Part II Statistical Mechanics

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Abstract

> Anyone who wants to analyze the properties of matter in a real problem might want to start by writing down the fundamental equations and then try to solve them mathematically. Although there are people who try to use such an approach, these people are the failures in this field . . .

Statistical mechanics is the art of turning the microscopic laws of physics into a description of Nature on a macroscopic scale.

Suppose you've got theoretical physics cracked. Suppose you know all the fundamental laws of Nature, the properties of the elementary particles and the forces at play between them. How can you turn this knowledge into an understanding of the world around us? More concretely, if I give you a box containing 10^{23} particles and tell you their mass, their charge, their interactions, and so on, what can you tell me about the stuff in the box?

There's one strategy that definitely won't work: writing down the Schrödinger equation for 10^{23} particles and solving it. That's typically not possible for 23 particles, let alone 10^{23}. What's more, even if you could find the wavefunction of the system, what would you do with it? The positions of individual particles are of little interest to anyone. We want answers to much more basic, almost childish, questions about the contents of the box. Is it wet? Is it hot? What colour is it? Is the box in danger of exploding? What happens if we squeeze it, pull it, heat it up? How can we begin to answer these kind of questions starting from the fundamental laws of physics?

The purpose of this course is to introduce the dictionary that allows you translate from the microscopic world where the laws of Nature are written to the everyday macroscopic world that we're familiar with. This will allow us to begin to address very basic questions about how matter behaves.

We'll see many examples. For centuries – from the 1600s to the 1900s – scientists were discovering "laws of physics" that govern different substances. There are many hundreds of these laws, mostly named after their discovers. Boyle's law and Charles's law relate pressure, volume and temperature of gases (they are usually combined into the ideal gas law); the Stefan-Boltzmann law tells you how much energy a hot object emits; Wien's displacement law tells you the colour of that hot object; the Dulong-Petit law tells you how much energy it takes to heat up a lump of stuff; Curie's law tells you how a magnet loses its magic if you put it over a flame; and so on and so on. Yet we now know that these laws aren't fundamental. In some cases they follow simply from Newtonian mechanics and a dose of statistical thinking. In other cases, we need to throw quantum mechanics into the mix as well. But in all cases, we're going to see how derive them from first principles.

A large part of this course will be devoted to figuring out the interesting things that happen when you throw 10^{23} particles together. One of the recurring themes will be that $10^{23} \neq 1$. More is different: there are key concepts that are not visible in the underlying laws of physics but emerge only when we consider a large collection of particles. One very simple example is temperature. This is not a fundamental concept: it doesn't make sense to talk about the temperature of a single electron. But it would be impossible

to talk about physics of the everyday world around us without mention of temperature. This illustrates the fact that the language needed to describe physics on one scale is very different from that needed on other scales. We'll see several similar emergent quantities in this course, including the phenomenon of phase transitions where the smooth continuous laws of physics conspire to give abrupt, discontinuous changes in the structure of matter.

Historically, the techniques of statistical mechanics proved to be a crucial tool for understanding the deeper laws of physics. Not only is the development of the subject intimately tied with the first evidence for the existence of atoms, but quantum mechanics itself was discovered by applying statistical methods to decipher the spectrum of light emitted from hot objects. However, physics is not a finished subject. There are many important systems in Nature – from high temperature superconductors to black holes – which are not yet understood at a fundamental level. The information that we have about these systems concerns their macroscopic properties and our goal is to use these scant clues to deconstruct the underlying mechanisms at work. The tools that we will develop in this course will be crucial in this task.

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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

1.1.1.1 Energy Storage

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

$$U = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 , \tag{1.1}$$

where m is the atomic mass and $\mathbf{v}_i$ is the velocity of the ith 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:

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

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

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

$$pV = N k_B T \qquad \text{Ideal gas law} \tag{1.3}$$

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

where p is the pressure and γ 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 moles 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.

1.1.1.2 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

$$\mathrm{d}U = đW \quad (= -p\,\mathrm{d}V \quad \text{if the compression is reversible}), \tag{1.5}$$

where we have used conservation of energy to state that the work done, $đW$, must be equal to the change in the internal energy of the gas.[1] The slash through the symbol đ

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[1] 1The sign of $đW$ 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 $đW$ relates to $\mathrm{d}U$, where U is the system energy. Positive work means that the system energy goes up, and vice-versa

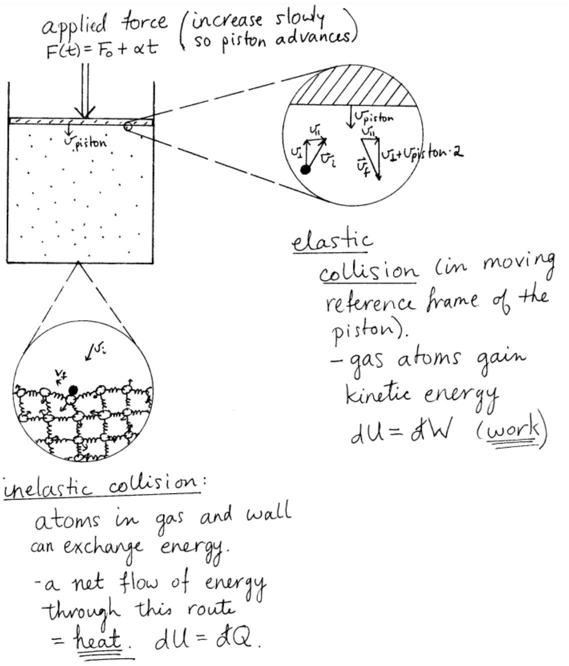
applied force (increase slowly so piston advances)
F(t) = F₀ + αt
v piston
v piston
v∥
v⊥
v_i
v∥
v_f
v⊥ + v piston · 2
elastic collision (in moving reference frame of the piston).
– gas atoms gain kinetic energy
dU = đW (work)
v_i
v_f
inelastic collision:
atoms in gas and wall can exchange energy.
- a net flow of energy through this route = heat. dU = đQ.

Fig. 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.

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, $đW$ 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."

Microscopic ↔ 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

   $$\mathrm{d}U = đQ \quad (= T\,\mathrm{d}S \quad \text{if the heat flow is reversible}), \tag{1.6}$$

   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

$$\mathrm{d}U = \mu \, \mathrm{d}N \,, \tag{1.7}$$

where μ is called the "chemical potential", defined as the change in energy when you bring an extra particle into the system:

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

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 μ 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, $pV = Nk_BT$, is replaced by

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

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 $-N^2a/V^2$ 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.

1.1.2.1 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

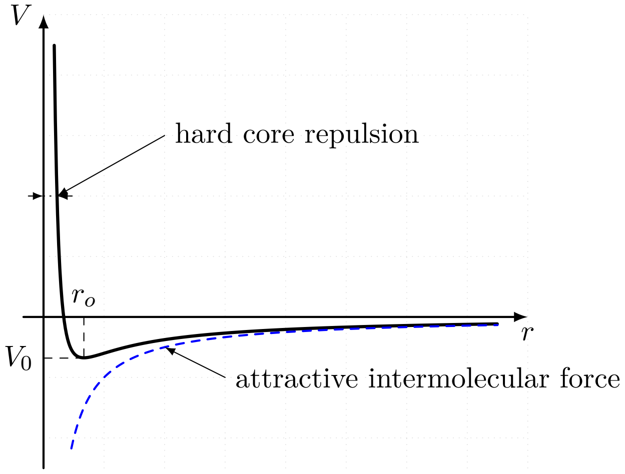

Fig. 1.2: The inter-molecular potential for a Van der Waals gas.

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 Section 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.

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 $\mathbf{m} + \mathrm{d}\mathbf{m}$ 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 proportional to $(\mathbf{m} \cdot \boldsymbol{\nabla})\mathbf{H}$. 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 $W' = -\mu_0 \int_0^{H_1} \mathbf{m}(\mathbf{H})\,\mathrm{d}\mathbf{H}$. 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, $W_1 = \mu_0 \int \mathbf{m}_1\,\mathrm{d}\mathbf{H} = \mu_0 \mathbf{m}_1 \mathbf{H}_1$, giving a net work $W = \mu \int \mathbf{H}\,\mathrm{d}\mathbf{m}$. 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:

$$\text{đ}W = \mu_0 \mathbf{H}\,\mathrm{d}\mathbf{m} \tag{1.10}$$

This contrasts with the work done during the first part of the process only: $\text{đ}W' =$

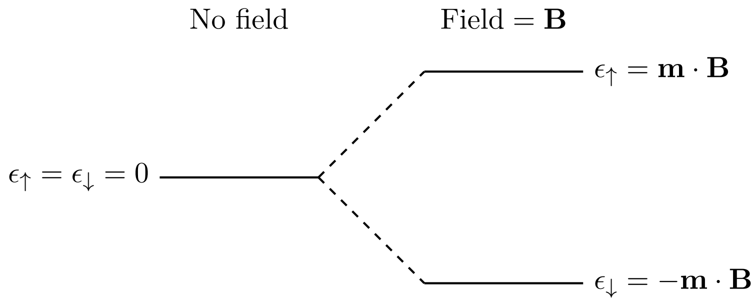
No field
Field = $\mathbf{B}$
$\epsilon_\uparrow = \mathbf{m}\cdot\mathbf{B}$
$\epsilon_\uparrow = \epsilon_\downarrow = 0$
$\epsilon_\downarrow = -\mathbf{m}\cdot\mathbf{B}$

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

$-\mu_0\mathbf{m}\,\mathrm{d}\mathbf{H}$. The difference between the two expressions is the change in the potential energy of the dipole moment in an applied field, $-\mu_0\,\mathrm{d}(\mathbf{mH})$, 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 (see Fig. 1.3).

1.1.3.1 Energy Storage

How does the expression for the work on a macroscopic substance (Eq. (1.10)) 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 $-\mu_0\mathbf{mH}$, 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 $U_{\text{pot}} = \mu_0(N_\uparrow - N_\downarrow)\mathbf{m}_d H$, 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.

1.1.3.2 Energy Flow In and Out of the System

Macroscopic ↔ Microscopic Energy Flow 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 $\mathrm{d}U = -\mu_0\,\mathrm{d}(\mathbf{mH})$.. 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 $đW' = -\mu_0 \mathbf{m}\,\mathrm{d}\mathbf{H}$.. Setting $\mathrm{d}U = đQ + đW'$, we find that heat is extracted during this process:

$$đQ = \mathrm{d}U - đW' = -\mu_0\,\mathrm{d}(\mathbf{mH}) + \mu_0 \mathbf{m}\,\mathrm{d}\mathbf{H} = -\mu_0 \mathbf{H}\,\mathrm{d}\mathbf{m}\,. \tag{1.11}$$

How does this tally with the approach outlined earlier, which gave a work $đW = \mu_0 \mathbf{H}\,\mathrm{d}\mathbf{m}$? 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 $\mu_0 \mathbf{H}\,\mathrm{d}\mathbf{m}$. This still gives $đQ = -\mu_0 \mathbf{H}\,\mathrm{d}\mathbf{m}$, so heat is extracted.

Even if no heat was exchanged between the surroundings and the sample, heat must have left the spin system, because $đQ$ 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?

Microscopic ↔ Microscopic Energy Flow 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 nth excited state is

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0. \tag{1.12}$$

1.1.4.1 Energy Storage

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

1.1.4.2 Energy Flow In and Out of the System

Macroscopic to microscopic energy flow would be accomplished by changing ω_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 μ, 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 know 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 Chapter 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

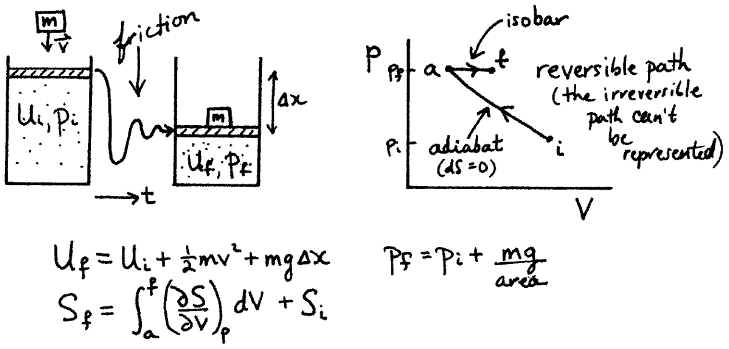
m
v
U_i, p_i
friction
Δx
m
U_f, p_f
→t
isobar
P
p_f
a
f
reversible path
(the irreversible path can't be represented)
p_i
adiabat
($dS=0$)
i
V
$U_f = U_i + \frac{1}{2}mv^2 + mg\Delta x$
$S_f = \int_a^f \left(\frac{\partial S}{\partial V}\right)_p dV + S_i$
$p_f = p_i + \frac{mg}{\text{area}}$

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

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

$$\mathrm{d}S = \frac{\text{đ}Q_{\text{rev}}}{T} \quad \text{or, for a finite change,} \quad \Delta S = \int_i^f \frac{\text{đ}Q_{\text{rev}}}{T} \tag{1.13}$$

According to this equation, to find the difference in entropy between two states, we integrate along any *reversible* path connecting those states. See 1.5 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

$$\Phi(p, T, V, N_1, N_2, \cdots) = 0. \tag{1.14}$$

(E.g., for an ideal gas, $pV - Nk_BT = 0$.) 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.

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.

1.3.1 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 80K isotherm, the path $A-E$E, rather than the path $A-B-C-D-E$.[2]

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.

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[2] 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.

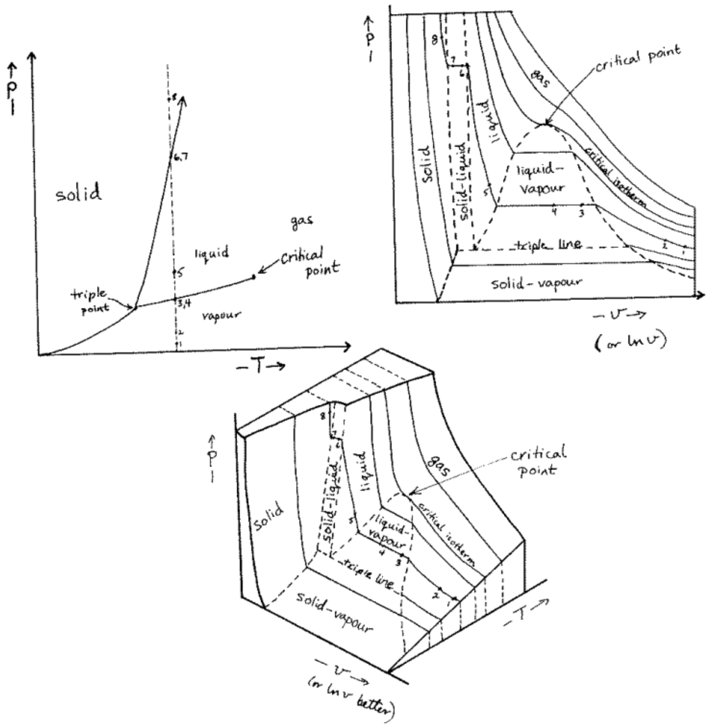
p
T
solid
liquid
gas
vapour
triple point
critical point
8
6,7
5
3,4
2
1
p
solid
solid-liquid
liquid
gas
critical point
critical isotherm
liquid-vapour
triple line
solid-vapour
V
(or ln V)
p
solid
solid-liquid
liquid
gas
critical point
liquid-vapour
critical isotherm
triple line
solid-vapour
V
(or ln V better)
T

Fig. 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.

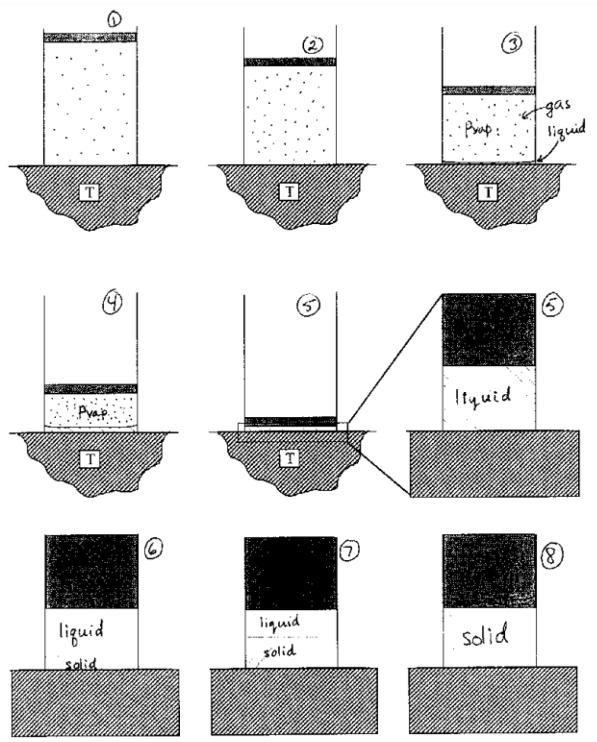
①
②
③
gas
liquid
Pvap
T
④
Pvap
⑤
⑤
liquid
⑥
liquid
solid
⑦
liquid
solid
⑧
solid

Fig. 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.

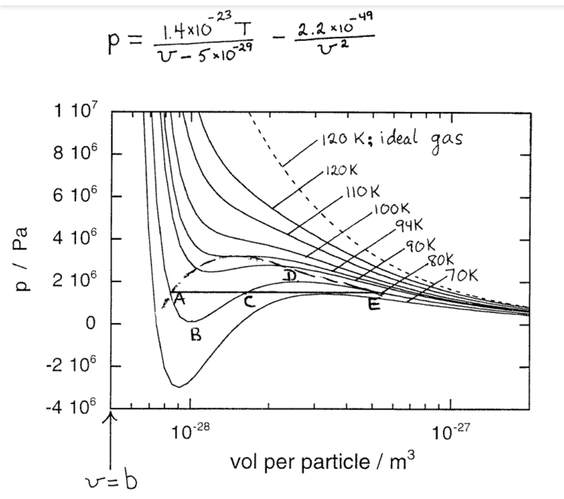

Fig. 1.7: Isotherms of the van der Waals equation of state.

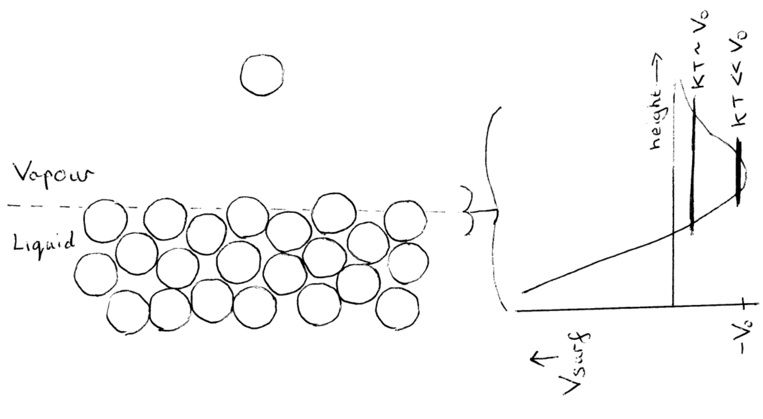
Vapour
Liquid
height →
kT ~ V_0
kT << V_0
← V_surf
−V_0

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

1.4 The Laws of Thermodynamics

- **0^{th} Law** The 0^{th} 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^{st} 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^{nd} 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^{rd} 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.

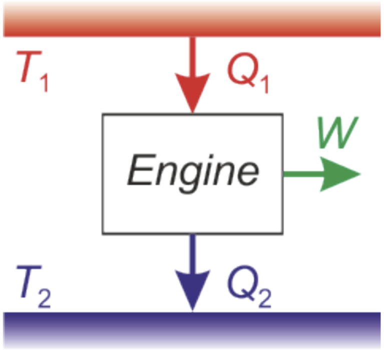

Fig. 1.9: Schematic representation of a heat engine operating between a hot reservoir at temperature T_1 and a cold reservoir at temperature T_2.

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.

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 $\mathrm{d}S = đQ/T$, 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 $T_1, \cdots, T_N$ 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

$$\sum \frac{Q_n}{T_n} \leq 0. \tag{1.15}$$

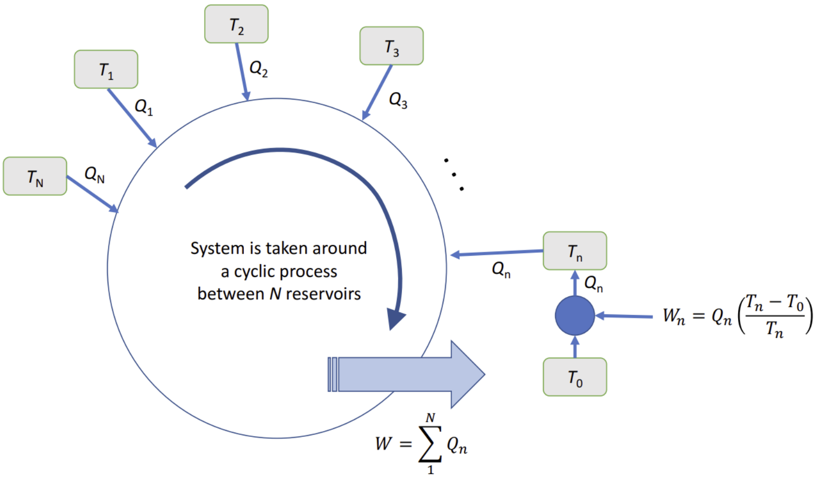
T_1
T_2
T_3
T_N
Q_1
Q_2
Q_3
Q_N
System is taken around a cyclic process between N reservoirs
Q_n
T_n
Q_n
$W_n = Q_n \left(\frac{T_n - T_0}{T_n}\right)$
T_0
$W = \sum_1^N Q_n$

Fig. 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 $Q_1, \cdots, Q_N$ 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.

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, $\sum \Delta Q/T \to \int \text{đ}Q/T$, can be used to define a function of state (because when you do that integral around a closed loop in parameter space, it gives zero). This leads to Clausius' definition of the entropy as a new function of state:

$$\mathrm{d}S = \text{đ}Q_{\mathrm{rev}}/T, \tag{1.16}$$

$$S_B - S_A = \int_A^B \text{đ}Q_{\mathrm{rev}}/T, \tag{1.17}$$

where $\text{đ}Q_{\mathrm{rev}}$ 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 $\oint \text{đ}Q/T$ 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 $\text{đ}Q/T$ 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 from A to B potentially irreversible, but the return reversible, we find for the entire loop:

$$\oint \text{đ}Q/T \leq 0, \tag{1.18}$$

and hence

$$\int_a^B \text{đ}Q/T \leq \int_A^B \text{đ}Q_{\mathrm{rev}}/T, \tag{1.19}$$

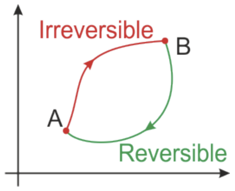

Fig. 1.11: Considering the entropy change between two states A and B. Because the loop integral of $đQ/T$ is ≤ 0, $S_B - S_A \geq \int đQ/T$ along the irreversible path. If the system is actually isolated, then the r.h.s. is $= 0$, implying that the entropy will stay the same or increase, but cannot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

but the latter gives the entropy change; therefore:

$$\Delta S = S(B) - S(A) \geq \int_A^B đQ/T. \tag{1.20}$$

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 ΔS 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:

$$\Delta S_{\text{total}} \geq 0. \tag{1.21}$$

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, $|Q_c| > \left|Q_c^{(\text{rev})}\right|$. Note that $Q_c < 0$. Therefore, the change in the total entropy of system plus reservoir is positive:

$$\Delta S_{\text{total}} = \underbrace{\Delta S_{\text{reservoir}}}_{-(Q_h/T_h + Q_c/T_c)} + \underbrace{\Delta S_{\text{system}}}_{=0} > 0. \tag{1.22}$$

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 $\Delta S_{\text{total}} > 0$.

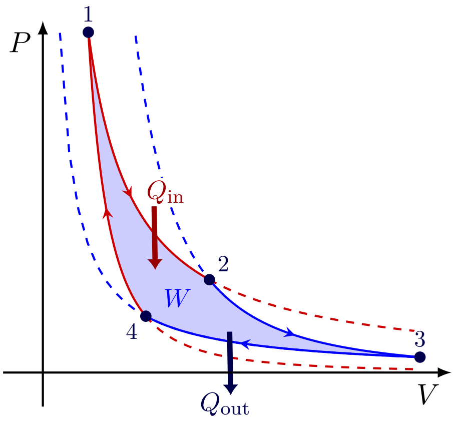

Fig. 1.12: A Carnot cycle. 1 → 2: Isothermal expansion; heat absorbed from high temperature reservoir Q_{in}; work is done on surroundings. 2 → 3: Adiabatic expansion; $\Delta Q = 0$; work is done on surroundings, medium cools. 3 → 4: Isothermal compression; heat given out to cold reservoir Q_{out}; work is done by surroundings. 4 → 1: Adiabatic compression; $\Delta Q = 0$; work is done by surroundings, medium warms.

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

$$\mathrm{d}U = \text{đ}Q + \text{đ}W, \tag{1.23}$$

where the work term $\text{đ}W$ can in general account for not just the 'volume work' $-p\,\mathrm{d}V$, but also other forms of work such as the magnetic work $\mu_0 H\,\mathrm{d}m$, the electrical work $V\,\mathrm{d}Q$ and the 'particle work', or 'chemical work' $\mu\,\mathrm{d}N$, where μ 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)

$$\begin{aligned} \text{đ}W &= -p\,\mathrm{d}V + \mu\,\mathrm{d}N\,, & (1.24)\\ \text{đ}Q &= T\,\mathrm{d}S\,, & (1.25)\\ \implies \mathrm{d}U &= T\,\mathrm{d}S - p\,\mathrm{d}V = \mu\,\mathrm{d}N\,, & (1.26) \end{aligned}$$

all for reversible changes only. But $\mathrm{d}S$, $\mathrm{d}V$ and $\mathrm{d}N$ are differentials of functions of state, so *provided that we are talking about a change between two equilibrium states*,

$$\boxed{\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,,} \tag{1.27}$$

always, 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, μ are “derived quantities”:

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \tag{1.28}$$

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. (1.27) 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 λ we can write $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$, so that

$$\begin{aligned}
U(S,V,N) &= \frac{\partial(\lambda U(S,V,N))}{\partial\lambda} \\
&= \left(\frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda S)}\right)_{\lambda V,\lambda N}\frac{\partial(\lambda S)}{\partial\lambda} + \left(\frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda V)}\right)_{\lambda S,\lambda N}\frac{\partial(\lambda V)}{\partial\lambda} \\
&\quad + \left(\frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda N)}\right)_{\lambda S,\lambda V}\frac{\partial(\lambda N)}{\partial\lambda} \\
&= \frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda S)}S + \frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda V)}V + \frac{\partial U(\lambda S,\lambda V,\lambda N)}{\partial(\lambda N)}N. \qquad (1.29)
\end{aligned}$$

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

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

But we know from Eq. (1.27) that

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

hence it must be true that

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

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 μN term is essential! This equation can be generalised to the case where several species of particle are present by replacing μN 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 $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$, but Eq. (1.32) gives $\mathrm{d}U = T\,\mathrm{d}S + S\,\mathrm{d}T - p\,\mathrm{d}V - V\,\mathrm{d}p + \mu\,\mathrm{d}N + N\,\mathrm{d}\mu$. Both of these equations can only be true at the same time if

$$N\,\mathrm{d}\mu = -S\,\mathrm{d}T + V\,\mathrm{d}p\,, \qquad (1.33)$$

$$\Longrightarrow \mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p\,, \qquad (1.34)$$

where s and v are the entropy and volume per particle (now intensive, as is the chemical potential μ). 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, $\mathrm{d}S \geq 0$, 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*.

2.1.1 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.

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, as shown in Fig. 2.2. The entropy statement of the Second Law is

$$\begin{aligned}\mathrm{d}S_{\mathrm{tot}} &= \mathrm{d}S_1 + \mathrm{d}S_2 \\ &= \frac{\mathrm{d}U_1 + p_1\,\mathrm{d}V_1 - \mu_1\,\mathrm{d}N_1}{T_1} + \frac{\mathrm{d}U_2 + p_2\,\mathrm{d}V_2 - \mu_2\,\mathrm{d}N_2}{T_2} \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\mathrm{d}U_1 \geq 0, \end{aligned} \tag{2.1}$$

   where we have used $\mathrm{d}V_i = 0$ (constant volume), $\mathrm{d}N_i = 0$ (constant particle number), and $\mathrm{d}U_2 = -\,\mathrm{d}U_1$ (energy conservation). This equation means that if T_1 is greater than T_2, $\mathrm{d}U_1$ is negative and heat flows from 1 to 2, but if T_1 is less than T_2, $\mathrm{d}U_1$ 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.

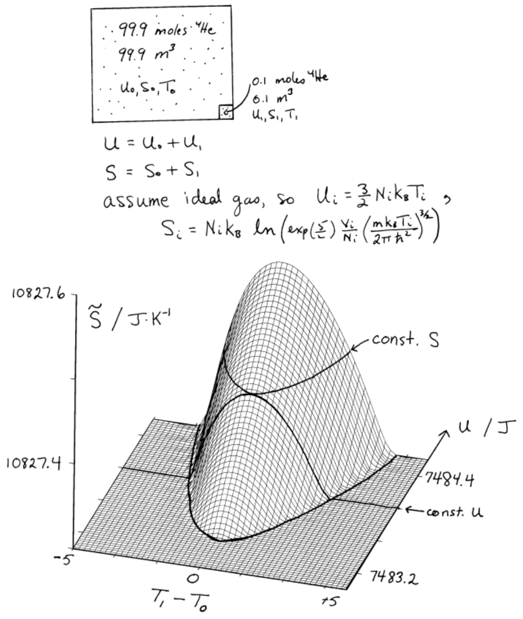

Fig. 2.1: A small section of the $(S - U - (T_1 - T_0))$ surface for a volume of ideal gas partitioned by an adiathermal wall. We imagine that we can transfer energy across the partition (using external heat engines for example) and then we calculate the total entropy, using the SackurTetrode expression (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.

2. Similarly, from $\mathrm{d}S \geq 0$ 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 shown in Fig. 2.3).

   The entropy statement of the Second Law of thermodynamics gives

   $$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2 = \frac{\mathrm{d}U_1 + p_1\,\mathrm{d}V_1 - \mu_1\,\mathrm{d}N_1}{T_1} + \frac{\mathrm{d}U_2 + p_2\,\mathrm{d}V_2 - \mu_2\,\mathrm{d}N_2}{T_2} \geq 0. \tag{2.2}$$

   The total energy is fixed, so $\mathrm{d}U_1 + \mathrm{d}U_2 = 0$, and the volumes are fixed so that $\mathrm{d}V_1 = \mathrm{d}V_2 = 0$. Particle number is also conserved, so $\mathrm{d}N_1 = -\,\mathrm{d}N_2$, and the law of increase of entropy reduces to

   $$(\mu_2 - \mu_1)\,\mathrm{d}N_1 \geq 0. \tag{2.3}$$

   Therefore if $\mu_2 > \mu_1$ then $\mathrm{d}N_1 > 0$, and particles flow from 2 to 1, whereas if $\mu_2 < \mu_1$, then $\mathrm{d}N_1$ and particles flow from 1 to 2. Hence

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

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

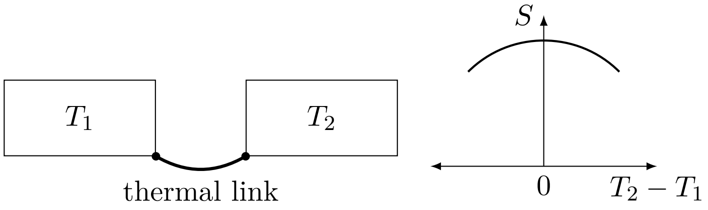

Fig. 2.2: Two systems connected by a thermal link. The heat flows from the hotter to the colder body and at equilibrium $T_1 = T_2$.

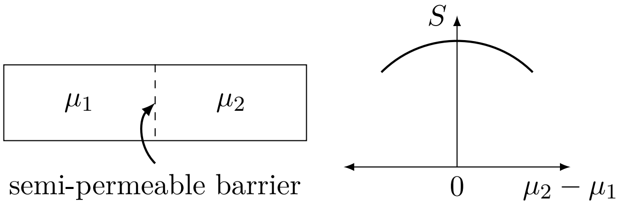

Fig. 2.3: A container is divided into two parts by a membrane which is permeable to salt but not to water. On the left of the semi-permeable membrane the water contains some salt, and on the right is pure water. The entropy is maximised when $\mu_1 = \mu_2$, i.e., the salt concentrations are equal.

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

$$\begin{aligned} \mathrm{d}S_{\text{tot}} &= \mathrm{d}S + \mathrm{d}S_R \geq 0 \\ &= \mathrm{d}S + \frac{\mathrm{d}U_R + p_R\,\mathrm{d}V_R - \mu_R\,\mathrm{d}N_R}{T_R} \qquad (2.5) \\ &= \frac{T_R\,\mathrm{d}S - \mathrm{d}U - p_R\,\mathrm{d}V + \mu_R\,\mathrm{d}N}{T_R}, \qquad (2.6) \end{aligned}$$

where we have used conservation of energy, volume and particle number, which give $\mathrm{d}U_R = -\,\mathrm{d}U$, $\mathrm{d}V_R = -\,\mathrm{d}V$ and $\mathrm{d}N_R = -\,\mathrm{d}N$.

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, $\mathrm{d}V_R = -\mathrm{d}V$, still, but $\mathrm{d}N_R = 0$. 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, $\mathrm{d}N_R = 0$, on the reservoir entropy in Eq. (2.5) above can be achieved in Eq. (2.6) 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, $\mathrm{d}T_R = 0$, $\mathrm{d}p_R = 0$ and $\mathrm{d}\mu_R = 0$. We can therefore bring all of the differentials to the front, i.e., $p_R\,\mathrm{d}V = \mathrm{d}(p_R V)$. We now define the new object, called *availability* A, as $\mathrm{d}A = -T_R\,\mathrm{d}S_{\mathrm{tot}}$ which means:

$$\boxed{\begin{aligned} \mathrm{d}A &= \mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N \\ &= (T - T_R)\,\mathrm{d}S - (p - p_R)\,\mathrm{d}V + (\mu - \mu_R)\,\mathrm{d}N \end{aligned}} \tag{2.7}$$

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 μ_R act as the corresponding "forces". Since they are constant, we can integrate and obtain:

$$A = U - T_R S + p_R V - \mu_R N. \tag{2.8}$$

Since we have $\mathrm{d}S_{\mathrm{tot}} \geq 0$ and T_R is assumed constant, we must conclude that

$$\mathrm{d}A \leq 0. \tag{2.9}$$

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 $\mathrm{d}A = 0$ 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: $S_{\mathrm{Boltz}} = k_B \ln \Omega$, where Ω is the statistical weight or degeneracy, can be used to motivated 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:

$$P(X) \propto e^{-\frac{A(X)}{k_B T}}. \tag{2.10}$$

2.2.2 Availability = Useful Work

The availability function in Eq. (2.8) 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, μ_R. So, in general, the system can be at temperature $T = (\partial A/\partial S)_{V,N} \neq T_R$, pressure $p = -(\partial A/\partial V)_{S,N} \neq p_R$ and chemical potential $\mu = (\partial A/\partial N)_{S,V} \neq \mu_R$. 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. (2.8) and allowing for $\mathrm{d}U_R$ not to be $= -\,\mathrm{d}U$, but rather putting $\mathrm{d}U_R + \mathrm{d}U = -\,\mathrm{d}W_{\mathrm{extr}}$, the amount of work extracted in the process. Alternatively, we can go directly for $-\,\mathrm{d}W_{\mathrm{extr}} = \mathrm{d}U + \mathrm{d}U_R$ and replace U by $A + T_R S - p_R V + \mu_R N$:

$$\begin{aligned} -\,\mathrm{d}W_{\mathrm{extr}} &= \mathrm{d}U + \mathrm{d}U_R = \mathrm{d}(A + T_R S - p_R V + \mu_R N) + T_R\,\mathrm{d}S_R - p_R\,\underbrace{\mathrm{d}V_R}_{=-\mathrm{d}V} + \mu_R\,\underbrace{\mathrm{d}N_R}_{=-\mathrm{d}N} \\ &= \mathrm{d}A + T_R\,\underbrace{\mathrm{d}(S + S_R)}_{\geq 0}\,. \end{aligned} \tag{2.11}$$

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_{extr} matches the reduction in the availability, or exergy:

$$\Delta W_{\mathrm{extr}} = -\Delta A. \tag{2.12}$$

2.2.3 Legendre Transformations

The natural variables of A as in Eq. (2.8) are S, V, N (because these are the natural variables of U), as well as T_R, p_R, μ_R. In equilibrium, the condition $\mathrm{d}A = 0$ for all variations of S, V, N then produces $(\partial A/\partial S)_{V,N} = (\partial U/\partial S)_{V,N} - T_R = T - T_R = 0 \implies T = T_R$, 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 $S = S_{\mathrm{eq}}$, 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_{eq}, V_{eq}, N_{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, μ_R, which are equal to T, p, μ in equilibrium.

This is an application of *Legendre transformations*. If we have a function $f(x)$ so that $\mathrm{d}f = f'\,\mathrm{d}x$, 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

$$\mathrm{d}g = f'\,\mathrm{d}x - y\,\mathrm{d}x - x\,\mathrm{d}y\,. \tag{2.13}$$

If we further look for the minimum of g w.r.t. x, we find it for $f' = (\partial f/\partial x)_{x=x_0} = y$. 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 $\mathrm{d}g_0 = (f' - y)\,\mathrm{d}x - x_0\,\mathrm{d}y = -x_0\,\mathrm{d}y$. 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 $(\partial V/\partial x)_{x=x_0,W} = 0$, i.e. $kx_0 = W$. This fixes the *equilibrium potential energy* for a given W as $V_0(W) = \frac{1}{2}kx_0^2 - Wx_0 = -\frac{1}{2}W^2/l$, and $\mathrm{d}V_0 = -x_0\,\mathrm{d}W$.

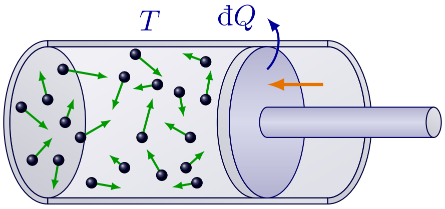

Fig. 2.4: Reversible compression of a monatomic ideal gas connected to a reservoir at constant temperature. Fixed temperature T implies constant internal energy U (Molecules in an ideal gas are assumed to have zero interaction with each other and so have only kinetic energy directly determined by T), and so $đQ = -đW$.

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

$$\mathrm{d}F = \left[\left(\frac{\partial U}{\partial S}\right)_{V,N} - T_R\right] \mathrm{d}S - S\,\mathrm{d}T_R - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,, \tag{2.14}$$

which for constant T_R is zero, when $(\partial U/\partial S)_{V,N,S=S_{\mathrm{eq}}} = T = T_R$, fixing the equilibrium entropy S_{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

$$\mathrm{d}F_{\mathrm{eq}} = -S_{\mathrm{eq}}\,\mathrm{d}T_R - p\,\mathrm{d}V + \mu\,\mathrm{d}N\,. \tag{2.15}$$

Focusing solely on the equilibrium properties and replacing T_R by T and S_{eq} by S, this can be written as $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$, the well-known expression for the Helmholtz free energy, on which more is in Section 2.3. 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

$$\mathrm{d}A_{\mathrm{eq}} = -S_{\mathrm{eq}}\,\mathrm{d}T_R + V_{\mathrm{eq}}\,\mathrm{d}p_R - N_{\mathrm{eq}}\,\mathrm{d}\mu_R \tag{2.16}$$

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 (Subsection 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, μ 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:

internal energy	U	$=$	$TS - PV + \mu N,$	$\mathrm{d}U$	$=$	$T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$
enthalpy	H	$=$	$U + pV,$	$\mathrm{d}H$	$=$	$T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$
Helmholtz free energy	F	$=$	$U - TS,$	$\mathrm{d}F$	$=$	$-S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$
Gibbs free energy	G	$=$	$U - TS + pV,$	$\mathrm{d}G$	$=$	$-S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$
grand potential	Φ	$=$	$F - \mu N,$	$\mathrm{d}\Phi$	$=$	$-S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$

Table 2.1: The most commonly encountered potentials for a gas. The variables which are differentiated are the "natural variables" of the corresponding thermodynamic potential. A thermodynamic potential takes its minimum value in equilibrium under the conditions that its natural variables are held fixed.

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, $U = \frac{3}{2}Nk_BT$, 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:

$$\mathrm{d}U = 0 \qquad \Longrightarrow \qquad \text{đ}Q = -\text{đ}W. \tag{2.17}$$

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,

$$\begin{aligned} \text{đ}W &= \mathrm{d}U - T\,\mathrm{d}S \\ &= \mathrm{d}(U - TS)_T \quad \text{if } T \text{ is constant} \\ &\equiv (\mathrm{d}F)_T \end{aligned} \tag{2.18}$$

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 transformations*, see Subsection 2.2.3). For a gas the most commonly encountered potentials are included in Table 2.1. The variables which are differentiated in Table 2.1 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:

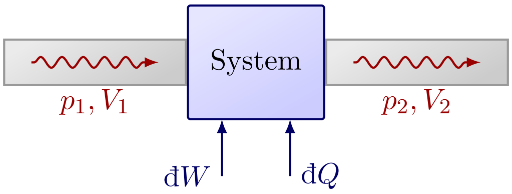

Fig. 2.5: A schematic flow process.

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., $đQ = 0$, $đW = 0$, $\mathrm{d}N = 0$). 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.

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, $\mathrm{d}p = 0$, constant entropy means that $\mathrm{d}S = 0$, while constant particle number means that $\mathrm{d}N = 0$. Therefore

$$\begin{aligned}(\mathrm{d}A)_{p,S,N} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{p,S,N} \\ &= \mathrm{d}(U + pV)_{p,S,N} \quad (\text{used } \ \mathrm{d}S = 0, \mathrm{d}N = 0, p = p_R) \\ &\equiv \mathrm{d}(H)_{p,S,N}\,, \qquad (2.19)\end{aligned}$$

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

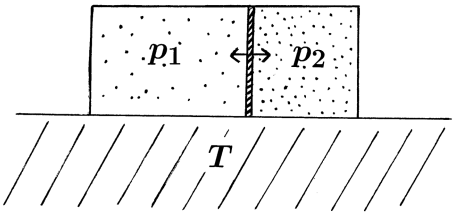

Fig. 2.6: Two gases initially at pressures p_1 and p_2 are separated by a movable barrier. The temperature is fixed and equal to T. The barrier moves under the pressure forces until the Helmholtz free energy reaches its minimum value, which occurs when $p_1 = p_2$.

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 Fig. 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: $\mathrm{d}T = 0$ because the temperature is fixed; $\mathrm{d}V = 0$ because the volume is fixed; and $\mathrm{d}N = 0$. We can then write

$$\begin{aligned}(\mathrm{d}A)_{T,V,N} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{T,V,N} \\ &= \mathrm{d}(U - TS)_{T,V,N} \quad (\text{used } T = T_R, \mathrm{d}T = 0) \\ &\equiv \mathrm{d}(F)_{T,V,N}\,, \end{aligned} \tag{2.20}$$

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

$$\begin{aligned} F &= F_1 + F_2 \\ &= (U_1 - T_1 S_1) + (U_2 - T_2 S_2). \end{aligned} \tag{2.21}$$

Using $T_1 = T_2 = T$ and $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$ we have

$$\mathrm{d}F = -p_1\,\mathrm{d}V_1 - p_2\,\mathrm{d}V_2\,. \tag{2.22}$$

Since $\mathrm{d}V_2 = -\,\mathrm{d}V_1$ the equilibrium condition becomes

$$\mathrm{d}F = 0 = -(p_1 - p_2)\,\mathrm{d}V_1 \qquad \Longrightarrow \qquad p_1 = p_2. \tag{2.23}$$

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

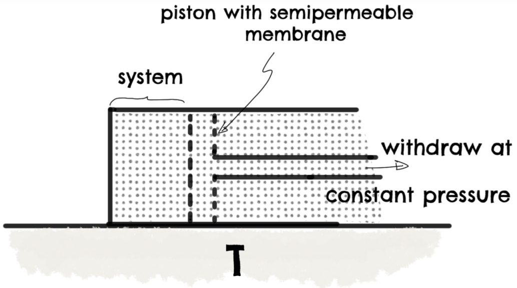

Fig. 2.7: Adding particles at constant T and p.

2.3.4 Gibbs Free Energy G: Equilibrium at Constant Temperature, Pressure and Particle Number

If p, N and T are constant then

$$\begin{aligned}(\mathrm{d}A)_{T,p,N} &= \mathrm{d}(U - TS + pV)_{T,p,N} \\ &\equiv \mathrm{d}(G)_{T,p,N}\,, \end{aligned} \tag{2.24}$$

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

$$G = \mu N \tag{2.25}$$

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 $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N = \mu\,\mathrm{d}N$. This means in effect that the chemical potential in a pure phase is the Gibbs free energy per particle. Moreover, from $G = \mu N$ we find $\mathrm{d}G = \mu\,\mathrm{d}N + N\,\mathrm{d}\mu = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$. Therefore we can write

$$\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p\,, \tag{2.26}$$

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

2.3.5 Grand Potential Φ: Equilibrium at Constant Temperature, Volume and Chemical Potential

Under these conditions we have

$$\begin{aligned}(\mathrm{d}A)_{T,V,\mu} &= (\mathrm{d}U - T_R\,\mathrm{d}S + p_R\,\mathrm{d}V - \mu_R\,\mathrm{d}N)_{T,V,\mu} \\ &= \mathrm{d}(U - TS - \mu N)_{T,V,\mu} \\ &\equiv \mathrm{d}(\Phi)_{T,V,\mu} \end{aligned} \tag{2.27}$$

where Φ is the *grand potential.* Minimum availability in this case corresponds to minimum grand potential.

Name	Helmholtz Free Energy	Gibbs Free Energy	Grand Potential	
	$F = U - TS$	$G = U - TS + pV = \mu N$	$\Phi = F - \mu N = -pV$	$\Phi_2 = G - \mu N = 0$
Differential	$-S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$	$-S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N$	$-S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$	$-S\,\mathrm{d}T + V\,\mathrm{d}p - N\,\mathrm{d}\mu = 0$
Minimised when constraints are	T, V, N	T, p, N	T, V, μ	Cannot be varied: T, p, μ 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 systems held at fixed temperature.

Name	Internal Energy	Enthalpy		
	U	$H = U + pV$	$\Phi_3 = U - \mu N$	$\Phi_4 = H - \mu N = TS$
Differential	$T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$	$T\,\mathrm{d}S + V\,\mathrm{d}p + \mu\,\mathrm{d}N$	$T\,\mathrm{d}S - p\,\mathrm{d}V - N\,\mathrm{d}\mu$	$T\,\mathrm{d}S + V\,\mathrm{d}p - N\,\mathrm{d}\mu$
Constant for isolated system when constraints are	V, N	p, N	V, μ	p, μ
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. ΔH is the heat energy in phase and chemical changes	Unimportant, not realised in practice	

Table 2.3: Potentials important for thermally isolated systems.

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 Section 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

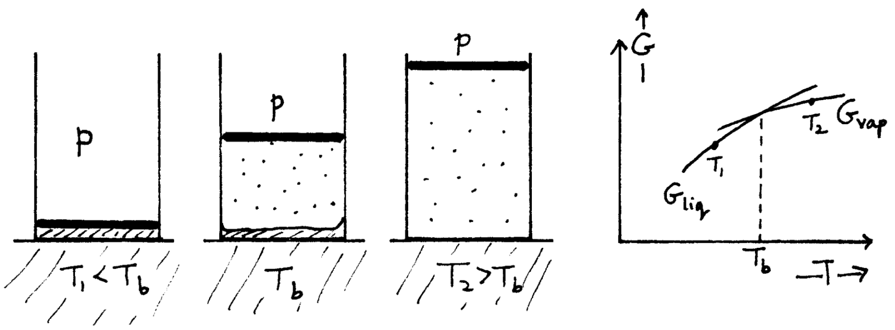

Fig. 2.8: The condition for a phase transition is that the Gibbs free energies of competing phases cross. The extrapolation of the Gibbs free energy of a phase to beyond the region in which that phase is stable is justified, for a short distance at least, by the metastability of supercooled and superheated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

transition will occur when the two functions cross. 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:

$$\begin{aligned} G &= G_l + G_v \\ \mathrm{d}G = 0 &\Rightarrow \mathrm{d}G_l = -\,\mathrm{d}G_v \\ \Longrightarrow\ -S_l\,\mathrm{d}T + V_l\,\mathrm{d}p + \mu_l\,\mathrm{d}N_l &= S_v\,\mathrm{d}T - V_v\,\mathrm{d}p - \mu_v\,\mathrm{d}N_v \\ \Longrightarrow\ \mu_l\,\mathrm{d}N_l &= -\mu_v\,\mathrm{d}N_v \qquad (T, p \text{ are constant}). \end{aligned} \tag{2.28}$$

Matter conservation requires $\mathrm{d}N_l = -\,\mathrm{d}N_v$, so that

$$\mu_l = \mu_v. \tag{2.29}$$

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

$$T_l = T_v, \quad \text{or, similarly,} \quad p_l = p_v, \tag{2.30}$$

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

2.4.0.1 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), $\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p$, where s and v are the entropy and volume per particle.[2] 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.

The condition for phase equilibrium is

$$\begin{aligned} \mu_v(E) &= \mu_l(A) \\ \text{but} \quad \mu_v(E) &= \mu_l(A) + \int_A^E \left(\frac{\partial \mu}{\partial p}\right)_T \mathrm{d}p \\ &= \mu_l(A) + \int_A^E v\,\mathrm{d}p\,. \end{aligned} \tag{2.31}$$

The first and last lines are true provided that

$$\int_A^E v\,\mathrm{d}p = 0, \tag{2.32}$$

---

[1] 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, $g\,\mathrm{d}m = \mu\,\mathrm{d}N$. To further confuse things for you, *Adkins* calls g the "chemical potential", and he defines a quantity μ 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 μ to our μ, use $\mu_{Adkins}\,\mathrm{d}N = \mu\,\mathrm{d}N$. Where n is the number of moles, and N is the number of molecules.

[2] This equation can only be applied to a pure phase, mixtures are more complicated.

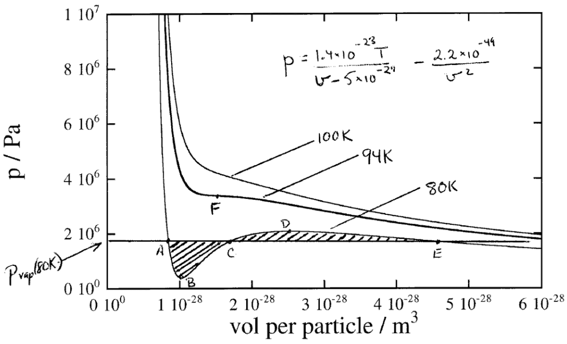

Fig. 2.9: Isotherms of the van der Waals gas (see also Section 1.3). As shown in Eq. (2.32), the vapour pressure is fixed by the requirement that the two shaded regions have equal areas if the chemical potentials of the two phases are equal.

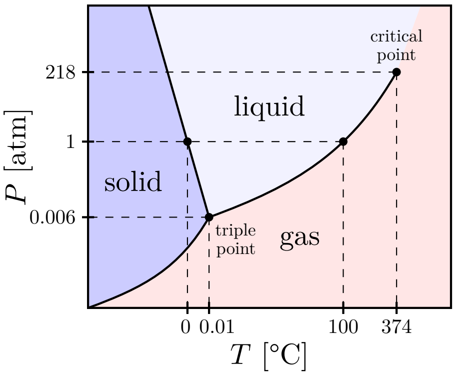

Fig. 2.10: Phase coexistence lines for water in the (p, T) plane. The Clausius-Clapeyron equation (2.35) gives an expression for the gradient of the phase boundaries, $\frac{\mathrm{d}p}{\mathrm{d}T} = L_m/(T\Delta v_m)$.

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.

2.4.0.2 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.

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

$$\mathrm{d}\mu_1 = v_1\,\mathrm{d}p - s_1\,\mathrm{d}T \tag{2.33}$$

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 $\mathrm{d}\mu_1 = \mathrm{d}\mu_2$, we have

$$v_1\,\mathrm{d}p - s_1\,\mathrm{d}T = v_2\,\mathrm{d}p - s_2\,\mathrm{d}T$$

$$\Longrightarrow \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{T\Delta s}{T\Delta v} \equiv \frac{L}{T\Delta v}, \tag{2.34}$$

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:

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L_m}{T\Delta v_m}. \tag{2.35}$$

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., Δv_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 Δv (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)

$$p = \sum_i p_i \quad \text{where} \quad p_i \frac{N_i k_B T}{V}. \tag{2.36}$$

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 $\mathrm{d}U$):

$$\begin{aligned} \text{integrate} \quad \mathrm{d}S &= \frac{\mathrm{d}U}{T} + \frac{p\,\mathrm{d}V}{T} = \frac{C_v\,\mathrm{d}T}{T} + \frac{Nk_B\,\mathrm{d}V}{V} \\ \text{obtain} \quad S &= C_v \ln T + Nk_B \ln V + S_0. \end{aligned} \tag{2.37}$$

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 $\mathrm{d}H$ instead of $\mathrm{d}U$), or simply replace $V = Nk_BT/p$ in Eq. (2.37) 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:

$$S = C_p \ln T - Nk_B \ln p + S_0 \tag{2.38}$$

where the integration constant S_0 is not the same as in Eq. (2.37).

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

$$\begin{aligned}\Delta S = S - S_{\text{pure}} &= -k_B \sum_i N_i \ln(p_i/p) \\ &= -k_B \sum_i N_i \ln c_i = -N k_B \sum_i c_i \ln c_i, \end{aligned} \tag{2.39}$$

where $c_i = N_i/N = p_i/p$ is the concentration of the i^{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 μ, 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 $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$, and considering a process at constant T we have

$$\left(\frac{\partial G}{\partial p}\right)_T = V = \frac{N k_B T}{p}, \tag{2.40}$$

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

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V = \frac{k_B T}{p}. \tag{2.41}$$

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

$$\mu(T, p) = \mu(T, p_0) + k_B T \ln \frac{p}{p_0}. \tag{2.42}$$

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

$$G = \sum_i G_i. \tag{2.43}$$

Using $(\partial G_i/\partial p_i)_{T,N_i} = V$ 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):

$$\begin{aligned} G_i(p_i, T) &= G_i(p, T) + \int_p^{p_i} V\,\mathrm{d}p \\ &= G_i(p, T) + N_i k_B T \int_p^{p_i} \frac{\mathrm{d}p}{p} \\ &= G_i(p, T) + N_i k_B T \ln \frac{p_i}{p} \\ &= G_i(p, T) + N_i k_B T \ln c_i. \end{aligned} \tag{2.44}$$

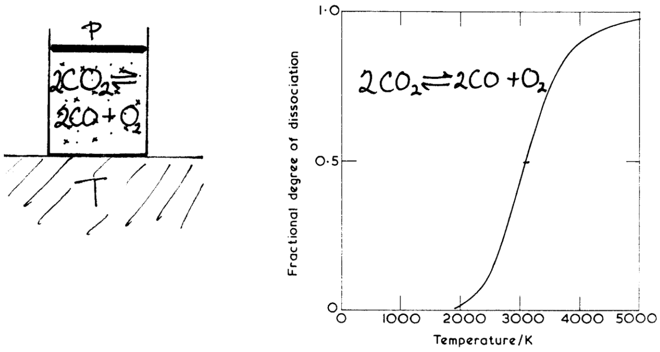

Fig. 2.11: Chemical reaction at constant temperature and pressure. At a given temperature and pressure the relative amounts of the chemical components are functions of state. In our example, at high temperatures CO_2 breaks down into CO and O_2.

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

$$\boxed{\mu_i(p_i,T) = \mu_{0i}(p,T) + k_B T \ln c_i.} \tag{2.45}$$

That is, the chemical potential of the ith 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

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}N_i \quad \text{we have} \quad \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{l\neq i}}. \tag{2.46}$$

So for two components i and j

$$\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,N_{l\neq j}} = \frac{\partial^2 G}{\partial N_i \partial N_j} = \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T,p,N_{l\neq i}}. \tag{2.47}$$

2.5.0.1 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 CO_2 (see Fig. (2.11)).

$$2CO_2 \rightleftharpoons 2CO + O_2. \tag{2.48}$$

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

$$\begin{aligned}(\mathrm{d}A)_{T,p} &= \mathrm{d}U - T\,\mathrm{d}S + p\,\mathrm{d}V \\ &= \mathrm{d}(U - TS + pV) \quad \text{constant temperature and pressure} \\ &= \mathrm{d}G = 0.\end{aligned} \tag{2.49}$$

where

$$G = \sum_i G_i = \sum_i \mu_i N_i. \tag{2.50}$$

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

$$\mathrm{d}G = \sum_i \mu_i\,\mathrm{d}N_i = 0, \tag{2.51}$$

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

$$\sum_i \nu_i\mu_i = 0, \tag{2.52}$$

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

2.5.0.2 The Equilibrium Constant

Combining $\sum_i \nu_i$ and Eq. (2.45) gives

$$\sum_i \nu_i\mu_{0i} + k_BT\sum_i \nu_i \ln c_i = 0 \tag{2.53}$$

$$\Longrightarrow \sum_i \nu_i\mu_{0i} + k_BT\ln\left(\prod_i c_i^{\nu_i}\right) = 0. \tag{2.54}$$

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

$$\boxed{K_c(T) = \prod_i c_i^{\nu_i},} \tag{2.55}$$

where

$$\ln K_c(T) = -\frac{1}{k_BT}\sum_i \nu_i\mu_{0i}(T,p). \tag{2.56}$$

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:

$$K_c = \frac{c^2_{\mathrm{CO}_2}}{c^2_{\mathrm{CO}}c_{\mathrm{O}_2}}. \tag{2.57}$$

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 (2.48), 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

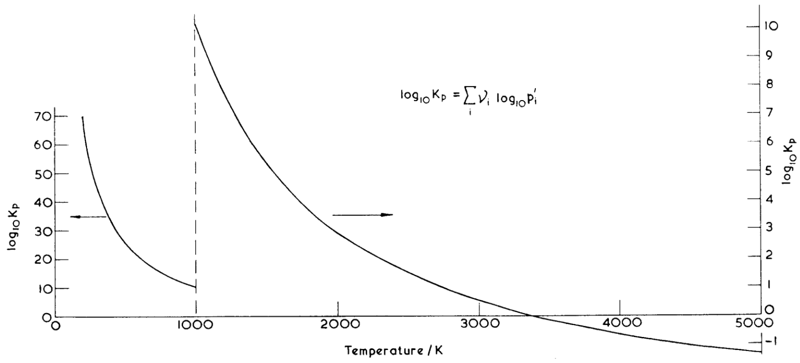

Fig. 2.12: Equilibrium constant for the $2CO_2 \rightleftharpoons 2CO + O_2$ reaction (following Hayward, *Equilibrium Thermodynamics*).

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.

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 'degenracy 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

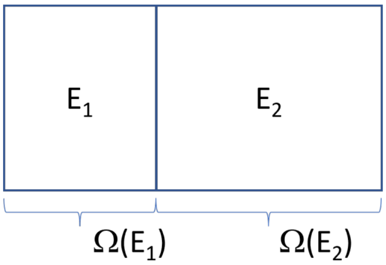

Fig. 3.1: A partition of the total energy E between two subsystems.

has not been solved in a satisfactory manner, but see Appendix A.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

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

$$E = E_1 + E_2, \tag{3.1}$$

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

$$\Omega(E;E_1) = \Omega_1(E_1)\Omega_2(E_2), \tag{3.2}$$

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

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

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

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

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

$$\beta = \left.\frac{\partial \ln \Omega(E)}{\partial E}\right|_{E=U}. \tag{3.5}$$

It is natural to expect that β is related to the temperature. Recalling the relationship

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

we can therefore make the identifications:

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

where the quantities on the left hand sides of Eq. (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

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

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

$$S = k_B ln 2\Omega = k_B \ln 2 + k_B \ln \Omega. \tag{3.9}$$

However, Ω 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 Ω 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,

$$S = -k_B \sum_i P_i \ln P_i, \tag{3.10}$$

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 (2.39) 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

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i 1/\Omega \ln 1/\Omega = k_B ln\Omega = S_B, \tag{3.11}$$

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

$$\Omega = \frac{N!}{N_1!N_2!\cdots N_m!}. \tag{3.12}$$

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

$$S = k_B \ln \Omega, \tag{3.13}$$

and using Stirling's approximation we obtain

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

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 (2.39) 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.[1] 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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[1] 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.

3.5.1 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 ith 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 $\Omega_R(U-E_1)$ 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:

$$\begin{aligned} P_i \propto 1 \times \Omega_R(U-E_i) &= e^{ln\Omega_R(U-E_i)} \\ &= \exp\Big(\ln\Omega_R(U) - E_i\Big(\frac{\partial \ln\Omega_R(U)}{\partial U}\Big) + \cdots\Big) \\ &\simeq e^{\ln\Omega_R(U)}e^{-\beta E_i}, \end{aligned} \tag{3.15}$$

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

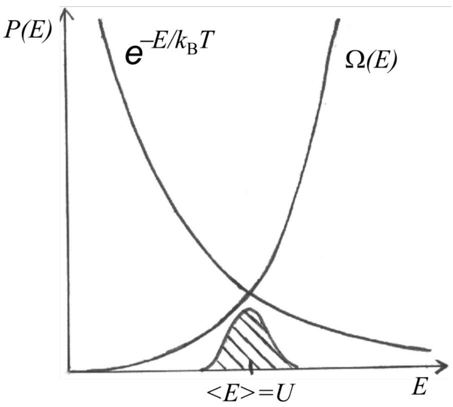

Fig. 3.2: The probability, $P(E)$, that a system has energy E is proportional to the product of the statistical weight, $\Omega(E)$, and the Boltzmann factor. $P(E)$ is sharply peaked around the mean value of U, the shaded area regarded as a Gaussian.

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,

$$Z = \sum_{\text{all states } i} e^{-\beta E_i}. \tag{3.16}$$

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:

$$P_i = \frac{1}{Z} e^{\beta E_i}. \tag{3.17}$$

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:

$$P(E_i) \propto \Omega(E_i) e^{-\beta E_i}. \tag{3.18}$$

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 $\mathrm{d}P/\mathrm{d}E_i = 0$. 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:

$$P(E) \propto e^{-\beta[E - k_B T \ln \Omega(E)]}. \tag{3.19}$$

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.

3.5.2 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:

$$\begin{aligned} P_i(E_i, N_i) &\propto e^{\ln \Omega_R(U-E_i, N-N_i)} \\ &\sim \exp\left(\ln \Omega(U,N) - E_i\left(\frac{\partial \ln \Omega_R(U,N)}{\partial U}\right)_N - N_i\left(\frac{\partial \ln \Omega_R(U,N)}{\partial N}\right)_U + \cdots\right) \\ &\sim e^{\ln \Omega_R(U,N)} e^{-\beta(E_i - \mu N_i)}, \end{aligned} \tag{3.20}$$

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

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_U = -k_B T\left(\frac{\partial \ln \Omega}{\partial N}\right)_U. \tag{3.21}$$

Normalising, we obtain the Gibbs probability distribution:

$$P_i(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i - \mu N_i)}, \tag{3.22}$$

where the new normalisation factor Ξ 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 (3.16), but also over all possible number of particles the system might have (ultimately, $N_i \in 0 \div N$, where N might be infinity):

$$\Xi = \sum_{N_i} \sum_i e^{-\beta(E_i[N_i] - \mu N_i)} \tag{3.23}$$

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 Ξ. All the thermodynamic potentials can then be obtained from Z or Ξ, 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.

3.6.0.1 Canonical Ensemble

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

$$P_i = \frac{e^{-\beta E_i}}{Z}, \tag{3.24}$$

where the partition function is

$$Z = \sum_{\text{all states } i} e^{-\beta E_i} = \sum_{\text{microstates } E} \Omega(E_i) e^{-\beta E_i} = \sum_{\text{microstates } E} e^{-\beta(E_i - TS(E_i))}, \tag{3.25}$$

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:

$$Z \approx e^{-\beta(U - TS(U))}, \quad \text{hence} \quad F = -k_B T \ln Z. \tag{3.26}$$

Or look at it from the equilibrium Gibbs entropy angle:

$$S = -k_B \sum_i P_i \ln P_i = -k_B \sum_i P_i \left(-\frac{E_i}{k_B T} - \ln Z \right) \equiv \frac{U}{T} + k_B \ln Z, \tag{3.27}$$

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

$$U = \sum_i E_i P_i(E_i) = -\frac{\partial}{\partial \beta} \ln Z. \tag{3.28}$$

3.6.0.2 Grand Canonical Ensemble

Here the microstate probabilities are given by

$$P_i = \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi}, \tag{3.29}$$

where the grand partition function is

$$\Xi = \sum_{N_i} \sum_i e^{-\beta(E_i - \mu N_i)}. \tag{3.30}$$

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

$$P_i = \frac{1}{\Xi}\Omega(E_i, N_i)e^{-\beta(E_i - \mu N_i)} = \frac{1}{\Xi}e^{-\beta(E_i - TS(E_i,N_i) - \mu N_i)}, \tag{3.31}$$

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

$$\begin{aligned} TS &= -k_B T \sum_i P_i \ln P_i = -k_B T \sum_i P_i\{-(E_i - \mu N_i)/k_B T - \ln \Xi\} \\ &= U - \mu N + k_B T \ln \Xi, \end{aligned} \tag{3.32}$$

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 $\mathrm{d}\Phi = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$ we then obtain the entropy, pressure and average particle number from

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}, \quad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}, \quad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}. \tag{3.33}$$

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

3.6.0.3 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 ϵ. 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

$$F(n) = E(n) - TS(n) = n\epsilon - k_B T \ln\left(\frac{(N+n)!}{N!n!}\right). \tag{3.34}$$

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

$$F = n\epsilon - k_B T[(N+n)\ln(N+n) - N\ln N - n\ln n]. \tag{3.35}$$

Minimising with respect to n gives

$$\frac{\partial F}{\partial n} = \epsilon - k_B T \ln\left(\frac{N+n}{n}\right) = 0 \tag{3.36}$$

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

$$n_{eq} = \frac{N}{e^{\epsilon/k_B T} - 1} \simeq N e^{-\epsilon/k_B T}. \tag{3.37}$$

Typically ϵ might be about 1eV, 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:

$$F_{eq}(T, N) = N k_B T \ln\left(1 - e^{-\epsilon/k_B T}\right). \tag{3.38}$$

3.6.0.4 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 $\mathrm{d}U_1 = T\,\mathrm{d}S_1 + B\,\mathrm{d}m$ (see Subsection 1.1.3), from which we can obtain the relevant free energy F_1, which incorporates the constraints (T, B), by a Legendre transformation: $F_1 = U_1 - TS_1 - mB$:

$$\mathrm{d}F_1 = -S\,\mathrm{d}T - m\,\mathrm{d}B\,. \tag{3.39}$$

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

$$Z_1 = \sum_i e^{-\beta E_i} = e^{+\beta m_0 B} + e^{-\beta m_0 B} = 2\cosh\left(\frac{m_0 B}{k_B T}\right). \tag{3.40}$$

We have

$$F_1 = -k_B T \ln Z_1 = -k_B T \ln\left(e^{+\beta m_0 B} + e^{-\beta m_0 B}\right) \tag{3.41}$$

and from Eq. (3.39) we obtain

$$m = -\left(\frac{\partial F_1}{\partial B}\right)_T = m_0 \tanh\left(\frac{m_0 B}{k_B T}\right), \tag{3.42}$$

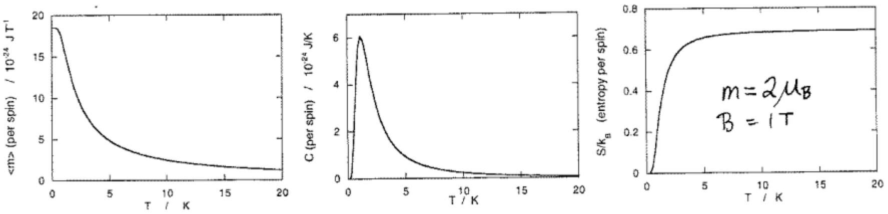

Fig. 3.3: The mean magnetisation, m, per spin, the heat capacity per spin, c, and the entropy per spin, s/k_B, for a two-level system.

which is the average magnetic moment of a site. We now calculate s. From Eq. (3.39) we have

$$S_1 = -\left(\frac{\partial F_1}{\partial T}\right)_B = k_B \ln\left(1 + e^{-2\beta m_0 B}\right) + \frac{1}{T}\frac{2m_0 B}{e^{2\beta m_0 B} + 1}, \tag{3.43}$$

and we obtain the heat capacity C_1 from

$$C_1 = T\left(\frac{\partial S_1}{\partial T}\right)_B = \frac{(m_0 B)^2}{k_B T^2 \cosh^2(\beta m_0 B)}. \tag{3.44}$$

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).

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

$$F(r) = -2rm_0B - k_BT\ln\Omega(r) = -2rm_0B - k_BT[N\ln N - r\ln r - (N-r)\ln(N-r)]. \tag{3.45}$$

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

$$r_{eq} = \frac{N}{1 + e^{-2m_0B/k_BT}}, \tag{3.46}$$

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

$$m_{eq} = \frac{1}{N}\cdot\frac{1}{2}m_0(2r - N) = m_0\tanh\left(\frac{m_0B}{k_BT}\right), \tag{3.47}$$

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. (3.41).

3.6.0.5 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:

$$Z = \sum_i \exp\Big(-\frac{E_i}{k_BT}\Big) = \sum_{n=0}^{\infty} \exp\Big(-\Big(n+\frac{1}{2}\Big)\frac{\hbar\omega_0}{k_BT}\Big) = \frac{e^{-\frac{1}{2}\hbar\omega_0/k_BT}}{1-e^{-\hbar\omega_0/k_BT}}, \tag{3.48}$$

$$\implies F_{eq} = -k_BT\ln Z = \frac{\hbar\omega_0}{2} = k_BT\ln\Big(1-e^{-\hbar\omega_0/k_BT}\Big), \tag{3.49}$$

$$\implies S = -\Big(\frac{\partial F}{\partial T}\Big)_V = -k_B\ln\Big(1-e^{-\hbar\omega_0/k_BT}\Big) + \frac{\hbar\omega_0}{T}\frac{e^{-\hbar\omega_0/k_BT}}{1-e^{-\hbar\omega_0/k_BT}}, \tag{3.50}$$

$$\implies U = F + TS = -\frac{\partial}{\partial\beta}\ln Z = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT}-1}. \tag{3.51}$$

This is Planck's formula for the energy of black-body radiation in a mode of frequency ω_0. The mean number of photons with energy $\hbar\omega_0$ is directly related to the energy; $\langle n_{\hbar\omega_0}\rangle = (U-\frac{1}{2}\hbar\omega_0)/\hbar\omega_0 = 1/(e^{\hbar\omega_0/k_BT}-1)$

3.6.0.6 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,

$$\begin{aligned} \mathrm{d}S &= -k_B\sum_i(\mathrm{d}P_i\ln P_i + \mathrm{d}P_i) \\ &= -k_B\sum_i\Big(\mathrm{d}P_i\Big(-\frac{E_i}{k_BT}-\ln Z\Big)+0\Big) \\ &= k_B\sum_i\frac{E_i\,\mathrm{d}P_i}{k_BT}, \end{aligned} \tag{3.52}$$

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

$$T\,\mathrm{d}S = \sum_i E_i\,\mathrm{d}P_i\,. \tag{3.53}$$

This is the reversible heat flow $đQ_{\text{rev}}$. But in general $U = \sum_i E_iP_i$, so from $\mathrm{d}U = T\,\mathrm{d}S + đW$ we conclude that the reversible work is

$$đW_{\text{rev}} = \sum_i P_i\,\mathrm{d}E_i\,. \tag{3.54}$$

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 $đW$ 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

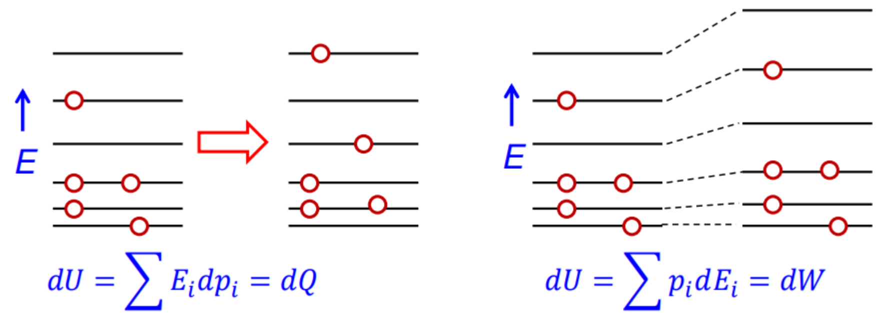

Fig. 3.4: We have $U = \sum p_i E_i \implies \mathrm{d}U = \sum E_i\,\mathrm{d}p_i + \sum p_i\,\mathrm{d}E_i$, and also that $\mathrm{d}U = \text{đ}Q + \text{đ}W$. Thus the internal energy can conceptually be changed in two ways: moving particles to other states- i.e. transfering energy (heat) to particles; and keeping state occupation the same, but changing state energies – i.e. doing work on the system. Hence, we see that the reversible heat flow, $\text{đ}Q_{\text{rev}} = \sum_i E_i\,\mathrm{d}P_i$, comes from the change in the probability distribution while the reversible work, $\text{đ}W_{\text{rev}} = \sum_i P_i\,\mathrm{d}E_i$, comes from the change in the energy levels.

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 Ω 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 Section 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 $t + \mathrm{d}t$. 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, $X = (\mathbf{r}_1, \cdots, \mathbf{r}_N; \mathbf{p}_1, \cdots, \mathbf{p}_n)$, 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 $\mathrm{d}\Gamma$ surrounding the point $\{\mathbf{r}_i, \mathbf{p}_i\}$. The infinitesimal volume is given by

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

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 $\mathrm{d}x\,\mathrm{d}p$. 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 A.2 it is shown that ϱ 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.

4.1.0.1 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 $E + \mathrm{d}E$, 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 $(\mathrm{d}\Gamma\,/\,\mathrm{d}E)\,\mathrm{d}E$, so we define the microcanonical entropy $S(E)$ as

$$S = k_B \ln\left(\frac{\mathrm{d}\Gamma(E)}{\mathrm{d}E}\,\mathrm{d}E\right). \tag{4.2}$$

Moreover we can define the Gibbs entropy as $S = -k_B \int \varrho \ln \varrho \,\mathrm{d}\Gamma$, 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:

$$\boxed{\begin{aligned} \varrho &= \frac{e^{-\beta E(\{\mathbf{p}_i,\mathbf{q}_i\})}}{Z_{cl}}, &(4.3)\\ Z_{cl} &= \int e^{-\beta E(\{\mathbf{p}_i,\mathbf{q}_i\})}\,\mathrm{d}\Gamma\,. &(4.4)\end{aligned}}$$

We mentioned earlier that the factor of $2\pi\hbar$ in the definition of Γ was not important. From Eq.s (4.3) and (4.4) it is clear that if we multiply Γ 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

$$Z_1 = \int e^{-\beta E(\mathbf{p},\mathbf{r})}\,\mathrm{d}\Gamma = \int e^{-p^2/2mk_BT}\frac{\mathrm{d}^3r\,\mathrm{d}^3p}{(2\pi\hbar)^3}$$
$$= \frac{V}{(2\pi\hbar)^3}\int_0^\infty e^{-p^2/2mk_BT}4\pi p^2\,\mathrm{d}p$$
$$= \left(\frac{k_BTm}{2\pi\hbar}\right)^{3/2}V. \tag{4.5}$$

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

$$Z_1 = \int \mathrm{d}^3r \left(\int_{-\infty}^{\infty} e^{-p_x^2/2mk_BT}\frac{\mathrm{d}p_x}{2\pi\hbar}\right)^3 = V\left(\sqrt{\frac{k_BTm}{2\pi\hbar}}\right)^3. \tag{4.6}$$

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:

$$\Omega = V/\lambda^3, \quad \text{where the length scale } \lambda \text{ is:} \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}. \tag{4.7}$$

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 ($m\bar{v} = \sqrt{mk_BT}$). 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 λ^3 inside a fixed V. It's not that surprising, if you look at this result in such a way.

The average energy of the particle is

$$U_1 = -\frac{\partial}{\partial\beta}\ln Z_1 = \frac{3}{2}k_BT. \tag{4.8}$$

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

$$S_1 = -\left(\frac{\partial F_1}{\partial T}\right)_V = -\frac{\partial}{\partial T}(-k_BT\ln Z_1) = k_B\ln Z_1 + \frac{3}{2}k_B = k_B\ln\left(\frac{V}{\lambda^3}e^{3/2}\right). \tag{4.9}$$

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. (4.9), 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

$$S_N^{\text{wrong}} = NS_1 = Nk_B \ln\left(Ve^{3/2}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right), \tag{4.10}$$

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

$$Z_N^{\text{wrong}} = Z_1^N. \tag{4.11}$$

Unfortunately Eq. (4.10) 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. (2.38)) led to the extensive Sackur-Tetrode formula for the entropy of an ideal gas.

The lack of extensivity of Eq. (4.10) 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. (4.10) predicts that the total entropy changes, which cannot be correct, while Eq. (2.38) predicts that it is unchanged.

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

$$Z_N = \frac{1}{N!}Z_1^N, \tag{4.12}$$

so that, for large systems, the free energy is

$$F = -k_BT\ln Z_N = -Nk_BT(\ln Z_1 - \ln N + 1). \tag{4.13}$$

In particular, the entropy now becomes

$$S = -\frac{\partial F}{\partial T} = Nk_B \ln\left(\frac{V}{N}\exp\left(\frac{5}{2}\right)\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right), \tag{4.14}$$

which is extensive and is exactly the Sackur-Tetrode formula (2.44) 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^{wrong} by $N!$.

Eq. (4.14) is consistent with Eq. (2.37), but now we have an explicit formula for the unknown integration constant S_0 which appeared in the earlier derivation. We will derive the SackurTetrode 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. (4.14) does not satisfy the Third Law of Thermodynamics, as the entropy does not go to zero as $T \to 0$ (when quantum effects would take over).

4.2.0.1 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. (4.12) provides:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N. \tag{4.15}$$

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:

$$U = -\frac{\partial}{\partial\beta}\ln Z; \qquad F = -k_BT\ln Z. \tag{4.16}$$

To find U you need to differentiate Z with respect to temperature (or its inverse, β) and that is "hiding" under the square-root in the de Broglie wavelength $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$. 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 $U = \frac{3}{2}Nk_BT$. This is great, but only useful for one thing: to evaluate the heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk_B. \tag{4.17}$$

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 $F = F(T, V, N)$:

$$F = -Nk_BT\ln\left(\frac{V}{\lambda^3}\right) + Nk_BT\ln N - Nk_BT = Nk_BT\ln\left(\frac{N\lambda^3}{Ve}\right), \tag{4.18}$$

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 Eq. (4.18). 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 μ:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V}, \tag{4.19}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_BT\ln\left(\frac{N\lambda^3}{V}\right). \tag{4.20}$$

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 (4.20) 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. (2.45) 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 Section 4.5). This resonates with our old $\mu = k_BT\ln c$ 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

$$\mathcal{H} = Aq^2 + \Delta\mathcal{H}(Q), \tag{4.21}$$

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

$$\varrho(q)\,\mathrm{d}q = \frac{e^{-\beta Aq^2}\,\mathrm{d}q \int e^{-\beta\Delta\mathcal{H}}\,\mathrm{d}Q}{\int e^{-\beta Aq^2}\,\mathrm{d}q \int e^{-\beta\Delta\mathcal{H}}\,\mathrm{d}Q} = \frac{e^{-\beta Aq^2}\,\mathrm{d}q}{\int e^{-\beta Aq^2}\,\mathrm{d}q} = \frac{e^{-\beta Aq^2}\,\mathrm{d}q}{\sqrt{\pi k_B T/A}}. \tag{4.22}$$

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

$$U = \left\langle Aq^2 \right\rangle + \left\langle \Delta\mathcal{H}(Q) \right\rangle, \tag{4.23}$$

and, using Eq. (4.22), we obtain

$$\left\langle Aq^2 \right\rangle = \frac{\int Aq^2 e^{-\beta Aq^2}\,\mathrm{d}q}{\int e^{-\beta Aq^2}\,\mathrm{d}q} = \frac{\frac{\sqrt{\pi}}{2\beta^{3/2}}}{\frac{\sqrt{\pi}}{\beta^{1/2}}} = \frac{1}{2}k_B T. \tag{4.24}$$

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. (4.8) 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 $k_B T \gg \hbar\omega_0$.

4.3.0.1 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,

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(\mathbf{r}_1, \cdots, \mathbf{r}_N), \tag{4.25}$$

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:

$$\varrho(v_{x,i})\,\mathrm{d}v = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\beta\frac{1}{2}mv_{x,i}^2}\,\mathrm{d}v_{x,i} \tag{4.26}$$

the corresponding factor in the partition function is $1/\lambda$, and the mean energy is still $\frac{1}{2}k_BT$ 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 ω_0. Following Eqs. (3.48) and (3.50) we have

$$S = -k_B \ln\left(1 - e^{-\hbar\omega_0/k_BT}\right) + \frac{\hbar\omega_0}{T}\frac{e^{-\hbar\omega_0/k_BT}}{1 - e^{-\hbar\omega/k_BT}}. \tag{4.27}$$

Or simply calculate the partition function:

$$Z = \sum_i \exp\left(-\frac{E_i}{k_BT}\right) = \sum_{n=0}^{\infty} \exp\left(-(n + \frac{1}{2})\frac{\hbar\omega_0}{k_BT}\right) = \frac{e^{-\frac{1}{2}\hbar\omega_0/k_BT}}{1 - e^{-\hbar\omega_0/k_BT}}, \tag{4.28}$$

and then find $S = -\, \mathrm{d}F/\mathrm{d}T$, or $U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$.

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

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = N\frac{\hbar^2\omega_0^2}{k_BT^2}\frac{e^{\hbar\omega_0/k_BT}}{(e^{\hbar\omega_0/k_BT} - 1)^2} = Nk_B\left(\frac{\Theta_{\mathrm{v}}}{T}\right)^2\frac{e^{\Theta_{\mathrm{v}}/T}}{(e^{\Theta_{\mathrm{v}}/T} - 1)^2}, \tag{4.29}$$

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

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

$$\epsilon_J = \frac{\hbar^2 J(J+1)}{2I}, \quad J = 0, 1, 2, \cdots, \tag{4.30}$$

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

$$Z = \sum_{J=0}^{\infty} (2J+1)\exp\left(-\frac{\hbar^2 J(J+1)}{2Ik_BT}\right). \tag{4.31}$$

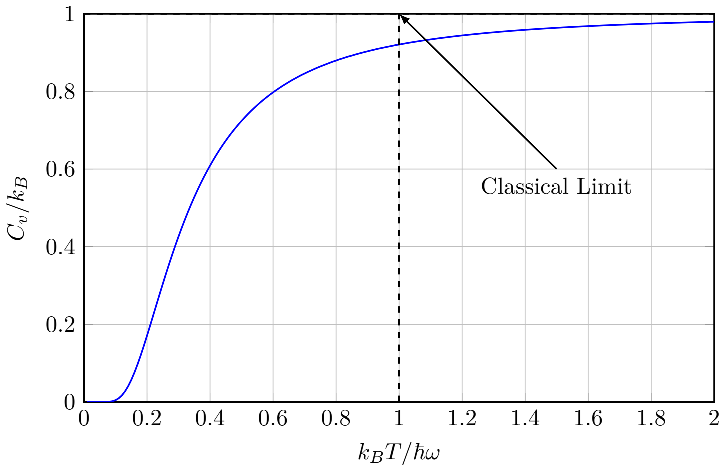

Fig. 4.1: The heat capacity of a harmonic oscillator as a function of temperature.

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

$$Z \simeq 1 + 3\exp\left(-\frac{\hbar^2}{Ik_BT}\right) + \cdots . \tag{4.32}$$

The Helmholtz free energy at low temperatures is given by

$$F = -k_BT\ln Z \simeq -3k_BT\exp\left(-\frac{\hbar^2}{Ik_BT}\right). \tag{4.33}$$

The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 3k_B\exp\left(-\frac{\hbar^2}{Ik_BT}\right) + \frac{3\hbar^2}{IT}\exp\left(-\frac{\hbar^2}{Ik_BT}\right), \tag{4.34}$$

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

$$C_\mathrm{r} = T\left(\frac{\partial S}{\partial T}\right)_V = 12Nk_B\left(\frac{\Theta_\mathrm{r}}{T}\right)^2\exp\left(-\frac{2\Theta_\mathrm{r}}{T}\right), \tag{4.35}$$

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

$$C_\mathrm{r} \simeq Nk_B. \tag{4.36}$$

The full result is shown in Fig. 4.2.

Normally $\Theta_\mathrm{r} \ll \Theta_\mathrm{v}$. 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:

$$\begin{array}{ccc} 0 \ll T \ll \Theta_\mathrm{r} & \text{translational motion:} & C_v = \frac{3}{2}Nk_B, \quad C_p = \frac{5}{2}Nk_B \\ \Theta_\mathrm{r} \ll T \ll \Theta_\mathrm{v} & \text{translational, rotational motion:} & C_v = \frac{5}{2}Nk_B, \quad C_p = \frac{7}{2}Nk_B \\ \Theta_\mathrm{v} \ll T & \text{translational, rotational, vibrational motion:} & C_v = \frac{7}{2}Nk_B, \quad C_p = \frac{9}{2}Nk_B. \end{array} \tag{4.37}$$

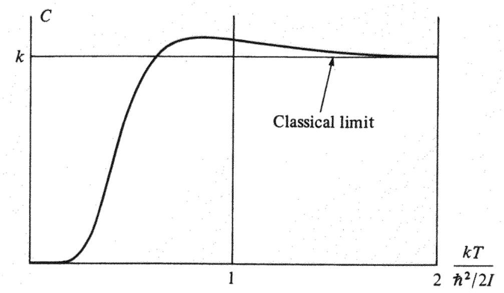

Fig. 4.2: The rotational heat capacity as a function of temperature.

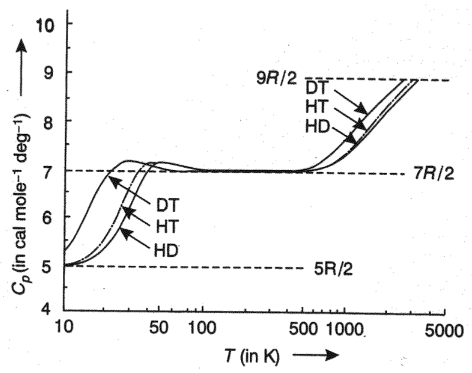

Fig. 4.3: The rotational-vibrational heat capacities at constant pressure, C_p, for the diatomic gases DT, HT, and HD, as a function of temperature.

Note that in the flat part of the curves, where $\Theta_\mathrm{r} \ll T \ll \Theta_\mathrm{v}$, 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!

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. (4.18) and (4.20) for the free energy and chemical potential. Please note how both these expressions, as in fact the entropy (4.14), depend on the combination of parameters (in a 3-dimensional system):

$$\frac{N\lambda^3}{V} = \frac{N}{V}\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2}. \tag{4.38}$$

You can look at this expression and have a scheme illustrated in Fig. 4.4 in mind. Clearly, the ratio in Eq. (4.38) 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 $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$ which, in turn, can be achieved by lowering the temperature $(T \to 0)$,

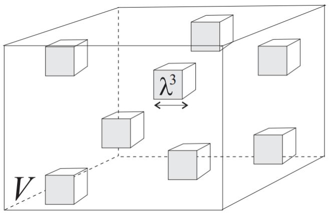

Fig. 4.4: Particles of "size" λ^3 filling the box of volume V.

or by considering lighter particles $m \to 0$). 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.

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_BT (ignoring 'rare' fluctuations). From $\epsilon_{\mathbf{k}} = \hbar^2k^2/2m$ the wavevector for which the kinetic energy of our classical particles matches k_BT is, therefore:

$$k_{\text{max}} \sim \sqrt{\frac{2mk_BT}{\hbar^2}}. \tag{4.39}$$

This would correspond to a wavelength $\lambda_{\text{max}} = \frac{2\pi}{k_{\text{max}}} = \frac{2\pi\sqrt{\hbar^2}}{\sqrt{2mk_BT}}$, which is close to the *thermal de Broglie wavelength* introduced earlier (Eq. (4.7)), up to a factor of order one. In different textbooks the thermal de Broglie wavelength is given with various factors of π floating around, but the most systematic approach for calculating this important quantity, based on the singleparticle partition function $Z_1 = V/\lambda^3$ gives, as shown earlier (Eq. (4.7)):

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}. \tag{4.40}$$

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

$$\langle n \rangle = \frac{\text{number of particles}}{\text{number of accessible energy levels}} = \frac{N}{4/3\pi k_{\text{max}}^3}\frac{(2\pi)^3}{V}, \tag{4.41}$$

and the behaviour is classical when $\langle n \rangle \ll 1$. From Eq. (4.41)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 Section 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 $(\frac{1}{2}, \frac{3}{2}, \cdots)$ and Bose particles or bosons which have integer spins $(0, 1, 2, \cdots)$. Examples of fermions include protons, neutrons, electrons, muons, neutrinos, quarks, and the ^{3}He atom. Examples of bosons include photons, pions, mesons, gluons, and the ^{4}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,

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

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 $|\mathbf{k}_1\rangle$. 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

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

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.[1]

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

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[1] 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.

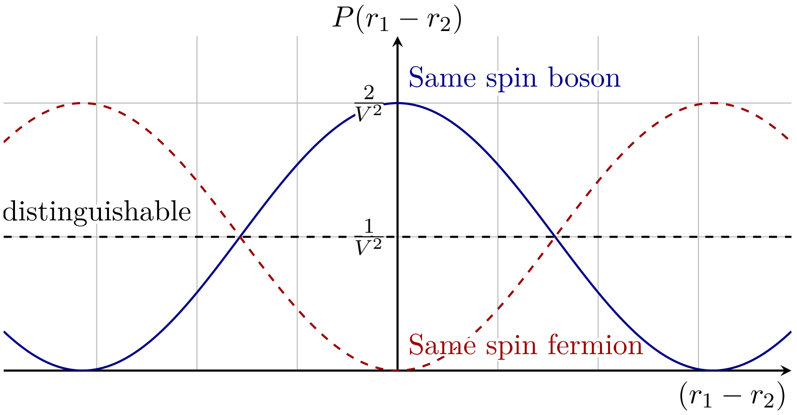

Fig. 5.1: The pair-correlation functions for two fermions of the same spin and for two bosons of the same spin.

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 $\mathbf{r}_2$,

$$\begin{aligned}P_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2) &= \Psi^*_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)\Psi_{\mathbf{k}_1,\mathbf{k}_2}(\mathbf{r}_1,\mathbf{r}_2)\\ &= \frac{1}{2}\Big(1+1\pm\delta_{s_1,s_2}\Big\{e^{-i\mathbf{k}_1\cdot(\mathbf{r}_1-\mathbf{r}_2)}e^{-i\mathbf{k}_2\cdot(\mathbf{r}_2-\mathbf{r}_1)}+e^{-i\mathbf{k}_2\cdot(\mathbf{r}_1-\mathbf{r}_2)}e^{-i\mathbf{k}_1\cdot(\mathbf{r}_2-\mathbf{r}_1)}\Big\}\Big)\\ &= (1\pm\delta_{s_1,s_2}\cos\{(\mathbf{k}_1-\mathbf{k}_2)\cdot(\mathbf{r}_1-\mathbf{r}_2)\}). \qquad (5.3)\end{aligned}$$

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.

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 $\varepsilon_1, \varepsilon_2, \cdots$, whose occupation numbers we denote by $n_1, n_2, \cdots$. The partition function is then

$$Z(T,V,N) = \sum_{n_1,n_2,\cdots}^{N} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}, \qquad (5.4)$$

where the sum is over all sets of occupation numbers, $n_1, n_2, \cdots$, which satisfy $n_1 + n_2 + \cdots = N$. 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 $0, 1, 2, \cdots$. The condition $n_1 + n_2 + \cdots = N$ leads to considerable mathematical difficulties, because it means that the sums over $n_1, n_2, \cdots$ in Eq. (5.4) are not independent.

Suppose we multiply Eq. (5.4) by $e^{\beta\mu N}$, where $\beta = 1/k_B T$ and μ is the chemical potential, and then sum over N,

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} Z(T, V, N) e^{\beta\mu N} = \sum_{N=0}^{\infty} \sum_{n_1, n_2, \cdots}^{N} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots - \mu N)}. \tag{5.5}$$

We recognise Ξ as being the grand partition function, first defined in Eq. (3.23). Noting that $N = n_1 + n_2 + \cdots$, we write

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

The sums are over all sets of the n_i such that $n_1 + n_2 + \cdots = N$, and over all N. This is equivalent to summing over all $n_1 + n_2 + \cdots$ without the constraint that $n_1 + n_2 + \cdots = N$, 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 $n_1 + n_2 + \cdots = N$, and write

$$\begin{aligned}
\Xi(T, V, \mu) &= \sum_{n_1, n_2, \cdots} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots - \mu(n_1 + n_2 + \cdots))} \\
&= \sum_{n_1, n_2, \cdots} e^{-\beta(\varepsilon_1 - \mu)n_1} e^{-\beta(\varepsilon_2 - \mu)n_2} \cdots \\
&= \left[\sum_{n_1} e^{-\beta(\varepsilon_1 - \mu)n_1}\right] \left[\sum_{n_2} e^{-\beta(\varepsilon_2 - \mu)n_2}\right] \cdots \\
&= \Pi_i \Xi_i. \qquad (5.7)
\end{aligned}$$

The last line, Eq. (5.7), shows that the grand partition function is just the product of the grand partition functions Ξ_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 μ. 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

$$\boxed{\Xi_{\mathbf{k}} = \sum_n e^{-\beta(n\varepsilon_{\mathbf{k}} - n\mu)} = \sum_n \left(e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}\right)^n.} \tag{5.8}$$

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 ∞. 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,

$$\beta(\varepsilon_{\mathbf{k}} - \mu) \gg 1, \tag{5.9}$$

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

$$\Xi^{\mathrm{cl}}_{\mathbf{k}} \approx 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} + \cdots . \tag{5.10}$$

If the Eq. (5.9) 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. (5.10) we obtain the grand potential for a given level of energy of an ideal classical gas:

$$\Psi_{\mathbf{k}} = -k_B T \ln \Xi^{\mathrm{cl}}_{\mathbf{k}} = -k_B T \ln\Big(1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}\Big) \simeq -k_B T e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \tag{5.11}$$

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

$$\langle n_{\mathbf{k}} \rangle = -\left(\frac{\partial \Psi_{\mathbf{k}}}{\partial \mu}\right)_{T,V} \simeq e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \tag{5.12}$$

which is the *Maxwell-Boltzmann distribution*. From Eq. (5.9) 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. (5.11) 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 Eq. (3.16), because the other aspect of grand statistical summation (over the number of particles) is effectively done for each microstate in Eq. (5.10). So for a continuous classical gas in 3-dimension this summation over the available phase space is the same as in Eq. (4.5):

$$\Phi = \sum_{\mathbf{k}} \Phi_{\mathbf{k}} = \int \Phi(\varepsilon) \frac{\mathrm{d}^3 r\, \mathrm{d}^3 p}{(2\pi\hbar)^3} = -k_B T \int_0^\infty e^{-\beta(\varepsilon - \mu)} g(\varepsilon)\, \mathrm{d}\varepsilon\,, \tag{5.13}$$

where, after a change of variables, we write the measure of integration as $g(\varepsilon)\,\mathrm{d}\varepsilon$ which is the number of eigenstates with energy between ε and $\varepsilon + \mathrm{d}\varepsilon$. 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 ε we differentiate $\varepsilon = p^2/2m$, which gives

$$\mathrm{d}p = \sqrt{\frac{m}{2\varepsilon}}\,\mathrm{d}\varepsilon\,. \tag{5.14}$$

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

$$\int \frac{\sigma\,\mathrm{d}^3r\,\mathrm{d}^3p}{(2\pi\hbar)^3} = 4\pi\int_0^\infty \frac{\sigma V}{(2\pi\hbar)^3}p^2\,\mathrm{d}p = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{\varepsilon}\,\mathrm{d}\varepsilon\,, \tag{5.15}$$

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

$$\begin{aligned}\Phi &= -k_BT\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}e^{\beta\mu}\int_0^\infty \sqrt{\varepsilon}e^{-\beta\varepsilon}\,\mathrm{d}\varepsilon\\ &= -k_BT\frac{\sigma V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}e^{\beta\mu}2\int_0^\infty x^2e^{-x^2}\,\mathrm{d}x\\ &= -k_BT\sigma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}e^{\beta\mu}\\ &= -k_BT\frac{\sigma V}{\lambda^3}e^{\beta\mu},\end{aligned} \tag{5.16}$$

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

$$N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = \frac{\sigma V}{\lambda^3}e^{\beta\mu}, \tag{5.17}$$

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:

$$\mu = k_BT\ln\left(\frac{N\lambda^3}{\sigma V}\right). \tag{5.18}$$

This is, of course, the same as the result obtained from the canonical ensemble and differentiating the free energy, Eq. (4.20), apart from the extra spin-degeneracy factor σ accounted for here.

The Maxwell Distribution If we substitute this expression for μ into Eq. (5.12) 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 ε is given by

$$P(\varepsilon)\,\mathrm{d}\varepsilon = \frac{1}{N}\langle n_{\mathbf{k}}\rangle\,g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{1}{N}e^{-\beta(\varepsilon-\mu)}g(\varepsilon)\,\mathrm{d}\varepsilon = \frac{1}{N}\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{N\lambda^3}{\sigma V}e^{-\beta\varepsilon}\sqrt{\varepsilon}\,\mathrm{d}\varepsilon\,, \tag{5.19}$$

where we have substituted for $g(\varepsilon)$, from Eq. (5.15), and $e^{\beta\mu}$ from Eq. (5.18). Substituting the classical expression for the kinetic energy, $\varepsilon = \frac{1}{2}mv^2$, and rearranging we obtain

$$P(v)\,\mathrm{d}v = \left(\frac{m}{2\pi k_BT}\right)^{3/2}e^{-\beta mv^2/2}4\pi v^2\,\mathrm{d}v\,, \tag{5.20}$$

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:

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

which is the usual ideal gas law. We got the last equality by substituting for μ from Eq. (5.18).

The Entropy of an Ideal Gas Finally, let us obtain the entropy from

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V} = k_B \frac{\sigma V}{\lambda^3} e^{\mu/k_B T}\left(\frac{5}{2} - \frac{\mu}{k_B T}\right). \tag{5.22}$$

Substituting for μ gives

$$S = k_B N \ln\left(\exp\left(\frac{5}{2}\right)\frac{\sigma V}{N\lambda^3}\right) = k_B N \ln\left(e^{5/2}\frac{\sigma V}{N}\left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}\right). \tag{5.23}$$

This is the Sackur-Tetrode expression for the entropy of an ideal classical gas yet again; we derived it in Section 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 (5.5). We have already calculated and discussed the canonical partition function

$$Z = \frac{1}{N!} Z_1^N, \quad \text{therefore} \quad \Xi = \sum_{N=0}^{\infty} \frac{1}{N!}\left(Z_1 e^{\beta\mu}\right)^N = \exp\left(Z_1 e^{\beta\mu}\right), \tag{5.24}$$

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:

$$\Xi = \exp\left(\frac{V}{\lambda^3} e^{\beta\mu}\right) = \exp\left(V\left[\frac{m k_B T}{2\pi\hbar^2}\right]^3 e^{\beta\mu}\right), \tag{5.25}$$

$$\implies \Phi = -k_B T Z_1 e^{\beta\mu} = -k_B T V \left[\frac{m k_B T}{2\pi\hbar^2}\right]^3 e^{\beta\mu}, \tag{5.26}$$

which is the expression (5.16), 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 ε_{int} is (see Section 4.4),

$$\varepsilon_{\text{int}} = \left(n + \frac{1}{2}\right)\hbar\omega_0 + \frac{\hbar^2 J(J+1)}{2I}, \tag{5.27}$$

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 ε_{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)

$$\begin{aligned}\Xi_{\mathbf{k}} &= 1 + \sum_{\text{int}} e^{-\beta(\varepsilon_{\mathbf{k}} + \varepsilon_{\text{int}} + \varepsilon_{\text{ext}} - \mu)} \\ &= 1 + e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)} e^{-\beta\varepsilon_{\text{ext}}} \sum_{\text{int}} e^{-\beta\varepsilon_{\text{int}}} \\ &\equiv 1 + Z_{\text{int}} Z_{\text{ext}}(h) e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)},\end{aligned} \tag{5.28}$$

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

$$\Phi_{\mathbf{k}}(h) = -k_B T \ln \Xi_{\mathbf{k}}(h) \simeq -k_B T Z_{\text{int}} Z_{\text{ext}}(h) e^{-\beta(\varepsilon_{\mathbf{k}} - \mu)}, \tag{5.29}$$

where the last equivalence holds in the classical limit only. We have seen this form in Eqs. (5.16) and (5.26) just above. Carrying through the same calculation as in Eq. (5.16) etc., we find the chemical potential for fixed particle number N,

$$\mu = k_B T \left[\ln\left(\frac{N(h)\lambda^3}{\sigma V}\right) - \ln Z_{\text{int}} - \ln Z_{\text{ext}}(h) \right], \tag{5.30}$$

where the possible dependence of particle number on the height h is also emphasised. 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_{int} is independent of height. In equilibrium µ must also be independent of height, and from Eq. (5.30) we can see that $N(h)$ must therefore be of the form

$$N(h) = N(0)e^{-mgh/k_BT}. \tag{5.31}$$

The density therefore drops exponentially with height.

5.6 Equilibrium Constant for Chemical Reactions

In Section 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

$$K_N(T) \equiv \prod_i N_i^{\nu_i}, \tag{5.32}$$

where ν_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. (5.30) for each species as

$$\mu_i = k_BT\Big(\ln N_i - \ln Z_1^i\Big), \tag{5.33}$$

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 μ_i in the condition for chemical equilibrium, $\sum_i \nu_i\mu_i = 0$, which gives

$$\sum_i \nu_i\mu_i = \sum_i \nu_i k_BT\Big(\ln N_i - \ln Z_1^i\Big) = 0, \tag{5.34}$$

and therefore

$$K_N(T) = \prod_i N_i^{\nu_i} = \prod_i \left(Z_1^i\right)^{\nu_i}. \tag{5.35}$$

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 Section 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 ε. 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, μ_s, and equating it to that of the vapour, μ_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.

- **Canonical Ensemble:** The partition function for N adsorbed molecules is

  $$Z_N = \frac{N_s!}{(N_s - N)!N!} z_s^N e^{-\beta(-N\varepsilon)}. \tag{5.36}$$

  Using Stirling's approximation we obtain

  $$F = -k_B T \ln Z_N = -N\varepsilon - k_B T[N \ln z_s + N_s \ln N_s - (N_s - N)\ln(N_s - N) - N \ln N]. \tag{5.37}$$

  The chemical potential is then

  $$\begin{aligned} \mu_s = \frac{\partial F}{\partial N} &= -\epsilon - k_B T\left(\ln z_s + \ln\left(\frac{N_s - N}{N}\right)\right) \\ &= -\epsilon + k_B T \ln\left(\frac{N}{(N_s - N)z_s}\right) \\ &= -\epsilon + k_B T \ln\left(\frac{\theta}{(1-\theta)z_s}\right). \end{aligned} \tag{5.38}$$

- **Grand Canonical Ensemble:** The surface sites are independent and therefore we consider a single site. The grand partition function is

  $$\Xi = \sum_i e^{-\beta(E_i - \mu_s N_i)} Z_{\text{int}}^{(i)}, \tag{5.39}$$

  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 $E_1 = -\epsilon$). $_{\text{int}}^{(i)}$ 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

  $$\Xi = 1 + z_s e^{\beta(\epsilon + \mu_s}. \tag{5.40}$$

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

  $$\theta = \frac{N}{N_s} = -\left(\frac{\partial \Phi}{\partial \mu_s}\right)_{T,V} = \frac{z_s e^{\beta(\epsilon+\mu_s}}{1 + z_s e^{\beta(\epsilon+\mu_s}}. \tag{5.41}$$

  Rearranging we obtain

  $$\mu_s = -\epsilon + k_B T \ln\left(\frac{\theta}{(1-\theta)z_s}\right) \tag{5.42}$$

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

The chemical potential of an ideal gas is given by Eq. (5.18):

$$\mu_v = k_B T \ln\left(\frac{N\lambda^3}{V}\right) = k_B T \ln\left(\frac{p}{k_B T}\lambda^3\right). \tag{5.43}$$

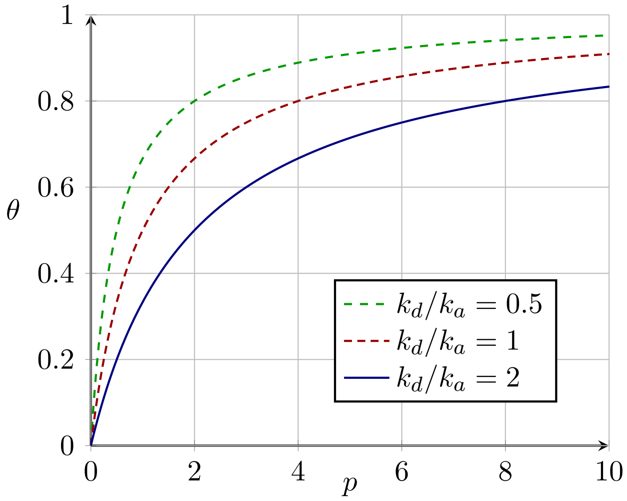

Fig. 5.2: Langmuir isotherms for different ratios of the rate constants, k_d/k_a.

Equating μ_v and μ_s we obtain the Langmuir adsorption isotherm,

$$p = \frac{\theta}{1-\theta}\frac{k_B T}{z_s \lambda^3} e^{-\beta\epsilon}. \tag{5.44}$$

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

$$\frac{\mathrm{d}\theta_a}{\mathrm{d}t} = k_a p(1-\theta), \tag{5.45}$$

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 θ due to desorption is just a basic decay:

$$\frac{\mathrm{d}\theta_d}{\mathrm{d}t} = -k_d\theta, \tag{5.46}$$

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

$$\frac{\mathrm{d}\theta_a}{\mathrm{d}t} + \frac{\mathrm{d}\theta_d}{\mathrm{d}t} = 0, \tag{5.47}$$

and therefore

$$p = \frac{\theta}{1-\theta}\frac{k_d}{k_a}, \tag{5.48}$$

which is illustrated in Fig. 5.1. Eq. (5.44) 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 θ is not too large.

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

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

and the grand potential is

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

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

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

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

$$\begin{aligned} S_{\mathbf{k}} &= -\left(\frac{\partial \Phi_{\mathbf{k}}}{\partial \mu}\right)_{V,\mu} \\ &= k_B \ln\left(1 + e^{-\beta(\varepsilon_{\mathbf{k}}-\mu)}\right) + \frac{k_B \beta(\varepsilon_{\mathbf{k}} - \mu)}{1 + e^{\beta(\varepsilon_{\mathbf{k}}-\mu)}} \\ &= -k_B[\langle n_{\mathbf{k}} \rangle \ln \langle n_{\mathbf{k}} \rangle + (1 - \langle n_{\mathbf{k}} \rangle) + \ln(1 - \langle n_{\mathbf{k}} \rangle)]. \end{aligned} \tag{6.4}$$

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.

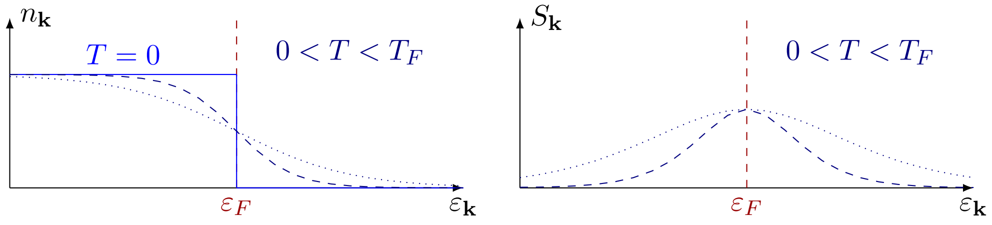

Fig. 6.1: The average occupation and entropy of an energy level as a function of energy in a Fermi gas at zero temperature (solid blue line) and at a finite temperature $T \ll T_F$ (dashed dark blue line).

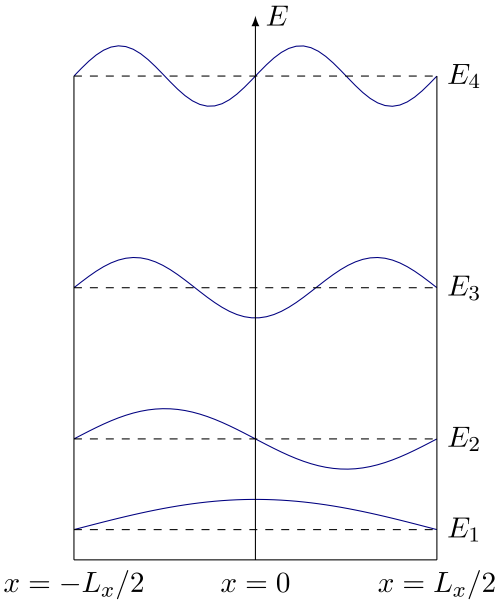

Fig. 6.2: The four lowest-energy eigenfunctions for a particle in a box.

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

$$\Psi = \left(\frac{2}{L_x}\frac{2}{L_y}\frac{2}{L_z}\right)^{1/2} \sin(k_x x)\sin(k_y y)\sin(k_z z). \tag{6.5}$$

The associated eigenenergies are

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2). \tag{6.6}$$

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

$$\Delta k_x \Delta k_y \Delta k_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}, \tag{6.7}$$

where V is the volume of the box.

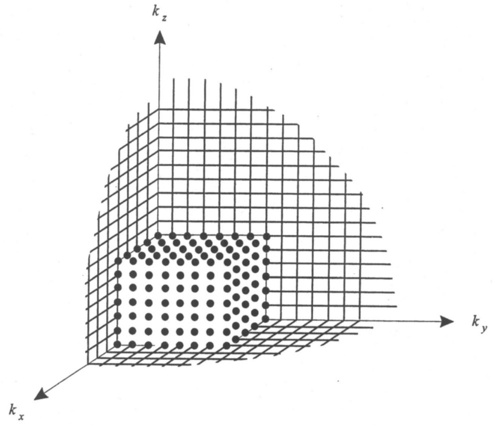

Fig. 6.3: The allowed k-values for a box with hard walls.

We will transform sums over quantum states into integrals over momentum or energy, in which case we need the density of allowed **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):

$$\text{density} = \frac{\sigma}{\Delta k_x \Delta k_y \Delta k_z} = \frac{\sigma V}{\pi^3}. \tag{6.8}$$

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:

$$\psi(x + L_x, y, z) = \psi(x), \tag{6.9}$$

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

$$\psi = \frac{1}{\sqrt{L_x L_y L_z}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{6.10}$$

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:

$$\Delta k_x \Delta k_y \Delta k_z = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V} \tag{6.11}$$

$$\text{density} = \frac{\sigma}{\Delta k_x \Delta k_y \Delta k_z} = \frac{\sigma V}{(2\pi)^3}. \tag{6.12}$$

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 **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:

$$\sum_{\text{states}} = \int \mathrm{d}\Gamma = \int \frac{\mathrm{d}^3x\,\mathrm{d}^3k}{(2\pi)^3}. \tag{6.13}$$

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 ε we use

$$\boxed{\sum_{k_x,k_y,k_z} f(\varepsilon_{\mathbf{k}}) \to \frac{\sigma V}{8\pi^3}\int_0^\infty f(\varepsilon_{\mathbf{k}}) 4\pi k^2\,\mathrm{d}k = \int_0^\infty g(\varepsilon) f(\varepsilon)\,\mathrm{d}\varepsilon\,,} \tag{6.14}$$

where $g(\varepsilon)\,\mathrm{d}\varepsilon$ is the density of states, which is given by Eq. (5.15) 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 ε and face the consequences. We will use Eq. (6.14) 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 ε (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:

Chapter 7

Ideal Bose Gases

Chapter 8

Non-ideal Gases and Liquids

Chapter 9

Phase Equilibria and Transitions

Chapter 10

Fluctuations in Equilibrium

CHAPTER 11

Elements of Stochastic Physics

Appendix A

Appendix

A.1 Microscopics of Irreversibility

A.2 Liouville's Theorem

A.3 Fluctuation-Dissipation Theorem and Wiener-Khinchin Theorem

A.4 Stirling's Approximation