$$

This shows that, as postulated in the previous examples, the fluctuating Langevin force indeed has a uniform power spectrum, like white noise, and that the intensity of the Langevin force is given by the damping constant.

## 11.4 Working with probability distributions

One would like to have a more universal approach to stochastic processes which could, for instance, have a different friction law or a different form of external force. Let us re-formulate the theory of Brownian motion in a different manner, via the probability distribution.

### 1D random walk

For simplicity, we start with 1-dimensional motion: a particle moving in back and forth along a line,  $x(t)$ . Such a motion is analogous to the 1-dimensional *random walk*, a problem which you have seen several times in this and last year's courses. If the particle may hop from one point to one of its two neighbouring points with equal probability, we then ask what is the probability that after  $N$  such steps the particle reaches a certain distance,  $x$ , from the point where it had started. By labelling the moves to the right as  $N_+$  and to the left as  $N_-$  (with  $N_+ + N_- = N$ ) and the length of an elementary step as  $a$ , the distance  $x$  can be expressed as

$$x = a(N_+ - N_-) = a(2N_+ - N) \quad (11.25)$$

from which the number of steps to the right, say, is equal to  $N_+ = \frac{1}{2}N + \frac{1}{2}(x/a)$ . Denoting the transition time per elementary step by  $\tau$ , the total time of motion is  $t = N\tau$ . The probability of finding the configuration with  $N$  trials out of which  $N_+$  are "successful" is, as usual,

$$P(N_+, N) = \frac{N!}{N_+!(N - N_+)!} \left(\frac{1}{2}\right)^N. \quad (11.26)$$

because both possibilities, steps to the right and to the left, have the same probability of  $1/2$ . Now, the necessary simplifying assumption, equivalent to the assumption made in the previous section about the sufficiently long time since the beginning of motion, is that the numbers of steps (both  $N$  and  $N_+$ ) are large. Using the Stirling formula  $N! \approx e^{-N} N^N \sqrt{2\pi N}$  we obtain

$$P(N_+, N) = \sqrt{\frac{N}{2\pi N_+(N - N_+)}} e^{N \ln N - N_+ \ln N_+ - (N - N_+) \ln(N - N_+) - N \ln 2} \quad (11.27)$$

Now one should get rid of unimportant  $N_+$  in favour of the displacement  $x$ , using (11.25), and expand the probability  $P(N_+, N)$  in powers of the parameter  $\epsilon = \frac{x}{aN} = (x\tau/at)$ , which we

assume to be small for a free random walk of many steps. Do the algebra as an exercise to obtain, keeping only terms up to second order in exponential,

$$\begin{aligned} P(N_+, N) &= \sqrt{\frac{2}{\pi N}} \sqrt{\frac{1}{1 - (x/aN)^2}} \exp\left[-\frac{x^2}{2a^2 N}\right] \\ &= 2a \sqrt{\frac{1}{4\pi D t}} \exp\left[-\frac{x^2}{4Dt}\right] \equiv 2a P(x, t) \end{aligned} \quad (11.28)$$

where the abbreviation  $D = a^2/2\tau$  is used. Note, that we should have in mind letting  $\tau$  and  $a$  go to zero, recovering the continuum description, but keeping fixed the ratio  $D$ . This is already looking familiar, reminding about the diffusion profiles evolving with time, or the problem of 1-dimensional rubber elasticity from *1B Thermodynamics*. But let us make a few more steps. First, changing from the summation over the number of discrete steps to the integration is, taking into account (11.25),

$$\begin{aligned} \sum_{N_1}^{N_2} \dots &= \int_{N_1}^{N_2} \dots dN_+ = \int_{x_1}^{x_2} \dots \frac{dx}{2a} \\ \text{so that } \sum_{N_1}^{N_2} P(N_+, N) &= \int_{x_1}^{x_2} P(x, t) dx \end{aligned} \quad (11.29)$$

where  $P(x, t)$  is the proper continuous probability density defined in Eq. (11.28):  $P(x, t) dx$  gives the probability of finding the particle after time  $t$  in the interval  $x \dots x + dx$  (having started at  $x = 0$  at  $t = 0$  in our picture). We now recover the key result about the 1-dimensional Brownian motion:  $\langle x(t)^2 \rangle = 2D t$ . It is clear that the ratio of microscopic parameters of random walk motion,  $D = a^2/2\tau$  plays the role of the diffusion constant, compare with Eq. (11.8).

The consideration in more than one dimension is analogous and, in fact, the results can be deduced immediately. Dividing this into three separate random walks, along  $x$ ,  $y$  and  $z$  directions, one multiplies the probabilities of statistically independent processes, and thus obtains as before  $\langle \mathbf{r}^3 \rangle = 3\langle x^2 \rangle = 6D t$ .

## Diffusion equation

Clearly the random walk resembles the diffusion process and it is time we establish an explicit connection. Let us return to the 1-dimensional discrete representation of a random walk the free Brownian particle is performing. Assign a number  $m$  to the current position the particle occupies after  $N + 1$  steps (simply define  $m = x/a$  so that  $m = 0, \pm 1, \pm 2, \dots$ ) and denote the probability of this occurrence as  $P(m, N + 1)$ . In order to arrive at this point  $m$ , the particle must have been at either  $m + 1$  or  $m - 1$  after  $N$  steps; there it arrived with probabilities  $P(m + 1, N)$  or  $P(m - 1, N)$ . Thus the probability  $P(m, N + 1)$  consists of two parts stemming from two possibilities for the particle to jump into  $m$  with corresponding *transition probabilities*, denoted as  $w(m, m + 1)$  and  $w(m, m - 1)$ :

$$P(m, N + 1) = w(m, m - 1)P(m - 1, N) + w(m, m + 1)P(m + 1, N) . \quad (11.30)$$

Of course,  $w(m, m + 1) = \frac{1}{2}$  and  $w(m, m - 1) = \frac{1}{2}$  for our 1-dimensional free Brownian motion. Note that Eq. (11.30) is actually valid for the general case, provided  $w(m, m + 1) + w(m, m - 1) =$

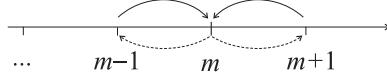


Figure 11.4: The scheme of ‘detailed balance’ – the change in probability  $P(m)$  is due to the difference between the *rate in*, Eq. (11.30), and the *rate out*:  $-(w_+ + w_-)P(m)$ .

1, that is, the particle is certain to hop out of the position  $m$  on the next time-step. Now, subtract  $P(m, N)$  from both sides of (11.30), see Fig. 11.4, and then divide it by the elementary time interval  $\tau = t/N$ . We have then

$$\begin{aligned} \frac{P(m, N+1) - P(m, N)}{\tau} &= \frac{1}{\tau} w(m, m-1)P(m-1, N) + \frac{1}{\tau} w(m, m+1)P(m+1, N) \\ &\quad - \frac{1}{\tau}[w(m-1, m) + w(m+1, m)]P(m, N) \\ \frac{\partial P(m, t)}{\partial t} &= \frac{1}{2\tau} [P(m-1, t) - 2P(m, t) + P(m+1, t)] , \end{aligned} \quad (11.31)$$

where in our case all  $w$ ’s = 1/2, which is implemented in Eq. (11.31). Now, let us re-write this equation again, this time paying attention to the fact that the expression in square brackets is the discrete representation of second derivative:

$$\frac{\partial P(m, t)}{\partial t} = \frac{1}{2\tau} \frac{\partial^2 P(m, t)}{\partial m^2} . \quad (11.32)$$

Now, replacing the index  $m$  by a continuous variable,  $m = x/a$ , we have at last

$$\frac{\partial P(x, t)}{\partial t} = \left( \frac{a^2}{2\tau} \right) \frac{\partial^2 P(x, t)}{\partial x^2} \quad (11.33)$$

(because the discrete probability and the continuous probability density are linearly related:  $P(m, t)\Delta m = P(x, t)\Delta x$ , where  $\Delta m = 1$  and  $\Delta x = a$ ). This is the 1-dimensional diffusion equation with the diffusion constant  $D = a^2/\tau$  defined, as before, as the constant limit at  $a \rightarrow 0$ ,  $\tau \rightarrow 0$ . We already know its fundamental solution, which is given by Eq. (11.28) !

By analogy, we can deduce the corresponding equation for a 3-dimensional diffusion process (by considering separately the process along the three Cartesian coordinates)

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = D \nabla^2 P(\mathbf{r}, t) \quad (11.34)$$

The diffusion equation has an immense importance in physics in general. One has only to look at a direct analogy with heat transfer (which is just the diffusion of “fast” molecules in the medium), and at the Schrödinger equation, which is exactly Eq. (11.34) only with imaginary time, or  $D = i\hbar/m$ .

## 11.5 Diffusion in external potentials

We have already examined the Brownian motion in external potential, but it was done from the Langevin equation, at a microscopic level. Now we are dealing with the probability function of the whole process,  $P(\mathbf{r}, t)$  and the kinetic equation that governs it. The simplest physical

example of diffusion under external force is the problem of particle sedimentation in solution. In this case, the force acting on the particles is constant (just  $mg$ ) and we can readily modify the earlier analysis of probability flow. Go back to Eq. (11.30) and Fig. 11.4, and now assume that the transition probabilities are not equal: independently of where the particle is on the  $x$ -scale, we take

$$w(m, m-1) = \frac{1}{2} - \epsilon \quad \text{and} \quad w(m, m+1) = \frac{1}{2} + \epsilon , \quad (11.35)$$

so that there is a preference for the particles to drift ‘down’ (from  $m+1$  to  $m$ ) as opposed to move ‘up’. Repeating the procedure that led to Eq. (11.32) we now have

$$\frac{\partial P(m, t)}{\partial t} = \frac{1}{2\tau} \frac{\partial^2 P(m, t)}{\partial m^2} + \frac{2\epsilon}{\tau} \frac{\partial P(m, t)}{\partial m} \quad (11.36)$$

$$\text{or } \frac{\partial P(x, t)}{\partial t} = D \frac{\partial^2 P(x, t)}{\partial x^2} + C \frac{\partial P(x, t)}{\partial x} , \quad (11.37)$$

where the new coefficient  $C = 2\epsilon a/\tau$  may itself depend on position, if  $\epsilon$  depends on position. We take  $\epsilon$  and thereby  $C$  to be constant for the time being. The presence of an external constant force has resulted in an additional term in the diffusion equation. There is a standard method of solving Eq. (11.37), based on the substitution

$$P(x, t) = \phi(x, t) \exp \left[ -\frac{C}{2D}(x - x_0) - \frac{C^2}{4D}t \right] ,$$

with the results shown in Fig. 11.5, but we can reach a better understanding of this phenomenon if we just look at the steady state of this process. In the limit of  $t \rightarrow \infty$  we expect no time-dependence left in the probability distribution (or the concentration of particles), so that Eq. (11.37) becomes

$$0 = D \frac{\partial^2 P(x)}{\partial x^2} + C \frac{\partial P(x)}{\partial x} \quad (11.38)$$

We can integrate this up vs.  $t$  and obtain  $0 = D \frac{\partial P(x)}{\partial x} + CP(x) + K$ , with  $K$  a constant of integration. However, this constant of integration can be fixed, because we know that for some very large  $x$ , both  $P$  and  $P'$  have to be = 0. Hence  $K$  must be = 0 as well, giving.

$$0 = D \frac{\partial P(x)}{\partial x} + CP(x) , \quad \text{i.e.} \quad P_{\text{eq.}}(x) = P_0 e^{-(C/D)x} . \quad (11.39)$$

If we recall the other definition of the diffusion constant,  $D = k_B T / \gamma$ , then the steady state distribution of particles in the gravity potential will take the form

$$P_{\text{eq.}}(x) = P_0 \exp \left( -\frac{mgx}{k_B T} \right) , \quad (11.40)$$

as long as we assign  $C = mg/\gamma$ , or the earlier parameter  $\epsilon = mg\tau/2\gamma a$ . This is the equilibrium Boltzmann distribution with the gravitational potential energy  $mgx$ , which we could have guessed from the outset.

The requirement that the equilibrium probability distribution (in the steady state, at  $t \rightarrow \infty$ ) reproduces the Boltzmann form,  $P_{\text{eq.}} \propto \exp[-E(x)/k_B T]$ , with  $E(x)$  the corresponding potential

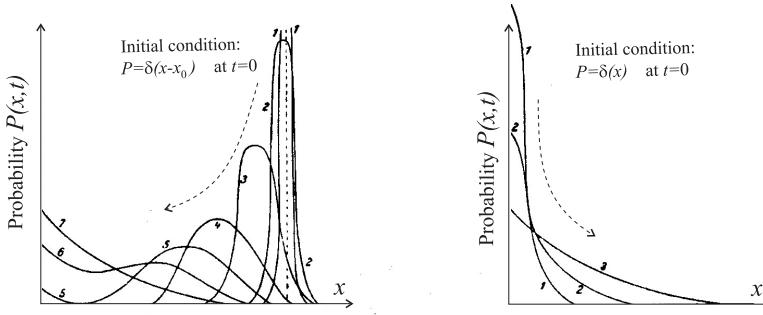


Figure 11.5: The time-evolution of particle concentration  $c(x, t)$ , proportional to the probability, during sedimentation. The left panel shows particles “sinking” from an initial delta-function distribution at  $x = x_0$ , and the right panel shows particles being “lifted” by the thermal excitation having started from a delta-function distribution at  $x = 0$ .

energy of the particle at point  $x$ , helps us understand the form of the generalised diffusion equation. Reproducing the argument in (11.39) we can say:

$$0 = D \frac{\partial P(x)}{\partial x} + \frac{1}{\gamma} \left( \frac{dE}{dx} \right) P(x), \quad (11.41)$$

$$\text{so that } \frac{dP}{P} = -\frac{1}{\gamma D} dE \quad \text{and} \quad P_{\text{eq.}}(x) = P_0 e^{-E(x)/k_B T}, \quad (11.42)$$

where the negative derivative  $f = -dE/dx$  is the external force acting on the particle. This means that the full, time-dependent, generalised diffusion equation can be written as

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left( \frac{1}{\gamma} \frac{dE}{dx} + D \frac{\partial}{\partial x} \right) P(x, t) \quad (11.43)$$

$$\text{or} \quad \frac{\partial P(x, t)}{\partial t} = -\frac{\partial}{\partial x} \left[ \frac{1}{\gamma} f(x) P(x, t) \right] + D \frac{\partial^2 P(x, t)}{\partial x^2}, \quad (11.44)$$

which go by the name of the *Fokker-Planck equation*. Note that its steady-state limit solution reproducing the equilibrium Boltzmann distribution is only valid when the external potential energy  $E(x)$  has a minimum: the free Brownian particle (at  $f = 0$ ) has no equilibrium position to act as reference point and follows the classical diffusion behaviour described by Eqs. (11.8) and (11.28).

The generalised diffusion equation (11.44) can also be written in a form that reproduces the continuity equation that you have seen in the context, e.g., of charge density in electromagnetism:

$$\frac{\partial P(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x}, \quad (11.45)$$

$$\text{with} \quad J(x, t) = -D \frac{\partial P(x, t)}{\partial x} + \frac{1}{\gamma} f(x) P(x, t) = -D e^{-\beta E(x)} \frac{\partial}{\partial x} \left[ e^{\beta E(x)} P(x, t) \right] \quad (11.46)$$

where  $J(x, t)$  represents the net current for the probability  $P(x, t)$ , or equivalently, the particle concentration  $c(x, t)$ . This net current arises as the sum of the *diffusion current*  $-D \frac{\partial P(x, t)}{\partial x}$ , which is driven by a probability (or concentration) gradient – as in Fick’s law – and the *drift current*  $\frac{1}{\gamma} f(x) P(x, t)$ , which is driven by the applied force. The equivalent second form of writing the total current can be checked by differentiation, and implementing  $D = k_B T/\gamma$ . For the force-free Brownian motion, the total current is just the diffusion current, i.e. the negative gradient of concentration:  $J = -D \nabla c(x, t)$ .

## The Kramers problem: escape over a potential barrier

As a final illustration of the application of principles of Brownian motion we shall consider the problem of the escape of particles over potential barriers. The solution to this problem has important implications on a variety of physical, chemical and astronomical problems, known as the *thermal activation*.

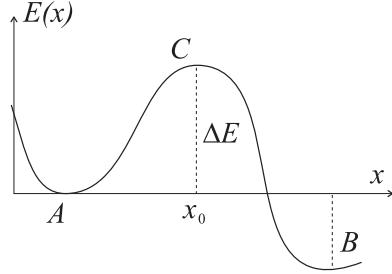


Figure 11.6: The potential energy profile of the Kramers problem. The key parameter is the height of the energy barrier,  $\Delta E$ , at a position  $x_0$ .

As usual, for simplicity limiting ourselves to a 1-dimensional problem, consider a particle moving in a potential field ( $x$ ) shown in Fig. 11.6. We suppose that the particles are initially caught in the *metastable* state at  $A$ , and we wish to find the rate at which the particles will escape from this state over the potential, as a result of thermal motion.

Let us concentrate on the long-time limit of this process, when the steady current of particles is established. Eq. (11.46) tells us that, at constant current  $J$ , integration between points  $A$  and  $B$  along the  $x$ -axis gives:

$$J \cdot \int_A^B e^{\beta E(s)} ds = -D \left[ e^{\beta E(x)} P(x) \right]_A^B, \quad (11.47)$$

where on the right-hand side the integral of the full derivative  $d/dx$  just gives us the difference between the initial and final values of the argument. Let us now approximate the potential near the metastable equilibrium point  $A$  as  $E(x) \approx E_A + \frac{1}{2}K_A x^2$ . The number of particles in the vicinity of  $A$  can be estimated from taking

$$dN_A = P(x_A) e^{-\beta E_A} dx$$

and integrating the Gaussian exponential  $e^{-\beta E_A}$  to obtain:

$$N_A \approx P(x_A) \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta K_A x^2} dx = P(x_A) \sqrt{\frac{2\pi k_B T}{K_A}}. \quad (11.48)$$

Considering point  $B$ , we can safely neglect its contribution to Eq. (11.47) if we assume the potential well  $E_B(x)$  is deep enough (the end-point being an “infinite sink” of particles). Then (since  $E(x_A) = 0$ ) the steady state current takes the form

$$J \approx \frac{DP(x_A)}{\int_A^B e^{\beta E(s)} ds}; \quad \text{rate} = \frac{J}{N_A} = D \sqrt{\frac{K_A}{2\pi k_B T}} \frac{1}{\int_A^B e^{\beta E(s)} ds}. \quad (11.49)$$

The principal contribution to the integral in denominator arises only from the very small region near the potential barrier  $C$ . Although the exact solution of Kramers problem may depend on

the particular shape of the potential  $E(x)$ , a very good estimate may be obtained by simply assuming the parabolic form near the maximum:  $E_C \approx \Delta E - \frac{1}{2}K_C(x-x_0)^2$ . On this assumption, with a sufficient degree of accuracy we have

$$\int_A^B e^{\beta E(s)} ds \approx e^{\Delta E/k_B T} \int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta K_C(x-x_0)^2} dx = e^{\Delta E/k_B T} \sqrt{\frac{2\pi k_B T}{K_C}}. \quad (11.50)$$

Combining Eqs. (11.49) and (11.50) we obtain the rate of particles transit over the barrier (equivalent to the rate of leaving the metastable state  $A$ ):

$$\text{rate} = \frac{J}{N_A} = D e^{-\Delta E/k_B T} \frac{\sqrt{K_A K_C}}{2\pi k_B T} = \frac{\sqrt{K_A K_C}}{2\pi\gamma} \cdot e^{-\Delta E/k_B T}. \quad (11.51)$$

This expression gives the probability, per unit time, that a particle originally in the potential hole  $A$ , will escape to  $B$  by crossing the barrier at  $C$ . The prefactor fraction is determined by various microscopic features of the system, but the most important fact to pay attention to is the exponential. This is the form representing the *thermal activation*, often known as the empirical Arrhenius law which one encounters in a variety of physical situations.



# Chapter 12

## Miscellaneous additional bits

### 12.1 Appendix 1: Microscopics of irreversibility

Can we derive the law of increase of entropy from the underlying microscopic laws such as Newtonian mechanics or quantum mechanics? This is a difficult question and I will discuss it in terms of a simple model, an isolated container ( $U$  constant) of gas consisting of  $N$  point particles obeying Newtonian mechanics. It is very important in physics to start with the simplest possible model which is relevant to the problem at hand. It is possible to derive the PEEP for such a system from Newtonian mechanics, and the proof is given in Appendix 2. This is helpful but it doesn't tell us about the approach to equilibrium and the law of increase of entropy.

If we write the jump rate between two microstates,  $i$  and  $j$ , as  $\nu_{ij}$ , and assume that the jump rates for the processes  $i \rightarrow j$  and  $j \rightarrow i$  are the same, then  $\nu_{ij} = \nu_{ji}$ . If the probability of being in microstate  $i$  is  $p_i$  then the probability of jumping from  $i$  to any other microstate is  $\sum_j \nu_{ij} p_i$  and the probability of jumping from any other microstate into state  $i$  is  $\sum_j \nu_{ji} p_j$ , so that overall we obtain Fermi's "master equation",

$$\begin{aligned}\frac{dp_i}{dt} &= \sum_j (-\nu_{ij} p_i + \nu_{ji} p_j) \\ &= \sum_j \nu_{ij} (p_j - p_i).\end{aligned}\tag{12.1}$$

In dynamic equilibrium  $\frac{dp_i}{dt} = 0$  so that, as long as none of the  $\nu_{ij}$  are zero (accessibility), equilibrium must correspond to  $p_i = p_j$ , i.e., the postulate of equal equilibrium probabilities (PEEP). The master equation not only predicts the PEEP, it also shows *irreversibility*. The master equation predicts that if the probabilities,  $p_i$ , are not equal to their equilibrium values then processes occur which drive them towards equilibrium. The master equation correctly shows how systems approach equilibrium. All that remains is to derive the master equation from the underlying microscopic physical laws! Here comes the disappointment, unfortunately it is *not possible* to derive the master equation in this way.

Consider a classical gas of molecules in an isolated container. The molecules obey Newton's laws, which have time reversal symmetry, so if we start off with all the molecules at one end of the container, make a film of the subsequent motion in which the molecules spread out over the

container and play it backwards (equivalent to reversing all the velocities) nothing looks wrong, they are still obeying Newton's laws. The Schrödinger equation of quantum mechanics also obeys *time reversal symmetry* and therefore it is not possible to derive the master equation from classical or quantum mechanics without some additional assumptions. Some of the equations of physics are irreversible, such as the diffusion equation and the Navier-Stokes equation, but these describe macroscopic phenomena and they already have the Second Law of Thermodynamics built into them. The success of these equations can be used as evidence that the Second Law is correct, but they cannot be invoked to derive it.

### Law of increase of entropy

This leads us to the greatest paradox of thermal and statistical physics, which Boltzmann sought to answer. How can irreversibility arise from the underlying time-reversible equations of motion? This problem is still not resolved to everyone's satisfaction. I will present a view which I hope is not too controversial, but certainly some will argue with it.

Consider a gas of  $N$  particles obeying Newtonian mechanics within an isolated container ( $U = \text{constant}$ ) which has upper and lower chambers joined by a hole. A sequence of snapshots of the gas is shown in Fig. 12.1. The first snapshot on the left shows a low entropy non-equilibrium state with all the gas in the lower chamber. If we start the system off from this state then we expect gas to move through the hole into the upper chamber so that equilibrium is approached where the gas is evenly distributed between the upper and lower chambers. The final state is then one of high entropy. Why does the gas prefer to be in the equilibrium state shown in the last snapshot on the right of Fig. 12.1?

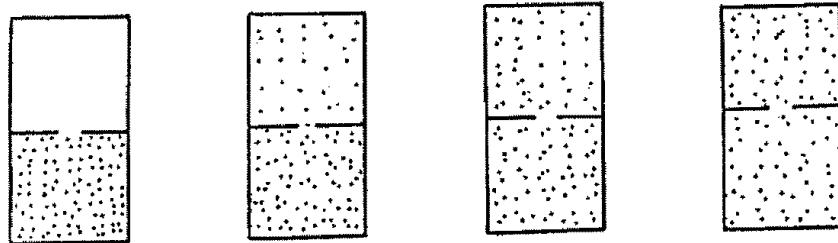


Figure 12.1: Four snapshots of a gas in a box approaching equilibrium.

To answer this question we use arguments based on the phase space introduced in §4.1.<sup>1</sup> Each snapshot in Fig. 12.1 shows a microstate of the system (I haven't shown the velocities of the particles) which is a member of a *macrostate*  $\Gamma(X)$  consisting of very many microstates which "look like" the snapshot. Let me try and make this notion more precise. Suppose the gas contains  $10^{23}$  molecules and we divide up the system into  $10^9$  small boxes. In equilibrium each box contains on average  $10^{23}/10^9 = 10^{14}$  molecules. In equilibrium the number of molecules in each box fluctuates about the mean value, but fluctuations of the size of the snapshot on the left of Fig. 12.1 are never seen. We can define a macrostate by specifying the number of particles in each box, to within some range. One can associate a Boltzmann entropy with each macrostate,

$$S_B(X) = k_B \ln |\Gamma(X)|, \quad (12.2)$$

where  $|\Gamma(X)|$  is the volume of phase space occupied by the *macrostate*  $\Gamma(X)$ .

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<sup>1</sup>Note that because we are assuming that the energy of our system is constant the trajectory of the point representing the system's microstate is confined to a constant energy surface of the phase space.

The different macrostates occupy different volumes of the phase space and the equilibrium macrostate occupies a much greater volume of phase-space than any other macrostate. The ratio of the phase space volumes,  $|\Gamma(X)|$ , for the macrostates on the right and left snapshots in Fig. 12.1 is roughly  $2^N = 2^{10^{23}}$ . We expect that if the system starts off in the macrostate corresponding to the snapshot on the left it will move with a probability of essentially unity into the much larger region of phase space corresponding to the equilibrium macrostate. In other words, the macrostate on the right of Fig. 12.1 is immensely more probable than the one on the left.

Many objections were raised to these ideas. Loschmidt noted that the form of Newton's laws means that the time-reversed solution is also valid. Zermelo noted that according to the Poincaré recurrence theorem almost all microstates will return to their initial microstate after a long enough period of time (which, however, for macroscopic systems turns out to be longer than the age of the universe). These objections illustrate the fact that there are points in phase space which do not have proper thermodynamic behaviour, but in fact they form a vanishingly small fraction of the total number of points.

Let us revisit the idea of watching a classical gas move towards equilibrium and then playing the film backwards. If we reverse all the velocities when the gas has attained equilibrium then obviously it just returns to its original state, which was far from equilibrium. The important point to realise is that this is totally irrelevant to the argument! We would not notice anything unphysical when we watched the film played backwards because Newton's laws are still obeyed, but starting conditions such that the system quickly moves far away from equilibrium are highly improbable, as once more I assert that most points in phase space just don't behave like that!

Modern computers have made it possible to simulate the time evolution of a gas of particles obeying Newton's laws. The number of particles and the simulation time must be kept fairly small so that the evolution is (almost) reversible. However, the results fully support Boltzmann's arguments.

Another important thing to notice is what Boltzmann's arguments *don't* involve. There was no mention of the precise nature of the dynamics, we only said that the molecules obeyed Newtonian mechanics. We have not used the PEEP. Nor have we mentioned quantum mechanics, which Boltzmann didn't know about. Of course matter obeys quantum mechanics rather than classical mechanics, but the introduction of quantum mechanics into the problem of the gas in a container only obscures the central issues. We *ought* to be able to explain this phenomenon within classical mechanics. Nor have we invoked "our limited knowledge of the microscopic state of the system", which is clearly irrelevant within a classical framework. Finally we have also not invoked residual interactions with the surroundings, although in practice these can never be entirely removed.

### **The arrow of time**

We have explained why entropy increases with time. Now comes the difficult part of the argument. Why should there be an "arrow of time" in our universe which says that time moves forwards, if the microscopic laws of physics are reversible? This is a rather controversial topic and a proper discussion of it is outside the scope of this course. The basic idea is that just after the Big Bang the universe was in a low entropy state; the arrow of time that we experience may simply be the continuing tendency of the universe to move away from this special state.<sup>2</sup>

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<sup>2</sup>For a more detailed discussion see J. Lebowitz, *Physics Today*, Sept. 1993, p.32

## 12.2 Appendix 2: Liouville's theorem

The state of a classical system at some given time is determined by its position in the  $6N$ -dimensional phase space. The trajectory of the system in the phase space is determined by the equations of motion which, in the Hamiltonian formulation, are:

$$\frac{\partial q_i}{\partial t} = \frac{\partial \mathcal{H}}{\partial p_i} \quad \frac{\partial p_i}{\partial t} = -\frac{\partial \mathcal{H}}{\partial q_i}, \quad (12.3)$$

where  $\mathcal{H}$  is the Hamiltonian function giving the system energy:  $E = \mathcal{H}(\{q_i, p_i\})$ . The classical equivalent of the quantum probability distribution is obtained by defining a *probability density*  $\varrho(\{q_i, p_i\})$  in the  $6N$  dimensional phase space.<sup>3</sup>

To obtain *Liouville's equation* we use the continuity relation, which states that probability is conserved,

$$\frac{\partial \varrho}{\partial t} + \nabla \cdot (\varrho \mathbf{v}) = 0. \quad (12.4)$$

The divergence term gives

$$\begin{aligned} \nabla \cdot (\varrho \mathbf{v}) &= \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i} \left( \varrho \frac{\partial q_i}{\partial t} \right) + \frac{\partial}{\partial p_i} \left( \varrho \frac{\partial p_i}{\partial t} \right) \right\} \\ &= \sum_{i=1}^{3N} \left\{ \frac{\partial q_i}{\partial t} \frac{\partial \varrho}{\partial q_i} + \frac{\partial p_i}{\partial t} \frac{\partial \varrho}{\partial p_i} \right\} + \sum_{i=1}^{3N} \left\{ \varrho \frac{\partial^2 q_i}{\partial q_i \partial t} + \varrho \frac{\partial^2 p_i}{\partial p_i \partial t} \right\} \end{aligned}$$

The second term in brackets is identically equal to zero, from Hamilton's equations, so Liouville's equation is

$$\frac{\partial \varrho}{\partial t} + \sum_{i=1}^{3N} \left\{ \frac{\partial q_i}{\partial t} \frac{\partial \varrho}{\partial q_i} + \frac{\partial p_i}{\partial t} \frac{\partial \varrho}{\partial p_i} \right\} = 0. \quad (12.5)$$

We now derive *Liouville's Theorem*, which states that in equilibrium the probability density  $\varrho$  is constant along the trajectories of the system in phase space. We are interested in the equilibrium ensemble, so  $\partial \varrho / \partial t = 0$ , and we obtain

$$\sum_{i=1}^{3N} \left\{ \frac{\partial q_i}{\partial t} \frac{\partial \varrho}{\partial q_i} + \frac{\partial p_i}{\partial t} \frac{\partial \varrho}{\partial p_i} \right\} = 0. \quad (12.6)$$

In other words, as we travel along the trajectory in phase space the probability density doesn't change.

This is a very important result, because the trajectories in phase space are lines of constant internal energy of the system, so it tells us that in equilibrium the probability density depends only on the energy, so states with the same energy have the same probability, which is the PEEP.

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<sup>3</sup>Probability density means what it says: you have to multiply by a volume element to get a probability.

## 12.3 Appendix 3: Fluctuation-dissipation theorem and Wiener-Khinchin theorem

Following on from section 11.3, we can obtain a very useful and general result about the relation between the frequency spectrum of fluctuations in a dynamic system and the response function of this system. First, we operate in the time-domain and argue that the expectation value of the fluctuating variable  $x(t)$  is given by the history of forces that have acted on it:

$$\langle x(t) \rangle = \langle x \rangle_0 + \int_{-\infty}^t f(t') \alpha(t-t') dt' , \quad (12.7)$$

where  $\langle x \rangle_0$  is the average value  $x$  assumes in the absence of the applied force  $f$ , and  $\alpha(t-t')$  gives the response of the dynamical system we are modelling at time  $t$ , provided it was exposed to a  $\delta$ -function force at time  $t'$ . This is the Fourier transform of the frequency-dependent response function  $\alpha_\omega$ , mentioned above, and it is also called Green's function.

We now choose a specific form for  $f(t)$ , namely an infinitesimal perturbation that switches on at  $t = -\infty$  and switches off at  $t = 0$ :

$$f(t) = f_0 \theta(-t)$$

where  $\theta(t)$  is the Heaviside step function.

We can express the expectation value of  $x$  at time  $t$  by integrating over all possible values that  $x$  may have at time  $t$ , weighted with their corresponding likelihood. These likelihoods, in turn, are obtained by integrating over all values  $x'$  at time 0, weighted with their likelyhoods and multiplied further by the probability that these values of  $x'$  would evolve into  $x$  at time  $t > 0$ :

$$\langle x(t) \rangle = \int \int dx' dx x P(x, t; x', 0) W(x', 0) \quad (12.8)$$

Here,  $P(x, t; x', 0)$  is the conditional probability that the system will evolve to value  $x$  at time  $t$ , if it had value  $x'$  at time  $t = 0$ , and  $W(x', 0)$  is the probability that the system had value  $x'$  at time  $t = 0$ . This is a special case of the more general result

$$\langle g(x(t)) h(x(0)) \rangle = \int \int dx' dx g(x) h(x') P(x, t; x', 0) W(x', 0) \quad (12.9)$$

We can find  $W(x', 0)$  in equilibrium from statistical mechanics:

$$W(x', 0) = \frac{e^{-\beta(E_0(x') - f_0 x')}}{\int e^{-\beta(E_0(x'') - f_0 x'')} dx''} \underset{\text{Taylor expand}}{\approx} \frac{e^{-\beta E_0(x')}(1 + \beta f_0 x')}{\int e^{-\beta E_0(x'')}(1 + \beta f_0 x'') dx''} \quad (12.10)$$

$$= \frac{e^{-\beta E_0(x')}(1 + \beta f_0 x')}{\int e^{-\beta E_0(x'')} dx'' (1 + \beta f_0 \langle x' \rangle_0)} = W_0(x') (1 + \beta f_0 (x' - \langle x' \rangle_0)) \quad (12.11)$$

Here,  $\langle \dots \rangle_0$ , which we abbreviate in the following with  $\overline{\dots}$ , denotes an average with respect to the unperturbed system, without applied force  $f(t)$ . This average is determined by the unperturbed energy  $E_0(x)$ , which produces the unperturbed probability distribution  $W_0(x)$ .

Putting this expression for  $W(x', 0)$ , which is accurate for infinitesimal perturbations  $f$  – and our test perturbation was designed to be infinitesimal – back into Eq. 12.8 then gives the expectation value for  $x(t)$  as

$$\langle x(t) \rangle = \int \int dx' dx (x - \bar{x} + \bar{x}) P(x, t; x', 0) W_0(x', 0) (1 + \beta f_0(x' - \bar{x})) = \quad (12.12)$$

$$= \langle (x(t) - \bar{x} + \bar{x})(1 + \beta f_0(x - \bar{x})) \rangle_0 = \bar{x} + \beta f_0 \langle (x(t) - \bar{x})(x(0) - \bar{x}) \rangle_0 \quad (12.13)$$

$$= \bar{x} + \beta f_0 A(t) , \quad (12.14)$$

where  $A(t) = \langle (x(t) - \bar{x})(x(0) - \bar{x}) \rangle_0$  is called the *autocorrelation function* of the variable  $x(t)$ .

Earlier on, when first considering the effect of a perturbing force  $f(t)$  on our system, namely in Eq. 12.7, the expectation value of  $x(t)$  was related to the response function of the system. We can now combine that equation with our most recent result to obtain:

$$\langle x(t) \rangle - \bar{x} = \beta f_0 A(t) = \int_{-\infty}^t f(t') \alpha(t - t') dt' \underset{\tau=t-t'}{=} f_0 \int_0^\infty \theta(\tau - t) \alpha(\tau) d\tau = f_0 \int_t^\infty \alpha(\tau) d\tau \quad (12.15)$$

Taking the derivative w.r.t.  $t$  on both sides, we obtain the key result:

$$\frac{dA}{dt} \theta(t) = -\frac{1}{\beta} \alpha(t) \quad (12.16)$$

The step function  $\theta(t)$  ensures that  $\alpha(t) = 0$  for  $t < 0$ , which is required by causality. We find that the time derivative of the autocorrelation function is determined by the response function.

### 12.3.1 Wiener-Khinchin theorem

To take this further, we need to study the behaviour of our system in the frequency domain. We use the following conventions for the treatment of Fourier series for a variable  $y(t)$ :

$$y(t) = \frac{1}{\sqrt{t_0}} \sum_\omega y_\omega e^{-i\omega t} \quad (12.17)$$

$$y_\omega = \frac{1}{\sqrt{t_0}} \int_{-t_0/2}^{t_0/2} y(t) e^{i\omega t} dt \quad (12.18)$$

$$\omega = \frac{2\pi}{t_0} n \text{ with } n = \text{integer} \quad (12.19)$$

$$\sum_\omega \xrightarrow[t_0 \rightarrow \infty]{} \frac{t_0}{2\pi} \int d\omega , \quad (12.20)$$

where the Fourier integrals are carried out over a time interval  $t_0$ , producing a grid of allowed frequencies spaced  $2\pi/t_0$ . Because the physical variable  $y(t)$  is real-valued, we can use  $y^*$  instead of  $y$ , when convenient.

We find that for two frequencies  $\omega$ ,  $\Omega$  and for correlation functions that are invariant under translation,  $\langle y(t + \tau)y(t) \rangle = \langle y^*(t + \tau)y(t) \rangle = \langle y^*(\tau)y(0) \rangle$ :

$$\langle y_{\omega+\Omega}^* y_{\omega} \rangle = \frac{1}{t_0} \int_{-t_0/2}^{t_0/2} \int_{-t_0/2}^{t_0/2} \langle y^*(t_1)y(t_2) \rangle e^{i(\omega+\Omega)t_1} e^{i\omega t_2} dt_1 dt_2 = \quad (12.21)$$

$$(\text{setting } t_1 = t_2 + \tau) = \frac{1}{t_0} \int d\tau dt_2 \langle y^*(t_2 + \tau)y(t_2) \rangle e^{-i(\omega+\Omega)(t_2+\tau)} e^{i\omega t_2} \quad (12.22)$$

$$= \frac{1}{t_0} \underbrace{\int dt_2 e^{-i\Omega t_2}}_{=t_0 \text{ for } \Omega=0} \int d\tau \langle y^*(\tau)y(0) \rangle e^{-i\omega\tau} e^{-i\Omega\tau} \quad (12.23)$$

$$= \delta_{\Omega,0} \int d\tau \langle y^*(\tau)y(0) \rangle e^{-i\omega\tau} \quad (12.24)$$

We see two results: firstly, the frequency components of our fluctuating variable  $y(t)$  are uncorrelated: a finite result is only obtained for the average  $\langle y_{\omega_1}^* y_{\omega_2} \rangle$ , when  $\omega_1 = \omega_2$ . This is a consequence of the translational invariance of the correlation function. Secondly, the power spectrum  $\langle y_{\omega}^* y_{\omega} \rangle$  of our process turns out to be given by the Fourier transform of the autocorrelation function. This is the essence of the Wiener-Khinchin theorem.

### 12.3.2 Power spectrum of fluctuations given by imaginary part of the response function

We can use the Wiener Khinchine theorem to revisit the earlier result Eq. 12.16:

$$\alpha(t) = -\beta \frac{dA}{dt} \theta(t) \quad (12.25)$$

$$\alpha_{\omega} = \int_{-\infty}^{\infty} \alpha(t) e^{i\omega t} dt \quad (12.26)$$

$$= -\beta \int_0^{\infty} \dot{A} e^{i\omega t} dt = (\text{integration by parts}) \quad (12.27)$$

$$= i\omega\beta \int_0^{\infty} A(t) e^{i\omega t} dt + \beta A(0) = (A(t) \text{ is real and even function}) \quad (12.28)$$

$$= i\omega \frac{\beta}{2} \int_{-\infty}^{\infty} A(t) e^{i\omega t} dt - \omega\beta \int_0^{\infty} A(t) \sin(\omega t) dt + \beta A(0) , \quad (12.29)$$

where the rearrangement in the last step follows from the fact that  $A(t)$  is a real and even function. We can now relate the real and imaginary parts of the response function  $\alpha_{\omega}$  to properties of the fluctuation spectrum:

$$\alpha'_{\omega=0} = \beta \langle |x(0) - \bar{x}|^2 \rangle = \beta \langle |\delta x|^2 \rangle , \quad \alpha''_{\omega} = \omega \frac{\beta}{2} \langle |\delta x_{\omega}|^2 \rangle , \quad (12.30)$$

The last step follows from the Wiener-Khinchin theorem, and we write  $\delta x = x - \bar{x}$ . Rearranging this slightly, we obtain the power spectrum of fluctuations around the mean,  $\langle |\delta x_{\omega}|^2 \rangle$ , from the imaginary part of the response function. The variance of the fluctuations, in turn, is given by the real part of the response function:

$$\langle |\delta x|^2 \rangle = k_B T \alpha'_{\omega=0} , \quad \langle |\delta x_{\omega}|^2 \rangle = \frac{2k_B T}{\omega} \alpha''_{\omega} \quad (12.31)$$

The first of these two expressions already followed from the equipartition theorem and was introduced in Eq. 11.19, but the second is new; this is the classical version of the fluctuation-dissipation theorem.

## 12.4 Appendix 4: Short biographies

**John Dalton** (1766-1844). Born in Eaglesfield in the Lake District, he was the son of a Quaker weaver. He began teaching at the age of 12 in a Quaker school in his home town. He taught at Kendal from 1781 and then went to teach mathematics and physical sciences at New College, Manchester. His first published work on meteorology attracted little attention. In 1794 he presented the earliest known paper on colour blindness, a condition from which he himself suffered. Dalton's most important contribution was his atomic theory which can be summarised as follows. (1) All matter consists of tiny particles which are indestructible and unchangeable. (2) Elements are characterised by the mass of their atoms, and when elements react, their atoms combine in simple, whole-number ratios. In 1808 he published the first part of "A New System of Chemical Philosophy" in which he listed the atomic weights of a number of known elements relative to the weight of hydrogen. Dalton arrived at his atomic theory through a study of the physical properties of gases. In the course of this investigation he discovered Dalton's law.



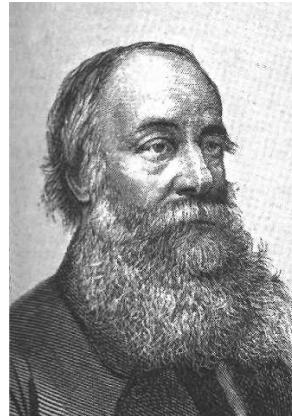
**Sadi Carnot** (1796-1832). Born in Paris, his father was a member of the Directory, the French Revolutionary government (1795-1799), and minister of war under Napoleon in 1799, and minister of the interior during Napoleon's Hundred Days rule in 1815. At 16 Carnot entered the Ecole Polytechnique and after graduating he studied military engineering. He began his work on thermodynamics because of his interest in designing steam engines. In 1824 Carnot published his book on steam engines which includes his description of the "Carnot cycle" and the "Carnot engine". He developed "Carnot's theorem" (all heat engines operating in reversible cycles are equally efficient and any degree of irreversibility reduces the efficiency). At that stage Carnot believed, quite wrongly, that heat was an indestructible substance (caloric), nevertheless, Carnot's theorem is correct and was very important in the development of the Second Law. He died in a cholera epidemic aged 36.



**Benoit Paul Emile Clapeyron** (1799-1864). Born in Paris, he studied at the Ecole Polytechnique, subsequently training as an engineer at the Ecole des Mines along with his friend Gabriel Lamé. Clapeyron and Lamé went to Russia for 10 years to teach mathematics to engineers and to lead construction work, during which they published joint mathematical and engineering work. They returned to France at the dawn of the railway age. Clapeyron constructed the first railway line connecting Paris to Saint-Germain and designed steam engines and metal bridges. In 1844 he was appointed professor at the Ecole des Ponts et Chaussées. Clapeyron devised a graphical representation of the Carnot cycle which influenced Thomson and Clausius in their work on the Second Law. Based on some of his ideas, Clausius later formulated the Clausius-Clapeyron equation.



**James Prescott Joule** (1818-1889). Born in Salford, he was the son of a prosperous brewery owner. He was educated by private tutors before studying under the chemist John Dalton. From 1837 to 1856 he worked in the family brewery, but in his spare time he studied electricity. In 1840 he formulated Joule's law of electrical heating (the heat generated is  $\propto I^2$ ). This led him to measure the heat produced through the action of falling weights, his famous "paddle wheel" experiment. His conclusion was that all systems contain energy which can be converted from one form to another, but the total energy of a closed system remains constant, which is the content of the First Law of Thermodynamics. He fell on hard times and, after an appeal by leading scientists of the day, was granted a civil list pension of £200 per annum in 1878. The unit of energy, the Joule, is named in his honour



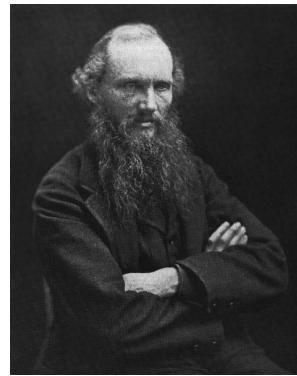
**Hermann Ludwig Ferdinand von Helmholtz** (1821-1894). Born in Potsdam, he was the son of a schoolteacher. Helmholtz was interested in physics, but his family was not well off so he studied medicine instead, for which he received a scholarship on condition that after graduating he worked for the Prussian army. He joined a military regiment at Potsdam in 1843, but spent his spare time on research, showing that muscle force was derived from chemical and physical principles. In 1847 he published his ideas in an important paper which studied the mathematical principles behind the conservation of energy. His scientific work was well regarded and he was released from the army to become professor of physiology at Königsberg in 1849. Subsequently he took up medical positions at Bonn in 1855, and Heidelberg in 1858, before taking up a professorship of physics at Berlin in 1882, subsequently becoming head of his own institute. He also did important work on physiological optics and physiological acoustics, vortex motion in fluids, acoustics including musical theory and the perception of sound, and electrodynamics. He was awarded the inheritable prefix "von" by Kaiser Wilhelm I, in 1882.



**Rudolf Julius Emmanuel Clausius** (1822-1888). Born in Koslin, Prussia (now Kozalin, Poland), he studied physics and mathematics in Berlin. He received his doctorate in 1848 for work on explaining the blue colour of the sky and the red colours of sunrise and sunset, although it turned out to be based on incorrect physics. In 1850 Clausius first published the basic idea of the Second Law of Thermodynamics. In 1865 he defined and named the quantity "entropy". The equation for the First Law,  $dQ = dU + dW$ , is due to Clausius, and he introduced the concept of  $U$ , later known as the internal energy. When Clausius was nearly 50 years of age he took part in the Franco-German war, receiving a serious leg wound and the Iron Cross. He was also involved in various disputes with British physicists concerning precedence for some of the ideas of thermodynamics.



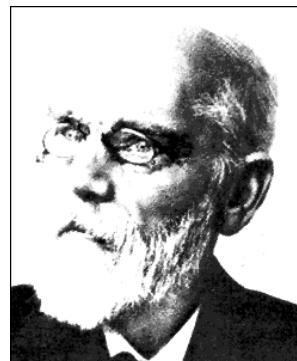
**Lord Kelvin (William Thomson)** (1824-1907). Born in Belfast, he attended Glasgow University from the age of 10, starting university level work at 14, in astronomy, chemistry and physics. Thomson moved to Cambridge, where he obtained a first class degree in mathematics and became a fellow of Peterhouse, and then to Paris where he met Biot, Cauchy, Liouville, and Sturm. In 1846 he was appointed Professor of Natural Philosophy at Glasgow University, helped by his father's influence, a position he held until 1897. He played major roles in the development of the Second Law of Thermodynamics, temperature scales, electromagnetic theory of light, and hydrodynamics. He also invented the mirror galvanometer. He achieved fame and wealth from his involvement in laying trans-atlantic cables for telegraph communication. The Kelvin temperature scale was named after him.



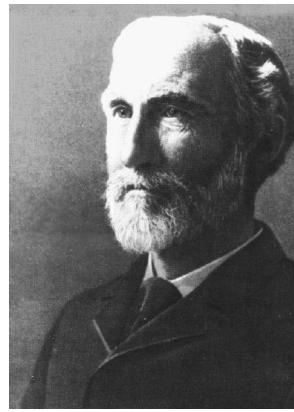
**James Clerk Maxwell** (1831-1879). Born in Edinburgh and attended Edinburgh University before studying mathematics at Trinity College, Cambridge. He held professorships in Aberdeen and then London before becoming the first Cavendish Professor of Physics at Cambridge in 1871. Maxwell showed that Saturn's rings consisted of small solid particles. He also made significant contributions to the kinetic theory of gases, but his most important achievements were in the extension and mathematical formulation of the theory of electromagnetism.



**Johannes Diderik van der Waals** (1837-1923). Born in Leyden in The Netherlands, he became a school teacher. In his spare time he studied at Leyden University and obtained teaching certificates in mathematics and physics. In 1873 he obtained his doctorate for a thesis which contained his famous equation of state, work which was recognised by, among others, Maxwell, and in 1876 he was appointed as the first Professor of Physics at Leyden. He made other important contributions such as The Law of Corresponding States (1880) and the Theory of Binary Solutions (1890). He was awarded the Nobel Prize for Physics in 1910 for his work on the equation of state for gases and liquids.



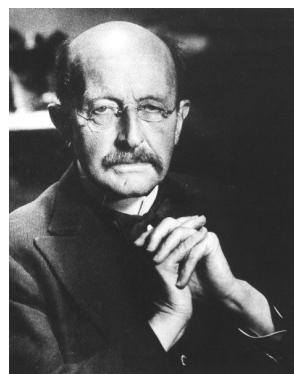
**Josiah Willard Gibbs** (1839-1903). Born in New Haven, Connecticut, the son of a professor of sacred literature at Yale. He obtained a doctorate in engineering from Yale in 1863 for a study of the design of gears. Afterwards he taught Latin and Natural Philosophy at Yale for three years. Gibbs spent 1866-1869 in Europe, studying in Paris, Berlin and Heidelberg. In 1871 he was appointed professor of mathematical physics at Yale, before he had published any work. In mathematics he wrote on quaternions and was influential in developing vector analysis. Gibbs also contributed to crystallography, the determination of planetary and comet orbits, and electromagnetic theory. His most important work was on thermal and statistical physics where he introduced geometrical methods, thermodynamic surfaces, criteria for equilibrium, the Gibbs free energy, the chemical potential, Gibbs statistical entropy, ensembles, and gave a complete treatment of the phase equilibrium of heterogeneous substances.



**Ludwig Boltzmann** (1844-1906). Born in Vienna, the son of a tax official. Boltzmann's doctorate on the kinetic theory of gases was awarded in 1866, and he became an assistant to his teacher, Josef Stefan. He taught at Graz, Heidelberg and Berlin, studying under Bunsen, Kirchhoff and Helmholtz. He held chairs of mathematics and physics at Vienna, Graz, Munich and Leipzig. Boltzmann developed statistical mechanics independently of Gibbs, working on the statistical definition of entropy and attempting to derive the Second Law of Thermodynamics from the principles of mechanics. He was also one of the first to recognise the importance of Maxwell's electromagnetic theory. His work was opposed by many European scientists who misunderstood his ideas. Boltzmann had always suffered from powerful mood swings and, depressed and in bad health, he hanged himself while on holiday with his wife and daughter. Within a few years of his death many of his ideas were verified by experiment.



**Max Planck** (1858-1947). Planck was born in Kiel, Germany, his father being a professor of law. Planck's family moved to Munich where he attended school and then university before studying in Berlin under Helmholtz and Kirchhoff. He returned to Munich where he received his doctorate on the Second Law of Thermodynamics, taught at the University of Munich (1880-1885), was appointed to a chair in Kiel, and in 1889 he succeeded Kirchhoff in the chair of Theoretical Physics at Berlin. Planck studied thermodynamics, examining the distribution of energy among different wavelengths. In 1900 Planck obtained his famous radiation formula by combining the formulae of Wien and Rayleigh. Within two months Planck had deduced his formula theoretically, renouncing classical physics and introducing the quanta of energy. The theory met resistance until Niels Bohr used it to calculate positions of spectral lines in 1913. Planck received the Nobel Prize for Physics in 1918. Subsequently Planck worked in science administration. He remained in Germany during World War II, during which time his son Erwin was executed for plotting to assassinate Hitler.



**Pierre Duhem** (1861-1916). Born in Paris, the son of a commercial traveller. He studied at the Ecole Normale and in 1884 he published his first paper on electrochemical cells. Duhem submitted his doctoral thesis in 1884 in which he defined the criterion for chemical reactions in terms of free energy. This work replaced the incorrect theory of Marcellin Berthelot, but Berthelot arranged for Duhem's thesis to be rejected. Duhem boldly published his rejected thesis in 1886, and successfully submitted a second thesis on magnetism in 1888. Duhem worked at Lille from 1887 until he moved to Rennes in 1893, but he quickly moved on to Bordeaux in 1894. A move to Paris was blocked by Berthelot who had become Minister of Education. Duhem was interested in hydrodynamics, elasticity, mathematical chemistry, and mechanics, but his most important contributions were to thermodynamics. He also wrote on the history and philosophy of science, where his views were strongly influenced by his Catholicism.



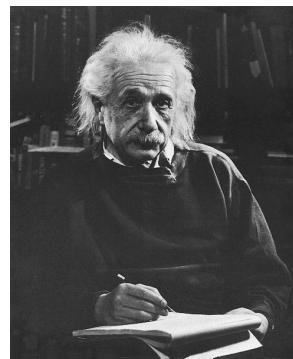
**Walther Hermann Nernst** (1864-1941). Nernst was born in Briesen, West Prussia, the son of a district judge. He studied physics and mathematics at the Universities of Zürich, Berlin and Graz, before moving to Würzburg, where in 1887 he obtained a doctorate with a thesis on electromotive forces produced by magnetism in heated metal plates. He joined Ostwald at Leipzig University and in 1894 he became a professor at Göttingen, moving to Berlin in 1905, where he remained until his retirement in 1933. He made fundamental contributions to electrochemistry, the theory of solutions, solid state chemistry, photochemistry, and thermodynamics and thermochemistry, including developing the Third Law of Thermodynamics. For his work in thermochemistry he received the Nobel Prize for Chemistry in 1920.



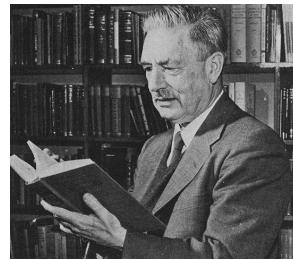
**Constantin Carathéodory** (1873-1950). He was born in Berlin where he entered the University in 1900. He received his Ph.D. in 1904 from the University of Göttingen working under Hermann Minkowski. Subsequently he took up a post at the University of Smyrna (now Izmir in Turkey), then moved to Athens and in 1924 to Munich, where he stayed for the rest of his career. Carathéodory made contributions to mathematics, relativity and optics, as well as reformulating the Second Law.



**Albert Einstein** (1879-1955). Born in Ulm, Germany, his family moved to Munich. Einstein failed an entrance examination for a local school, so he moved to a school in Arrau, Switzerland, and entered the Swiss National Polytechnic in Zürich, graduating in 1900. He worked as a teacher, but in 1902 joined a patents office in Bern, earning a doctorate in 1905 from the University of Zürich for theoretical work on determining the sizes of molecules. In 1905 he completed five papers that would change the world for ever. Spanning three quite distinct topics – relativity, the photoelectric effect and Brownian motion – he laid foundations to modern quantum mechanics, statistical physics and field theory. In 1908 he became a lecturer at the University of Bern, and held professorships at Zürich (1909-11, 1912-13), Prague (1911-12), and Berlin (1913-32). In 1915 he published his definitive version of general relativity. When British eclipse expeditions in 1919 confirmed his predictions Einstein became world famous. He received the Nobel Prize in 1921 for his work on the photo-electric effect. He left Germany for Princeton in 1932, working on unified theories of physics. In 1952 the Israeli government offered him the post of president, which he refused.



**Peter Joseph William Debye** (1884-1966). Born in Maastricht, he obtained a degree in electrical technology from the Aachen Institute of Technology in 1905. He worked as an assistant for two years before moving to Munich, where he obtained his doctorate in 1908 and became a lecturer in 1910. In 1911 he became Professor of Theoretical Physics at Zürich, and subsequently he worked at Utrecht, Göttingen, Zürich (again), Leipzig, and Berlin. He introduced the concept of the molecular electric dipole moment, which led to a new understanding of ionisation and molecular structure. For this and related work he was awarded the 1936 Nobel Prize for Chemistry. He emigrated to the USA in 1940, becoming Professor of Chemistry at Cornell, where he mostly researched into the light-scattering process.



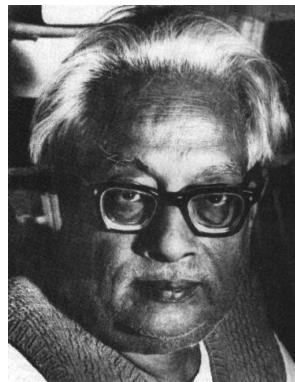
**Erwin Schrödinger** (1887-1961). His father ran a small linoleum factory in Erdberg, Austria. He studied mathematics and physics at the University of Vienna, receiving a doctorate on the conduction of electricity on the surface of insulators in moist air. He then undertook voluntary military service until he obtained an assistantship at Vienna. During World War I he saw active service in Italy and Hungary, receiving a citation for outstanding service, but in 1917 he returned to Vienna, where he worked on colour theory, and moved to Jena and then Zürich in 1921. He began to study atomic structure and quantum statistics and was influenced by de Broglie's thesis. In 1926 he published his revolutionary wave mechanics. In 1927 he moved to Berlin but left in 1933 and moved from place to place, finally settling in Dublin in 1939. In 1933 he was awarded the Nobel Prize and in 1935 his famous Schrödinger's cat paradox appeared. He published work on a unified field theories, but was devastated by Einstein's criticism of this work. He also wrote various books including "What is life?", before returning to Vienna in 1956.



**Louis-Victor Pierre Raymond duc de Broglie** (1892-1987). Born in Dieppe, he studied history at the Sorbonne in Paris. He intended a career in the diplomatic service, but became interested in mathematics and physics and was awarded a degree in theoretical physics in 1913. When World War I broke out he joined the army, serving in the telegraphy section at the Eiffel Tower. After the war he returned to the Sorbonne and became interested in quantum theory. In his doctoral thesis of 1924, “Researches on the quantum theory”, he proposed the particle-wave duality. He taught at the Sorbonne, becoming Professor of Theoretical Physics at the Henri Poincaré Institute in 1928. The wave nature of the electron was confirmed experimentally in 1927, and de Broglie was awarded the Nobel Prize in 1929. From 1932 he was also Professor of Theoretical Physics at the Sorbonne, where he taught until he retired in 1962.



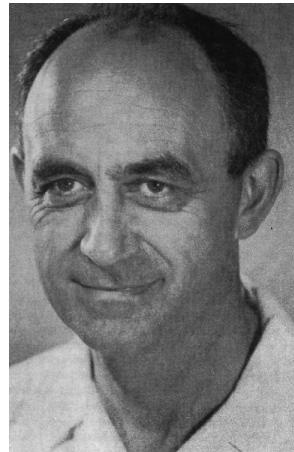
**Satyendra Nath Bose** (1894-1974). Bose studied at the University of Calcutta, becoming a lecturer in 1916. In 1921 he was appointed as a Reader at the University of Dacca. In 1923 he wrote a paper on Planck’s radiation law which was rejected by the Philosophical Magazine of London. He sent a copy of his paper to Einstein, his accompanying letter starting “Respected Sir, I have ventured to send you the accompanying article for your perusal and opinion.” Einstein saw the importance of Bose’s work, translated it into German and recommended that it for publication in the German journal Zeitschrift für Physik. Bose toured Europe, visiting Paris and Berlin, where he worked with Einstein and met Schrödinger and Heisenberg. Returning to Dacca he became Professor and Head of the Department of Physics, before moving back to Calcutta. Dirac coined the term “boson” for particles obeying Bose-Einstein statistics.



**Wolfgang Ernst Pauli** (1900-1958). Born in Vienna, the son of a doctor, his godfather was the physicist and philosopher Ernst Mach. He wrote his first paper on general relativity, aged 18. He worked under Sommerfeld in Munich and was awarded a doctorate in 1921. After working as Max Born’s assistant in Göttingen he moved to the University of Hamburg. He formulated the exclusion principle in 1925, which states that no two electrons can exist in the same quantum state. In 1927 he introduced the Pauli spin matrices. He was appointed Professor of Theoretical Physics in Zürich in 1928, and in 1930 he postulated the existence of the neutrino, which was first observed experimentally in 1959. He visited Michigan and the Institute for Advanced Study at Princeton before returning to Zürich. In 1940 he proved the spin-statistics theorem, which states that fermions have half-integer spin and bosons integer spin. He returned to Princeton and in 1945 was awarded the Nobel Prize in for his discovery of the exclusion principle. In 1946 he returned to Zürich, and wrote an important paper on the CPT theorem. He was also known for the “Pauli Effect” - his mere presence would lead to equipment breaking, which rather amused him!



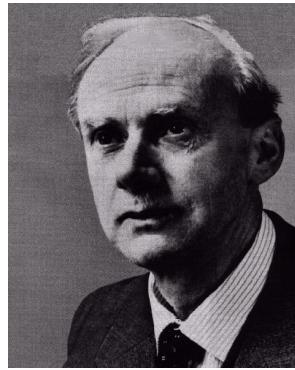
**Enrico Fermi** (1901-1954). Born in Rome, he was the son of a civil servant. Fermi studied at Pisa, gaining his doctorate in physics in 1922. He visited Max Born in Göttingen and Ehrenfest in Leyden, returning to Italy in 1924 as a lecturer at the University of Florence. In 1926 he discovered “Fermi statistics”, and in 1927 he was elected Professor of Theoretical Physics at the University of Rome. His theory of beta decay introduced the “weak force” into physics, and he was awarded the Nobel Prize in 1938 for his work on nuclear reactions. He emigrated to the USA and was appointed Professor of Physics at Columbia University (1939-1942). When nuclear fission was discovered by Hahn and coworkers in 1939, Fermi recognised the possibility of a chain reaction and directed the first controlled nuclear chain reaction in Chicago in 1942. He played an important role in the Manhattan Project for the development of the atomic bomb. In 1946 he accepted a professorship at the Institute for Nuclear Studies of the University of Chicago, turning his attention to high-energy physics. He died from stomach cancer in 1954.



**Werner Karl Heisenberg** (1901-1976). Born in Würzburg, he studied theoretical physics at the University of Munich, gaining a doctorate in 1923. He studied with Sommerfeld, also spending time at Göttingen with Born and at Copenhagen with Bohr. At age 25 he was appointed Professor of Theoretical Physics in Leipzig. Heisenberg invented matrix quantum mechanics in 1925, his Uncertainty Principle in 1927, and by 1932, when he was awarded the Nobel prize, he was applying quantum theory to the atomic nucleus. During the Second World War he headed the unsuccessful German nuclear bomb project. In 1941 he was appointed Professor of Physics at the University of Berlin. After the war he was interned in Britain, but returned to Germany in 1946 as director of the Max Planck Institute for Physics and Astrophysics at Göttingen, remaining in post when the institute moved to Munich in 1958. He devoted much of his time to reviving research in West Germany, and he also wrote and lectured on the philosophy of physics.



**Paul Adrien Maurice Dirac** (1902-1984). Dirac's father was a teacher from Switzerland, while his mother was English. He studied electrical engineering at the University of Bristol, but his real passion was mathematics. He was unable to take up a scholarship at St John's College, Cambridge, for financial reasons, so he studied mathematics at Bristol, obtaining first class honours in 1923. He then worked at Cambridge with Fowler on quantum statistical mechanics. Dirac realised that Heisenberg's uncertainty principle was a statement of the non-commutativity of quantum mechanical observables, which formed part of his doctoral thesis awarded in 1926. He visited Copenhagen, Göttingen and Leiden, before returning to Cambridge as a Fellow of St John's in 1927. In 1928 he published the Dirac equation for spin-1/2 relativistic particles, in 1930 he published "The principles of Quantum Mechanics", and in 1931 he predicted the existence of antimatter. He shared the 1933 Nobel Prize with Schrödinger. He became Lucasian Professor of Mathematics at Cambridge in 1932. Dirac worked on uranium separation and nuclear weapons during World War II. In 1969 Dirac retired from Cambridge, taking up positions at the University of Miami and Florida State University.



**Lev Davidovitch Landau** (1908-1968). Born in Baku, Azerbaijan, he was the son of a petroleum engineer and a physician. He entered Baku University in 1922, aged 14, before moving to Leningrad State University in 1924. After graduating in 1927 he continued research at the Leningrad Physico-Technical Institute. From 1929-1931 he visited Germany, Switzerland, England and, especially, Copenhagen, working under Bohr. In 1932 Landau became the head of the Theoretical Department of the Ukrainian Physico-Technical Institute at Kharkov, and in 1935 he also became head of Physics at the Kharkov Gorky State University. In 1937 Landau went to Moscow to become Head of the Theory Division of the Physical Institute of the Academy of Sciences. He also spent a year in prison during Stalin's regime. Landau's work covered many branches of theoretical physics, including low-temperature physics, phase transitions, atomic and nuclear physics and plasma physics. He was awarded the Nobel Prize for Physics in 1962 "for his pioneering theories for condensed matter, especially liquid helium". In 1962, Landau was involved in a car accident and was unconscious for six weeks, and from which he never fully recovered.

