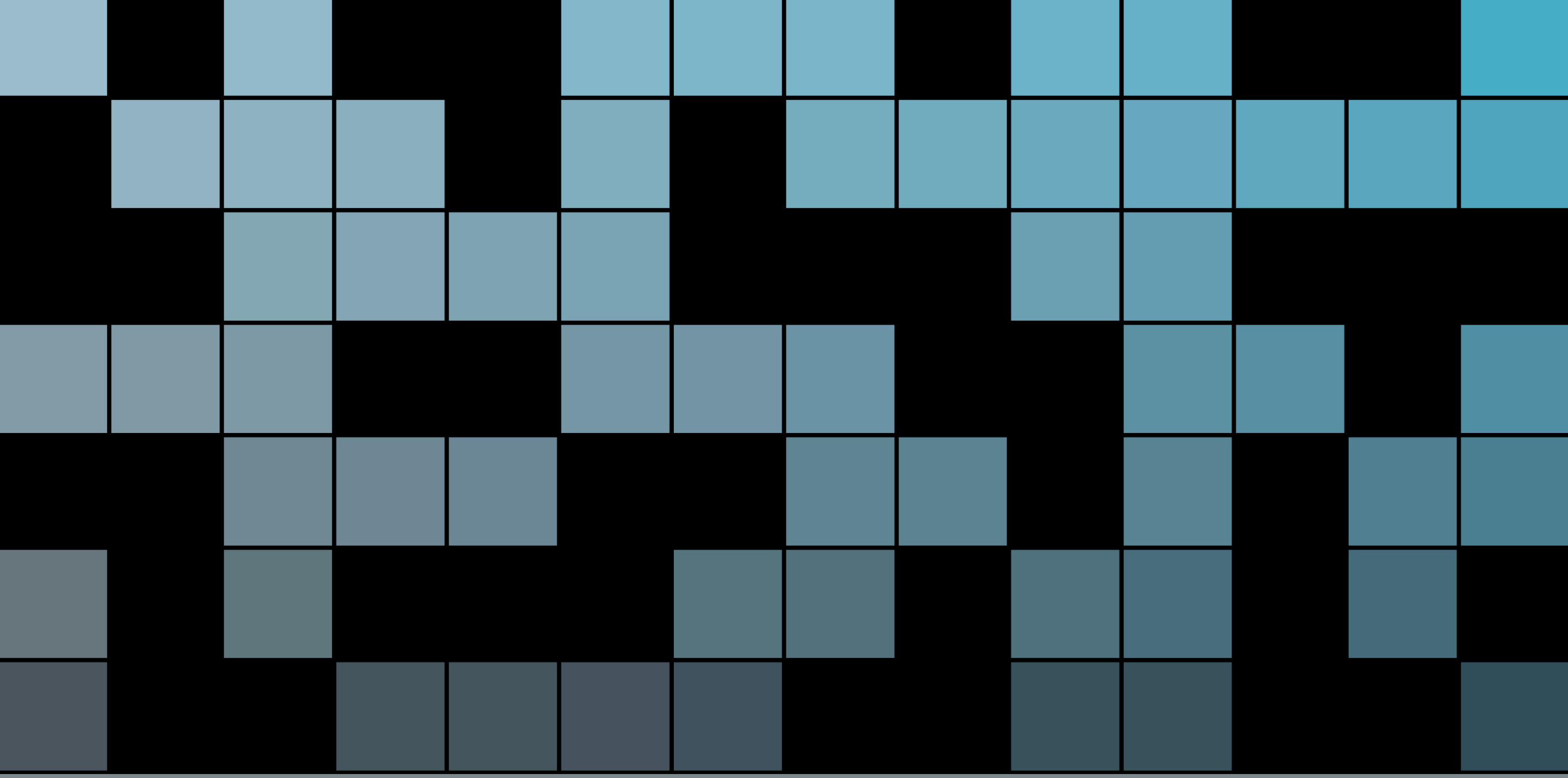

Lecture Notes on Thermodynamics & Statistical Mechanics

UNIVERSITY OF OXFORD

Part of the A1 Second Year Course

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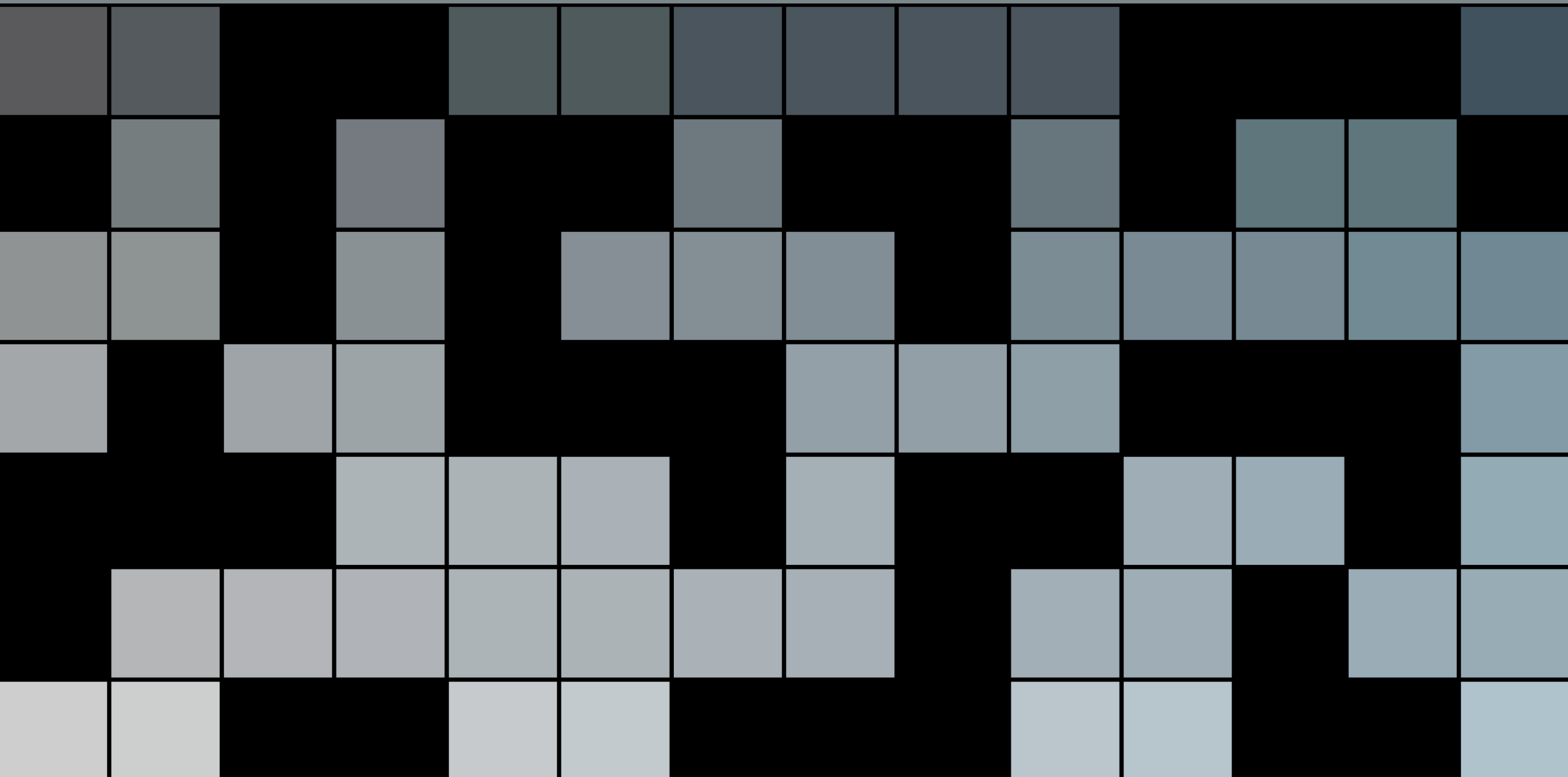

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I

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1. Introduction

Thermodynamics is the study of how heat moves around in ‘macroscopic’ objects. Throughout these lectures, we will talk a lot about *laws* and *models*. Models are a *simplified*, empirical description of a real system which generally develops overtime as our knowledge progresses. In contrast, laws derive from fundamental principles of Physics and thus apply[*] *universally*. Examples of laws are: the energy conservation law, Newton’s laws of motion, but also quantum mechanics, special and general relativity, etc ... Examples of models include: the ideal gas, the Bohr atom etc ...

One important thing to remember is that what looks obvious to the modern physicist, was not so in the 18th and early 19th century, when Thermodynamics was developed! For instance, the description of matter as made of atoms and molecules — although an old philosophical idea — in terms of statistical mechanics was yet to be invented. Quantum mechanics and special relativity did not exist. In short, there was no microscopic underpinning of Thermodynamics. Even the concept of energy was blurry, with the French chemist, Lavoisier, proposing the existence of a weightless conserved fluid called ‘caloric’ (a.k.a. ‘heat’ in modern language). Rumford had observed that cannons were heated by friction during boring, which showed that mechanical work could be turned into heat, but it was Joule who was the first to perform a careful experiment which determined the mechanical equivalent of heat, using a paddle wheel apparatus.

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[*] with caution ...

2. The zeroth law of Thermodynamics

2.1 Thermodynamical systems

Before we embark on deriving the laws of thermodynamics, it is necessary to define the main vocabulary we will be using throughout these lectures.

> **Definition 2.1.1 — 'Thermodynamical system' (or 'system').** Whatever "macroscopic" part of the Universe we select for study.

"Macroscopic" here means made of a large number of particles, N, i.e. $N \geq \mathcal{N}_A \simeq 6.02 \times 10^{23}$, with $\mathcal{N}_A$ the Avogadro number. This is very important as some properties (eg. temperature) do not apply for single particles.

As an isolated system is not a very realistic concept (apart if one studies the Universe as a whole!), one is led to define the

> **Definition 2.1.2 — 'Surroundings of a system' (or 'surroundings').** This is simply the vicinity of a system.

Generally the surroundings will be much larger than the system itself, so will not be treated in the same way. The system and its surroundings are separated from one another by a *boundary*. Together, system and surroundings form what is called the

> **Definition 2.1.3 — 'Total system'.** This is a thermodynamical system which can be considered as *isolated* to a good approximation.

Graphically, one can summarise this definitions as follows:

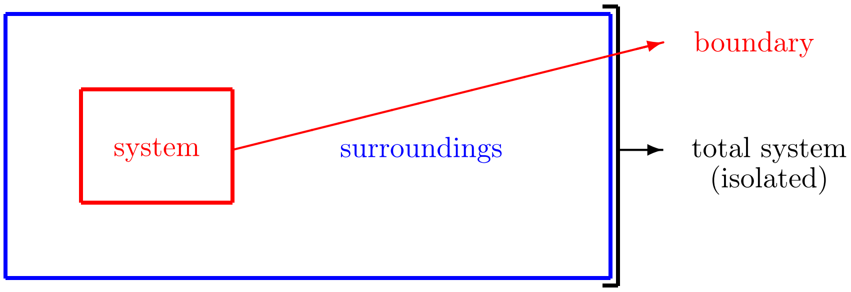

Figure 2.1: Schematic diagram of a thermodynamical system.

R There will exist multiple possible choices to define system and surroundings in any given thermodynamical problem: choose wisely!

2.2 Thermodynamical (macro) versus micro states

When a theory or a measurement provides a complete description of a system, one says that the system's *state* is determined. For a thermodynamical (or macroscopic) system, all there is to know about it can be summarised by four *thermodynamical variables*. Two of these, the pressure, p, and the temperature, T, are called *intensive* variables as they do not depend on the amount of material in the system. The other two, the volume, V, and the number of particles, N, are *extensive* variables and depend on the amount of material in the system.

Obviously, the micro states (positions and momenta of all the particles that compose the system) are not determined by these four variables. However, any micro state which gives rise to the same values for these four variables cannot be differentiated in terms of thermodynamics (see example in Fig. 2.2).

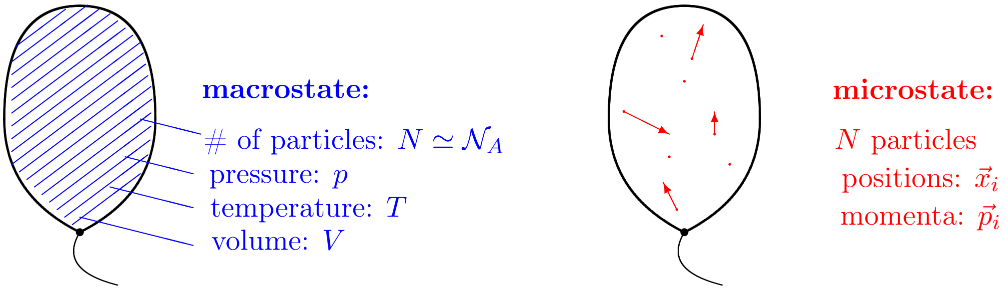

Figure 2.2: Example of macrostates and microstates: inflatable balloon.

We will start these lectures by considering *closed* systems, i.e. systems with $N = \mathrm{C}^{\mathrm{st}}$, for simplicity and come back to systems where the number of particles can vary after we have discussed the fundamental laws of thermodynamics.

2.3 Thermodynamical equilibrium

One says that a system is in *thermodynamical equilibrium* if all its thermodynamical variables (p, V, T) are:

- well defined (i.e. they have the same value throughout the system: see Fig. 2.3 for an example)
- do not vary with time (i.e. if external factors do not change. and you look at the system at two different time instants, p, V, T, will have the same values)

Note that the *micro* states of the system will be different, as particles are not “frozen in place”, but their changes compensate. One therefore says that micro states are **not** functions of state.

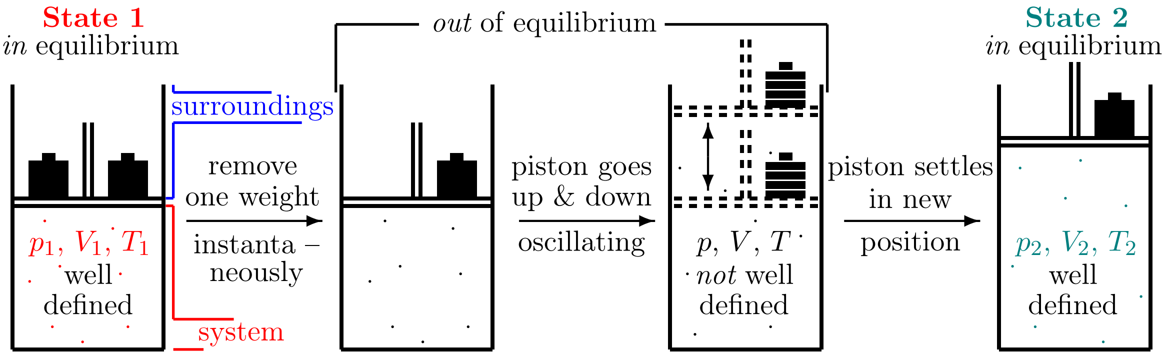

Figure 2.3: Example of a system in and out of equilibrium: gas is enclosed in a container whose top is a piston initially balanced by two identical weights. One of the weights is then removed instantaneously.

One way to visualise this is to draw a $p-V$ *diagram* (see Fig 2.4). We will be using these a lot!

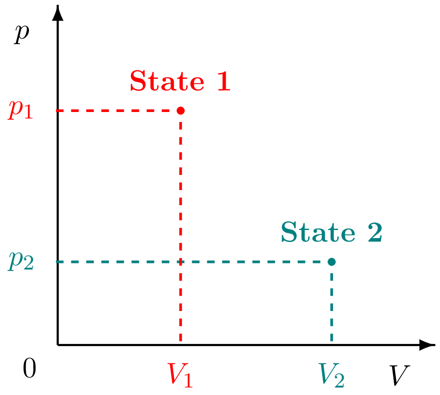

Figure 2.4: $p-V$ diagram for the gas enclosed in the container presented in Fig 2.3. Whilst one can mark the two (well defined) macro states, it is *impossible* to draw the path taken by the system to go from **State 1** to **State 2**!

R *Micro* states are always well defined as one can always specify the positions and momenta of all particles at any point in time, regardless of whether the system is in equilibrium. It is the *macro* states which are only well defined when the system is in thermodynamical equilibrium.

2.4 Equation of state

For systems in thermodynamical equilibrium, it has been established, both experimentally (*Boyle’s law* for gases) and via Statistical Mechanics (as you will see later in this course), that only 2 of the 3 thermodynamical variables are *independent*. The third one can be determined by using the *equation of state* which is a single equation involving all 3 variables, and thus constrains their values.

■ **Example 2.1** The ideal gas equation of state $pV = nRT$ or $pV = Nk_BT$ where n is the amount of substance in moles, $R = 8.314$ J K^{-1} mol^{-1} the molar gas constant, and $k_B = R/\mathcal{N}_A = 1.381 \times 10^{-23}$ J K^{-1} the *Boltzmann constant*. ■

R The equation of state *only* applies to systems in thermodynamical equilibrium and does *not* favour one thermodynamical variable over another: the choice is yours!

2.5 The zeroth law

Using both the definition of thermodynamical equilibrium and of the equation of state previously given, one realises that there are essentially two ways for a system to be *out of equilibrium*:

- p, V, T are well defined (they are the same throughout the system) but do not lie on the equation of state*
- p or T vary from one point of the system to another

Whenever a system gets out of equilibrium, it undergoes a spontaneous macroscopic change to reach a new thermodynamical equilibrium. Situation two (p and T differing in different part of the system) is the most common in thermodynamical problems.

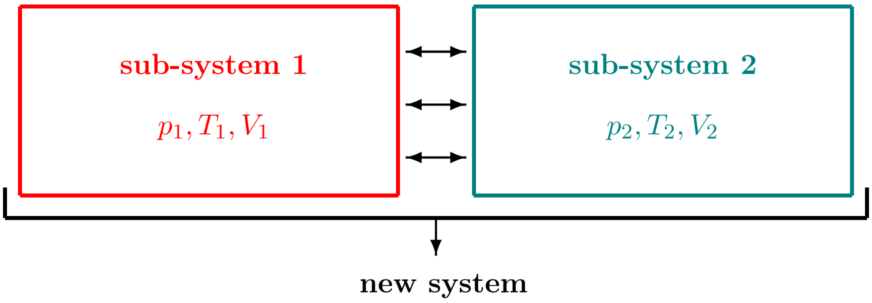

Figure 2.5: Schematic diagram of two thermodynamical sub-systems which are brought into contact (along the double arrows) and interact to form a new thermodynamical system.

Imagine two sub-systems each in a different thermodynamical equilibrium state initially, say with p_1, V_1, T_1 and p_2, V_2, T_2 respectively, as illustrated in Fig 2.5. When these two sub-systems are brought into contact and allowed to interact, they will form a single system which is out of equilibrium, as per situation two. A spontaneous change will ensue, so that the combined system achieves equilibrium. At this point, the sub-systems 1 and 2 will have the same p, V, T throughout but with values different from both p_1, V_1, T_1 and p_2, V_2, T_2.

Now imagine that both sub-systems start with the same p, V, T values. When they are brought into contact, nothing happens because the combined system is already in

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[*] This is the case, for instance of (transient) non-equilibrium states of a system which are close enough to the equilibrium state so that their pressure and temperature can be well defined, or of meta-stable non-equilibrium states. Examples of these latter are water with below freezing temperature at standard pressure, or diamond, which can co-exist at standard p, T alongside the true carbon equilibrium state in these conditions: graphite. We will discuss such non-equilibrium states in more detail when we study the liquid-gas phase transition at the end of these lectures.

thermodynamical equilibrium with p, V, T the same throughout. We therefore say that the sub-systems are in equilibrium with one another. This leads to:

Law 1 — The zeroth law of Thermodynamics. If A, B and C are different thermodynamical systems and A is in thermodynamical equilibrium with B and B is in thermodynamical equilibrium with C, then A is in thermodynamical equilibrium with C.

In other words, thermodynamical states exist and thermodynamics is macroscopically complete as a theory. It also establishes why thermometers work and can be used to give a definition of temperature.

How do we bring these sub-systems "into contact"[†]? It turns out that for *closed* systems made of a *pure* substance in a *single phase*, there exists two kinds of contact, each associated with a different kind of equilibrium and a different intensive thermodynamical variable.

1. **Mechanical contact.** Associated with p and *mechanical equilibrium*. To realise this kind of contact, the wall which ends up separating the two sub-systems in Fig. 2.5 once they touch must be allowed to move (but not let particles go through). A typical example is that of gas on two sides of a container with different pressures $p_1 > p_2$. The pressure difference exerts a net macroscopic force, $\mathcal{F} = (p_1 - p_2) \times (\text{area of the wall})$, which pushes the wall towards side 2. So if the wall can move, then side 1 expands, side 2 is compressed, and energy (volume) is transferred from side 1 to side 2 in the form of *work*, until the pressures become equal on both sides.
2. **Thermal contact.** Associated with T and *thermal equilibrium*. That's the one relevant for thermometers! In this case, the wall between the two sides must be *diathermal* (thermally conductive). If the two sub-systems in Fig. 2.5, with $T_1 > T_2$, are brought in contact, energy in the form of *heat* flows from the hotter (side 1)to the cooler one (side 2) until the temperatures become equal on both sides.

Note that most of the real world systems consist of more than one substance/phase (gas, liquid or solid) and often are open (N is not constant). In that case, another form of contact exists, called **diffusive contact** and associated with another intensive thermodynamical variable, the *chemical potential*, μ. The equilibrium reached via diffusive contact is called *diffusive equilibrium* and the wall separating the two sub-systems in that case must be *permeable*, i.e. able to let particles through. The energy transferred between side 1 and side 2 is directly linked to the amount of material flowing through the wall: $\mu \Delta N$. If we start from $\mu_1 > \mu_2$, this migration of particles from side 1 to side 2 will end when the chemical potentials on both sides are equal. We will come back to this type in equilibrium in the later part of the course, but it is something you should keep in the back of your mind.

R You can easily convince yourself that the number of particles, N, is an independent thermodynamical variable, as you can change the macroscopic state of a system by adding more material without changing either p or T. This is straightforward to see when considering the ideal gas law $pV = Nk_BT$: changing N proportionally to V leaves p and T unchanged, but obviously V (and N) have changed, so the macroscopic state of the system has changed. This is impossible to achieve if N remains fixed, i.e. the system is closed.

[†] "Contact" here is not to be taken literally, as for instance a sub-system could be irradiated by another located at a great distance from it, like the Earth by the Sun, and we would still consider that these sub-systems are in contact.

3. The first law of Thermodynamics

With the previous definitions in hand, we are now equipped to tackle the first law of thermodynamics.

3.1 Thermodynamical change

Because thermodynamical systems are generally in mechanical and/or thermal contact with their surroundings, nothing really happens until there is a *change* in external factors. Generally, this gives rise to a change in thermodynamical state: at least one of the two independent thermodynamical variables of the system will change its value. If we denote the initial value of a thermodynamical quantity X (function of state) by the subscript i and its final value by the subscript f, we will write the change $\Delta X = X_f - X_i$. Note that the function of state of the surroundings will also change.

One of the major reasons why thermodynamical processes are complicated in general is that there are *two* independent variables[*]. So we need a description of what both variables are doing to be complete. However, thermodynamical changes often occur under the constraint that one variable is fixed. We will give a more mathematical description of thermodynamical changes later in the course.

3.2 The first law

Law 2 — The first law of Thermodynamics. The internal energy of an *isolated* system is conserved under *any* thermodynamical change.

> This is the macroscopic version of the familiar energy conservation law of physics. This law applies to an *isolated* system, i.e. according to our previous definitions to the *total system* constituted by the system plus its surroundings. In other words, whatever internal energy is gained by the system itself must be lost by its surroundings and vice-versa.

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[*] This explains why we will often use $p - V$ or $p - T$ diagrams to mark states and path to states.

We saw from the zeroth law that there are two kinds of energy that can be transferred between a thermodynamical system and its surroundings:

1. *work*, W, by mechanical contact
2. *heat*, Q, by thermal contact

This leads us to rewrite the first law for *any* thermodynamical system (i.e. not necessarily isolated), as:

Law 3 — The first law of Thermodynamics (bis). Under *any* thermodynamical change,

$$\Delta U = Q + W$$

where U is the internal energy of the system (function of state), Q is the heat *added to* the system and W the work done *on* the system[†]. According to the first law we thus have $Q_{\text{surr}} = -Q$ and $W_{\text{surr}} = -W$, where the subscript 'surr' indicates the system's surroundings.

3.3 Internal energy

How to calculate the total amount of energy that a system contains? Here we will somewhat 'cheat' a bit and go back to the microscopic scale to develop an understanding of it.

The energy E_l of a particle l, according to the fundamental laws of physics, is either in *kinetic* or *potential* form, which we will write $E_{l,K}$ and $E_{l,P}$ respectively. As we will be discussing molecules in thermodynamics and statistical mechanics, it is also convenient to introduce an *internal state* energy $E_{l,I}$ (which is really composed of *intra*-molecular kinetic and potential energies reflecting the structure of the molecule). $E_{l,K}$ is associated with the translational (centre of mass) motion of the molecule and $E_{l,P}$ refers to the *inter*-molecular interactions (between different molecules).

R For an ideal *mono-atomic* gas, we only have $E_{l,K}$ as particles have no internal structure and they do not collide/interact with one another by assumption!

So the total internal energy of a system is simply:

$$E = \sum_{l} (E_{l,K} + E_{l,P} + E_{l,I})$$

This energy remains constant over time only if the system is *isolated*. This is not the case for most thermodynamical systems which usually are in thermal/mechanical contact with their surroundings, so energy flows in and out of the system even when this latter is in thermodynamical equilibrium. So strictly speaking, E *cannot* be a thermodynamical variable. However, for thermodynamical systems in equilibrium, energy fluctuations are small and quick (you will qualify this statement in statistical mechanics), so that one can define:

$$U = \langle E(t) \rangle = \frac{1}{\Delta t} \int_0^{\Delta t} E(t)\ \mathrm{d}t$$

as a true thermodynamical variable and call it the *internal energy* of the system (in the sense of 'the energy internal to the system').

[†] You will sometimes encounter the first law written $\Delta U = Q - W$, where W is the work done *by* the system. It's a convention. A mnemonic way to remember what the sign is, is that from the system's perspective, if work is done *on* it, its internal energy *increases*: you get a '+' sign.

3.4 Functions of state vs functions of path

U like the other thermodynamical quantities (V, p, T, N) is a *function of state*, in the sense that it only depends on the thermodynamical state of the system. By contrast, Q and W *cannot* be assigned to a state but only to thermodynamical processes, i.e. to changes of state. For this reason they are called *functions of path*. **It makes absolutely no sense whatsoever to say that a system 'has' heat or work!** A system exchanges heat or does work but it does *not* store work or heat: they are energy *in transit*!

Mathematically, this means that for any function of state X, if the thermodynamical variables (V, p, T, N) go from (V_i, p_i, T_i, N_i) to (V_f, p_f, T_f, N_f), the change in X is:

$$\Delta X = \int_{V_i,p_i,T_i,N_i}^{V_f,p_f,T_f,N_f} \mathrm{d}X = X(V_f, p_f, T_f, N_f) - X(V_i, p_i, T_i, N_i)$$

i.e. the change depends only on the end points, the initial and final states of the system and *not* on the path the system took to get there. In other words, $\mathrm{d}X$ is an *exact differential* and functions of state have exact differentials.

R X can be trivial: a simple thermodynamical variable like V, p, T, N.

Mathematical reminder: Let $f_1(x,y)\,\mathrm{d}x + f_2(x,y)\,\mathrm{d}y$ be the change undergone by a function when its variables x and y change to $x + \mathrm{d}x$ and $y + \mathrm{d}y$. This change is an *exact differential* if it can be written as the differential of a differentiable single-valued function $f(x,y)$, i.e. $f_1(x,y) = (\partial f/\partial x)_y$ *and* $f_2(x,y) = (\partial f/\partial y)_x$.

By contrast, a thermodynamical quantity X represented by an *inexact differential* will be noted $\text{đ}X$.

■ Example 3.1

- $f(x,y) = xy \to \mathrm{d}f = \mathrm{d}(xy) = x\,\mathrm{d}y + y\,\mathrm{d}x$
- $\text{đ}g = y\,\mathrm{d}x$

Now consider a path going from $(x_i, y_i) = (0,0)$ to $(x_f, y_f) = (1,1)$. The change in f is given by

$$\Delta f = \int_{(0,0)}^{(1,1)} \mathrm{d}f = \int_{(0,0)}^{(1,1)} \mathrm{d}(xy) = \Big[xy \Big]_{(0,0)}^{(1,1)} = 1$$

no matter which path you decided to consider. In the same way, we can write that the change in g is

$$\Delta g = \int_{(0,0)}^{(1,1)} y\,\mathrm{d}x.$$

However, in this case, let us consider path (i) which is the straight line connecting $(0,0)$ to $(1,1)$, and path (ii) which first goes from $(0,0)$ to $(1,0)$ horizontally and then from $(1,0)$ to $(1,1)$ vertically (see Fig 3.1). In the first case, we have:

$$\Delta g^{(i)} = \int_0^1 x\,\mathrm{d}x = \left[\frac{x^2}{2}\right]_0^1 = \frac{1}{2}$$

whilst in the second case,

$$\Delta g^{(ii)} = \int_{(0,0)}^{(1,0)} 0\,\mathrm{d}x + \int_{(1,0)}^{(1,1)} y\,\mathrm{d}x = 0$$

since $\mathrm{d}x = 0$ in the second integral, as $x = 1$ is fixed. ■

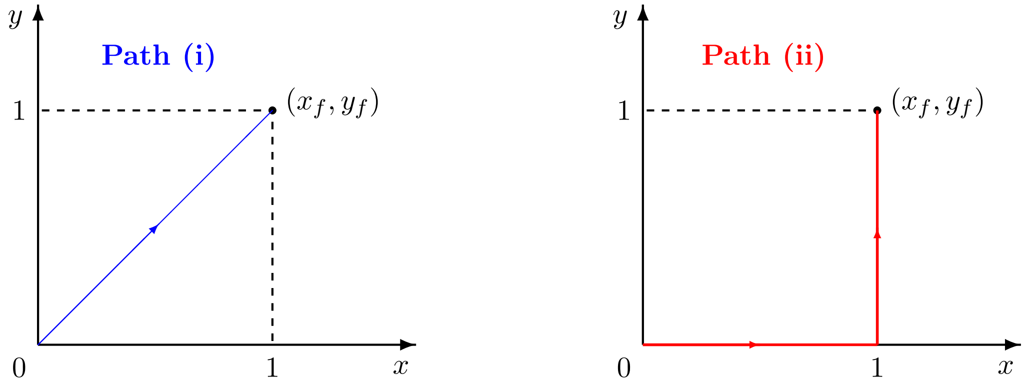

Figure 3.1: Paths (i) and (ii) considered in Example 3.1

R If you replace x by V and y by p in the previous example you get $đg = p\,\mathrm{d}V = -đW$. This behaviour of functions of path will be extremely useful when we consider cycles (loops in $p-V$ diagrams), because Q and W will generally be non nil, which means work/heat will be produced every time the system goes around the loop!

This property leads us to rewrite the first law in differential form:

Law 4 — The first law of Thermodynamics (differential form). Under an infinitesimally small thermodynamical change,

$$\mathrm{d}U = đQ + đW$$

R Note that the term 'infinitesimal change' is only appropriate to describe what happens to U, *not* Q or W, because, as we said previously, changes in heat and work have no meaning! $đQ$ and $đW$ simply represent infinitesimal amounts of heat and work.

3.5 Definition of work & heat

According to the laws of mechanics, the infinitesimal amount of work done, when moving a macroscopic object against an opposing force, $\vec{F}$, is given by $đW = \vec{F}\cdot \mathrm{d}\vec{h}$, with $\mathrm{d}\vec{h}$ the infinitesimal displacement of the object. In Thermodynamics, $\vec{F}$ is imparted by the system's surroundings and the macroscopic object is the separating wall (which can be set in motion if mechanical equilibrium is to be achieved). As pressure is force divided by surface area of the mobile wall, and displacement becomes volume when multiplied by this surface area, we obtain that $đW = -p_{\mathrm{surr}}\,\mathrm{d}V$[‡].

R There exists other kinds of work (electrical, magnetic) where we will have to go back to the previous, more general definition of $đW = \vec{F}\cdot \mathrm{d}\vec{h}$, but in Thermodynamics, $p\,\mathrm{d}V$ work is the most common kind.

So for any thermodynamical process, we can *define* the ($p\,\mathrm{d}V$ or expansion) work as:

$$W \equiv \int_{V_i}^{V_f} -p_{\mathrm{surr}}(V)\,\mathrm{d}V$$

[‡] Note the sign: $đW > 0$ if the volume is reduced! Also note the use of p_{surr}, rather than p, because p_{surr} is *always* well defined, unlike p (recall our example of the out-of-equilibrium cylinder when we removed one of the weights holding the piston down).

where $p_{\text{surr}}(V)$ specifies the path taken by the system to go from the initial to the final state. Note that this might be difficult to calculate!

R This definition of work means that there are *two* conditions to be met for $p\,\mathrm{d}V$ work to be non-nil: the volume of the system *must* change *and* the pressure of the surroundings *must* be non-zero! We will come back to this latter when we discuss the Joule expansion.

Again we stress that other types of work exist which are *isochoric* (the volume of the system does not change), like rubbing your hands against one another. We will also often encounter specific thermodynamical processes which occur at mechanical equilibrium between system and surroundings, i.e. where $p = p_{\text{surr}}$, in which case the distinction between the two pressures is useless and we will thus use p rather than p_{surr} to calculate the work. However, if in doubt, always come back to the original definition, which holds regardless of the thermodynamical process considered.

As for heat, its preferred definition is from the first law of Thermodynamics and the definition of work: $Q = \Delta U - W$, i.e. whatever is left over when work is subtracted from the internal energy change of the system. It is always well defined, since ΔU and W are always well defined. It is also a practical definition: this is how you will calculate Q in thermodynamical problems!

R This definition of heat is only valid if there are no other forms of energy transfer, i.e. the system is closed.

3.6 Constructing new thermodynamical quantities

Following what we did for the definition of Q, we can derive new thermodynamical quantities directly at the macroscopic level (unlike what we did for U). Most of these will be partial derivatives of other functions of state, because of the existence of two independent thermodynamic variables.

Mathematical reminder: Let any three variables x, y, z, satisfy a relation $f(x, y, z) = 0$. We then have:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z}$$

which is called the *reciprocal* theorem and is valid for any pair of variables, and

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

which is called the *reciprocity* theorem.

Arguably the most important example of such new thermodynamical quantities is the *heat capacity* [§], C. By definition, C, is the amount of heat that must be supplied to a system to raise its temperature by $\mathrm{d}T$ [unit J K^{-1}]. Mathematically, we write this definition as $C \equiv đQ/\mathrm{d}T$.

[§] Note the ill-fitting name ‘capacity’, when we have repeatedly made the point that heat cannot be stored by a system!

R Obviously, the more of a substance you have, the more heat you will need, so a more fundamental quantity than C is the *specific heat capacity*, $c \equiv C/m$, which is the heat capacity per unit mass. Also, given how we have defined heat, the definition of C is ambiguous: the amount of heat you will need will depend on whether you are doing work on the system, and if so, how much.

Plugging in the infinitesimal version of the first law in the definition of C, one gets:

$$C = \frac{\mathrm{d}U - \text{đ}W}{\mathrm{d}T}$$

Immediately, you see that even if U is a function of T alone (careful, this is not always the case!) work can be anything, so C as well! In practice though, two circumstances are more likely to arise than others:

1. no work is done on or by the system, i.e. $\text{đ}W = 0$, which usually means that the volume of the system does not change. In that case, C is called the heat capacity *at constant volume* and denoted $C_V \equiv (\partial U/\partial T)_V$.
2. the system expands and does work *on* its surroundings (this means $\text{đ}W < 0$ and you will need to add more heat to compensate for the energy lost as work, so $C > C_V$), but p_{surr} is constant. In that case, C is called the heat capacity *at constant pressure* and denoted C_p.

If we assume the system remains in mechanical equilibrium with its surroundings, we can then write:

$$C_p = \frac{\mathrm{d}U - (-p\mathrm{d}V)}{\mathrm{d}T} = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{3.1}$$

R Note that in general $(\partial U/\partial T)_V \neq (\partial U/\partial T)_p$ (see Exercise 3.1 below)!

Exercise 3.1 From the definition of dU/dT in terms of the two independent variables (V,T) and (p,T) show that:

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

■

So we have that (using the result of Exercise 3.1):

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \quad \text{and} \quad \frac{C_p}{C_V} = \gamma$$

where γ is called the *adiabatic index* (we'll see its usefulness later).

■ **Example 3.2** Let us calculate C_V and C_p for an ideal gas.
In that case, the equation of state is $pV = nRT$ and $U(T)$ is a function of T alone (you'll prove it in statistical mechanics). If this ideal gas is mono-atomic (no structure, no E_I), then $U = 3/2\,nRT$. We thus deduce straightforwardly that $(\partial U/\partial V)_T = 0$ and $(\partial V/\partial T)_p = nR/p$. This, in turn, yields $C_p - C_V = nR$ and given that $C_V = (\partial U/\partial T)_V = 3/2\,nR$, $C_p = 5/2\,nR$ and $\gamma = 5/3$. Note that one retrieves $C_p > C_V$ as expected. ■

4. Thermodynamical processes & Carnot engine

4.1 Quasi-static & reversible processes

Let us go back to our example of a thermodynamical system in and out of equilibrium (Fig. 2.3). The removal of a large weight created an out of equilibrium situation where macro states were ill-defined, and one could not draw the path followed by the system on a $p - V$ diagram. Let us now replace the weights by piles of very fine pebbles* and proceed to remove them one-by-one, as illustrated in Fig. 4.1. The piston moves up infinitesimally. This is called a *quasi-static* process. It happens so slowly that the system stays in equilibrium and the thermodynamical variables remain well defined at all times.

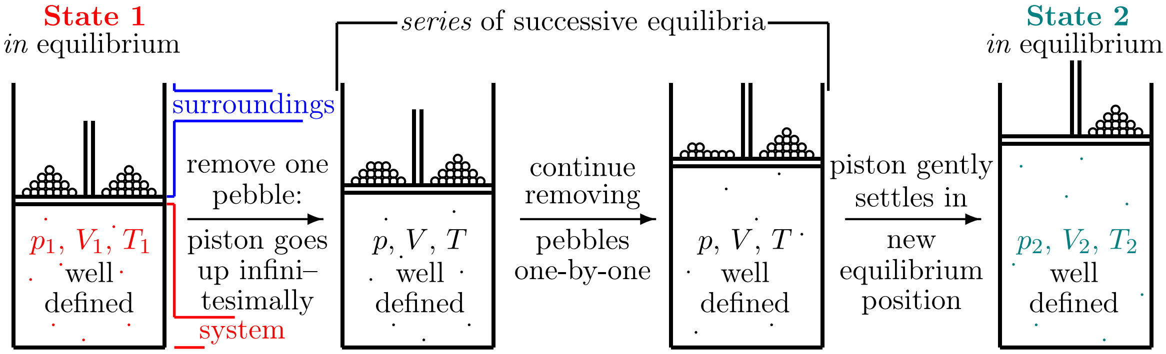

Figure 4.1: Example of a system undergoing a quasi-static process: gas is enclosed in a container whose top is a piston initially balanced by a given weight. Infinitesimal amounts of weight are then removed gradually.

R Strictly speaking, if the system stayed in the same equilibrium, nothing would happen. So this process is to be understood as the system going through a series of successive equilibria which are very close but different. The slowness at which these equilibria must take place can seem limiting (and certainly is) but if you consider the mechanical equilibrium of a gas for instance, the *relaxation time* of the system is comparable to

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*This is a thought experiment, so you can make these pebbles as fine as you like.

the time it takes for sound waves to propagate across, and these are quite fast (~ 330 m/s for air in standard p, T conditions).

One can now draw the path followed by the system on a $p - V$ diagram (see Fig. 4.2).

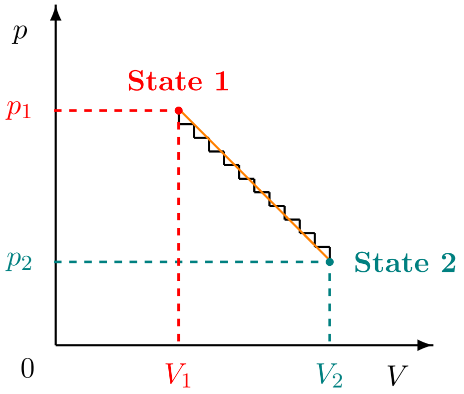

Figure 4.2: $p - V$ diagram for the gas enclosed in the container presented in Fig 4.1. It is now possible to draw the path taken by the system to go from **State 1** to **State 2**, taking infinitesimal steps which ultimately converge to the orange solid line as the step size goes to zero!

Now if we further assume that during such a quasi-static process there is *no hysteresis* of any kind (i.e. no friction of the piston on the walls of the canister as it goes up), when one adds the pebbles that were removed back on top of the piston, the system will go back to its original state. Such a process is then said to be *reversible*.

By contrast, if friction is involved, the system will not be able to retrace its exact steps without extra external intervention, and the process is then *irreversible*. Note that this does *not* mean that you cannot bring the system back to its original state. You can. Simply not by the *same* path. In our example, one will have to add more pebbles than were removed.

From our previous definition of work, it is obvious that for a quasi-static process, $p_{\text{surr}} = p$, as the system is always in equilibrium with p well defined at all times. So the work done by the expanding system when the pebbles are removed is $đW = -p\mathrm{d}V$ and the total work along the path from the initial state (pebbles on) to the final state (pebbles off) simply is the area under the curve (see Fig.4.3).

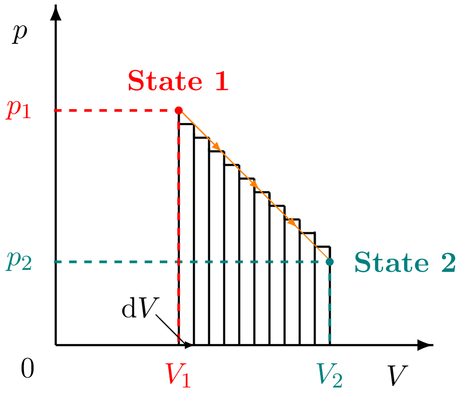

Figure 4.3: Work done by the gas enclosed in the container presented in Fig 4.1 as it expands when the pebbles are removed. The amount of work clearly is the area underneath the orange curve. Note the arrows which mark the direction taken: if the process is reversible, these will point in the other direction as the system is compressed going from **State 2** to **State 1**. As a result, only the sign of the work done will change in this case.

Mathematically, this writes as:

$$W = -\sum_{pebbles} p \, \mathrm{d}V = -\int_{V_i}^{V_f} p(V) \, \mathrm{d}V < 0$$

If the process is reversible, by the same arguments, adding the pebbles back one by one, we will go back from the final state to the initial state along the same path (in the other direction), compressing the gas, so:

$$W = -\sum_{pebbles} p \, (-\mathrm{d}V) = -\int_{V_f}^{V_i} p(V) \, \mathrm{d}V > 0$$

as expected, because work is done on the system. As a consequence, going back and forth on the *same* path, no work is done!

Otherwise, if the path is *not* the same, the work done will be the area enclosed within the loop (see Fig.4.4).

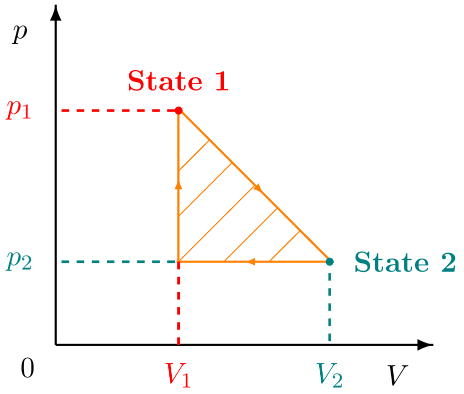

Figure 4.4: Work done (orange hatched area) going from **State 1** to **State 2** and back to **State 1**, if two different paths are taken to go back and forth (follow the arrows). This is simply the difference between the areas under the forward path and the reverse path.

Note that $\Delta U = 0$ no matter how many times you go back and forth, and no matter which path is taken, as long as you go back to the original state of the system. This is called a *cycle* and arguably the most famous and important one is named the *Carnot cycle* after the French engineer who discovered it whilst looking to optimise steam engines in the 19^{th} century.

4.2 The Carnot cycle

Let us go back to our piston and pebbles system depicted on Fig.4.1 and modify it as described on Fig 4.5.

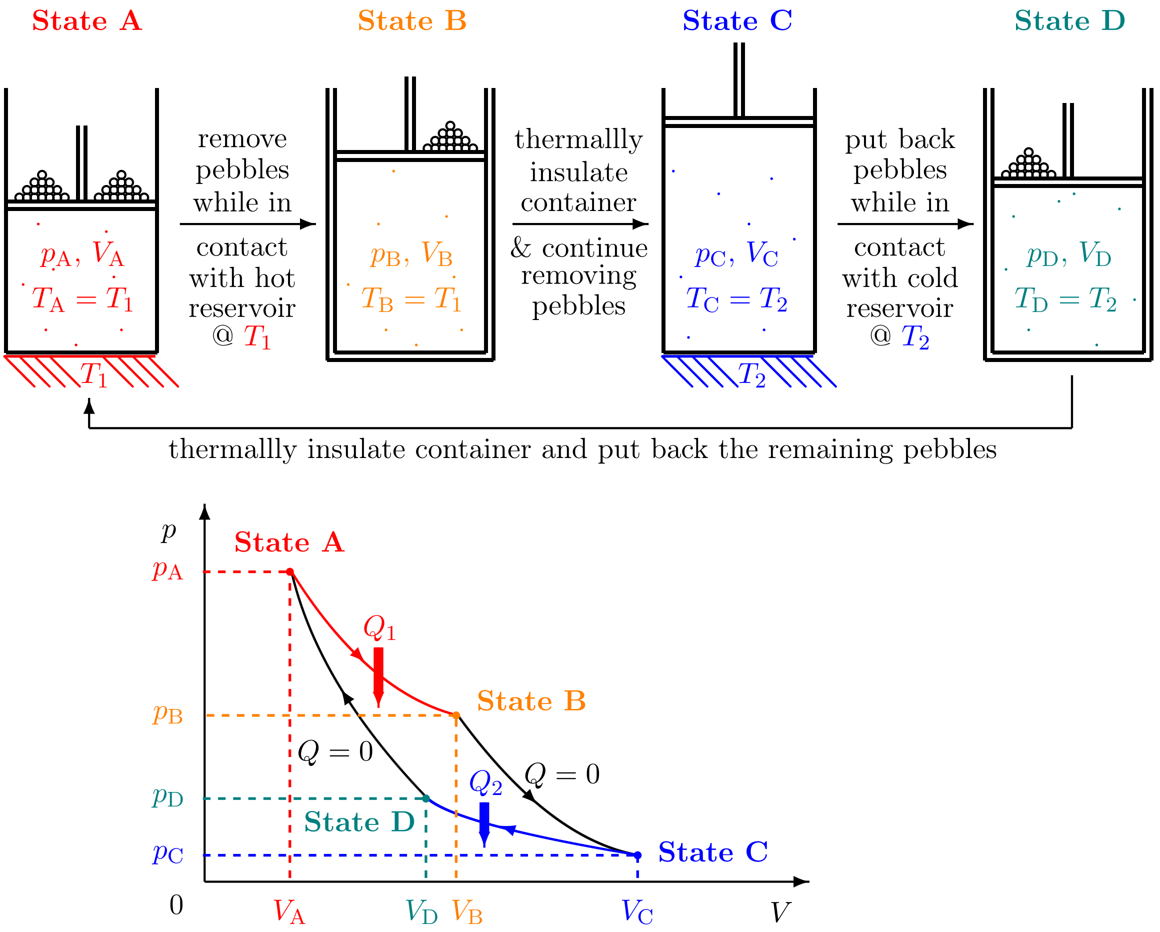

Figure 4.5: Carnot cycle for an ideal gas (top part of the figure) together with its $p - V$ diagram representation (bottom part).

As the system is in thermal contact with a *reservoir*[†] from State A to State B, its temperature remains constant on that path, and $T_B = T_1 = T_A$. It is called an *isothermal* process and given the equation of state of the ideal gas, it describes a hyperbola in the $p - V$ diagram (red curve in bottom part of Fig. 4.5 which is called an *isotherm*). As one is removing some pebbles on top of the piston, the gas expands, so that $V_B > V_A$ and $p_B < p_A$. We have previously established that the amount of work done by the gas is the area under the path in the $p - V$ diagram, $W_{AB} < 0$. For an ideal gas, the internal energy U is a function of the temperature alone, so the change in internal energy along an isothermal path, $\Delta U = 0$. Therefore, the first law allows us to write that the amount of heat $Q_1 = -W_{AB} > 0$ (thick red arrow entering the cycle in Fig. 4.5). This is quite an intuitive result: the system must draw heat from the reservoir to do work if it is to operate at a constant temperature.

From State B to State C, one continues to remove pebbles, but this time from a container which is thermally insulated rather than in contact with a reservoir. This means that $Q = 0$ on this path, and the process is called *adiathermal*. If it is also reversible (as is our

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[†] Basically this is a bath where one can dump/draw as much heat as one wants without changing its temperature. Oftentimes, it is also called a *thermostat* and we will use both terms interchangeably in these lectures.

case here), then it is called *adiabatic* (black curve in the bottom part of Fig. 4.5, called an *adiabat*[‡]). Work is still being done by the gas as it expands (the area under the B → C path is non nil), so $V_{\rm C} > V_{\rm B}$, $p_{\rm C} < p_{\rm B}$ and $W_{\rm BC} < 0$. Applying the first law yields $\Delta U = W_{\rm BC} < 0$ and therefore, as for an ideal gas $U \propto T$, we have $T_{\rm C} = T_2 < T_1$: the gas has cooled.

Now we start reversing processes to get back to the original state and complete the cycle. From State C to State D, we place the system back in contact with a reservoir, but this time a cold one, with temperature $T_2 = T_{\rm C}$. We then put back some of the pebbles. Reasoning in a similar manner than for the A → B path, albeit in the reverse direction as the system is now compressed, we conclude that $T_{\rm D} = T_2 = T_{\rm C}$, $V_{\rm D} < V_{\rm C}$, $p_{\rm D} > p_{\rm C}$ and $W_{\rm CD} > 0$. $\Delta U = 0$ along this isotherm therefore the first law tells us that $Q_2 = -W_{\rm CD} < 0$ (thick blue arrow exiting the cycle in Fig. 4.5): the system has dumped heat in the reservoir.

Finally, we remove the reservoir, thermally insulate the system and put back the remaining pebbles to go from State D back to the original State A. Similarly to what took place on the B → C path, $Q = 0$ on this adiabat (the other black curve in the bottom part of Fig. 4.5) and as the gas is compressed further, $V_{\rm A} < V_{\rm D}$, $p_{\rm A} > p_{\rm D}$, $W_{\rm DA} > 0$. Applying the first law, we deduce $\Delta U = W_{\rm DA} > 0$ and thus $T_{\rm A} = T_1 > T_2$ for our ideal gas: it has heated.

Summarising what happened along one entire Carnot cycle loop, we have $\Delta T = \Delta U = 0$ and $W_{\rm tot} = W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} < 0$ ($W_{\rm tot}$ is the area within the cycle ABCD in Fig. 4.5) so that $Q_{\rm tot} = -W_{\rm tot} = Q_1 + Q_2 > 0$.

R When one talks about "released heat" or "work performed by the system", one usually assumes that these quantities are positive, i.e. equal to $-Q_2$ and $-W_{\rm tot}$ with our convention.

One can use this cycle to understand where the concept of *entropy* comes from, and this is how we will approach it in these lectures. This is referred to as the Carnot engine.

4.3 The Carnot engine

R You would *never* implement a *real* engine this way!

- **Principle:** Heat is transferred from a hot to a cold reservoir, doing work in the process.
- **Schematics:**

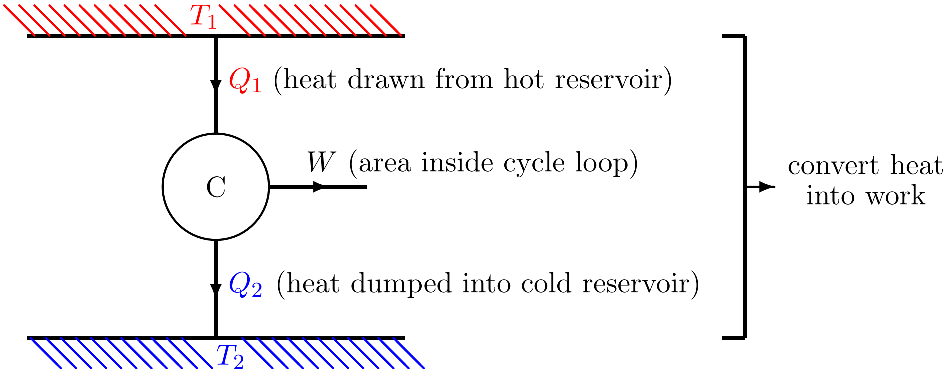

Figure 4.6: Diagram of a (Carnot) engine, C.

[‡] We will see later why this black adiabat has been drawn steeper than the red isotherm on Fig. 4.5.

R With the convention we have adopted, everything that flows *into* the engine is *positive*, and everything that flow *out of* it is *negative*. So we have taken the absolute values of all the quantities and are using the arrows to obtain their signs, i.e. in our notation for the Carnot cycle, the quantities of Fig. 4.6 read as: $W = |W_{\text{tot}}| = -W_{\text{tot}}$, $Q_1 = |Q_1| = Q_1$ and $Q_2 = |Q_2| = -Q_2$.

Keep going round the cycle doing more work every time. This is possible because Q and W are *not* variables of state: you cannot tell at any point how much heat and work are in the system!

- **Question:** How efficient is the Carnot engine?

To answer this question, we first need to define the *efficiency*, η. Going back to the cycle presented on Fig. 4.5, this is simply:

$$\eta = \frac{\text{work done}}{\text{energy given or heat in}} = \frac{-W_{\text{tot}}}{Q_1}$$

so that

$$\boxed{\eta = \frac{Q_1 - |Q_2|}{Q_1} = 1 - \frac{|Q_2|}{Q_1}} \tag{4.1}$$

Carnot realised that the efficiency is maximised if all processes are reversible and later showed that all reversible engines operating between the same temperatures T_1 and T_2 have the same efficiency[§].

R This can be understood as a formulation of the second law of Thermodynamics: $\eta < 1$ means you cannot break even, $|Q_2|$ has to be strictly positive! It is also related to the absolute temperature scale (see calculation of efficiency for an ideal gas below).

So what is the efficiency of a Carnot engine for an ideal gas?

- From $A \to B$: $T = T_1 = \text{C}^{\text{st}}$ so $\text{d}U = 0$ and the first law yields $đQ = -đW$. The process is reversible so $p = p_{\text{surr}}$ and $đW = p\text{d}V$, so $đQ = p\text{d}V$. Integrating:

$$Q_1 = \int_{V_A}^{V_B} p(V)\text{d}V = \int_{V_A}^{V_B} \frac{nRT_1}{V}\text{d}V = nRT_1 \ln\left(\frac{V_B}{V_A}\right) > 0 \text{ since } V_B > V_A$$

- From $B \to C$: $đQ = 0$ so the first law (+ reversible process) yields $\text{d}U = đW = -p\text{d}V$. For a mono-atomic gas $U = 3/2\, nRT$, so $\text{d}U = 3/2\, nR\text{d}T$, and using the ideal gas equation of state, one gets $3/2\,\text{d}T = -T\text{d}V/V$, so separating variables and integrating:

$$\frac{3}{2}\int_{T_2}^{T_1} \frac{\text{d}T}{T} = -\int_{V_B}^{V_C} \frac{\text{d}V}{V} \to \frac{3}{2}\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_B}{V_C}\right) \quad \text{i.e.} \quad \frac{T_2}{T_1} = \left(\frac{V_B}{V_C}\right)^{2/3}$$

R This adiabatic expansion can be written in the more general form $TV^{\gamma-1} = \text{C}^{\text{st}}$, using the adiabatic index γ, which is, as we have already seen equal to 5/3 for a mono-atomic gas. Equivalently, one can use the alternative form $pV^{\gamma} = \text{C}^{\text{st}}$, which explains why the adiabat is steeper than the isotherm on Fig. 4.5 ($5/3 > 1$).

[§] We will prove it as well in the next section, where we introduce the second law of Thermodynamics!

- From $C \to D$: $Q_2 = nRT_2 \ln\left(V_D/V_C\right) < 0$ since $V_D < V_C$
- From $D \to A$: $T_1/T_2 = \left(V_D/V_A\right)^{2/3}$

From $B \to C$ and $D \to A$, we conclude that $V_B/V_C = V_A/V_D$ and therefore that $\ln(V_B/V_A) = -\ln(V_D/V_C)$, so that $|Q_2|/Q_1 = T_2/T_1$ and in turn:

$$\eta = 1 - \frac{T_2}{T_1} \tag{4.2}$$

R

- This expression makes it clear that there must exist an absolute temperature scale. Otherwise if $T_2 < 0$, we have $\eta > 1$ and one could extract more work from heat that the amount one absorbs!
- We will show later that this expression is valid for *all* reversible engines.
- Note that $Q_1/T_1 + Q_2/T_2 = 0$ along the cycle ... Is this a new variable of state?
- It can be shown that the expression is also valid for non-ideal gases and other substances.
- η depends only on the temperature ratio, and *not* on the properties of the engine itself!

5. The second law of Thermodynamics

The concept of engine efficiency naturally leads to the second law of thermodynamics. The first law was a generalisation of the principle of energy conservation. It told us which processes were energetically possible, but not every process which is energetically possible does actually occur in nature. For instance, you have never seen a hot stone spontaneously cool down and use the thermal energy to jump in the air!

5.1 Statements of the second law

This leads us to postulate that there exists another fundamental guiding principle in nature which defines an "arrow" of time, making energy flow in a certain direction, irreversibly, in macroscopic systems even though on a microscopic scale the fundamental equations of physics are time reversible. The thermodynamical property associated with this principle is called *entropy* (term coined by Clausius), and can only be fully understood at the microscopic level. You will see in the Statistical Mechanics part of this course how it is linked to the fact that the most likely macro-state of a system is the one corresponding to the largest number of micro-states, but to help you grasp the idea, let us look at the following example.

■ **Example 5.1 — System of 100 coins in a box.** Consider a system composed of a hundred true coins contained in a box. There are $2^{100} \simeq 10^{30}$ possible micro-states associated with this system (each coin is either heads or tails). The macro-state of this system is the total number of heads or tails. Now the macro-state with all 100 coins heads has only 1 micro-state associated with it, whereas the macro-state with 50 coins heads and 50 coins tails has $\sim 10^{27}$. Which one is the most likely to be realised if you shake the box? Imagine a thermodynamical system which consists of $\mathcal{N}_A$ coins instead of just 100! ■

In these Thermodynamics lectures, we will follow a chain of classical arguments which lead to a definition of entropy which is equivalent to that you will derive in statistical mechanics* but starting from a more intuitive and practical standard. This is an assumption

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*You can actually prove this equivalence quite easily for ideal gases, so I leave it to you as an exercise to about nature which is so well funded that it has become a law.

Law 5 — Clausius statement of the second law. No process is possible whose *sole result* is the transfer of heat from a colder to a hotter body.

Some of you might think: but what about fridges? Well, in a fridge, an engine has to *do work* to perform such a heat transfer!

The previous remark leads us to another formulation of the second law:

Law 6 — Kelvin-Planck statement of the second law. No *cyclic* process is possible whose sole result is the complete conversion of heat into work.

The word "cyclic" is Planck's only contribution to the statement, but it is key: one can obviously convert all heat into work in a single step, but then the system will not be back in the same state!

We will prove that these two statements are equivalent shortly, but note how Kelvin's statement is reminiscent of (Carnot) engines. It tells us that an engine efficiency cannot be 100%, but the real question is: how high can it be?

5.2 Carnot's theorem

Theorem 5.2.1 — Carnot's theorem. No engine operating between two given temperatures can be more efficient than a Carnot engine.

• **Proof:** Imagine somebody claims to have built an engine E, which is more efficient than Carnot's. It means that for the same quantity of heat taken from the hot reservoir, it produces slightly more work. Now consider a reverse Carnot engine, $\mathrm{C_R}$, which converts work into a heat transfer from the cold reservoir to the hot reservoir (simply change the direction of going around the Carnot cycle, which is reversible by definition). Use the work provided by engine E to drive $\mathrm{C_R}$, as illustrated on the diagram below (Fig. 5.1):

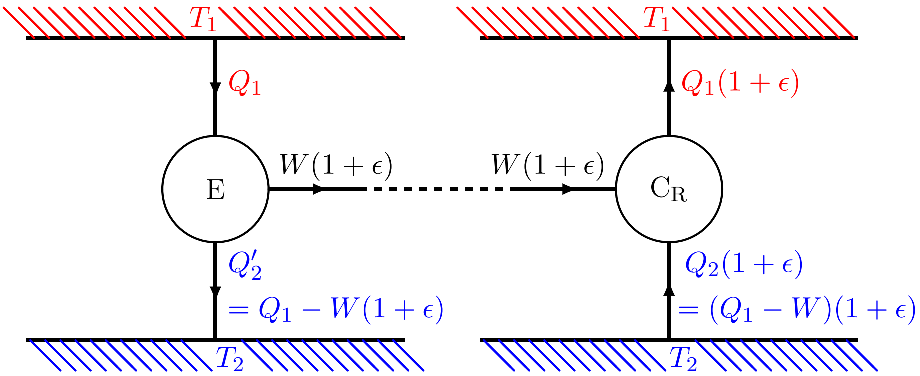

Figure 5.1: Schematic diagram of an engine E driving a reverse Carnot engine $\mathrm{C_R}$.

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be done after you have seen the statistical mechanics definition of entropy.

The diagram on Fig. 5.1 simplifies to:

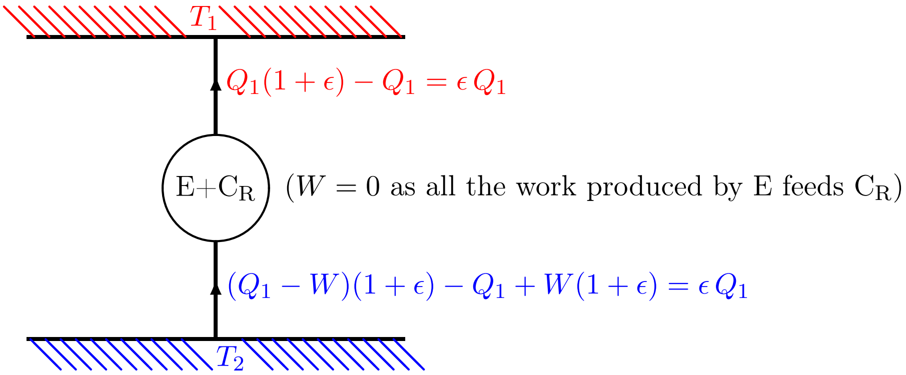

Figure 5.2: Simplified version of diagram on Fig. 5.1.

So you have obtained a simple heat transfer from the cold reservoir to the hot one, which contradicts Clausius' statement of the second law of thermodynamics. To be more explicit this would mean that you could cool food in your fridge without having to plug it in! Now that's what I call cheap energy! We must therefore conclude that the Carnot engine is the most efficient.

Corollary 5.2.2 — Carnot's corollary. All reversible engines have the same efficiency as the Carnot engine.

- **Proof:** Let R be a reversible engine, and use the Carnot engine, C, to drive it backwards:

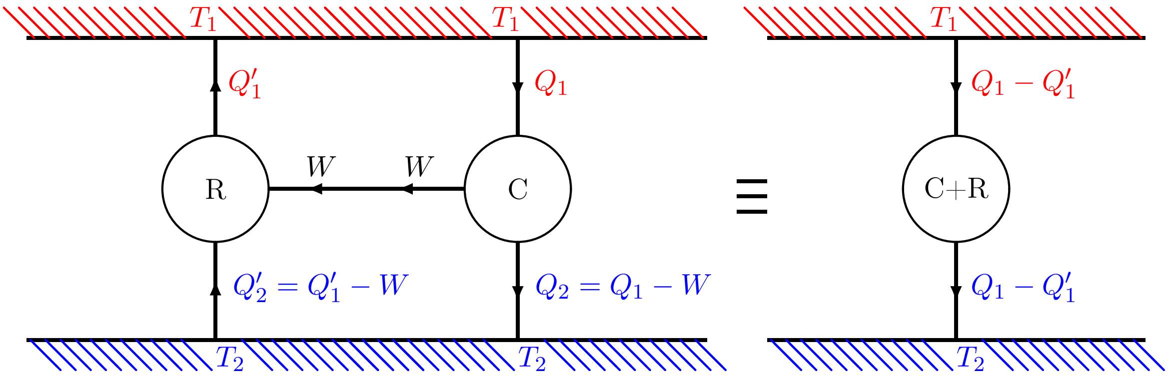

Figure 5.3: Schematic diagram of a Carnot engine C driving a reverse engine R.

Now assume that the efficiency of the reversible engine is such that[†]

$$\eta_R = 1 - \frac{Q'_2}{Q'_1} < \eta_C = 1 - \frac{Q_2}{Q_1}$$

Since $Q_2 = Q_1 - W$ and $Q'_2 = Q'_1 - W$, this implies that $W/Q'_1 < W/Q_1$ and simplifying by W, that $Q'_1 > Q_1$. This means that heat must be flowing from the cold reservoir to the hot one, in violation of Clausius' statement of the second law. We must therefore conclude that $\eta_R = \eta_C$.

[†] We have already proven that η_R cannot be larger than η_C

5.3 Equivalence of Clausius' & Kelvin's statements

• **Proof ad absurdum:** Let us consider an hypothetical engine E which violates Kelvin's statement of the second law, and use it to drive a reverse Carnot engine $\mathrm{C_R}$:

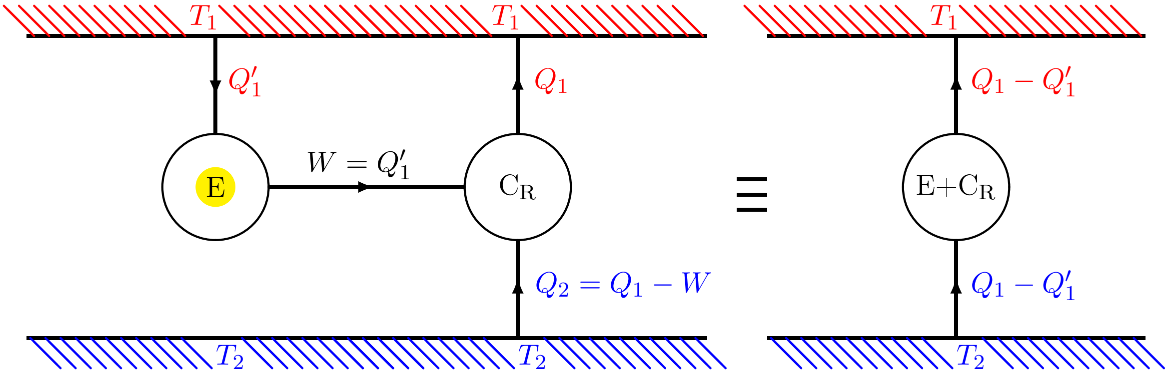

Figure 5.4: Schematic diagram of a hypothetical engine E which violates Kelvin's statement of the second law driving a reverse Carnot engine $\mathrm{C_R}$.

Applying the first law, we have $W = Q'_1$ and $Q_1 = W + Q_2 > W$ since $Q_2 > 0$. So $Q_2 = Q_1 - Q'_1 > 0$ and heat is extracted from the cold reservoir and simply transferred to the hot one, contradicting Clausius' statement of the second law.

Now consider an hypothetical engine E' which violates Clausius' statement of the second law and connect it to a Carnot engine C:

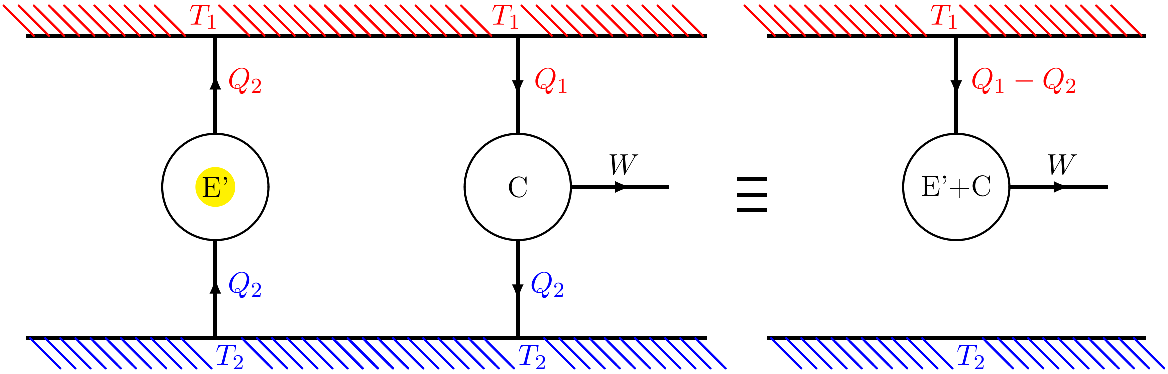

Figure 5.5: Schematic diagram of a hypothetical engine E' which violates Clausius' statement of the second law connected to a Carnot engine C.

The first law tells us that $W = Q_1 - Q_2 > 0$ so that all the heat is converted into work, which violates Kelvin-Planck's statement of the second law.

We therefore conclude that Kelvin's and Clausius' statements of the second law are equivalent.

5.4 Engine driven backwards & real engines

We have already seen reverse engines in the previous section, but here we detail what is the main difference between engines and reverse engines, namely the definition of efficiency.

5.4.1 Refrigerator

This is a device that uses work to transfer heat from a low temperature reservoir to a high temperature one.

■ **Example 5.2** In a household refrigerator, work is done by an electrical compressor which transfers heat from the food storage compartment (cold reservoir) to the kitchen (hot reservoir). ■

If we assume that all the processes involved in the operation of a refrigerator are reversible, then we have an *ideal* refrigerator: this is simply a Carnot engine running in reverse. So the ideal refrigerator is called a Carnot refrigerator and can be schematically depicted as follows:

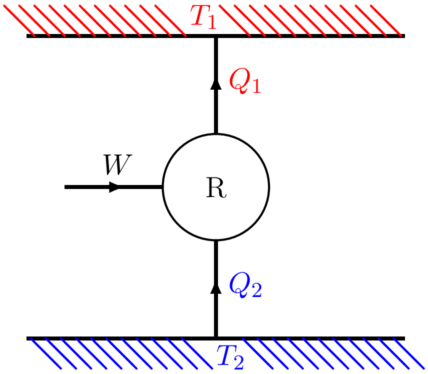

Figure 5.6: Schematic diagram of a refrigerator R.

The difference with the Carnot engine is that the efficiency of the Carnot refrigerator is defined differently, as the amount of heat extracted from the cold reservoir for a given amount of work. This efficiency is called the *coefficient of performance* (COP), η, and mathematically reads:

$$\eta = \frac{Q_2}{W} \tag{5.1}$$

Obviously, the larger the COP, the more efficient the refrigerator is. Applying the first law of Thermodynamics to the Carnot refrigerator, one gets $W = Q_1 - Q_2$ so that

$$\eta_{\text{CR}} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

where one uses the ideal gas in the same manner as for the Carnot engine to obtain the last equality (left as an exercise). Note that η_{CR} can be > 1!

R An air conditioning device is the same as a refrigerator, except that in this case the cold reservoir is the house and the hot reservoir the outside world!

5.4.2 Heat pump

It is basically also a refrigerator, but one which is used to pump heat from a cold reservoir to a place where one wants to add heat (hot reservoir).

■ **Example 5.3** The cold reservoir can be the ground several meters deep, and the reservoir to “heat”, a house. ■

The reason why a heat pump is not classified as a refrigerator once again has to do with the definition of efficiency. Indeed, the goal for using a heat pump is to warm up the “hot” reservoir rather than cool the “cold” one (although you can of course do both at the same time). This means that the COP for a heat pump is defined as:

$$\eta = \frac{Q_1}{W} \tag{5.2}$$

i.e. how much heat one can transfer to the hot reservoir for a given amount of work. Now since $Q_1 > W$, this means that η is always > 1! This is why heat pumps are attractive (however mind the capital costs). In other words, it is always possible to turn work into heat with 100% efficiency (e.g. an electric fire), but a heat pump will provide more heat for the same amount of work. For the Carnot heat pump, one can easily show that $\eta_{\text{CH}} = T_1/(T_1 - T_2)$.

5.4.3 Real engines

So far, we have treated heat engines and refrigerators in an idealised way, deriving the theoretical limits of their performances. These are very useful for two reasons:

- they tell us how the efficiency of an engine depends on its operating temperature
- they serve as a benchmark for the efficiency of a real engine

Consider a real steam engine operating between $T_1 = 373$K (boiling point of water) and $T_2 = 320$K (condensing water above the engine). If you are getting a 14% efficiency from this real engine, it is quite pointless to spend a lot of efforts to make is better, as $\eta_C = 1 - T_2/T_1 \simeq 15\%$!

Exercise 5.1 In an Otto engine, the working substance is a gas composed of air and vaporised petrol. It is first injected in a cylinder of volume V_1 and compressed adiabatically by a piston to a smaller volume V_2. A spark plug then ignites the mixture, raising its temperature and pressure whilst the volume does not change (called an *isochoric* process). The high pressure pushes back the piston and the gas expands adiabatically to its original volume V_1, producing mechanical work in the process. Finally the hot exhaust gases are expelled and replaced by a fresh mix of air and petrol at lower temperature and pressure[a]. Assuming that the gas mixture is an ideal gas with adiabatic index $\gamma = 7/5$ and that all processes are reversible, draw the $p - V$ diagram for the Otto cycle and calculate its efficiency, η_{O}.

Ans: $\eta_{\text{O}} = 1 - (V_2/V_1)^{2/5}$. ■

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[a] We represent this latter step as a single step lowering p at constant V in the Otto cycle, but in reality the piston pushes the exhaust gas through a valve whilst drawing the fresh mix through another, expelling heat but doing no net work.

Obviously in a real engine, processes are not very reversible. For instance, in exercise 5.1, we discuss an ideal combustion engine, but in practice, real car engines will experience piston friction, heat loss and incomplete fuel combustion. This means that for a typical engine compression ratio of $V_1/V_2 \sim 8$, i.e. with $\eta_{\text{O}} = 0.56$, the real engine only achieves an efficiency $\eta \sim 25\%$.

R • Note that there is no “hot” reservoir connected to the Otto engine. Instead the thermal energy is produced internally by burning the fuel, which results in a high p and T gas, as if this gas had absorbed heat from an external source!
• The obvious way to make the Otto cycle more efficient is to increase the compression ratio. Unfortunately, if the gas mixture becomes too hot in the process, it will pre-ignite spontaneously. This is avoided in a Diesel engine by only compressing the

air and injecting the fuel when the air is hot enough to ignite it. In this way, real engines can reach an efficiency of $\eta \sim 40\%$.

5.5 Clausius' theorem and entropy

Let us go back to our Carnot cycle (bottom of Fig. 4.5). We know that Q is not a conserved quantity along the cycle because it is a function of path, *not* state. In particular for one cycle, we have $Q_{\text{tot}} = Q_1 - |Q_2| > 0$, so for k cycles, $Q_k = kQ_{\text{tot}}$.

However, we have added Q_1 at high temperature T_1 and removed Q_2 at low temperature T_2. So what if we defined a new variable, S by taking the ratio of these two quantities, such that $\Delta S = Q/T$? Along a full cycle (two isotherms and two adiabats) and for an ideal gas, we would then have:

$$\Delta S_{\text{tot}} = \frac{Q_1}{T_1} + 0 + \frac{Q_2}{T_2} + 0 = \frac{nRT_1}{T_1} \ln\left(\frac{V_B}{V_A}\right) + \frac{nRT_2}{T_2} \ln\left(\frac{V_D}{V_C}\right) = nR \ln\left(\frac{V_B V_D}{V_A V_C}\right) = 0$$

In other words, our new variable, S, is conserved along the Carnot cycle: it is a legit state variable! It turns out S is only valid as a state variable if all the processes involved are *reversible*, as we will now demonstrate.

Theorem 5.5.1 — Clausius' theorem. For *any closed* cycle:

$$\oint \frac{\text{đ}Q}{T} \leq 0 \ , \ \text{with equality for reversible cycles.}$$

• **Proof:** Let us consider the cycle ABCD drawn on Fig.5.7, where A→B is a general thermodynamical process[‡] (i.e. not necessarily reversible) but all the other processes in the cycle, i.e. B→C, C→D and D→A are reversible.

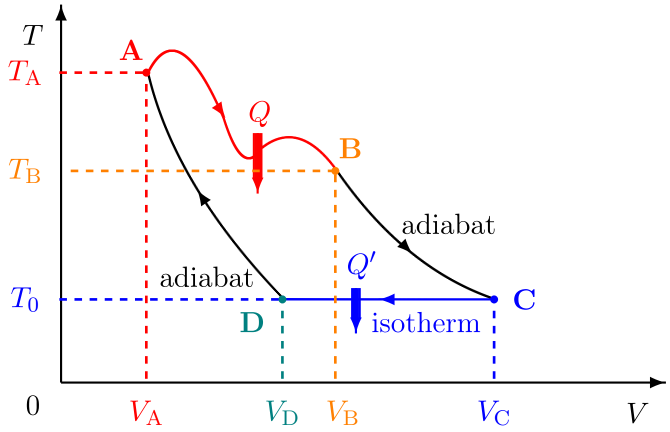

Figure 5.7: $T - V$ diagram of a cycle with a general, albeit quasi-static, process (A→B).

Let us then divide this cycle into k infinitesimal elementary Carnot sub-cycles (as depicted on Fig. 5.8), with $\text{đ}Q_i$ the infinitesimal amount of heat supplied to sub-cycle i by a hot

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[‡] Strictly speaking we are not considering the most general process possible since we want to be able to draw a path on a $p - V$ (or as it turns out a $T - V$ diagram), so this means we are considering a quasi-static process. However the idea behind the demonstration is that if our reasoning is valid for any non-reversible process for which we can draw a path, the results should also apply to any non-reversible process, regardless of whether we can draw the path the system takes explicitly. See e.g. *Thermodynamics* by A. Steane (section 8.3) for a more general version of this proof.

reservoir at temperature T_i, and $\text{đ}Q'_i$ the infinitesimal amount of heat dumped into the cold reservoir at temperature T_0 by the very same i^{th} sub-cycle.

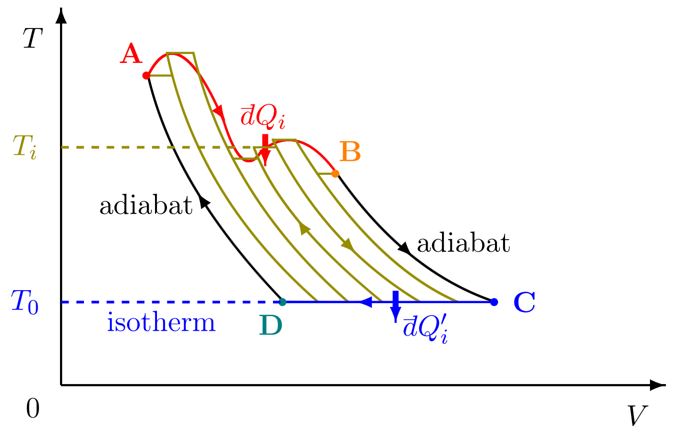

Figure 5.8: $T-V$ diagram of the Fig. 5.7 cycle, divided into infinitesimal elementary Carnot sub-cycles.

We know from Carnot's theorem that the efficiency of the general elementary sub-cycle will be smaller than that of the corresponding (reversible) Carnot sub-cycle, i.e.

$$\left(1-\frac{|\text{đ}Q'_i|}{\text{đ}Q_i}\right)=\left(1+\frac{\text{đ}Q'_i}{\text{đ}Q_i}\right)\;\leq\;\left(1-\frac{|\text{đ}Q'_i|}{\text{đ}Q_i}\right)_{\text{rev}}=\left(1+\frac{\text{đ}Q'_i}{\text{đ}Q_i}\right)_{\text{rev}}$$

since $\text{đ}Q'_i<0$. We also have demonstrated for an ideal gas (but this result holds for any substance) that $(\text{đ}Q'_i/\text{đ}Q_i)_{\text{rev}}=-T_0/T_i$ and therefore, injecting this relation in the previous inequality, we obtain that $\text{đ}Q_i/T_i\leq-\text{đ}Q'_i/T_0$ for *any* process A→B. Now for the A→B Carnot sub-processes, $(\text{đ}Q_i/T_i)_{\text{rev}}=-\text{đ}Q'_i/T_0$, so we conclude that for any general process A→B, one has $\text{đ}Q_i/T_i\leq(\text{đ}Q_i/T_i)_{\text{rev}}$.
Going around the full cycle ABCD on Fig. 5.8 thus yields:

$$\sum_i\left[\frac{\text{đ}Q_i}{T_i}+\frac{\text{đ}Q'_i}{T_0}\right]=\oint\frac{\text{đ}Q}{T}\;\leq\;\sum_i\left[\left(\frac{\text{đ}Q_i}{T_i}\right)_{\text{rev}}+\frac{\text{đ}Q'_i}{T_0}\right]=\sum_i[0]=\oint\left(\frac{\text{đ}Q}{T}\right)_{\text{rev}}=0$$

where we have replaced the discrete sum by a continuous integral, which is valid in the limit where the size of the infinitesimal sub-cycles goes to zero, to retrieve Clausius' theorem result.

This leads us to define the new state function *entropy*, S, in terms of reversible supply/rejection of heat at a given temperature. Indeed, since we have demonstrated that $\oint(\text{đ}Q/T)_{\text{rev}}=0$, we have that $\int_{\text{A}}^{\text{B}}(\text{đ}Q/T)_{\text{rev}}$ is independent of path. Or in other words, $(\text{đ}Q/T)_{\text{rev}}$ is an exact differential, and we can therefore write:

$$\mathrm{d}S\equiv\left(\frac{\text{đ}Q}{T}\right)_{\text{rev}}\tag{5.3}$$

which, in turn, implies that $\Delta S=\int_{\text{A}}^{\text{B}}\mathrm{d}S=S(\text{B})-S(\text{A})$, where S is the function of state we call entropy.

- It should be strange to you that we have to define entropy as a differential as it implies that we can only predict entropy changes ΔS, *not* absolute entropy S!

- This definition of entropy involves *reversible* processes, which is somewhat paradoxical when the most important application of entropy is the second law of thermodynamics, which concerns *irreversible* processes.
- It also provides very little physical understanding of what entropy is. People generally talk about "disorder" in the sense that an injection of extra heat at a given temperature will increase the number of micro-states available to the system and therefore its "disorder", but this is very vague and ultimately unsatisfying.

Two important concepts emerge from the introduction of the function entropy:

1. We have already seen that for adiathermal reversible (a.k.a. adiabatic) changes, $\text{đ}Q_{\rm rev} = 0$. Hence $\mathrm{d}S = 0$ and $S = \mathrm{C}^{\rm st}$, so these changes are *isentropic*.
2. The maximum entropy principle.

Focussing on this latter, let us consider a loop in a $p - V$ diagram made of an irreversible process (A→B) and a reversible one (B→A), as indicated on Fig 5.9.

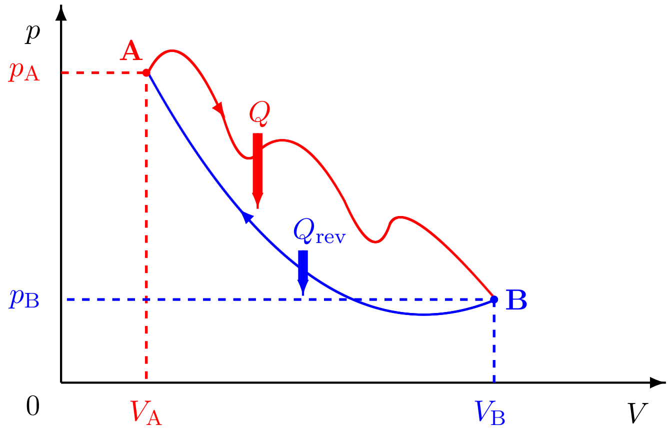

Figure 5.9: $p - V$ diagram of a cycle made of an irreversible process (A→B) followed by a reversible one (B→A).

According to Clausius' theorem, $\oint \text{đ}Q/T \leq 0$, so for the particular cycle of Fig. 5.9, $\int_{\rm A}^{\rm B} \text{đ}Q/T + \int_{\rm B}^{\rm A} (\text{đ}Q/T)_{\rm rev} \leq 0$ which can be re-written as $\int_{\rm A}^{\rm B} \text{đ}Q/T \leq \int_{\rm A}^{\rm B} (\text{đ}Q/T)_{\rm rev} = S({\rm B}) - S({\rm A}) = \Delta S$. Therefore, taking the infinitesimal limit of this latter expression, one has $\mathrm{d}S = (\text{đ}Q/T)_{\rm rev} \geq \text{đ}Q/T$ for *any* process. This has for important consequence that for a thermally isolated system, i.e. a system for which $\text{đ}Q = 0$, whatever process it undergoes (reversible, irreversible):

$$\boxed{\mathrm{d}S \geq 0} \tag{5.4}$$

This is another statement of the second law which says that the entropy of a thermally isolated system either stays the same (reversible case) or increases (irreversible case) under a thermodynamical change. This yields a direction of energy flow, an "arrow of time" and is referred to as the *principle of maximum entropy* as equation (5.4) can be stated as:
" **The entropy of a thermally isolated system tends to a maximum** ".

Applying what we have seen so far of Thermodynamics to the entire Universe, which can arguably be considered as the best example of a thermally isolated system, we deduce that $U_{\rm Univ} = \mathrm{C}^{\rm st}$ (first law: energy is conserved) and $S_{\rm Univ}$ can only increase (second law: principle of maximum entropy)! That is to say, (i) the Universe is out of equilibrium and is relaxing towards an equilibrium state which maximises its entropy and (ii) if the entropy decreases in some region of the Universe, it has to increase by *at least* the same amount in another!

5.6 Calculating entropy changes

So far things have been pretty abstract. In this section, we develop our intuition of entropy by calculating entropy changes in very specific and practical cases.

5.6.1 Heat transfer from a reservoir R to a system S

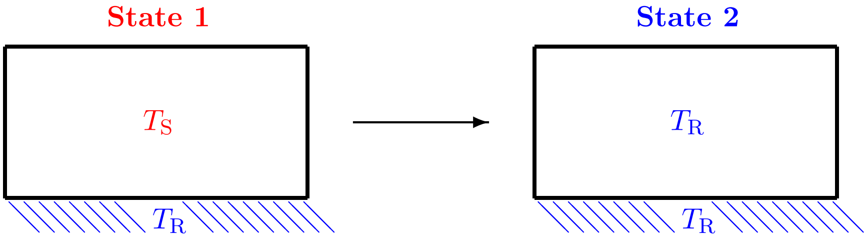

Figure 5.10: Transfer of heat between a system S, initially at temperature T_S (State 1) and a reservoir R at temperature T_R.

Fig. 5.10 depicts the process of heat transfer from a system S (rectangular box), initially at temperature T_S to a reservoir R at temperature T_R (hatched blue lines). This is an irreversible process in the sense that if one breaks the thermal contact in State 2, the temperature of the system will not in general revert to T_S (unless the system is brought in contact with another reservoir at temperature T_S). This is because $\Delta T = T_\mathrm{R} - T_\mathrm{S}$ is finite. However, the heat flow across the boundary of the reservoir, which occurs at constant temperature, is itself reversible.

To see this, let us assume that $T_\mathrm{S} > T_\mathrm{R}$, and that we have 2 reservoirs, the first one at temperature T_R, and the second one at $T_\mathrm{S} - (T_\mathrm{S} - T_\mathrm{R})/2$. Now let us bring the system in contact first with this second reservoir at temperature $T_\mathrm{S} - (T_\mathrm{S} - T_\mathrm{R})/2$ and then with the reservoir at temperature T_R, instead of performing the heat transfer in just one step. The temperature T of the system has decreased from T_S to T_R and the system has given heat to both reservoirs. Let us then reverse the process and bring the system back in contact with the second reservoir at temperature $T_\mathrm{S} - (T_\mathrm{S} - T_\mathrm{R})/2$. The temperature T of the system has increased from T_R to $T_\mathrm{S} - (T_\mathrm{S} - T_\mathrm{R})/2$, and heat has been given to it by the second reservoir.

In doing that, we have partially brought back the *total system* to its initial state: the temperature T of the system is still cooler than T_S and the reservoir at temperature T_R has received some heat from the system, but the reservoir at temperature $T_\mathrm{S} - (T_\mathrm{S} - T_\mathrm{R})/2$ is *back to its original state*. Heat exchange with a reservoir is therefore *reversible*.

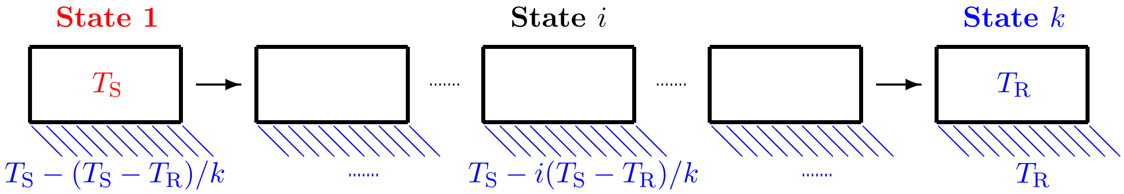

Figure 5.11: Transfer of heat between a system S, initially at temperature T_S (State 1) and k reservoirs regularly spaced in temperature between T_S and T_R.

Now let us repeat this experiment using k reservoirs equally spaced in temperature between T_S and T_R (see Fig. 5.11). Every time we reverse the thermal contacts, we bring back all the reservoirs to their original states, except the last one and the system itself.

In the limit $k \to \infty$, we have thus achieved reversible heat transfer! In other words, the condition for reversible heat transfer to take place between two bodies is that their temperatures only differ by an infinitesimally small amount $\mathrm{d}T$.

As we now have established that the heat transfer of a system from/to a reservoir is reversible, we can calculate the changes in entropy involved in the process. Using the definition of the heat capacity C, we have $đQ_{\mathrm{rev}} = C\mathrm{d}T$ and so, if we assume that C is independent of T (true for e.g. an ideal gas), we can write[§]:

$$\begin{aligned}\Delta S_{\mathrm{R}} &= \int_{T_{\mathrm{S}}}^{T_{\mathrm{R}}} \frac{-đQ_{\mathrm{rev}}}{T_{\mathrm{R}}} = \frac{C}{T_{\mathrm{R}}}\int_{T_{\mathrm{R}}}^{T_{\mathrm{S}}} \mathrm{d}T = C\,\frac{T_{\mathrm{S}}-T_{\mathrm{R}}}{T_{\mathrm{R}}}\\ \Delta S_{\mathrm{S}} &= \int_{T_{\mathrm{S}}}^{T_{\mathrm{R}}} \frac{đQ_{\mathrm{rev}}}{T} = C\int_{T_{\mathrm{S}}}^{T_{\mathrm{R}}} \frac{\mathrm{d}T}{T} = C\,\ln\left(\frac{T_{\mathrm{R}}}{T_{\mathrm{S}}}\right)\end{aligned}$$

for the change in entropy of the reservoir and the system, ΔS_{R} and ΔS_{S} respectively. Note that these changes in ΔS_{R} and ΔS_{S} can be either positive or negative depending on whether you bring the system in contact with a hot or a cold reservoir. However, if we consider the change of entropy of the total system consisting of system + reservoir (which we will call the Universe to emphasise that it is thermally isolated), we have $\Delta S_{\mathrm{Univ}} \geq 0$ no matter what! Let us prove it. We have:

$$\Delta S_{\mathrm{Univ}} = \Delta S_{\mathrm{R}} + \Delta S_{\mathrm{S}} = C\left[\ln\left(\frac{T_{\mathrm{R}}}{T_{\mathrm{S}}}\right) + \frac{T_{\mathrm{S}}}{T_{\mathrm{R}}} - 1\right]$$

Setting $X = T_{\mathrm{S}}/T_{\mathrm{R}}$ and evaluating the derivative $\mathrm{d}(\Delta S_{\mathrm{Univ}})/\mathrm{d}X = C(1-1/X)$, we find that it is nil for $X = 1$, which means that ΔS_{Univ} has an extremum for this value of X. Since the second derivative, $\mathrm{d}^2(\Delta S_{\mathrm{Univ}})/\mathrm{d}X^2 = C/X^2 > 0$ for $X = 1$, this extremum is a minimum. As $\Delta S_{\mathrm{Univ}}(1) = 0$, we therefore conclude that $\Delta S_{\mathrm{Univ}}(X) \geq 0$ whatever the value of X, in accordance with the principle of maximum entropy.

5.6.2 Joule expansion

In this second example, we consider a system consisting of 1 mole of ideal gas initially enclosed in a thermally insulated container of volume xV, where $0 < x < 1$. This gas is prevented from filling an empty container of volume $(1-x)V$, also thermally insulated, by a valve (see top diagram of Fig 5.12). The valve is then opened instantaneously, allowing the gas to expand into the second container and fill the whole volume V, as illustrated on the bottom diagram of Fig 5.12. This process, which is *irreversible*[¶], is called a *Joule expansion.*

The question is: what is the change in entropy during this Joule expansion?

This is far from trivial a question to ask because, in the same way that our system was thrown out of equilibrium when we removed the weight from the piston in Fig 2.3,

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[§] Being careful that for the reservoir, the heat transferred is the *opposite* of that of the system. Indeed, if, as we have assumed here, the system dumps heat into the reservoir then $đQ_{\mathrm{rev}} < 0$ as the system has lost heat, but from the point of view of the reservoir, this amount of heat is gained, and therefore $-đQ_{\mathrm{rev}} > 0$ for the reservoir.

[¶] Once again this does not mean that you cannot bring back all the gas inside the first container. You obviously can. But you are going to have to do work to get back to this state. For instance, if the back wall of the second container is a mobile piston, you will need to use this piston to push the gas back into the first container and *then* close the valve. It is not going to happen simply by closing the valve once the gas has filled the second container!

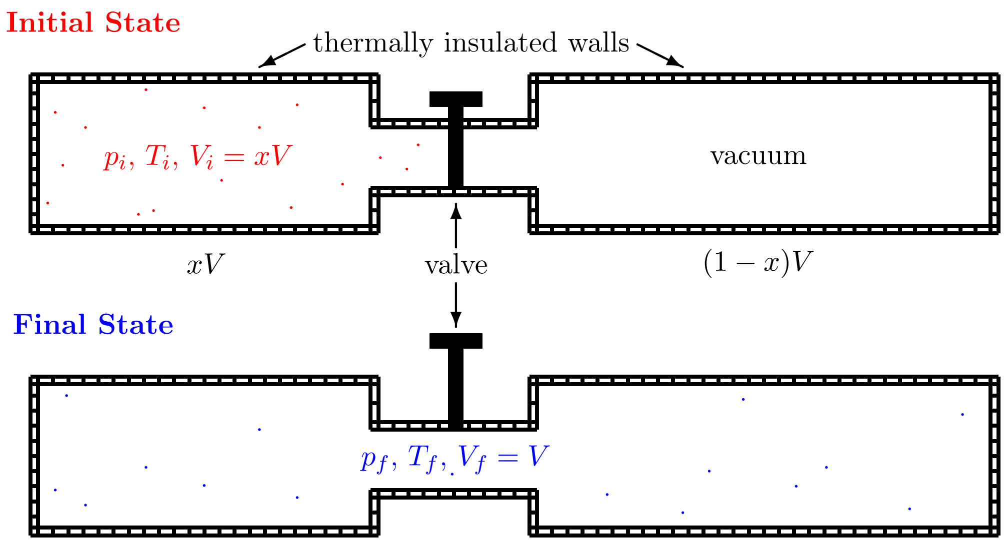

Figure 5.12: Joule expansion of 1 mole of gas initially enclosed in a container of volume xV (with $0 < x < 1$) into a container of volume V.

our gas is out of equilibrium immediately after we open the valve: we cannot define its pressure, volume, temperature etc ... until it has reached its new equilibrium state, filling both containers! In other words, we cannot draw the path taken by the system to go from its initial equilibrium state to its final equilibrium state in a $p - V$ diagram. So how do proceed to calculate the entropy change? Well, we use a 'trick' which always works because entropy is a function of state: we go from the initial to the final state along a *fictitious* reversible path! Once again, we are completely allowed to proceed this way because the entropy change does not depend on which path the system takes, but only on its end states.

Having said that, we still have to choose a convenient reversible path to link the initial and final equilibrium states. Let us then examine the process in more detail. The gas being ideal, we can write its equation of state in both equilibrium states as $p_iV_i = RT_i$ and $p_fV_f = RT_f$ (for 1 mole, $n_i = n_f = 1$). As the containers are thermally insulated, $Q = 0$. No work is done on or by the gas as it expands (the second container is empty therefore the gas is not pushing anything to fill it, this is a *free expansion*), so $W = 0$. The first law then tells us that $\Delta U = 0$ and since U can be expressed as a function solely of temperature for the ideal gas, we conclude that $\Delta T = 0$, i.e. $T_f = T_i$.

The Joule expansion of an ideal gas is therefore *isothermal*. Hence it makes sense for us to use a reversible isotherm (exactly like the one we used to join State A and State B in the Carnot cycle depicted on Fig 4.5) to connect the initial and final states of the Joule expansion in a $p-V$ diagram. Along that reversible isotherm, the first law yields $\mathrm{d}U = \text{đ}Q_{\rm rev} - p\mathrm{d}V = 0$, so that $\Delta S \equiv \int \text{đ}Q_{\rm rev}/T_i = \int_{V_i}^{V_f} p/T_i\,\mathrm{d}V = \int_{V_i}^{V_f} R/V\,\mathrm{d}V = R\ln(1/x) > 0$. Now what is key is that this is *also* the change in entropy undergone by the ideal gas during the real irreversible Joule expansion!

• Obviously the heat $Q_{\rm rev}$ absorbed by the system on the fictitious reversible isotherm is different from the heat Q truly absorbed by the system during the Joule expansion as $Q = 0$.
• So do *not* make the mistake to say $Q = 0$ for the Joule expansion therefore $\Delta S = Q/T = 0$! Remember: $\Delta S \geq Q/T$ for irreversible processes!

What about the entropy change of the Universe, ΔS_{Univ}? For the fictitious reversible isotherm, we have $\Delta S_{\text{Univ}} = \Delta S + \Delta S_{\text{surr}} = R\ln(1/x) - R\ln(1/x) = 0$, as the heat absorbed by the system is given to it by its surroundings, which must therefore lose exactly the same amount. For the Joule expansion, $\Delta S_{\text{Univ}} = \Delta S + \Delta S_{\text{surr}} = R\ln(1/x) + 0$ as the entropy of the surroundings does *not* change since the system is thermally isolated: the initial and final states of the surroundings are the same!

5.6.3 Gibbs paradox: the entropy of mixing

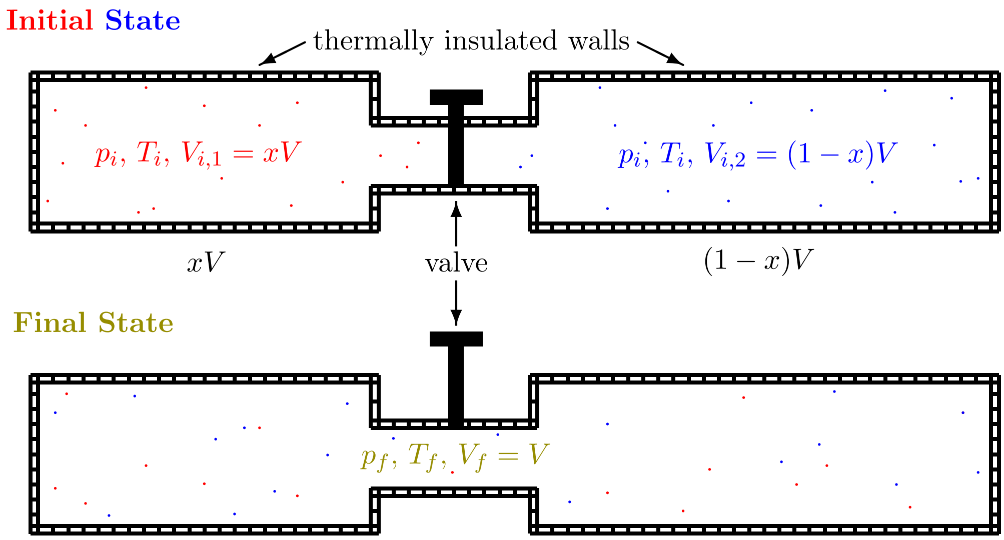

Figure 5.13: Expansion of two different gases initially enclosed in two containers of volume xV and $(1-x)V$ respectively, into a single container of volume V.

Let us now consider a third example, very similar to the Joule expansion, but with two different ideal gases (say gas 1 and gas 2) at the same pressure and temperature, p_i and T_i, in initially separated and thermally insulated containers of volume $V_{i,1} = xV$ and $V_{i,2} = (1-x)V$ respectively, with $0 < x < 1$ (see top diagram of Fig.5.13). When we open the valve, the two gases will mix spontaneously (this is the third kind of thermodynamical equilibrium, called *diffusive* equilibrium, which we will study in more detail later in these lectures when we discuss open systems).

Once again, the question is: what is the entropy change associated with such a process?

This is called the *entropy of mixing*. To determine it, we proceed exactly as we did for the Joule expansion and look at the process in more detail. As p_i and T_i are initially the same for both gases, writing the equation of state for each of them yields $p_i = N_1 k_B T_i / V_{i,1}$ and $p_i = N_2 k_B T_i / V_{i,2}$, from where we derive that $N_1 = xN$ and $N_2 = (1-x)N$ with $N = N_1 + N_2$ the total number of gas particles. Moreover, $T_f = T_i$ (the gases already are in thermal and mechanical equilibrium and the containers are thermally insulated), and so, as we did in the case of the Joule expansion, we can imagine going to the final equilibrium state where gas 1 and gas 2 are mixed homogeneously (see bottom diagram of Fig.5.13) via a reversible isothermal expansion of gas 1 from volume $V_{i,1} = xV$ to $V_f = V$ and of gas 2 from volume $V_{i,2} = (1-x)V$ to $V_f = V$. Along each of these two reversible paths, we will then have $\mathrm{d}U = 0$, so that $\text{đ}Q_{\text{rev}} = p\mathrm{d}V$ and $\mathrm{d}S = p\mathrm{d}V/T = Nk_B\mathrm{d}V/V$. The total entropy change is thus:

$$\Delta S = xNk_B \int_{xV}^{V} \frac{\mathrm{d}V_1}{V_1} + (1-x)Nk_B \int_{(1-x)V}^{V} \frac{\mathrm{d}V_2}{V_2} = -Nk_B\left[x\ln x + (1-x)\ln(1-x)\right]$$

As expected, if $x = 0$ or $x = 1$, i.e. only one gas is initially present and there is no expansion, $\Delta S = 0$. We also find (left as an exercise below) that the maximal entropy change occurs when the two gases initially occupy the same volume.

Exercise 5.2 Show that ΔS is maximal for $x = 1/2$. ■

This result can be intuitively understood at the microscopic level. Indeed, if x=1/2, this means that after mixing is completed, each gas particle can occupy twice the number of microstates as before (the volume available to them has doubled), so the total number of microstates has increased by a factor 2^N when considering all the particles. Therefore S must increase by a factor $Nk_B \ln 2$ ($S = k_B \ln \Omega$ as you will see in statistical mechanics, with Ω the number of microstates). The relation of entropy to information theory is starting to appear.

Let us dig a bit further and ask, after Gibbs, an apparently straightforward question: what if $x = 1/2$ but the two gases are identical to begin with? When we open the valve, the system already is in complete thermodynamical equilibrium (same pressure, temperature and particle number density throughout the system): surely nothing should happen and we should have $\Delta S = 0$ in that case! So where did we go wrong? This is referred to as *Gibbs' paradox* : the ability to distinguish particles matters when counting the number of microstates of a system and therefore when calculating entropy changes!

5.6.4 Maxwell's daemon: the connection of entropy to information theory

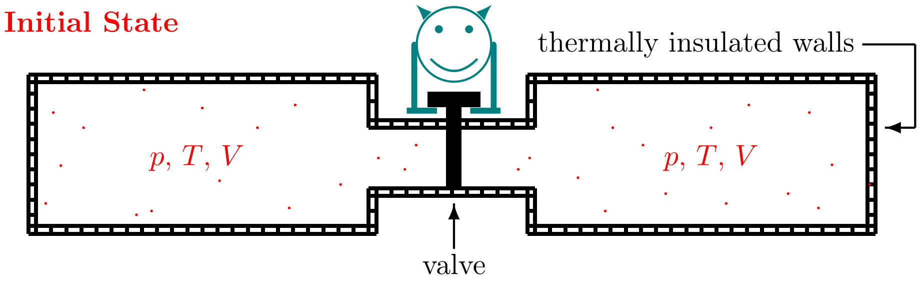

Figure 5.14: Maxwell's intelligent daemon is operating the valve to let specific particles through in order to violate the second law (see text for detail).

In this final example, we consider the same apparatus as in the Joule expansion again, but this time the initial states are identical on each side of the valve (see Fig. 5.14). If we open the valve, nothing happens, no work is done, there is no heat transfer, the process is clearly reversible and thus $\Delta S = 0$.

Now imagine an intelligent daemon is perched atop of the valve and opens and closes it to let fast particles move into the container on the right hand side and slow ones into the left hand side one. This creates a temperature difference (T is linked to the average kinetic energy of the particle distribution as you will see in the kinetic theory lectures), which can be used to run a reversible heat engine and produce useful work. Hence $\Delta S = -W/T \leq 0$

and it looks like the daemon, simply by converting information (their knowledge of the positions and velocities of the particles) into energy, has *decreased* the entropy of an *isolated* system, without performing any work, i.e. in flagrant violation of the second law of Thermodynamics!

This paradox took a long time to resolve (see e.g. Szilard (1929), Landauer (1961), Bennett (1983) for detail). To cut a long (but fascinating) story short, the daemon, which has to be included in the system, has to keep track (a memory) of all the positions and velocities that they measure. Due to the connection of entropy to information, if the daemon has to discard measurements at any point in time, they will create entropy (a minimal amount of $k_B T \ln 2$ heat is generated per bit of information lost as reasoned by Landauer and experimentally measured by Bérut et al (in *Nature*, 2012, 483, 187)) because it is an irreversible process. So the daemon must store information but cannot store it indefinitely: they must "write over" previous information at some point, generating at least as much entropy than they extract from the system in the process[‖].

[‖] A more quantitative resolution of this conundrum is discussed in *Thermodynamics* by A. Steane using the Szilard engine (chapter 9.5.1).

6. “Practical” Thermodynamics & free energy

6.1 The first law revisited

Using S, as previously defined, it is possible to re-write the first law of Thermodynamics in a much more elegant (and useful) way. Consider a *reversible* change, so that $\mathrm{d}U = \text{đ}Q + \text{đ}W$ can be written as:

$$\boxed{\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V} \tag{6.1}$$

Even though we have explicitly assumed reversibility to write this equation, it only involves functions of state, so is independent of path and therefore valid for *any* thermodynamical process, be it reversible or not! This equation is sometimes referred to as the *fundamental law* of Thermodynamics.

> **R** For an irreversible process we have $\text{đ}Q < T\mathrm{d}S$ and $\text{đ}W > -p\,\mathrm{d}V$, but when these infinitesimal heat and work are added together, $\mathrm{d}U$ is the *same* as for a reversible process, leading to an identical infinitesimal change in internal energy.

This begs for S to be treated as a fundamental thermodynamic variable like V, T and p, rather than a mere thermodynamical quantity. Indeed, considering the internal energy $U(S,V)$ as a function of the two independent thermodynamic variables S and V, equation (6.1) becomes a total differential for U. S and V are thus called *natural variables* for U. Looking closer at equation (6.1), each of the four thermodynamic variables, T, V, p and S appears once and by pair: T & S and p & V, one pair member intensive (T and p) and the other extensive (S and V). The variables in each pair are called *conjugate variables*, and their product (TS or pV) has the dimension of energy. In fact, mathematically, we can write:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V$$

and identify $T = (\partial U/\partial S)_V$ and $p = -(\partial U/\partial V)_S$ using equation (6.1).

6.2 Thermodynamical potentials

6.2.1 Definitions

Given that conjugate variables are constrained to appear together as a product with the dimension of energy, there exists only four possible choices for the pairs of independent thermodynamic variables, namely (S, V), (S, p), (T, V) and (T, p). It thus seems logical to conclude that there will exist a ‘natural’ energy-like quantity associated with each of these independent pair choices. These ‘natural’ energy-like quantities are called *thermodynamical potentials*. To obtain them, the ‘trick’ is to multiply pairs of conjugate variables and add or subtract them to U:

$$(S,V) \longrightarrow U : \textbf{Internal energy}$$

$$(S,p) \longrightarrow H = U + pV : \textbf{Enthalpy} \tag{6.2}$$

$$(T,V) \longrightarrow F = U - TS : \textbf{Helmholtz free energy} \tag{6.3}$$

$$(T,p) \longrightarrow G = U + pV - TS : \textbf{Gibbs free energy} \tag{6.4}$$

Note that the choice of conjugate variable products to add or subtract to U is not unique. For instance we could have decided to construct a thermodynamical potential as $U + 3pV - 5TS$. So how did we decide on these four combinations? Simply by looking at their differential forms. We know that $\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V$ (equation (6.1)), so that $\mathrm{d}U = 0$ if its natural variables S and V are fixed. We are thus naturally led to require that the same must hold for H, i.e. if its natural variables S and p are fixed then $\mathrm{d}H = 0$. This is verified straightforwardly by taking the differential of equation (6.2): $\mathrm{d}H = \mathrm{d}U + \mathrm{d}(pV) = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p = T\mathrm{d}S - \cancel{p\mathrm{d}V} + \cancel{p\mathrm{d}V} + V\mathrm{d}p$. As we did for U, we can write:

$$\mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_p \mathrm{d}S + \left(\frac{\partial H}{\partial p}\right)_S \mathrm{d}p$$

and identify $T = (\partial H/\partial S)_p$ and $V = (\partial H/\partial p)_S$ from the differential form of H. A similar reasoning applied to F (equation (6.3)) yields $\mathrm{d}F = \mathrm{d}U - \mathrm{d}(TS) = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T = \cancel{T\mathrm{d}S} - p\mathrm{d}V - \cancel{T\mathrm{d}S} - S\mathrm{d}T$, which is nil if its natural variables T and V are fixed. Writing

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_T \mathrm{d}V$$

we then identify $p = -(\partial F/\partial V)_T$ and $S = -(\partial F/\partial T)_V$ from the differential form of F. Finally, for G (equation (6.4)), we get $\mathrm{d}G = \mathrm{d}U + \mathrm{d}(pV - TS) = \cancel{T\mathrm{d}S} - \cancel{p\mathrm{d}V} + \cancel{p\mathrm{d}V} + V\mathrm{d}p - \cancel{T\mathrm{d}S} - S\mathrm{d}T$, which is equal to zero if T and p are fixed. Writing once again:

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p$$

we then identify $V = (\partial G/\partial p)_T$ and $S = -(\partial G/\partial T)_p$ from the differential form.

6.2.2 Physical meaning

- Enthalpy: the enthalpy of a system consists of its internal energy plus the work that is needed to make room for it in an *isobaric* environment. That is to say, it is the total energy that you would need to create the system out of nothing and place it in such an environment (the initial volume is 0 in that case so $\Delta V = V$). Conversely, H is the energy you would recover if you could annihilate the system: its internal energy plus the work done by the atmosphere to fill the volume it occupied.

Usually we deal with much less dramatic processes than creation or annihilation and look at changes undergone by the system. In that case, $\mathrm{d}H = T\mathrm{d}S \equiv \text{đ}\mathrm{Q}_{\mathrm{rev}}$ at constant p, i.e. using independent variables T and p, $\mathrm{d}H = (\partial H/\partial T)_p\,\mathrm{d}T = C_p\,\mathrm{d}T$ and $\Delta H = \int_{T_i}^{T_f} C_p\,\mathrm{d}T$ is the heat absorbed (reversibly) by the system in isobaric conditions (if no other work is done). These are easy conditions to be in: an open air system in the lab is usually at constant (atmospheric) pressure P_{atm}. Example: chemical reactions (*exothermic* if $\Delta H < 0$ and *endothermic* if $\Delta H > 0$).
Summarising, in an isobaric environment, $\Delta H = \Delta U + p\Delta V = Q + W + p\Delta V = Q - \cancel{p\Delta V} + W_{\mathrm{other}} + \cancel{p\Delta V}$, with $Q = T\Delta S$ for a reversible process and $Q < T\Delta S$ for an irreversible one. W_{other} stands for any non-$p\mathrm{d}V$ work (e.g. electrical).

- Helmholtz free energy: often we are not interested in the total amount of energy that can be recovered from the annihilation of a system but simply in the amount of work that can be recovered. Conversely, in an *isothermal* environment, the system can extract heat for *free* so all we need to provide to create the system from nothing is the extra work needed. So the Helmholtz free energy is the total energy needed to create the system *minus* the heat you can get for free from the isothermal environment. Equivalently, it is the amount of energy you can recover as work if you annihilate the system, given that you have to dump some heat in the environment to get rid of the system's entropy.
  Again, in practical situations, we deal with changes less dramatic than creation ex nihilo and $\mathrm{d}F = -p\mathrm{d}V$ for an isothermal reversible process. Therefore $\Delta F = -\int_{V_i}^{V_f} p\mathrm{d}V$ (> 0 if work is done on the system by its surroundings, and < 0 if work is done by the system on its surroundings) and we have assumed that there is no other work than $p\mathrm{d}V$ work. Note that if the change considered is irreversible, new entropy will be generated in the process and $\Delta F < W$.
  Summarising, in an isothermal environment, $\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$ where $W = p\mathrm{d}V\,\text{work} + W_{\mathrm{other}}$ and $Q = T\Delta S$ for a reversible process or $Q < T\Delta S$ for an irreversible one.
- Gibbs free energy: the work we talked about for F consisted of *all* work, including that done on the system by its surroundings. If a system is placed in an *isobaric and isothermal* environment, then the *non-*$p\mathrm{d}V$ work you need to do to create it, or that you can recover by annihilating it is given by G.
  Once again, focussing on practical changes, $\mathrm{d}G = 0$ for a reversible, isothermal and isobaric process, assuming no other work than $p\mathrm{d}V$. So G is conserved for phase transitions which take place at constant T and p and will thus be very useful to describe them (and chemical reactions as well).
  Summarising, in an isothermal and isobaric environment, $\Delta G = \Delta U - T\Delta S + p\Delta V = Q + W - T\Delta S + p\Delta V = Q - \cancel{p\Delta V} + W_{\mathrm{other}} - T\Delta S + \cancel{p\Delta V}$ where $Q = T\Delta S$ for a reversible process or $Q < T\Delta S$ for an irreversible one.
- Internal energy: We already gave its definition but if we consider its physical meaning in a similar manner than the three other thermodynamical potentials, focussing on a practical thermodynamical change, we have $\mathrm{d}U = T\mathrm{d}S \equiv \text{đ}\mathrm{Q}_{\mathrm{rev}}$ at constant V, i.e. using independent variables T and V, $\mathrm{d}U = (\partial U/\partial T)_V\,\mathrm{d}T = C_V\mathrm{d}T$. Thus $\Delta U = \int_{T_i}^{T_f} C_V\mathrm{d}T$ is the heat absorbed (reversibly) by the system in isochoric conditions (if no other work is done). Note that this is not very practical a change to measure, as in practice substances tend to expand when heated!
  Summarising, in an isochoric environment, $\Delta U = Q + W_{\mathrm{other}}$, with $Q = T\Delta S$ for a reversible process or $Q < T\Delta S$ for an irreversible one.

6.3 General conditions for thermodynamic equilibrium

Let us take stock and summarise what we have learned so far by updating the first diagram we drew (Fig 2.1).

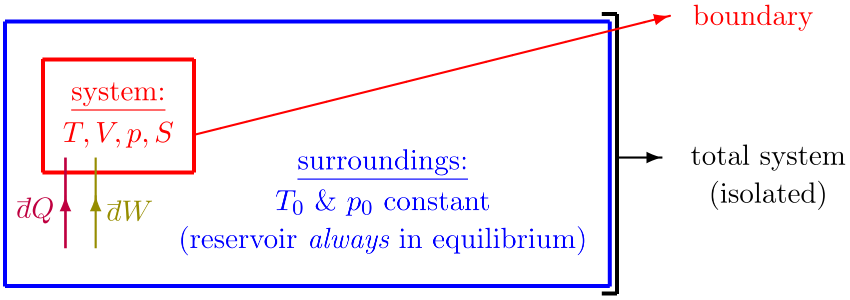

Figure 6.1: Updated schematic diagram of a thermodynamical system.

In the most general case, the system will be placed in thermodynamical contact (i.e. it will be able to exchange heat with / do work on) its surroundings. The question we want to ask is: what happens to this system when such transfers of energy take place? What equilibrium state will it reach?

To answer that question, let us first apply the first law to the total system. Its internal energy, U_{tot}, must be conserved as it is isolated, so any infinitesimal change $\mathrm{d}U_{\text{tot}} = 0$. In other words, any amount of internal energy gained by the surroundings must be lost by the system and vice-versa, which we write $\mathrm{d}U_{\text{surr}} = -\mathrm{d}U = T_0\,\mathrm{d}S_{\text{surr}} - p_0\,(-\mathrm{d}V)^*$. Rearranging this expression, we obtain $\mathrm{d}S_{\text{surr}} = -(\mathrm{d}U + p_0\,\mathrm{d}V)/T_0$.

The second law then tells us that the entropy of the total system, S_{tot}, can only increase. So any infinitesimal change $\mathrm{d}S_{\text{tot}} = \mathrm{d}S_{\text{surr}} + \mathrm{d}S \geq 0$. Multiplying this inequality by T_0 and using the expression for $\mathrm{d}S_{\text{surr}}$ obtained through the first law then yields: $-(\mathrm{d}U + p_0\,\mathrm{d}V - T_0\,\mathrm{d}S) \geq 0$. Finally, as p_0 and T_0 are constant, we obtain $\mathrm{d}A = \mathrm{d}(U + p_0 V - T_0 S) \leq 0$, where A is called the *availability* of the system. This means that as the system settles down to equilibrium, any change will result in a decrease of A: the equilibrium state is thus reached when A is *minimum*.

R The form of A is strangely reminiscent of that of the Gibbs free energy ...

Now, the type of equilibrium that the system will be able to reach depends on the constraints applied to it (the type of contacts it is allowed to have with its surroundings). So A will play the role of each of our four thermodynamical potentials in turn, depending on what these constraints are. More specifically if:

1. the system is thermally insulated and has a fixed volume (no thermal nor mechanical contact with the surroundings), we have $\mathrm{d}S = 0$ and $\mathrm{d}V = 0$. Therefore $\mathrm{d}A = \mathrm{d}U \leq 0$ and the system reaches equilibrium when its internal energy, U, is minimal.
2. the system is thermally insulated and has a fixed pressure (no thermal contact but mechanical contact with the surroundings is permitted), we have $\mathrm{d}S = 0$ and $\mathrm{d}p = 0$. Therefore $\mathrm{d}A = \mathrm{d}U + p_0\,\mathrm{d}V = \mathrm{d}H \leq 0$ and the system reaches equilibrium when its enthalpy, H, is minimal.

---

[*] We applied the fundamental form of the first law to the surroundings, hence the sign reversal for the infinitesimal volume: in the same way that whatever amount of internal energy gained by the surroundings must be lost by the system, any amount of volume $\mathrm{d}V$ gained by the surroundings must be lost by the system.

3. the system has a fixed temperature and volume (thermal contact with the surroundings is allowed, but not mechanical contact), we have $\mathrm{d}T = 0$ and $\mathrm{d}V = 0$. Therefore $\mathrm{d}A = \mathrm{d}U - T_0\,\mathrm{d}S = \mathrm{d}F \leq 0$ and the system reaches equilibrium when its Helmholtz free energy, F, is minimal.
4. the system has a fixed temperature and pressure (both thermal and mechanical contact with the surroundings are authorised), we have $\mathrm{d}T = 0$ and $\mathrm{d}p = 0$. Therefore $\mathrm{d}A = \mathrm{d}U + p_0\,\mathrm{d}V - T_0\,\mathrm{d}S = \mathrm{d}G \leq 0$ and the system reaches equilibrium when its Gibbs free energy, G, is minimal.

6.4 Maxwell's relations

These are very useful for essentially two reasons:

1. They relate partial derivatives representing quantities which are difficult to measure experimentally to partial derivatives which are easier to measure.
2. Taken as a whole, the set of them describe the constraints imposed on the four thermodynamical variables, T, S, V, p, owing to the fact that only two of them are independent. In that sense they play a role similar to that of an equation of state!

The mathematical idea behind these relations is that if $f(x, y)$ is a function of state, then

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

is an exact differential and therefore $(\partial(\partial f/\partial x)_y/\partial y)_x = (\partial(\partial f/\partial y)_x/\partial x)_y$, i.e. the order of differentiation w.r.t. x or y does not matter. Let us apply this property to each of the four thermodynamical potentials in turn.

Starting with $f = U$, $x = S$, $y = V$ we have $\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V$ with $T = (\partial U/\partial S)_V$, $p = -(\partial U/\partial V)_S$ so that the second derivatives yield the following equality:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{6.5}$$

Next, let us consider $f = H$, $x = S$ and $y = p$. We have $\mathrm{d}H = T\mathrm{d}S + V\,\mathrm{d}p$ with $T = (\partial H/\partial S)_p$, $V = (\partial H/\partial p)_S$ so that:

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{6.6}$$

For $f = F$, $x = T$ and $y = V$, $\mathrm{d}F = -S\mathrm{d}T - p\,\mathrm{d}V$ along with $S = -(\partial F/\partial T)_V$, $p = -(\partial F/\partial V)_T$, which yields:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{6.7}$$

Exercise 6.1 Show that the last Maxwell relation, associated with the Gibbs free energy, G, writes:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{6.8}$$

■

6.5 Thermodynamical coefficients

The main idea of this section is to illustrate that one can calculate the physical properties of a system (its thermodynamical coefficients) in terms of other experimentally known quantities, using the mathematical relations that link partial derivatives together (Maxwell relations, reciprocity and reciprocal theorems). We have already seen some of these coefficients, the heat capacities:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \text{ (use } \mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V \text{ divide by } \mathrm{d}T \text{ and hold } V \text{ constant)} \\ C_p &= \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \text{ (use } \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \text{ divide by } \mathrm{d}T \text{ and hold } p \text{ constant)} \end{aligned}$$

which play a special role in thermodynamics. These are well measured quantities for gas, liquids and solids (units [J K^{-1} mol^{-1}]).

Here, we will use them to calculate the compressibility of a system, κ. First, let us define what we mean by compressibility. It is the fractional change in volume of the system when we apply pressure to it. V and p are therefore the two thermodynamical quantities that will vary. As we have four thermodynamical variables, there will be two ways to vary them (two different constraints): either at fixed T (isothermally), or at fixed S (adiabatically). Mathematically we will write:

$$\begin{aligned} \kappa_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \\ \kappa_S &= -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S \end{aligned}$$

for the *isothermal compressibility* and the *adiabatic compressibility* respectively.
The ratio of these two compressibilities is:

$$\begin{aligned} \frac{\kappa_T}{\kappa_S} &= \frac{(\partial V/\partial p)_T}{(\partial V/\partial p)_S} = \frac{(\partial p/\partial T)_V\,(\partial T/\partial V)_p}{(\partial p/\partial S)_V\,(\partial S/\partial V)_p} = \frac{(\partial S/\partial V)_T\,(\partial p/\partial S)_T}{(\partial T/\partial V)_S\,(\partial p/\partial T)_S} \\ &= \frac{(\partial p/\partial S)_T\,(\partial T/\partial p)_S}{(\partial V/\partial S)_T\,(\partial T/\partial V)_S} = \frac{(\partial S/\partial T)_p}{(\partial S/\partial T)_V} = \frac{C_p}{C_V} = \gamma \end{aligned}$$

where we have successively applied the reciprocity theorem to both numerator and denominator; Maxwell's relations associated with F (first term) and G (second term) to the numerator and Maxwell's relations associated with U (first term) and H (second term) to the denominator; the reciprocal theorem to the first term of the numerator and the second term of the denominator; and finally the reciprocity theorem once more to both numerator and denominator.

To go one step further and explicitly calculate each compressibility, we need to specify the equation of state of the system. This is done in example 6.1 for the case of an ideal gas.

■ **Example 6.1** Explicit calculation of the compressibility of an ideal gas.
• Isothermal compressibility: $\mathrm{d}T = 0$, so $\mathrm{d}(pV) = 0 \to p\,\mathrm{d}V + V\mathrm{d}p = 0$ and $-V\mathrm{d}p/\mathrm{d}V = p$. Therefore $\kappa_T = 1/p$.
• Adiabatic compressibility: $\mathrm{d}S = 0$, so $\mathrm{d}(pV^\gamma) = 0 \to \gamma V^{\gamma-1} p\,\mathrm{d}V + V^\gamma \mathrm{d}p = 0$ and $-V\mathrm{d}p/\mathrm{d}V = \gamma p$. Therefore $\kappa_S = 1/(\gamma p)$. ■

6.6 Generalisation to open systems

So far, we have, for simplicity, ignored the fact that the amount of substance is a thermodynamic variable, and considered it fixed. Even in the case of the entropy of mixing, where we had two different ideal gases initially enclosed in thermally insulated containers that were then allowed to mix (see Fig 5.13), the total number of particles of the system, $N = N_1 + N_2$, was fixed.

This approach is fine to describe simple processes such as the expansion of a gas, but most thermodynamical systems are not so simple in reality: they can undergo phase transitions, or some chemical reactions may occur that lead to a change in N. Such systems will be called *open* systems. The question we then have to ask is: how does this affect the results we have derived so far?

To answer it, we have to establish whether N is independent of the other thermodynamical variables. As we have previously hinted, the answer to that question is that is clearly is: you can change the state of the system by adding new particles to it *without* changing its temperature or pressure. Convince yourself by considering the example of the ideal gas. The ideal gas equation of state is $pV = Nk_BT$, so if I change N proportionally to V, p and T remain constant, but since V has changed, the state of the system has changed! This would, of course, be impossible if I had only two independent variables.

Therefore, we have to conclude that, for an open system consisting of a *pure*[†] substance in a *single phase*[‡], there exist *three* independent variables.

In this context, N can only change as a result of *diffusion*, i.e. the migration of random particles in and out of the system. We will talk about *diffusive* thermodynamical contact between the system and its surroundings, which will have to be separated by a *permeable*[§] boundary to be able to reach *diffusive equilibrium*.

R Note that strictly speaking, even after a open system has come to diffuse equilibrium, particles continue to drift randomly. In other words, N is not constant over time but fluctuates, exactly like the true internal energy of the system, E. This means that, in the same way that we had to define the thermodynamic internal energy as $U = \langle E(t)\rangle$, we have to define $N = \langle N(t)\rangle$ as our thermodynamic number of particles. In practice, for very large systems ($N \sim \mathcal{N}_A$), N and its average over time are very nearly identical.

Now recall that an equilibrium for a different type of contact corresponds to a different *intensive* thermodynamic variable which is the same for the system and its surroundings (p for mechanical contact, T for thermal contact). Another way to say this is that thermodynamic variables come in conjugate pairs (p and V, T and S). So what is the conjugate variable of N? It's called the *chemical potential*, and is noted μ. We can easily deduce its properties: it must be intensive since N is extensive and must have the dimension of energy per particle since N is a number of particles and the product of two conjugate variables, like μN, must have the dimension of energy.

The energy transferred through diffusive contact, i.e. the analog of Q for thermal contact and W for mechanical contact is simply $\mu\Delta N$, where ΔN is the net number of particles transferred to or from the system. For this reason, even though any of the two variable can be chosen as the natural variable from each of the three pairs of conjugate variables, it is almost always N which is used for the (μ, N) pair[¶]. This means that we will

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[†] Otherwise we would have to introduce multiple N_i, where the index i indicates the substance.

[‡] Otherwise different phases could exchange particles even if the system was closed.

[§] This word is to be understood in the sense of a wall that lets particles go through but does not necessarily move or let heat in or out.

[¶] The one exception worth mentioning is the *Grand potential*, $\Omega(T, V, \mu) = F - \mu N$, which will be useful to describe general open systems, and whose total differential form will then be $\mathrm{d}\Omega = -S\mathrm{d}T - p\,\mathrm{d}V - N\mathrm{d}\mu$.

generalise our total differentials for the four thermodynamical potentials as:

$$\begin{aligned}
U(S,V,N) &\quad\rightarrow\quad \mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N \\
H(S,p,N) &\quad\rightarrow\quad \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \mu\,\mathrm{d}N \\
F(T,V,N) &\quad\rightarrow\quad \mathrm{d}F = -S\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N \\
G(T,p,N) &\quad\rightarrow\quad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\,\mathrm{d}N
\end{aligned}$$

The physical meaning of the chemical potential now appears a bit more clear: it measures the change in Gibbs free energy with respect to a change in N at constant T and p: $\mu \equiv (\partial G/\partial N)_{T,p}$.

- We could have used any of the thermodynamical potentials to define μ but G is more useful because the variables which are held constant, T and p, are the intensive variables which correspond to the other two equilibria, thermal and mechanical.
- Since G is extensive, $G(T,p,N) = NG_{N=1}(T,p)$, so why didn’t we simply define $\mu \equiv G_{N=1}(T,p)$ and dispense with μ altogether? The reason is that this would only work for a pure substance in a single phase: in more general situations $\mu \neq G_{N=1}(T,p)$.

The role that μ plays for diffusive contact can be understood in perfect analogy with that of T for thermal contact or p for mechanical contact. If $\mu \neq \mu_{\text{surr}}$, the system is out of diffusive equilibrium and this will lead to a net flow of particles crossing the permeable boundary with the surroundings, from the high μ to the low μ region, until $\mu = \mu_{\text{surr}}$, at which point diffusive equilibrium is reached.

We have seen that this process, like for the two other types of equilibrium, can be interpreted in terms of entropy (information). As we saw in the section where we discussed the general conditions for thermodynamical equilibrium, allowing for diffusive contact removes a macroscopic constraint on the system: it is no longer closed. The system will ‘take advantage’ of this new freedom by exploring the increased range of microstates available to it: particles will migrate between system and surroundings. This results in a macroscopic change of state for the system, i.e. a change in N. This change stops when the entropy of the *total* system is maximised, at which point thermodynamical equilibrium is restored. This is the classic story of thermodynamics!

6.7 Thermodynamics beyond expansion work

The examples that we have studied in these lectures (Carnot cycle, Joule expansion, etc...) all involved systems consisting of ideal gases. This might have given you the (false) impression that thermodynamics *only apply* to gases. Even though gas systems are without doubt very important thermodynamical systems, I thus want to conclude the first part of these lectures by dispelling such an impression. Indeed, the general thermodynamical concepts we have introduced can describe virtually *any* macroscopic system, whatever this system is made of.

The main idea is that “heat is heat” because it is related to temperature and entropy, which are *generic properties* of the system, in the sense that they can be defined and measured in the same way, whatever the system is made of.

By contrast, work can take a different form from $p\,\mathrm{d}V$, depending on the properties of the system. For example, we have already mentioned electrical or magnetic work. In general, we will write the work in differential form as $\text{đ}W = \mathcal{F}\mathrm{d}h$, where $\mathcal{F}$ is a kind of *intensive* generalised force (like p for the gas), and h is a kind of *extensive* generalised *internal*[‖] displacement (like V for the gas).

To be more specific, we can come up with the following (non-exhaustive) list of examples of thermodynamical systems:

- fluid: $\text{đ}W = p\,\mathrm{d}V$ with p the pressure and V the volume.
- elastic rod: $\text{đ}W = t\,\mathrm{d}L$ with t the tension and L the length.
- liquid film: $\text{đ}W = \gamma\,\mathrm{d}A$ with γ the surface tension and A the area.
- dielectric material: $\text{đ}W = \vec{E}\cdot\mathrm{d}\vec{p}_E$ with $\vec{E}$ the electric field and $\vec{p}_E$ the electric dipole moment.
- magnetic material: $\text{đ}W = \vec{B}\cdot\mathrm{d}\vec{m}$ with $\vec{B}$ the magnetic field and $\vec{m}$ the magnetic dipole moment.

> Not only do the electric and magnetic work involve a dot product between vectors, but a different differential form to that we have just defined will be used in most problems. This is due to the fact that the system (dielectric or magnetic material) will generally be plunged in an external (vacuum) field, and that we will only be interested in the work that is associated with changing the polarization/magnetization of the material rather than in the work associated with the change in the external field that such a change in polarization/magnetization will necessarily entail[**]. In other words, for uniform external fields, we will write the electric work as $\text{đ}W = -\vec{p}_E\cdot\mathrm{d}\vec{E}_{\mathrm{ext}}$, where $\vec{E}_{\mathrm{ext}}$ is the electric field that would be present in the absence of the dielectric material but if the charge remained the same, and the magnetic work as $\text{đ}W = -\vec{m}\cdot\mathrm{d}\vec{B}_{\mathrm{ext}}$ where $\vec{B}_{\mathrm{ext}}$ is the magnetic field that would be present in the absence of the magnetic material but if the magnetic flux remained the same.

You will encounter other specific examples of such systems in the problem sheet, but in this lecture I want to focus on the thermodynamics of the elastic rod.

Let us then consider a rod with a cross section A and length L. This rod can be made of any material: metal, rubber, etc... We then exert an infinitesimal tension $\mathrm{d}t$ on it, so that it elongates by an infinitesimal amount dL, as represented on Fig 6.2.

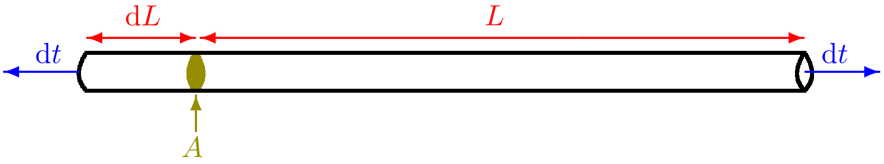

Figure 6.2: Diagram of an elastic rod of initial cross-section A and length L, stretched under infinitesimal tension $\mathrm{d}t$.

First, let us define the physical properties of the system using thermodynamical coefficients. The ratio of the *stress*, $\sigma \equiv \mathrm{d}t/A$, to the *strain*, $\epsilon \equiv \mathrm{d}L/L$, exerted on the rod is called *Young's modulus*, and if the stretching takes place at constant temperature, T, it is equal to $E_T \equiv \sigma/\epsilon = L/A\,(\partial t/\partial L)_T$. As σ and ϵ always have the same sign, $E_T > 0$. Another relevant thermodynamical coefficient is the linear expansivity of the rod at constant tension, i.e. its fractional change in length with temperature: $\alpha_t = 1/L\,(\partial L/\partial T)_t$. This coefficient will be positive if the rod extends when heated (e.g. a metal rod) and negative if

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[‖] In these lectures, we always (and always will) place ourselves in the reference frame where the system of interest is at rest with respect to the observer. In other words, the systems we study do not move: this means that the displacements we measure must be internal to these systems.

[**] For an in depth discussion of the subtleties of properly defining electric and magnetic work, see e.g. *Thermodynamics* by A. Steane (chap 14.5) or, for magnetic work, the footnote in the second part of these lectures devoted to paramagnets.

it contracts (e.g. a rubber band). Armed with these two coefficients, we can now ask how the tension of a rod held at constant length will change with temperature. Mathematically, this writes as $(\partial t/\partial T)_L = -(\partial t/\partial L)_T(\partial L/\partial T)_t = -AE_T\alpha_t$, where the first equality is obtained using the reciprocity theorem. So the tension will go down as a metal rod is heated but it will increase for a rubber band.

The first law in fundamental form reads $\mathrm{d}U = S\mathrm{d}T + t\,\mathrm{d}L$ and the Helmoltz free energy $\mathrm{d}F = -S\mathrm{d}T + t\,\mathrm{d}L$, so we can define the rod's entropy as $S = -(\partial F/\partial T)_L$ and its tension as $t = (\partial F/\partial L)_T$. We can measure how the entropy of the rod will change when its length changes at constant T by measuring how the tension changes as a function of temperature when its length is held constant: $(\partial S/\partial L)_T = -(\partial t/\partial T)_L = AE_T\alpha_t$ (the first equality is the Maxwell relation associated with F for the rod). As A is assumed to stay constant, stretching the rod increases its entropy if $\alpha_t > 0$, i.e. in the case of the metal, but entropy will decrease for the rubber band. This can be understood by analogy with the ideal gas. Extending the rod isothermally and reversibly by $\mathrm{d}L$ is analogous to the isothermal gas expansion in the Carnot cycle: an amount of heat $đQ_{\mathrm{rev}} = T\mathrm{d}S = ATE_T\alpha_t\mathrm{d}L$ will be absorbed by the rod if $\alpha_t > 0$ or released if $\alpha_t < 0$. Microscopically, for the metal, its crystalline structure is distorted and S increases (each atom can occupy more volume) and heat is absorbed, whereas for the rubber band, the stretching uncoils disordered chain segments and aligns them more with the applied tension: entropy decreases and heat is released.

Let us conclude this study by asking how the internal energy of the rod, U, changes under such an isothermal extension. This will serve, I hope, to highlight the pitfalls of thinking that all systems have an internal energy with similar properties to that of an ideal gas. Indeed, for an ideal gas, the answer to this question would be trivial: as its internal energy can be written as a function of temperature alone, an isothermal process cannot change its value. Not so for the rod. Applying the first law, we get $(\partial U/\partial L)_T = T(\partial S/\partial L)_T + t = ATE_T\alpha_t + t$ which will not be equal to zero in general!

II

Statistical Mechanics of Simple Systems

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10.1 General case
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7. Introduction

Up to now, everything you have done was:

- fairly general and abstract: you talked about systems, maximisation of entropy under constraints, or
- applied to pV systems (ideal gas).

The goal of these lectures on simple systems is to show you how powerful the Statistical Mechanics approach is by applying it to (relatively) simple (but still very useful), non-pV systems

The systems in question will conserve number of particles N and volume V (fixed external parameters) but will be in thermal contact with a thermostat (or heat bath) at fixed temperature T, with which they can exchange energy. In other words, the natural starting point to study them will be the canonical ensemble partition function:

$$\mathcal{Z}(\beta) = \sum_{\alpha} \exp(-\beta\epsilon_{\alpha}) \quad \text{with} \quad \beta = \frac{1}{k_B T} \tag{7.1}$$

which we interpret as the number of micro-states available to a system at a given temperature.

Why is the partition function of a system so important? Well, it contains all the information about the energy of the micro-states of the system, and you have seen that all thermodynamical equilibrium properties of the system can be derived from it, i.e. *all* the usual functions of state, including the equation of state, and heat capacity!

Why is this Statistical Mechanics approach so powerful? Well, if I give you the equation of state of one mole of ideal gas, $pV = RT$, and ask you what the heat capacity of the gas is at constant V, what would you answer? $3R/2$? That would be correct for a mono-atomic gas, but how do you know that the gas is mono-atomic? Its equation of state says nothing about that, but $\mathcal{Z}$ does!

Is it surprising? Well, not really. To construct $\mathcal{Z}$, you need to know all the quantum energy levels of a system. And what else is there to know? In general solving Shrödinger's equation for a complex system and getting its complete energy level spectrum is impossible, but one can do it for useful simple systems, and that is the subject of the next three lectures.

The path we will systematically follow to study these simple systems consists of three steps:

1. derive the single-particle partition function, $\mathcal{Z}_1$, being careful about any *level degeneracy*
2. combine the single-particle partition functions together to get the total partition function of the system, $\mathcal{Z}$, being careful as to whether the particles are *distinguishable or not* and can be considered as *independent or not*
3. derive the thermodynamical properties of the system from $\mathcal{Z}$

8. Paramagnetic solid

Consider a crystal of N identical atoms (or ions), each in a particular position, in equilibrium with a heat bath at temperature T. Since the atoms are localised, we can apply the statistics of distinguishable particles, even though these atoms are of the same kind. When no external magnetic field is present, virtually all the atoms of the crystal are in their fundamental state[*].

Let us call $\vec{J}$ the *total angular momentum* of an atom, i.e. the sum of the *total orbital angular momentum*, $\vec{L}$, and *total spin*, $\vec{S}$, of all its electrons, in its fundamental state. From your Quantum Mechanics lectures, you know that to this total angular momentum is associated a magnetic moment[†]:

$$\vec{\mu} = -g_J \mu_B \vec{J} \tag{8.1}$$

where

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{8.2}$$

is called the *Landé factor*[‡], J can take integer or half-integer values and $\mu_B = e\hbar/(2m_e)$ is the *Bohr magneton*, with e the elementary charge, $\hbar = h/(2\pi)$ the *reduced Planck constant* and m_e the rest mass of the electron. From this expression, it is clear that if $J \neq 0$, each atom possesses a permanent magnetic moment[§]. Again, from your Quantum Mechanics

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[*] To excite the electrons, e^-, of an atom, you need energies $k_B T \sim 1$ eV, i.e. temperatures around 10^4 K, so the probability of finding an excited atom at room temperature is negligible.

[†] If you prefer, think of the classical picture of the e^- "orbiting" the nucleus and thus creating a mini current loop which in turns creates the magnetic moment.

[‡] Although you will only study the spin-orbit coupling in detail when you take Atomic Physics or Condensed Matter in the 3rd year, you can already understand how such a factor comes about from your 2nd year Quantum Mechanics lectures, in particular the ones devoted to the resolution of the Stern-Gerlach experiment puzzle.

[§] Note that this is not the case for most materials. What exists in all materials (including those for which $J = 0$) is a *diamagnetic* effect (part of the 3rd year Condensed Matter course), where the e^- re-organise in an attempt to cancel the external magnetic field $\vec{B}_{\text{ext}}$ (when present), but this effect is generally small. This is also referred to as *Lenz's law*.

lectures, this means that e.g. the $z-$component of $\vec{J}$, J_z, can take $2J+1$ eigenvalues between $-J$ and $+J$. In other words, the fundamental energy level of the atom is $2J+1$ degenerate.

In the absence of an *external* magnetic field, all the states with different J_z will share the same energy level, and are thus equally likely to be populated. As the magnetic moment of each atom is proportional to J_z, the net magnetic moment of the crystal is nil. However, if we plunge our crystal in a *uniform*¶ external magnetic field, $\vec{B}_{\text{ext}} \neq \vec{0}$ aligned with the $z-$axis and pointing up, each atom is subject to the Hamiltonian:

$$H = -\vec{\mu} \cdot \vec{B}_{\text{ext}} = g_J \mu_B \, J_z B_{\text{ext}} \tag{8.3}$$

This lifts the degeneracy of the atoms fundamental state by splitting them into $2J+1$ regularly spaced energy sub-levels, between energies $-g_J\mu_B \, JB_{\text{ext}}$ and $+g_J\mu_B \, JB_{\text{ext}}$.

If the atoms in the crystal are sufficiently far from one another, the interaction between their magnetic momenta are negligible and they can be considered as *independent*. In that case, the magnetic properties of the crystal can be calculated from the model Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^{N} H_i = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{B}_{\text{ext}} = \sum_{i=1}^{N} g_J \mu_B \, J_z^{(i)} B_{\text{ext}} \tag{8.4}$$

which is simply the sum of the individual atom Hamiltonians given by equation (8.3). The crystal thus exhibits a magnetic moment which is aligned with the external field $\vec{B}_{\text{ext}}$, hence the name *para*magnetism.

8.1 Spin $\frac{1}{2}$ paramagnet

This is the special case where $J = S = 1/2$ and $L = 0$. This yields $g_J = 2$, so that the fundamental level of the atoms is split into two sub-levels with energies $\epsilon = \pm \, \mu_B B_{\text{ext}}$ in the presence of the external magnetic field $\vec{B}_{\text{ext}}$ (see Fig. 8.1). So, taking the first step in

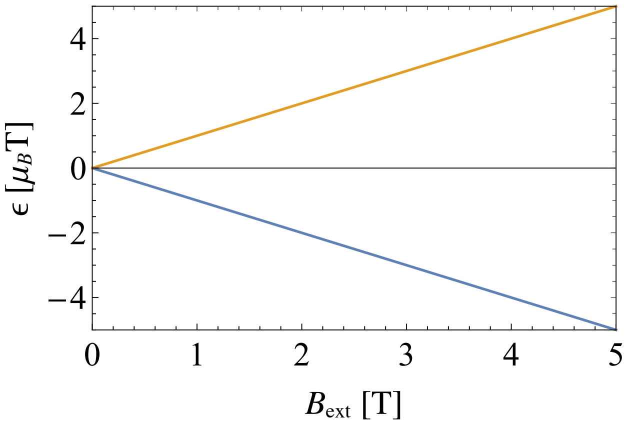

Figure 8.1: Sub-levels of energy split as a function of the external field strength, B_{ext}, with the blue line corresponding to magnetic dipoles pointing in the same direction as the field, and the orange line to dipoles pointing in the opposite direction. The zero point energy corresponds to the fundamental level in the absence of the field.

¶In order to avoid complicating our life by having to evaluate potentially nasty integrals to obtain the average magnetic field present in the volume occupied by the crystal.

our three step procedure, we calculate the single-particle partition function of the system by summing these two *non-degenerate* energy sub-levels:

$$\mathcal{Z}_1 = \exp(-\beta\mu_B B_{\text{ext}}) + \exp(+\beta\mu_B B_{\text{ext}}) = 2\cosh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right) \tag{8.5}$$

For the second step, recall that the atoms are *distinguishable* (because they are *localised*) *and independent*, so that the partition function of the system simply is the product of all the single-particle partition functions:

$$\mathcal{Z} = (\mathcal{Z}_1)^N \tag{8.6}$$

The third and final step consists in deriving the thermodynamical properties of the system from $\mathcal{Z}$. Let us start with the internal energy:

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = -N\mu_B B_{\text{ext}} \tanh\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right) \tag{8.7}$$

U is plotted in Fig. 8.2 both as a function of T (left panel) and B_{ext} (right panel), arguably the main conclusion we can draw is that the internal energy of the crystal *increases* when it is plunged in an external magnetic field (right panel).

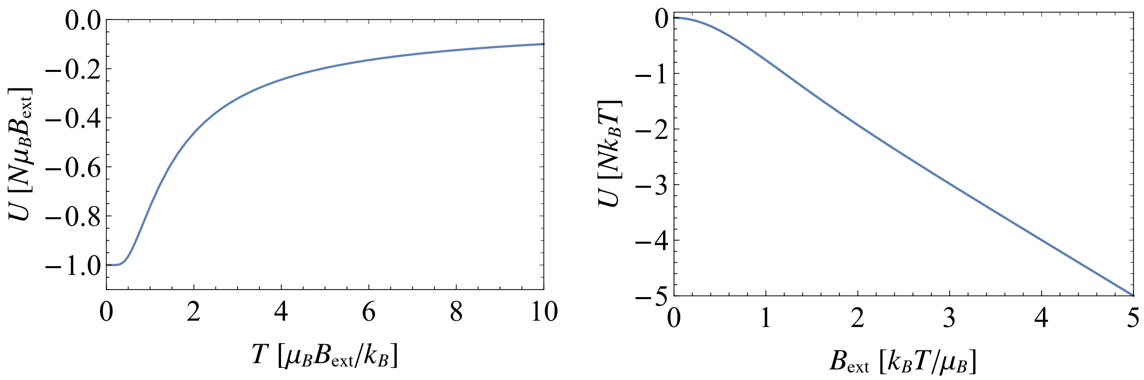

Figure 8.2: Internal energy of the paramagnet as a function of temperature T (left panel) at fixed B_{ext} and of the external field strength, B_{ext} at fixed T (right panel).

> We have not accounted for the internal energy contribution coming from other processes undergone by atoms in the crystal, such as vibrations. This will be the subject of the next lecture, and is only emphasised here to draw your attention on the arbitrariness of the energy zero point. We have chosen the internal energy of the crystal in the absence of an external field as zero, but of course the crystal has a non-nil internal energy in that case! In other words, only the difference in energy matters to study independent processes as the corresponding partition functions will simply multiply and the energies add up.

Looking at the left panel of Fig. 8.2 shows that at very low temperature and fixed $B_{\text{ext}} \neq 0$, $U = -N\mu_B B_{\text{ext}}$. This is exactly was we expect, the external field splits the level into two sub-levels, but at low T *all* the atoms must be in the ground state, i.e. their lowest energy level $-\mu_B B_{\text{ext}}$, which directly leads to $U = -N\mu_B B_{\text{ext}}$. As the system is heated and its T rises, some e^- are excited to the upper energy level $+\mu_B B_{\text{ext}}$ and U therefore increases. In the high temperature regime when $T \gg \mu_B B_{\text{ext}}/k_B$, the two sub-levels become very nearly equally populated and the internal energy goes back to the original $U = 0$, i.e. to its value in the absence of the external magnetic field.

Now, at fixed T (right panel of Fig. 8.2), for large B_{ext}, $\tanh(\beta\mu_B B_{\text{ext}}) \to 1$ and so $U \propto B_{\text{ext}}$. Again, this behaviour is expected: when B_{ext} is large, the energy gap between sub-levels is so large that very few atoms can populate the upper energy sub-level, even though the system has a finite T, and so $U = -N\mu_B B_{\text{ext}}$ again. For weaker B_{ext}, the situation is a bit more complicated, as some e^- are going to be thermally excited to the upper energy sub-level. However, in the regime $B_{\text{ext}} \ll k_B T/\mu_B$, $\tanh(\beta\mu_B B_{\text{ext}}) \to \beta\mu_B B_{\text{ext}}$ and we expect $U \propto -B_{\text{ext}}^2$.

What about the heat capacity[‖]?

$$\boxed{C_{B_{\text{ext}}} = \left(\frac{\partial U}{\partial T}\right)_{B_{\text{ext}}} = Nk_B\left(\frac{\mu_B B_{\text{ext}}}{k_B T}\right)^2 \frac{1}{\cosh^2\left(\mu_B B_{\text{ext}}/(k_B T)\right)}} \tag{8.8}$$

Looking at the high temperature regime, $T \to +\infty$ and for a fixed B_{ext}, we can derive a limit for $C_{B_{\text{ext}}} \simeq Nk_B\big(\mu_B B_{\text{ext}}/(k_B T)\big)^2 \to 0$. In the same way, the low temperature regime $T \to 0$, yields $C_{B_{\text{ext}}} \simeq Nk_B\big(2\mu_B B_{\text{ext}}/(k_B T)\big)^2 \exp\big(-2\mu_B B_{\text{ext}}/(k_B T)\big) \to 0$. We therefore predict a peak in the heat capacity of a paramagnet (see exercise 8.1 and Fig. 8.3 for detail)! Such a peak is actually observed in real systems: it is called the *Schottky* anomaly.

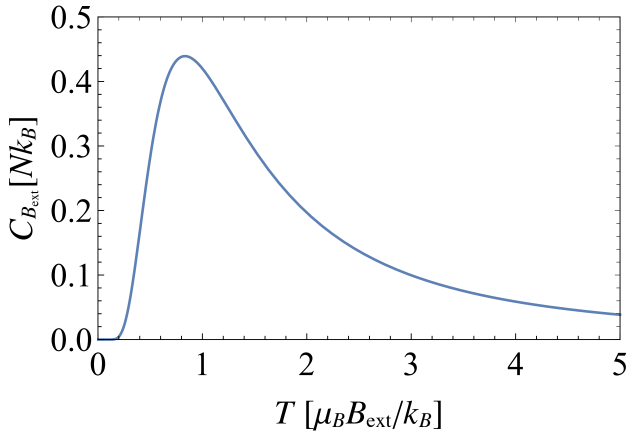

Figure 8.3: Heat capacity at constant external magnetic field for a spin half paramagnet. Note the presence of a peak centred on a specific temperature.

Exercise 8.1 Estimate the temperature, T_{max}, and the heat capacity, $C_{B_{\text{ext}}}^{\text{max}}$ of a spin half paramagnet plunged in an external magnetic field B_{ext}.
Ans: $T_{\text{max}} \simeq 0.83\,\mu_B B_{\text{ext}}/k_B$, $C_{B_{\text{ext}}}^{\text{max}} \simeq 0.44 Nk_B$ ■

R What is the order of magnitude for the temperature at the peak? For this you need to know that it is difficult to manufacture magnets capable of producing a magnetic field much stronger than $B_{\text{ext}} \sim 10$ Tesla, so as the magnitude of μ_B and k_B are similar, $T_{\text{max}} \sim 10$ K. The use of the Schottky anomaly plays an important role for cooling material at extremely low temperatures: if one can lower B_{ext} without heat

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[‖] Note that the volume of the crystal is fixed, so we are talking about heat capacity at constant B_{ext} rather than constant V.

> entering into the system, then T has to decrease proportionally for the magnetisation to remain constant. In this way, you can go down from 10 K to the mK level and even lower with *nuclear* dipoles as you gain a factor ~ 2000 in mass when replacing m_e in the Bohr magneton by m_p!

In general, the Helmholtz free energy will be more useful than any of the other thermodynamic potentials, because as you have already seen for the mono-atomic ideal gas and we will see time and again for other systems, it provides a direct route to their equation of state. The paramagnet is no different. Its Helmholtz free energy is:

$$\begin{aligned} F &= -k_B T \ln \mathcal{Z} \\ &= -N k_B T \ln \left(2 \cosh \left(\frac{\mu_B B_{\text{ext}}}{k_B T} \right) \right) \qquad (8.9) \end{aligned}$$

Now to the equation of state. For an ideal gas, it would be obtained by taking the partial derivative of F with respect to the volume at constant temperature, as $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$. For a paramagnet, its *total magnetic moment*, $\vec{m} \equiv \sum_{i=1}^{N} \vec{\mu}_i$, will play the role of p and (as we have already noted for the heat capacity), $\vec{B}_{\text{ext}}$ will play the role of V, even though given the intensive and extensive nature of these variables, one would naively have expected the reverse. In other words, we will write** $\mathrm{d}F = -S\,\mathrm{d}T - m\,\mathrm{d}B_{\text{ext}}$, so that its *magnetisation*

[**] As we have seen in the Basic Thermodynamics lectures, "heat is heat but work differs". However, for magnetic systems, there is always some confusion about writing the work as $-\vec{m}\cdot \mathrm{d}\vec{B}_{\text{ext}}$ or $+\vec{B}_{\text{ext}}\cdot \mathrm{d}\vec{m}$. This confusion arises because the *total* magnetic field, $\vec{B}$, is the sum of the external field and the one induced in the paramagnet, i.e. $\vec{B} = \vec{B}_{\text{ext}} + \vec{B}_{\text{ind}}$. These fields are generated by current densities $\vec{J} = \vec{J}_{\text{ext}} + \vec{J}_{\text{ind}}$ and all three (total, external (free) and induced (bound)), obey Ampère's law, $\vec{\nabla} \times \vec{B} = \mu_0 \vec{J}$, where μ_0 is the magnetic permeability in vacuum. To figure out the amount of work done *by* the crystal, we need to remove the contribution of the external field from the Hamiltonian of the system. Unfortunately, this task is not straightforward because Faraday's law requires that a back-electromotive force be generated in the device producing the *external* field when the *total* magnetic field of the system changes. In other words, work needs to be done to maintain the *external* current and field. This work, $đW = -\mathrm{d}t \int \vec{J}_{\text{ext}} \cdot \vec{E}\,\mathrm{d}^3x$, integrates to $W = \mu_0^{-1} \int \vec{B}_{\text{ext}} \cdot \vec{B}\,\mathrm{d}^3x$ when the *total* field increases from $\vec{0}$ to $\vec{B}$, with the integrals performed over *all* space and using Maxwell-Faraday's equation $\vec{\nabla} \times \vec{E} = -\partial \vec{B}/\partial t$ to turn the electromotive force into a magnetic field. As such work maintains the *external* current, it is an energy which pertains to the surroundings and *not* to the paramagnet itself, so it should be *subtracted* from the total magnetic energy which permeates the crystal: $1/(2\mu_0) \int \vec{B}^2\,\mathrm{d}^3x$. By virtue of the same reasoning, we should also subtract the magnetic energy present in the crystal which is *entirely* due to the presence of the external field, i.e. $1/(2\mu_0) \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$ and $-\mu_0^{-1} \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$, where the second term corrects for our inclusion of the external field work to maintain the external current in W. So the *net* effect of the presence of an external field is to *add* $1/(2\mu_0) \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$ to the internal energy of the paramagnet, and therefore the magnetic (free) energy which should appear in the Hamiltonian of this latter is $F_{\text{mag}} = 1/(2\mu_0) \int (\vec{B}^2 - 2\vec{B}_{\text{ext}} \cdot \vec{B} + \vec{B}_{\text{ext}}^2)\,\mathrm{d}^3x = 1/(2\mu_0) \int (\vec{B} - \vec{B}_{\text{ext}})^2\,\mathrm{d}^3x = 1/(2\mu_0) \int \vec{B}_{\text{ind}}^2\,\mathrm{d}^3x$.

On the other hand, it is customary to describe the response of a paramagnet to the presence of an external magnetic field by its magnetisation $\vec{M}$, such that $\vec{\nabla} \times \vec{M} = \vec{J}_{\text{ind}}$, and to introduce an auxiliary field $\vec{H} = \vec{B}/\mu_0 - \vec{M}$, for which $\vec{\nabla} \times \vec{H} = \vec{J}_{\text{ext}}$. These quantities are therefore linked to the induced and external magnetic fields by $\vec{M}^{\perp} = \vec{B}_{\text{ind}}/\mu_0$ and $\vec{H}^{\perp} = \vec{B}_{\text{ext}}/\mu_0$ respectively, where the subscript $^{\perp}$ denotes the transverse component of the vector fields, with zero divergence (the curl free longitudinal components of $\vec{M}$ and $\vec{H}$ are generally not specified, unless $\vec{M}$ is a local function of $\vec{B}$). Now let the external magnetic field vary by $\mathrm{d}\vec{B}_{\text{ext}}$. Although the charged particles in the crystal (and therefore the *total* field $\vec{B}$) will respond to such a change, *at first order*, the variation in the paramagnet energy comes *entirely* from its dependence on $\vec{B}_{\text{ext}}$ (the crystal sits at a stable energy minimum in the external field so the other terms are of higher order). The magnetic energy term in the Hamiltonian of the crystal that we previously derived thus varies by $\mathrm{d}F_{\text{mag}} = -\mu_0^{-1} \int (\vec{B} - \vec{B}_{\text{ext}}) \cdot \mathrm{d}\vec{B}_{\text{ext}}\,\mathrm{d}^3x$ to first order. Skipping over the transverse component subtlety and identifying $\vec{M}$ with $\vec{B}_{\text{ind}}/\mu_0$ *inside* the crystal, we then obtain $\mathrm{d}F_{\text{mag}} = -\int_V \vec{M} \cdot \mathrm{d}\vec{B}_{\text{ext}}\,\mathrm{d}^3x = -\vec{m} \cdot \mathrm{d}\vec{B}_{\text{ext}}$. However, another possible choice is to consider the cross term $\vec{B}_{\text{ind}} \cdot \vec{B}_{\text{ext}}$ as part of the internal energy of the crystal (i.e. to remove the external field magnetic energy $1/(2\mu_0) \int \vec{B}_{\text{ext}}^2\,\mathrm{d}^3x$ from the paramagnet internal energy but regard the work done by the external current to maintain the field as part of it), thus writing the magnetic energy part in the Hamiltonian as is given by[††]:

$$\begin{aligned} M &= -\frac{1}{V}\left(\frac{\partial F}{\partial B_{\rm ext}}\right)_T \\ &= \frac{N\mu_B}{V}\tanh\left(\frac{\mu_B B_{\rm ext}}{k_B T}\right) \end{aligned} \tag{8.10}$$

In the limit of small external magnetic fields (or high temperatures), i.e. $\mu_B B_{\rm ext} \ll k_B T$, this equation of state linking variables $M, B_{\rm ext}$ and T in a similar way as the ideal gas equation of state links P, V and T, yields what is known as

Law 7 — Curie's law of paramagnetism.

$$M = \frac{N\mu_B^2 B_{\rm ext}}{V k_B T} \tag{8.11}$$

On the other hand, for large magnetic fields (or low temperatures), $\mu_B B_{\rm ext} \gg k_B T$, all e^- will be in the ground state with magnetic moments parallel to and pointing in the direction of the external magnetic field so that the magnetisation will *saturate* at $M = N\mu_B$.

Another quantity often used to describe materials is their *magnetic susceptibility*, χ. It is a measure of the degree of magnetisation that the material will acquire when plunged in an external magnetic field. Magnetic susceptibility is a dimensionless quantity defined as:

$$\chi \equiv \mu_0\left(\frac{\partial M}{\partial B_{\rm ext}}\right)_T = \frac{\mu_0 N\mu_B^2}{V k_B T}\,{\rm sech}^2\left(\frac{\mu_B B_{\rm ext}}{k_B T}\right) \tag{8.12}$$

In the paramagnet case, we then have $\chi > 0$ and, as we have already seen, the induced magnetisation increases the magnetic field in the crystal[‡‡]. Moreover, in the case of small external fields, $\chi = \mu_0 N\mu_B^2/(V k_B T)$, so it is inversely proportional to the temperature only, i.e. it does *not* depend on $B_{\rm ext}$. Therefore, in this regime, where magnetisation is a linear function of the applied magnetic field (see equation (8.11)), one can rewrite the *total* field present in the crystal as $\vec{B} = \vec{B}_{\rm ext}\,(1+\chi)$.

Finally, the entropy of the spin half paramagnet is given by:

$$S = \frac{U-F}{T} = -\frac{N\mu_B B_{\rm ext}}{T}\tanh\left(\frac{\mu_B B_{\rm ext}}{k_B T}\right) + N k_B \ln\left(2\cosh\left(\frac{\mu_B B_{\rm ext}}{k_B T}\right)\right) \tag{8.13}$$

At high temperatures, $k_B T \gg \mu_B B_{\rm ext}$, we have $S \to N k_B \ln 2$ and in the regime of low temperatures, i.e. $k_B T \ll \mu_B B_{\rm ext}$, $S \to 0$. This is what we expect (from the arguably more intuitive microcanonical view of entropy), because at low T, *all* the e^- should be in the lowest energy state and there is only one way for them to do so (1 micro-state associated), whilst at high T, each of the two individual states is equally likely to be populated (and thus there are 2^N possible ways of achieving this situation).

$F'_{\rm mag} = 1/(2\mu_0)\int(\vec{B}^2 - \vec{B}^2_{\rm ext})\,{\rm d}^3x = 1/(2\mu_0)\int(\vec{B}^2_{\rm ind} + 2\vec{B}_{\rm ind}\cdot\vec{B}_{\rm ext})\,{\rm d}^3x$ instead of $F_{\rm mag} = 1/(2\mu_0)\int \vec{B}^2_{\rm ind}\,{\rm d}^3x$. In this case, one arrives at the other result: ${\rm d}F'_{\rm mag} = +\int_V \vec{B}_{\rm ext}\cdot{\rm d}\vec{M}\,{\rm d}^3x = +\vec{B}_{\rm ext}\cdot{\rm d}\vec{m}$. Both expressions for ${\rm d}F_{\rm mag}$ and ${\rm d}F'_{\rm mag}$ are correct, they simply depend on one's definition of the paramagnet internal energy: you now understand the source of the confusion for defining *infinitesimal* magnetic work! Note that we will use ${\rm d}F_{\rm mag}$ in these lectures, as it is easier in practice to vary an external magnetic field than to control the magnetisation of a crystal. We will also drop the vector notation, thus implicitly assuming that the magnetic dipoles fully align with the external field.

[††] Strictly speaking, as we established in the previous footnote, the magnetisation is the magnetic moment of the paramagnet per unit volume, so we should define it as $\vec{M} \equiv {\rm d}\vec{m}/{\rm d}^3x$, where ${\rm d}\vec{m}$ represents the infinitesimal magnetic moment contained in the infinitesimal volume element ${\rm d}^3x$. However, as the system is assumed homogeneous, we simply write $\vec{M} = \vec{m}/V$, with V the volume of the crystal.

[‡‡] Alternatively, if $\chi < 0$, the material will be called *diamagnetic* and the magnetic field permeating the material will be weakened by the induced magnetisation.

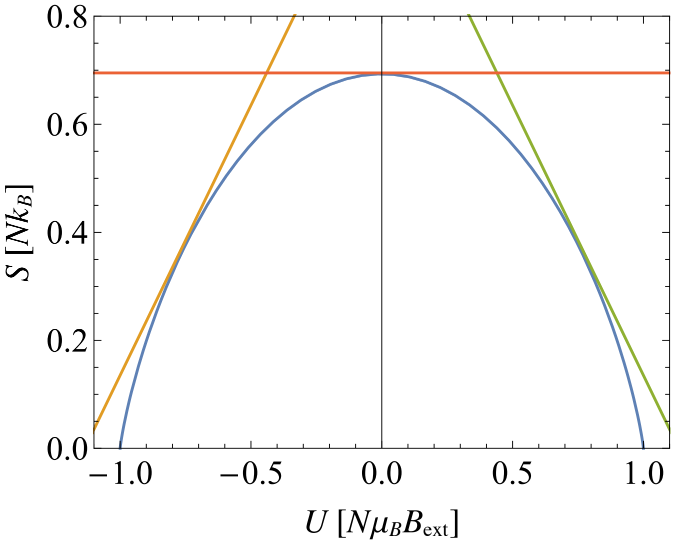

Figure 8.4: Entropy of a paramagnet as a function of internal energy for a fixed value of the external magnetic field. The temperature, $T = (\partial U/\partial S)_{B_{\text{ext}}}$, is given by the tangent to the curve at any point (orange, red and green lines). Note that this means T is negative in the quadrant where $U > 0$ (green line see text for detail).

From the thermodynamic definition of internal energy, $\mathrm{d}U = T\mathrm{d}S - M\mathrm{d}B_{\text{ext}}$, one readily obtains the temperature of the paramagnet as $T = (\partial U/\partial S)_{B_{\text{ext}}}$. Paramagnet entropy is plotted as a function of internal energy in Fig 8.4 for a system with N magnetic dipoles. Starting from the system in its *minimal* internal energy state ($U = -N\,\mu_B B_{\text{ext}}$) and progressively increasing its temperature whilst maintaining a constant external magnetic field, one reaches $U = 0$ only for an infinite temperature (horizontal tangent in red). However, if one starts with the system in its *maximal* energy state, with all the dipoles parallel to the external field but pointing in the other direction, i.e. $U = +N\,\mu_B B_{\text{ext}}$, one realises that the system will spontaneously evolve towards $U = 0$ and infinite temperature, despite its temperature remaining *negative* (see slope of the green tangent to the curve in Fig 8.4) throughout the process! There is nothing wrong with this behaviour, which is in fact typical of systems with a *capped internal energy*. In such systems, the multiplicity of microstates *decreases* as one approaches the maximum internal energy allowed, so their entropy decreases as well. This underlines that the fundamental physical quantity is the entropy, governed by the second law of Thermodynamics, *not* the temperature which merely reflects the "willingness" of a system to give away energy: in that sense a system with negative temperature is simply *hotter* than a system with infinite positive T! A concrete example of a system for which negative temperatures have been measured is nuclear paramagnets which are prepared in the lowest internal energy state initially (strong external magnetic field, low positive temperature regime), before the applied magnetic field is "instantaneously" reversed (see Purcell E. & Pound R., Physical Review, 81, p279 (1951)).

8.2 General case paramagnet

In general, a paramagnet will have a total angular momentum $J > 1/2$, and therefore a different number of energy levels than the spin half paramagnet. For instance, if $J = 2$, then $J_z = -2, -1, 0, 1, 2$ and we have five levels of energy instead of two. Apart from this, the calculation of the thermodynamical properties of a general paramagnet follows the same exact route we have taken for the particular case of the spin half paramagnet. Its single-particle partition function is obtained by summing over all the *non-degenerate* energy sub-levels:

$$\mathcal{Z}_1 = \sum_{J_z=-J}^{+J} \exp\left(-\frac{g_J\, J_z\, \mu_B B_{\text{ext}}}{k_B T}\right) = \frac{\sinh\left(\left(J+1/2\right)R\right)}{\sinh(R/2)} \tag{8.14}$$

where the last equality results from evaluating the finite sum of terms of a geometric progression with common ratio $R = g_J\, \mu_B B_{\text{ext}}/(k_B T)$.

The atoms of the general paramagnet are *distinguishable* (because they are *localised*) *and independent*, so that, once again, the partition function of the system simply is the product of all the single-particle partition functions:

$$\mathcal{Z} = (\mathcal{Z}_1)^N \tag{8.15}$$

Exercise 8.2 Following what was done for the spin half paramagnet, derive $U, C_{B_{\text{ext}}}$ and S from the partition function of the general paramagnet.
Ans:

$$\begin{aligned}
U &= -N g_J J \mu_B B_{\text{ext}} \left(\frac{2J+1}{2J}\coth\left(\frac{(2J+1)R}{2}\right) - \frac{1}{2J}\coth\left(\frac{R}{2}\right)\right) \\
C_{B_{\text{ext}}} &= N k_B \left(\frac{g_J J \mu_B B_{\text{ext}}}{k_B T}\right)^2 \left(\left(\frac{1}{2J\sinh\left(R/2\right)}\right)^2 - \left(\frac{2J+1}{2J\sinh\left((2J+1)R/2\right)}\right)^2\right) \\
S &= -\frac{N g_J J \mu_B B_{\text{ext}}}{T}\left(\frac{2J+1}{2J}\coth\left(\frac{(2J+1)R}{2}\right) - \frac{1}{2J}\coth\left(\frac{R}{2}\right)\right) \\
&\quad + N k_B \ln\left(\frac{\sinh\left(\left(J+1/2\right)R\right)}{\sinh(R/2)}\right)
\end{aligned}$$

■

Leaving the calculation of the other thermodynamic properties of the general paramagnet as an exercise (8.2), we directly jump to its magnetisation:

$$\begin{aligned}
M &= -\frac{1}{V}\left(\frac{\partial F}{\partial B_{\text{ext}}}\right)_T = \frac{k_B T}{V}\left(\frac{\partial \ln \mathcal{Z}}{\partial B_{\text{ext}}}\right)_T = \frac{g_J \mu_B}{V}\left(\frac{\partial \ln \mathcal{Z}}{\partial R}\right)_T \\
&= \frac{N g_J J \mu_B}{V}\, \mathcal{B}_J(RJ)
\end{aligned} \tag{8.16}$$

where

$$\mathcal{B}_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)\,x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \tag{8.17}$$

is called the *Brillouin function* of order J and is plotted for various values of J in Fig 8.5. Note that for $J = 1/2$, the Brillouin function reduces to an hyperbolic tangent and we recover our spin half paramagnet result. Beyond this, in the large magnetic field/low temperature regime, $R \gg 1$, $\mathcal{B}_J \to 1$ and the magnetisation saturates as all the magnetic dipoles align with $\vec{B}_{\text{ext}}$. Conversely, for small external magnetic fields/high temperatures, $R \ll 1$ and $\mathcal{B}_J \simeq (J+1)R/3$ and we recover *Curie's law*:

$$M = \frac{N\, g_J^2\, J(J+1)\mu_B^2 B_{\text{ext}}}{3V k_B T} \tag{8.18}$$

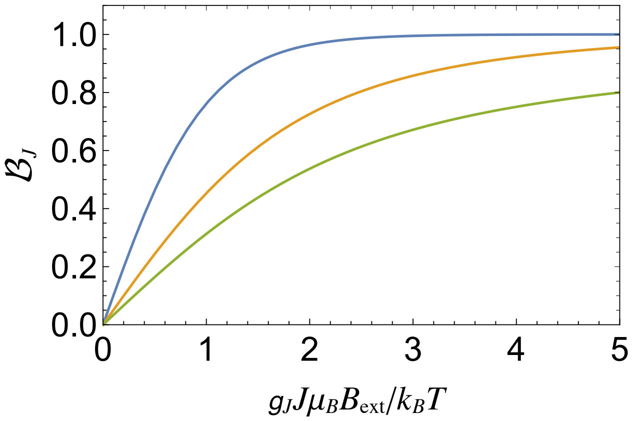

Figure 8.5: Brillouin function of various orders J as a function of the external magnetic field to temperature ratio, R. $J = 1/2$ in blue, $J = 2$ in orange and $J = \infty$ in green.

It turns out that $\mathcal{B}_J$ functions have been measured in the lab for crystals containing Cr^{3+}, Fe^{3+} and Gd^{3+} ions (see Henry W., Physical Review, 88, p559 (1952)). Note that these experiments are generally done at low temperatures as it is difficult to generate a strong external field to study the convergence to magnetisation saturation.

R

• $\mathcal{B}_\infty(x) = \coth x - 1/x$ is called the *Langevin function*, after french physicist Paul Langevin who explained paramagnetism (and diamagnetism) in 1905 *before* the emergence of Quantum Mechanics. This seems weird as one can actually prove (so called Bohr-van Leeuwen theorem) that *no* classical material can actually be magnetised (whether we are talking about para or diamagnetisation does not matter)! It turns out that Langevin got to the correct result because he had implicitly made the assumption that atoms were behaving like the Bohr atom in his derivation. Magnetisation is *purely* a quantum mechanical phenomenon.

• You will also hear about another kind of magnetism called *ferromagnetism* (and study it in the third year Condensed Matter course). This is the kind you are more likely to be familiar with, as it is "permanent", in the sense that ferromagnetic material continues to be magnetised after the applied external field has vanished. These ferromagnets include the common "fridge magnets". Essentially (restricting oneself to one domain/zone of the crystal where the magnetic field is aligned), ferromagnetism arises through the coupling of the spin of an atom with that of its neighbours: contrary to what we have seen for the paramagnet, the atoms *cannot* be considered independent. This coupling is generally modelled using a complicated *Heisenberg Hamiltonian* and it is customary to perform a mean field approximation (examples of which we will study in these lectures) to obtain a self-consistent implicit formula for the ferromagnet magnetisation: $M = N g_J \mu_B \tanh(g_J \mu_B B_{\mathrm{eff}}/(2k_B T))/(2V)$ with $B_{\mathrm{eff}} = B_{\mathrm{ext}} + \lambda M$.

9. Simple harmonic oscillators

The goal of this lecture is to model the vibrations of atoms in a crystal. As for the paramagnet in the previous lecture, let us consider a crystal made of N localised particles, so they are distinguishable even though they all are of the same kind. This crystal of fixed volume V is in thermal equilibrium with a thermostat at temperature T, so that the canonical ensemble is the natural choice to derive its thermodynamical properties.

In the simplest model, also known as *Einstein's model*, all the atoms of the crystal are assumed to be vibrating as *independent* simple harmonic oscillators at the same frequency in all three spatial dimensions (see Fig. 9.1). It should seem a strange model, as interactions between atoms *never* are negligible in solids. So why does the independent simple harmonic

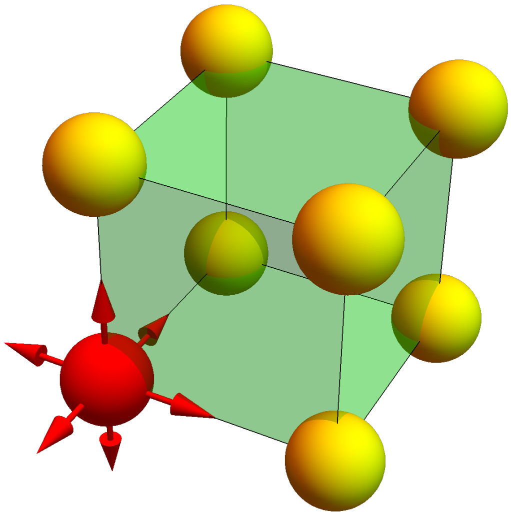

Figure 9.1: Schematic diagram of the three-dimensional vibrations (indicated by red arrows along the axes of symmetry) of atoms in a regular crystal.

oscillator model work at all? It is thanks to an approximation which is very commonly used in Statistical Mechanics: the *mean field* approximation.

To figure out how this approximation works, consider an atom that is part of the crystal. At zeroth order, it feels the $N-1$ other atoms *globally*, through a mean potential energy, $U_{\text{mean}}(\vec{r})$, which depends on its own position in the crystal, $\vec{r}$, but *not* on the position of the other atoms. Let us then define the position of this specific atom, $\vec{r}$, with respect to its equilibrium position in the crystal and let us assume (to simplify things) that the mean potential it sits in is *isotropic*, i.e. U_{mean} is only a function of the distance to equilibrium, r. As the atom will not stray very far from its equilibrium position in the crystal, let us expand $U_{\text{mean}}(r)$ around $r = 0$. This must be a *minimum* of the mean potential (necessary for the equilibrium to be stable), so we have:

$$\frac{\mathrm{d}U_{\text{mean}}(0)}{\mathrm{d}r} = 0 \quad \text{and} \quad \frac{\mathrm{d}^2U_{\text{mean}}(0)}{\mathrm{d}r^2} \equiv \kappa > 0 \tag{9.1}$$

At lowest order in r, we can thus write:

$$U_{\text{mean}}(r) = -U_0 + \frac{\kappa}{2}r^2 \tag{9.2}$$

where U_0 is the (positive) binding energy per atom in the crystal. Under such an approximation, each atom constitutes an *independent* simple harmonic oscillator since its energy is:

$$\varepsilon = \frac{\vec{p}^2}{2m} - U_0 + \frac{\kappa}{2}r^2 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{\kappa}{2}(x^2 + y^2 + z^2) - U_0 \tag{9.3}$$

where m is the mass of the atom and $\vec{p}$ its momentum. The crystal is thus composed of N such independent simple harmonic oscillators with the *same* angular frequency $\omega = \sqrt{\kappa/m}$.

9.1 The 1-D case

Before we embark upon the quest to solve the full three-dimensional case, let us assume that our simple harmonic oscillators can only oscillate in one dimension, say along the $z-$axis. We know from our Quantum Mechanics lectures that the solution of Schrödinger's equation in this case leads to the following spectrum of energy levels:

$$\epsilon_n = -U_0^{(1D)} + \left(n + \frac{1}{2}\right)\hbar\omega \tag{9.4}$$

where $n \in \mathbb{Z}^+$ is the level number, and $\hbar = h/(2\pi)$ the reduced Planck constant. Note that the superscript $^{(1D)}$ indicates that the potential minimum is different from that of the full three-dimensional case. In contrast to the paramagnet, you will notice that there is an *infinite* number of energy levels for the crystal. However, just like for a paramagnet, these energy levels are equally spaced which makes matters easier from a mathematical point of view.

Applying our now standard three step approach, we first derive the single-particle partition function of the crystal:

$$\mathcal{Z}_1 = \sum_{n=0}^{+\infty} \exp\left(\beta\left(U_0^{(1D)} - (n + 1/2)\hbar\omega\right)\right) \tag{9.5}$$

which is a geometric progression with an infinite number of terms so

$$\mathcal{Z}_1 = \exp\left(\beta U_0^{(1D)}\right) \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)} \tag{9.6}$$

Since the atoms in the crystal are distinguishable (localised) and independent, its partition function then reads:

$$\mathcal{Z} = (\mathcal{Z}_1)^N = \exp\big(N\beta U_0^{(1D)}\big)\left(\frac{1}{2\sinh\big(-\beta\hbar\omega/2\big)}\right)^N \tag{9.7}$$

Finally the third step consists in deriving the thermodynamical properties of the crystal. Its internal energy is:

$$\begin{aligned} U &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \\ &= N\left(-U_0^{(1D)} + \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\big(\hbar\omega/(k_BT)\big) - 1}\right) \end{aligned} \tag{9.8}$$

So when $k_BT \gg \hbar\omega$, $\exp\big(\hbar\omega/(k_BT)\big) \simeq 1 + \hbar\omega/(k_BT)$ and $U \simeq Nk_BT$, i.e. U is independent of the properties of the oscillators! This is a consequence of the *classical theorem of equipartition of energy*, which we will state and demonstrate right now: when $k_BT \gg \hbar\omega$, our quantum harmonic oscillators behave like classical harmonic oscillators.

Theorem 9.1.1 — Classical theorem of equipartition of energy. If the energy of a classical system is the sum of N *quadratic* terms, and the system is in contact with a heat reservoir at temperature T, then the mean energy of the system is $\langle E\rangle = Nk_BT/2$.

Proof. Consider a system whose energy has a quadratic dependence on some variable and is interacting with a heat reservoir at temperature T. This system is thus able to borrow energy from its surroundings and give it back. What mean thermal energy $\langle E\rangle$ does it have? Mathematically, this means that the energy of the system has the form $E(x) = Ax^2$, where A is a positive constant, and x is the variable[*]. Let us assume that x can take any continuous value. As previously derived in the Statistical Mechanics lectures, the probability $p(x)$ of the system having a particular energy Ax^2 under the constraint of constant mean energy is given by:

$$p(x) = \frac{\exp(-\beta Ax^2)}{\int_{-\infty}^{+\infty}\exp(-\beta Ax^2)\,\mathrm{d}x} \tag{9.9}$$

so that the mean energy of the system is:

$$\begin{aligned} \langle E\rangle &= \int_{-\infty}^{+\infty} E(x)p(x)\,\mathrm{d}x \\ &= \frac{\int_{-\infty}^{+\infty} Ax^2\exp(-\beta Ax^2)\,\mathrm{d}x}{\int_{-\infty}^{+\infty}\exp(-\beta Ax^2)\,\mathrm{d}x} \\ &= \frac{1}{2\beta} = \frac{k_BT}{2} \end{aligned} \tag{9.10}$$

where we have integrated by parts the numerator and then simplified away the denominator in the resulting expression. This is a remarkable result: the mean energy of the system is *independent* of the constant A and simply proportional to T! We leave it as an exercise to finish the proof, extending it to N quadratic terms (also called *modes* or *degrees of freedom*) by writing the energy of the system as $E = \sum_{i=1}^{N} A_i x_i^2$. ■

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[*] This is a very common situation in Physics, where x could be the velocity v, in which case the energy would be kinetic, or x could be the displacement of a mass attached to a spring, etc ...

Back to our one dimensional simple harmonic oscillator, we can now calculate its heat capacity at constant volume:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= N k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\big(\hbar\omega/(k_B T)\big)}{\Big(\exp\big(\hbar\omega/(k_B T)\big) - 1\Big)^2} \end{aligned} \tag{9.11}$$

• Note the similarity of the heat capacity of the crystal with that of the paramagnet: the $+$ sign in the term at the denominator for the paramagnet has become a $-$ sign here for the crystal, but otherwise the expressions are the same, provided you replace $2\mu_B B_{\text{ext}}$ by $\hbar\omega$.

• In a real system, the heat capacities due to magnetisation and oscillations will add up as they are independent from each other! This is also true for their internal energies. We will see how this additivity property works in more detail when we discuss the polyatomic gas.

9.2 The 3-D case

As each of the three directions of oscillation is independent, we can simply write the energy level spectrum of the crystal as:

$$\epsilon_{n_x,n_y,n_z} = -U_0^{(3D)} + \left(n_x + \frac{1}{2}\right)\hbar\omega + \left(n_y + \frac{1}{2}\right)\hbar\omega + \left(n_z + \frac{1}{2}\right)\hbar\omega \tag{9.12}$$

with n_x, n_y and $n_z \in \mathbb{Z}^+$ and independent of one another. So the three-dimensional single-particle partition function reads:

$$\mathcal{Z}_1^{(3D)} = \mathcal{Z}_1(x)\mathcal{Z}_1(y)\mathcal{Z}_1(z) = \left(\mathcal{Z}_1^{(1D)}\right)^3 \tag{9.13}$$

and similarly, the three-dimensional partition function is equal to

$$\mathcal{Z}^{(3D)} = \left(\mathcal{Z}^{(1D)}\right)^3 \tag{9.14}$$

Furthermore, as all thermodynamical potentials are functions of $\ln \mathcal{Z}$, we can directly write:

$$\begin{aligned} C_V^{(3D)} &= 3\, C_V^{(1D)} \\ &= 3\, N k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\big(\hbar\omega/(k_B T)\big)}{\Big(\exp\big(\hbar\omega/(k_B T)\big) - 1\Big)^2} \end{aligned} \tag{9.15}$$

Defining the *Einstein temperature*, $T_E \equiv \hbar\omega/k_B$, one can see that it depends on the properties of the crystal through the angular frequency $\omega \equiv \sqrt{\kappa/m}$, i.e. it decreases with the mass of the atoms and increases with the "spring constant" κ.

Note that $\kappa \equiv \mathrm{d}^2 U_{\text{mean}}(0)/\mathrm{d}r^2 \sim U_0/d^2$, where d is the distance between two neighbouring atoms. This distance is constant (up to a factor 2-3) for all materials, so κ is essentially a function of U_0, the depth of the potential well in which the atom is moving.

This leads to re-writing the three-dimensional heat capacity of the crystal as:

$$\boxed{C_V = 3\,Nk_B\left(\frac{T_E}{2T}\right)^2 \frac{1}{\sinh^2\left(T_E/(2T)\right)}} \tag{9.16}$$

where we have dropped the $^{(3D)}$ superscript for the sake of notation simplicity. Focussing on the high temperature regime, $T \gg T_E$, we get $C_V \simeq 3Nk_B$, which is independent of both temperature and the nature of the crystal considered! This is the so-called *Dulong & Petit law* discovered in 1819, and which we now know is a consequence of the classical theorem of equipartition of energy. In the low temperature regime, $T \ll T_E$, we have that $C_V \simeq 3\,Nk_B(T_E/T)^2\exp(-T_E/T)$ and $\lim_{T\to 0} C_V = 0$.

These considerations lead to the plot of C_V as a function of T displayed in Fig. 9.2.

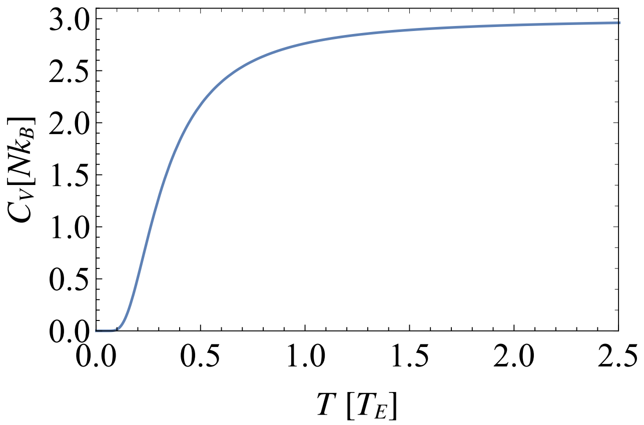

Figure 9.2: Heat capacity of a three-dimensional crystal due to atom vibrations, as a function of temperature.

R

- The importance of this simple Einstein model of a crystal *cannot* be underestimated. Indeed, it explicitly shows that the decrease in the heat capacity of solids at low temperature is *purely a quantum phenomenon*, like magnetisation!

- If you adjust the Einstein temperature for each crystal, it approximately reproduces the change in heat capacity as a function of temperature for *real* solids (see Einstein A., Annalen der Physik, 22, p87 (1907)).

A few things are worth emphasising about the limitations of this simple crystal model. For those of you who are (rightly) worried about the infinite number of energy levels, it must be noted that at *very* high temperatures, $T \gg U_0^{(3D)}/k_B$, the thermal energy overcomes the binding energy of the crystal and this latter *melts*. However, even before this catastrophic outcomes takes place, at lower thermal energies, the quadratic expansion of the potential will no longer be a valid approximation, and we will need to take into account higher order terms to provide an adequate description of the atom motion. So why sum over an infinity of energy levels even when the temperature is reasonable then? The reason is that the infinite sum converges very rapidly. Indeed, you can easily convince yourself that *any* energy level with an energy $> k_BT$ has a *very low* probability of being excited, so using the full infinite sum is an excellent approximation of the physically correct truncated sum.

At the other end of the temperature range, the Einstein model, while qualitatively correct, is quantitatively wrong at low temperatures. Experiments show that the heat capacity of solids goes to zero as $C_V \propto T^3$ rather than exponentially. As previously remarked, this exponential decay is a direct consequence of the existence of a minimal excitation quantum $\hbar\omega$, which is non-nil for the simple harmonic oscillator. This is the subject of the exercise below.

Exercise 9.1 Show that $C_V \propto \exp(-T_E/T)$ is an inevitable conclusion of the simple harmonic quantum oscillator model if $\hbar\omega \neq 0$. [hint: write the first two lowest energy levels of the system, ϵ_0 and ϵ_1, which are, by definition, such that $\epsilon_1 - \epsilon_0 = \hbar\omega$ and use them to calculate $\mathcal{Z}$ in the very low T limit.]
Ans: $C_V \simeq g_1/g_0\big(\hbar\omega/(k_BT)\big)^2 \exp\big(-\hbar\omega/(k_BT)\big)$ when $T \ll \hbar\omega/k_B$, with g_0 and g_1 the degeneracy coefficients of levels 0 and 1 respectively. ■

In other words, one can only hope to reproduce the experimental power law behaviour of the heat capacity at low temperatures if the energy level spectrum in the neighbourhood of the fundamental level, ϵ_0, is almost *continuous*. The solution of this conundrum is to realise, as Debye did, that the existence of a unique frequency of oscillation, ω, is linked to the assumption of *independence* of the oscillators. If one takes into account coupling terms, eigenfrequencies will differ from their initially identical values[†].

[†] Intuitively and physically, when an atom wanders away from its equilibrium position, it exerts a force on its neighbours, repelling those it is getting close to and attracting those it moves away from. These neighbours then act on their own neighbours and so on and so forth. So crystal vibrations are collective rather than individual at low temperature.

10. Polyatomic ideal gases

You have derived, in another part of the course, the partition function (and hence the thermodynamical properties) of the mono-atomic perfect gases. In this lecture, we will study the modifications that we need to introduce to describe an ideal gas composed of poly-atomic molecules[*]. Essentially, this means that we are going to take into account the *internal structure* of the gas particles instead of treating them as an ensemble of mathematical points. In other words, we will have to consider the extra degrees of freedom associated with the possibility that these particles/molecules can also vibrate and rotate ...

10.1 General case

Let us consider a gas of N *identical*, *non-interacting* molecules of mass m, enclosed in a recipient of fixed volume V, in contact with a thermostat at temperature T. We will assume that N is sufficiently large (so that the thermodynamic limit is reached), and that T is sufficiently large[†] and N/V sufficiently low (so that the mean occupation number of a single particle micro-state is low ($\ll 1$)).

> **R** This last assumption is also sometimes called the *Maxwell-Boltzmann approximation* as it yields the same partition function for bosons and fermions. The gas is therefore *classical* in the sense of *non-degenerate*.

We can then write the partition function of the gas as:

$$\mathcal{Z} = \frac{1}{N!}\mathcal{Z}_1^N \tag{10.1}$$

where the factorial of N term accounts for the fact that particles are *indistinguishable* and $\mathcal{Z}_1$ is the *single-particle partition function*. Up to this point, this is identical to what you have seen for the mono-atomic gas.

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[*] In truth, most of the lecture will focus on diatomic molecules for simplicity, but the way to generalise the results to molecules composed of more atoms will be outlined.

[†] Albeit lower than the ionization temperature of the gas ($T < 10^4$K).

Let us follow our three-step procedure and start with the first step of calculating $\mathcal{Z}_1$. As for the mono-atomic gas, the single particle Hamiltonian has a kinetic energy part, $\mathcal{H}_0 = \vec{p}^2/(2m)$, where $\vec{p}$ is the momentum of the particle, but also, and this is specific to poly-atomic gases, an internal structure part, which we won't make explicit for the moment and simply write as $\mathcal{H}_{\text{int}}$[‡]. In other words, we will write the single particle Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{int}} = \frac{\vec{p}^2}{2m} + \mathcal{H}_{\text{int}} \tag{10.2}$$

The internal degrees of freedom associated with $\mathcal{H}_{\text{int}}$ are *independent* of the translational motion degrees of freedom associated with $\mathcal{H}_0$[§].

> R Physically, you can understand this easily: it is only when molecules collide that a fraction of their translational kinetic energy can be transferred to rotational or vibrational internal motions (so called *inelastic* collisions). For ideal gases where collisions between particles are, by definition, ignored (*non-interacting* particles), such a coupling is thus neglected.

This means that a single-particle state, χ, will be defined by a monochromatic wave function with wave vector $\vec{k} = \vec{p}/\hbar$ which describes the eigenstates of $\mathcal{H}_0$, as in the mono-atomic gas case, *and* the quantum numbers describing the eigenstates of $\mathcal{H}_{\text{int}}$, i.e. the internal structure of the particle (including spin). In other words, if we label τ the ensemble of these internal structure quantum numbers, we have $\chi = \{\vec{k}, \tau\}$, and the corresponding energy levels are:

$$\varepsilon_\chi = \frac{\hbar^2 \vec{k}^2}{2m} + \epsilon_\tau \tag{10.3}$$

i.e. the sum of an eigenvalue of $\mathcal{H}_0$ and an eigenvalue of $\mathcal{H}_{\text{int}}$ (called η_τ here). So we have, using the usual notation $\beta = 1/(k_B T)$:

$$\begin{aligned}
\mathcal{Z}_1 &= \sum_\chi \exp(-\beta\varepsilon_\chi) \\
&= \sum_{\vec{k}} \sum_\tau \exp\left(-\beta\left(\frac{\hbar^2\vec{k}^2}{2m} + \epsilon_\tau\right)\right) \\
&= \frac{V}{(2\pi)^3} \int \sum_\tau \exp\left(-\beta\left(\frac{\hbar^2\vec{k}^2}{2m} + \epsilon_\tau\right)\right) \mathrm{d}^3k \\
&= \frac{V}{(2\pi)^3} \int \exp\left(-\beta\frac{\hbar^2\vec{k}^2}{2m}\right) \mathrm{d}^3k \times \left(\sum_\tau \exp(-\beta\epsilon_\tau)\right) \\
&= V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \times \xi(\beta)
\end{aligned} \tag{10.4}$$

where $\xi(\beta)$ is the single-particle partition function associated with the internal structure of the particle and we have taken advantage of the high enough temperature to replace the discrete sum over $\vec{k}$ by a continuous integral. In what follows, we will evaluate it explicitly for a diatomic molecule composed of two different atoms, but notice that $\xi(\beta)$ is *independent* of V.

[‡] We proceed this way because, as you will see, it will allow us to derive important results regarding the thermodynamical properties of a polyatomic gas which hold *regardless of the gas specific composition.*

[§] If you prefer, in Quantum Mechanics parlance, the operators $\mathcal{H}_{\text{int}}$ and $\mathcal{H}_0$ commute.

Having obtained $\mathcal{Z}_1$, we proceed to the second step of our procedure and calculate the partition function using equation (10.1):

$$\boxed{\mathcal{Z} = \frac{V^N}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2}\xi^N(T)} \tag{10.5}$$

Finally, in the third step, we derive thermodynamical quantities from $\mathcal{Z}$. As usual, we start with the Helmholtz free energy:

$$\begin{aligned} F &= -k_BT\ln\mathcal{Z} \\ &= -Nk_BT\left(\ln\frac{V}{N}+\frac{3}{2}\ln\frac{mk_BT}{2\pi\hbar^2}+1+\ln\xi(T)\right) \end{aligned} \tag{10.6}$$

where the final equality made use of the Stirling formula, $\ln N! \simeq N\ln N - N$.

R If you replace ξ by $2s+1$, you recover the mono-atomic case, as the spin s is the only internal degree of freedom of an atom.

F for a polyatomic gas has the same dependency on V than the mono-atomic gas F so

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} \tag{10.7}$$

meaning the ideal gas equation of state is valid *no matter* the internal structure of the molecules that compose it! However, the internal energy,

$$\begin{aligned} U &= -\frac{\partial\ln\mathcal{Z}}{\partial\beta} \\ &= Nk_BT\left(\frac{3}{2}+\frac{T}{\xi}\frac{\mathrm{d}\xi(T)}{\mathrm{d}T}\right) \end{aligned} \tag{10.8}$$

is the sum of two terms: one always equal to $3Nk_BT/2$ which corresponds to the translational degrees of freedom of the gas, and the other which corresponds to the internal degrees of freedom, which is *decoupled* from the other. So the heat capacity of ideal polyatomic gases at constant volume is *different* from that of ideal mono-atomic gases and in general will depend on temperature (but not on V). Indeed we have:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= Nk_B\left(\frac{3}{2}+\left(2-\frac{T}{\xi}\right)\frac{T}{\xi}\frac{\mathrm{d}\xi(T)}{\mathrm{d}T}+\frac{T^2}{\xi}\frac{\mathrm{d}^2\xi(T)}{\mathrm{d}T^2}\right) \end{aligned} \tag{10.9}$$

Exercise 10.1 Calculate the entropy, S, of a polyatomic gas. Does $S\to 0$ when $T\to 0$? Is this behaviour surprising?
Ans: $S = Nk_B\Big(\ln\left(V/N\right)+3\ln\left(mk_BT/(2\pi\hbar^2)\right)/2+5/2+\ln\left(\xi\right)+T/\xi\,\mathrm{d}\xi/\mathrm{d}T\Big)$. S does not go to zero when T does, because the classical gas approximation fails at low temperature, where quantum effects become important. ■

10.2 Freezing of internal degrees of freedom

Before we start explicitly calculating $\mathcal{H}_{\text{int}}$ terms, let us look at the low T behaviour of the contribution of the internal degrees of freedom to the gas properties.

In order to do this, we call ϵ_0 the lowest level of all the ϵ_τ possible energy levels (i.e. ϵ_0 is the fundamental level of internal structure), ϵ_1 the level just above it (i.e. ϵ_1 is the first excited level of internal structure), and define g_0 as the degree of degeneracy of ϵ_0 (i.e. g_0 is the number of independent quantum states with the same energy ϵ_0). If T is sufficiently low, i.e. $k_B T \ll \epsilon_1 - \epsilon_0$, all the terms in $\xi(\beta) = \sum_\tau \exp(-\beta\epsilon_\tau)$ are negligible in front of the g_0 first ones with energy ϵ_0, so that the internal structure single-particle partition function becomes $\xi(\beta) \simeq g_0 \exp(-\beta\epsilon_0)$, and its logarithm $\ln \xi \simeq -\beta\epsilon_0 + \ln g_0$. This means that at low T, all molecules are in the fundamental level of internal structure and as a consequence, all the properties of the polyatomic ideal gas reduce, by and large, to those of a mono-atomic ideal gas. The internal energy, U, is simply offset by a constant $N\epsilon_0$, but the heat capacity at constant volume, C_V is the same.

When this happens, one says that the internal degrees of freedom are *frozen* (or *blocked*). It is a pure quantum phenomenon, where the excitation of an internal mode is only possible if $k_B T$ is comparable or greater to the minimal excitation energy of that mode. By contrast, in a classical gas, *any* excitation energy is permitted.

10.3 Internal structure of polyatomic molecules

To a good approximation, the internal structure Hamiltonian is the sum of three independent terms:

$$\mathcal{H}_{\text{int}} = \mathcal{H}_e + \mathcal{H}_v + \mathcal{H}_r \tag{10.10}$$

where $\mathcal{H}_e$ is the Hamiltonian of the electrons of the molecule, $\mathcal{H}_v$ describes the vibrations of its atoms with respect to one another and $\mathcal{H}_r$ its rotational motion in space.

R We should add to this list a 4th term which describes the internal structure of the nuclei of the atoms which compose the molecule. However, the excitation energy of these nuclei are on the order of the MeV (or equivalently $T \sim 10^{10}$K). So the degrees of freedom associated with the nuclei are frozen and we neglect them in what follows.

10.3.1 $\mathcal{H}_e$

Even individual atoms possess an internal structure associated with discrete energy levels. However, the excitation energies of e^- in atoms and molecules are of the order of as few eV, i.e. several 10,000 K. So it is only at very high temperatures that the internal structure of atoms may play a role. Until the temperature reaches a few 1000 K, the degrees of freedom associated with e^- are frozen, so they are generally ignored.

R • Exceptions exist, like the *fine structure* of the fundamental level of atoms and molecules. Remember the paramagnet lecture, and consider an atom/molecule with $\vec{L}$ and $\vec{S}$, the total orbital angular momentum and total spin of its e^- respectively, which both have *non-nil* values in the fundamental state. This is not common, but if it occurs the fundamental level is split into fine structure sub-levels due to the coupling between $\vec{L}$ and $\vec{S}$. The number of these sub-levels is equal to the number of different possible values for the total angular momentum $\vec{J}$: $j = l+s, l+s-1, \cdots, |l-s|$. The energy difference between these sub-levels generally are around a few 10^{-2} eV, i.e. $T_e \sim$ a few 100 K, so when the temperature of the thermostat is of that order, one has to account for the fine structure when calculating $\mathcal{Z}_1$ (e.g. for the molecule N-O with

0.015 eV or $T_e \simeq 175$ K). If $T \gg T_e$, one can consider all the fine structure sub-levels as degenerate, and so the e^- degrees of freedom are frozen but with degeneracy factor $g_0 = (2l+1)(2s+1)$.

• Finally, note that the fundamental level of atoms/molecules can also have a *hyperfine structure* due to the coupling between nuclei spin and the angular momentum of e^-. However the differences in energy between hyperfine levels (6×10^{-6} eV or equivalently 7×10^{-2} K for the Hydrogen atom, and higher for other atoms but never above 1.5 K). One therefore "neglects" hyperfine structure and considers all hyperfine sub-levels as degenerate. For atoms with nuclei spin s_n, $\mathcal{Z}_1$ is multiplied by $(2s_n+1)$, and for molecules by $(2s_{n_i}+1)$ where n_i, with $i \in \mathbb{Z}^+$ are the nuclei of the atoms which compose the molecule.

10.3.2 $\mathcal{H}_v$ – Vibration of a diatomic molecule

Let us first consider a molecule composed of only two atoms. To study its structure we will use what is known as the *Born-Oppenheimer approximation*: we will assume that its nuclei, much more massive than the e^- are separated by a fixed distance, r. We then calculate the lowest energy value for the e^- corresponding to this spacing r between nuclei using Quantum Mechanics.

The energy of the system composed of the two nuclei and the e^- is a function $u(r)$ of the distance r, which, if the atoms can form a stable molecule, will possess a deep enough minimum for bound states to exist (see Fig. 10.1). The equilibrium distance, d, between the two nuclei corresponds to this minimum, as indicated on the figure. However, the nuclei can vibrate with respect to one another, so their separation distance r oscillates around d. This vibration is equivalent to the motion of a fictitious particle with reduced mass $m_r = m_1 m_2/(m_1+m_2)$, where m_1 and m_2 are the masses of the two nuclei, in the potential drawn on Fig 10.1.

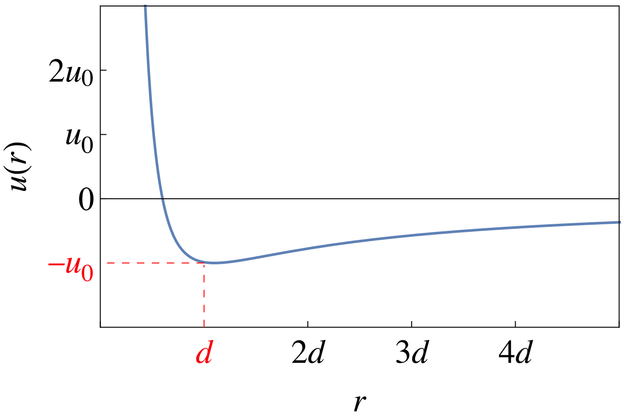

Figure 10.1: Potential energy of a diatomic molecule as a function of the distance r, between the two nuclei. Note the electrostatic repulsion (sharp rise) at short distances.

In the limit of small oscillations (or if you prefer in the limit of small extensions to the quantum wave function), from the lecture on the solid crystal, we recognize a one-dimensional harmonic oscillator with angular frequency $\omega = \sqrt{\kappa/m_r}$ where κ is the curvature of $u(r)$ at its minimum u_0, i.e. for the equilibrium distance d. So the vibration energy levels from the minimum u_0 are given by

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad \text{with} \quad n \in \mathbb{Z}^+ \tag{10.11}$$

and the level ϵ_n is *non-degenerate*, i.e. it corresponds to a unique quantum state of vibration. In this case, the single-particle partition function writes:

$$\xi_v(\beta) = \sum_{n=0}^{+\infty} \exp\big(-\beta(n+1/2)\hbar\omega\big) \tag{10.12}$$

and the associated internal energy:

$$U_v = -N\frac{\mathrm{d}\ln\xi_v}{\mathrm{d}\beta} = N\hbar\omega\left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1}\right) \tag{10.13}$$

The extra heat capacity of the gas due to molecule vibration thus reads:

$$\boxed{C_V^{(v)} = Nk_B\frac{\big(\hbar\omega/(2k_BT)\big)^2}{\sinh^2\big(\hbar\omega/(2k_BT)\big)} = Nk_B\frac{\big(T_v/(2T)\big)^2}{\sinh^2\big(T_v/(2T)\big)}} \tag{10.14}$$

where we have defined the *characteristic vibrational temperature* as $T_v \equiv \hbar\omega/k_B$. We can see that for $T \ll T_v$, we have $C_V^{(v)} \to 0$ like $Nk_B(T_v/T)^2\exp(-T_v/T)$. On the other hand, for $T \gg T_v$, $C_V^{(v)} \simeq Nk_B$, i.e. is independent of temperature, in line with the classical theorem of equipartition of energy applied to the one dimensional harmonic oscillator. These considerations lead to the diagram 10.2.

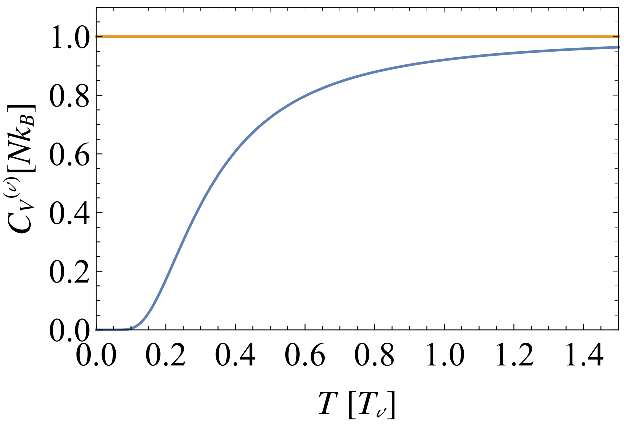

Figure 10.2: Heat capacity of a diatomic molecule due to vibration, as a function of temperature.

T_v increases when the inter-atomic forces increase, but varies between a few hundred K (463 K for the molecule Br_2) to a few 1000 K (6215 K for H_2).

– Vibration of a polyatomic molecule

If the molecules are composed of $q \in \{3, 4, \cdots, +\infty\}$ atoms, the number of degrees of freedom for vibrations q_v, i.e. the number of variables necessary to characterise the relative positions of their q nuclei, is $q_v = 3q - 6$. Indeed, one has to account for the positions of all nuclei of the molecule and remove the coordinates of its centre of mass (3 degrees of freedom corresponding to the translational motion), along with the 3 Euler angles[¶] necessary to describe the orientation of the molecule in space (associated with the degrees of freedom of rotational motion as we will see later on).

The potential energy $u(r)$ becomes $u(r_i)$ where the index $i \in \{q_v\}$ and the nuclei are located at equilibrium distances d_i. We are thus dealing with a system of q_v coupled harmonic oscillators, which can be shown to be equivalent to a fictitious system of q_v one-dimensional independent harmonic oscillators. So the generalisation from the diatomic molecule heat capacity to that of the polyatomic molecule is quite straightforward:

$$C_V^{(v)} = Nk_B \sum_{i=1}^{q_v} \frac{\big(T_{v,i}/(2T)\big)^2}{\sinh^2\big(T_{v,i}/(2T)\big)} \tag{10.15}$$

where $T_{v,i} \equiv \hbar\omega_i/k_B$ represents the different characteristic vibrational temperatures of the polyatomic molecule.

10.3.3 $\mathcal{H}_r$

Molecules also possess rotational excitation modes which correspond to their rotational kinetic energy in three-dimensional space. We will assume in what follows that distances between nuclei remain constant during the rotation of the molecule, i.e. the molecule behaves as a *rigid rotator*[‖].

– Rotation of a diatomic molecule

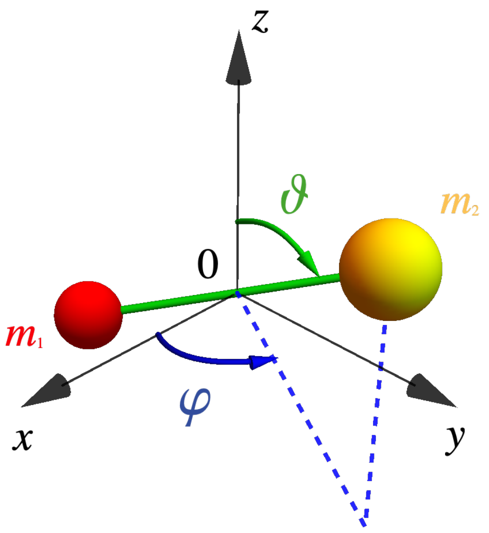

Figure 10.3: Schematic diagram of a diatomic molecule showing its orientation in three-dimensional space. The origin of the coordinate system is located at the centre of mass of the molecule. Distances r_1 and r_2 separate the origin from the nuclei of the molecule's atoms. The distance $d = r_1 + r_2$ separating the two nuclei is the length of the green rod.

[¶] Unless the molecule is linear, in which case 2 Euler angles are enough and $q_v = 3q - 5$ in this case.

[‖] In other words we neglect the centrifugal force felt by the nuclei during rotation.

As is clear from the diagram 10.3, the position of the centre of mass of the molecule is already accounted for in the degrees of freedom associated with the translational motion of the molecule, so its orientation in space is simply given by two Euler angles ϑ and φ.

The rotational kinetic energy of such a molecule, is, according to your Classical Mechanics lectures,

$$\epsilon_r = \frac{\mathcal{I}}{2}\left(\left(\frac{\mathrm{d}\vartheta}{\mathrm{d}t}\right)^2 + \left(\frac{\mathrm{d}\varphi}{\mathrm{d}t}\right)^2 \sin^2\vartheta\right) = \frac{\vec{L}^2}{2\mathcal{I}} \tag{10.16}$$

where $\vec{L}$ is the angular momentum of the molecule and $\mathcal{I}$ the moment of inertia with respect to its centre of mass, i.e. w.r.t. any axis going through the centre of mass and perpendicular to the molecule axis. For a diatomic molecule, we have[**] $\mathcal{I} = m_r\, d^2$, keeping the notation for the reduced mass m_r and equilibrium separation d that we introduced for these molecules in the lecture on vibrations.

So the Quantum Mechanics Hamiltonian associated to the rotation of such linear molecules is:

$$\mathcal{H}_r = \frac{\vec{\mathcal{L}}^2}{2\mathcal{I}} \tag{10.17}$$

where $\vec{\mathcal{L}}$ is the *orbital* angular momentum operator. From your Quantum Mechanics lectures, you know the stationary states of rotation. The corresponding wave functions are the so-called spherical harmonics $\mathcal{Y}_l^m(\vartheta,\varphi)$, where $l \in \mathbb{Z}^+$ and $m \in \{-l, \cdots, l\}$. The energy levels associated to these states depend only on l, *not* on m, i.e. these levels are $2l+1$ degenerate:

$$\epsilon_{l,m} = \frac{\hbar^2}{2\mathcal{I}} l(l+1) \tag{10.18}$$

and following what we did for vibrations, we introduce a *characteristic rotational temperature* $T_r \equiv \hbar^2/(2\mathcal{I}k_B)$.

R For light molecules with small $\mathcal{I}$, T_r can be quite high (85 K for H_2). However for the vast majority of molecules T_r is much lower, around a few K. So except for molecular hydrogen, one is practically always in the case where $T \gg T_r$, and the rotational degrees of freedom of the molecule are *not* frozen and can be treated classically (i.e. considered as continuous).

Let us consider a molecule made of two *different* atoms, like HCl. Its single-particle partition function is:

$$\begin{aligned}
\xi_r(\beta) &= \sum_{l=0}^{+\infty} \sum_{m=-l}^{+l} \exp(-\beta\epsilon_{l,m}) \\
&= \sum_{l=0}^{+\infty} (2l+1)\exp\left(-\beta\frac{\hbar^2}{2\mathcal{I}} l(l+1)\right) \\
&= 1 + 3\exp(-2\,T_r/T) + 5\exp(-6\,T_r/T) + 7\exp(-12\,T_r/T) + \cdots
\end{aligned} \tag{10.19}$$

There is no simple method to evaluate this infinite sum exactly, however two important remarks can be made. First, in the infrequent case where $T \le T_r$, one should remember

---

[**] Note that we neglect any rotation around the molecule axis because the moment of inertia in that case would be due to the e^- instead of the nuclei and therefore about 2000 times smaller given the mass difference.

that the terms of the sum decay rapidly, so that a good approximation can be obtained by considering only the first few ones and neglecting the rest. Second, in the most likely case where $T \gg T_r$, two consecutive terms are "close enough" to allow us to approximate the discrete sum over l by a continuous integral, thus writing:

$$\xi_r(\beta) \simeq \int_{l=0}^{+\infty} (2l+1) \exp\left(-\beta \frac{\hbar^2}{2\mathcal{I}} l(l+1)\right) \mathrm{d}l \tag{10.20}$$

which, after the change of variable $y = l(l+1)$ yields

$$\xi_r(T) \simeq \frac{T}{T_r} \tag{10.21}$$

The associated internal energy for $T \gg T_r$ thus reads:

$$U_r = -N \frac{\mathrm{d} \ln \xi_r}{\mathrm{d}\beta} = N k_B T \tag{10.22}$$

as expected from the classical equipartition of energy theorem since we have summed two quadratic terms (in the kinetic energy of rotation of the molecule, see equation (10.16)). In this high temperature regime, the extra heat capacity of the gas due to molecule rotation is thus simply:

$$C_V^{(r)} = N k_B \tag{10.23}$$

Exercise 10.2 Estimate $C_V^{(r)}$ in the low temperature regime ($T \leq T_r$) by assuming that all the other terms in the sum (10.19) are negligible in front of the first two. What is the limit of $C_V^{(r)}$ when $T \to 0$?

Ans: $C_V^{(r)} = 12 k_B (T_r/T)^2 \exp(-2T_r/T) / \big(1 + 3\exp(-2T_r/T)\big)^2$, so $\lim_{T\to 0}\ C_V^{(r)} = 0$. ■

Numerically evaluating the sum (10.19) (and given the limits at low and high T that we have previously estimated), we arrive to the following graph for the heat capacity of a diatomic molecule:

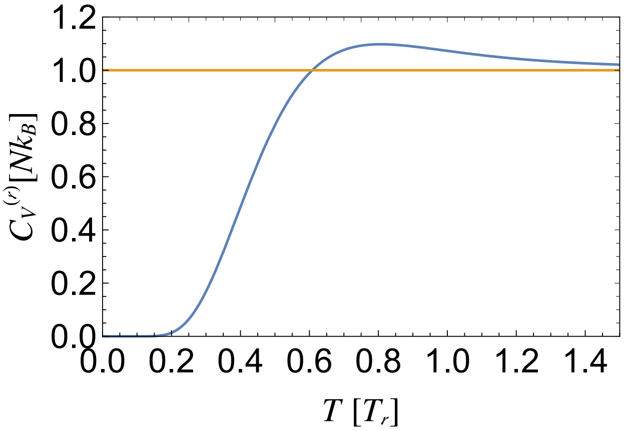

Figure 10.4: Heat capacity of a diatomic molecule due to rotation, as a function of temperature.

What if the two atoms constituting the molecule are *identical*, like H_2, O_2, N_2? In this case, one has to take into account the quantum principle of symmetrisation to count its states. The only states allowed are those which are symmetrical when the two nuclei are swapped if these nuclei are bosons with integer spin, or anti-symmetrical if the nuclei are fermions with half-integer spin. You can see that that while the translational motions can safely ignore this constraint as they deal with the motion of the centre of mass of the molecule and not the relative position of the two nuclei[††], this is not the case for rotations which can swap nuclei positions (e.g. $\vartheta \to \pi - \vartheta$ and $\varphi \to \pi + \varphi$). One can show that (left as an exercise), in that case, whether for bosons or fermions, if $T \gg T_r$, the single-particle partition function is:

$$\xi_r(T) \simeq (2s_n + 1)^2 \frac{T}{2T_r} \tag{10.24}$$

where s_n is the nuclear spin. Therefore both U_r and $C_V^{(r)}$ are the same as for a molecule with two different atoms.

– Rotation of a polyatomic molecule

What about if the molecule is composed of more atoms than just two? Well, we have to distinguish between two cases. First, and most simple, is the case where the molecule is *linear*. Then we can develop arguments like those we used for the diatomic molecule, leading to

$$\xi_r(T) \simeq \frac{1}{\sigma}\frac{T}{T_r} \tag{10.25}$$

where σ is called the *symmetry factor* and has values of 1 for non-symmetric molecules such as N_2O (N-N-O) or 2 for symmetric molecules such as CO_2 (O-C-O)[‡‡]. As a consequence, both U_r and $C_V^{(r)}$ are the same as for a diatomic molecule.

The second case is that of a *non-linear* molecule. It thus possesses three degrees of rotational freedom. Consider that it is rotating like a rigid block so we can apply the classical results of solid kinematics: we have to define three moments of inertia $\mathcal{I}_1$, $\mathcal{I}_2$ and $\mathcal{I}_3$ with respect to its principal axes of inertia. We need three Euler angles to characterise the rotation, and three characteristic rotational temperatures (one per moment of inertia) $T_{r,p} \equiv \hbar^2/(2k_B\mathcal{I}_p)$ with $p \in \{1,2,3\}$. In practice, we almost always have $T \gg T_{r,p}$ and therefore have:

$$\xi_r(T) \simeq \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T}{T_{r,1}}}\sqrt{\frac{T}{T_{r,2}}}\sqrt{\frac{T}{T_{r,3}}} \tag{10.26}$$

where σ is a symmetry factor exactly like in the case of a linear molecule, except its values are not limited to 1 or 2. For instance, the benzene molecule, C_6H_6 has $\sigma = 12$. More importantly however, this leads to $U_r = 3Nk_BT/2$ and $C_V^{(r)} = 3Nk_B/2$ in the high temperature regime, again in agreement with the classical theorem of equipartition of energy.

10.3.4 Putting C_V all together

As translational, rotational and vibrational motions are considered *independent* of one another, the total heat capacity at constant volume of the molecular gas, C_V is simply the

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[††] The same is true for vibrations which only depend on the distance r between nuclei and are therefore invariant upon the permutation of these latter.

[‡‡] You can understand this intuitively: if the molecule is symmetric, you do not change the single-particle partition function by swapping the symmetric nuclei, so you have to divide the total number of states by 2.

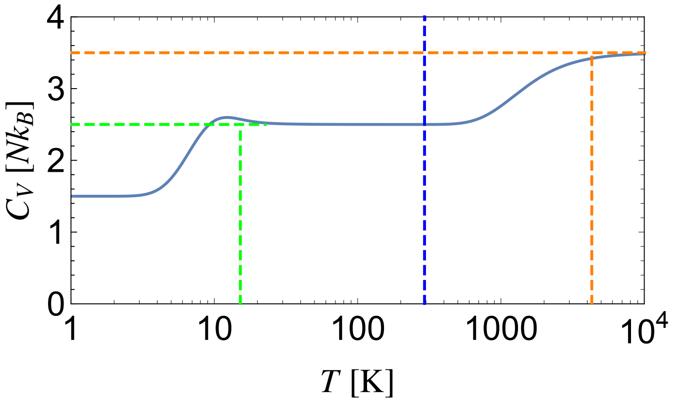

Figure 10.5: Total heat capacity of the HCl diatomic molecule ($T_r = 15.2$K and $T_v = 4303$K indicated by vertical green and orange dashed lines respectively) due to translational, rotational and vibrational motions, as a function of temperature. The blue vertical dashed line represents a typical lab temperature of 293K, and is given for reference.

sum of all the contributions. This yields in the high temperature regime ($T \gg T_{r,p}$):

$$\begin{aligned} C_V &= C_V^{(t)} + C_V^{(r)} + C_V^{(v)} \qquad (10.27) \\ &= \frac{3}{2} N k_B + \left\{ \begin{array}{ll} N k_B & \text{(linear molecule)} \\ \frac{3}{2} N k_B & \text{(non} - \text{linear molecule)} \end{array} \right. + N k_B \sum_{i=1}^{q_v} \frac{\left(T_{v,i}/(2T)\right)^2}{\sinh^2\left(T_{v,i}/(2T)\right)} \end{aligned}$$

where the different characteristic vibrational temperatures, $T_{v,i}$ are associated with the different vibrational modes which will be excited in turn as T increases. So some of them will be in the classical limit while others are still frozen! Finally, for a diatomic molecule, this sum of terms simplifies to $N k_B \left(T_v/(2T)\right)^2 / \sinh^2\left(T_v/(2T)\right)$ and contributes accordingly to the total C_V plotted in Fig. 10.5.

III

Thermodynamics of Radiation

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11. Electromagnetic waves & photons

We will consider here a system of photons, i.e. of the massless particles which are the quanta associated with the electro-magnetic field. The behaviour of such photon "gases" in thermal equilibrium can be analysed experimentally by measuring the thermodynamical properties of the electro-magnetic radiation.

R
- This is a very intuitive process: everybody knows that when you heat e.g. steel to make a sword, the metal radiates in the visible part of the electro-magnetic spectrum ... it glows red!
- As we will see, photons are special bosons: their number is not conserved, which gives them a very peculiar statistical behaviour: their chemical potential is nil.

Definition 11.0.1 We call *blackbody* a closed cavity which contains a photon gas in thermal equilibrium with a thermostat.

R
- It is easy to make a blackbody in practice. All one needs to do is to take a container of volume V and keep it at constant temperature T. A system of electro-magnetic waves is spontaneously created within the container, i.e. in Quantum Mechanical parlance, a system of photons. The physical quantities associated with this system can be measured by poking a hole of negligible size in one of the container walls and observe the characteristics of the radiation emitted through it[*].
- The characteristics of this radiation have been well known since the end of the 19th century, and their analysis led Planck in 1900 to formulate the "quantum hypothesis", starting point of the scientific revolution which led to the discovery of Quantum Mechanics[†].

---

[*] Also called blackbody radiation or thermal radiation.

[†] This is sometimes referred to as the "ultra-violet" catastrophe because as we will see, in the classical formulation of Maxwell's, each electro-magnetic wave behaves like an independent harmonic oscillator, and so an infinite number of them implies infinite energy, which is contributed mostly from short wavelengths, hence the ultra-violet name. This issue is resolved in Quantum Mechanics because quantum harmonic oscillators *cannot* take any continuous energy value.

11.1 Electro-magnetic eigenmodes of a container

Our starting point will be the classical theory of electro-magnetism, with the goal to use it to determine the individual quantum states that the system of photons can occupy. In other words we will follow in Planck's footsteps.

Let us consider, without loss of generality, an empty cubic container of size L. From a classical point of view, the most general electro-magnetic field that can exist inside this container is given by Maxwell's equations. Since these equations are linear, their general solution is a linear superposition of monochromatic elementary solutions that fulfil the boundary conditions imposed by the container walls. These monochromatic solutions are called the *eigenmodes* of the cavity.

Let us derive them. Consider the case were the walls of the cavity are perfectly reflecting[‡]: this enforces strict boundary conditions, in the sense that both the tangential component of the electric field, $\vec{E}$, and the normal component of the magnetic field, $\vec{B}$, must vanish at the walls[§]. Such boundary conditions allow to use simple progressive monochromatic plane waves to describe the spatial and temporal and dependence of all $\vec{E}$ and $\vec{B}$ field components, i.e. these two fields will be a sum of terms of the form $\exp\big(i(\vec{k}\cdot\vec{r}-\omega t)\big)$, where $\vec{k}$ is the wave vector, $\vec{r}$ is the position vector and ω is the angular frequency. Maxwell's equations in vacuum enforce $\|\vec{k}\| \equiv k = \omega/c$ with c the speed of light. The boundary conditions restrict the values of $\vec{k}$ to $k_x = n_x\,2\pi/L$, $k_y = n_y\,2\pi/L$, $k_z = n_z\,2\pi/L$, where n_x, n_y and $n_z \in \mathbb{Z}$[¶]. Maxwell's equations also imply that for each $\vec{k}$, the $\vec{E}$ and $\vec{B}$ fields of that wave are perpendicular to $\vec{k}$ and perpendicular to one another: this allows two independent polarization states in the plane perpendicular to $\vec{k}$.

In summary, an electro-magnetic eigenmode of our cubic cavity is characterized by an eigenvector $\vec{k}$ such that its components obey $k_x = n_x\,2\pi/L$, $k_y = n_y\,2\pi/L$, $k_z = n_z\,2\pi/L$ and a polarization state. Its angular frequency is given by $k = \omega/c$ and the most general electro-magnetic field that can exist in the cavity is a linear combination of eigenmodes thus defined. For macroscopic applications we want to know the number of eigenmodes, $g(\omega)\,\mathrm{d}\omega$, whose angular frequencies are comprised in the interval $[\omega, \omega + \mathrm{d}\omega]$. We can calculate this number by counting the number of eigenmodes whose wave vector $\vec{k}$ has a modulus between $[k, k + \mathrm{d}k]$. This number is $2 \times \big(L/(2\pi)\big)^3 \times 4\pi k^2\,\mathrm{d}k$, where the three multiplicative factors represent the number of polarization states, the inverse volume of an elementary cell and the volume of a spherical shell in $k-$space respectively. Replacing k by ω/c and $\mathrm{d}k$ by $\mathrm{d}\omega/c$, we obtain the *classical* spectral density of eigenmodes:

$$g(\omega) = \frac{L^3\omega^2}{\pi^2 c^3} = \frac{V\omega^2}{\pi^2 c^3} \tag{11.1}$$

11.2 Quantification of eigenmodes: photons

If we remained in the classical world, the amplitude of each eigenmode (i.e. of the corresponding $\vec{E}$ and $\vec{B}$ fields) and consequently its energy, could take any continuous value

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[‡] This is the case where the container is made of a perfect conductor.

[§] As usual, real life boundary conditions are more complex than that, but it is not necessary to know them perfectly to determine the macroscopic behaviour of the system. In other words, we can choose "perfect" boundary conditions, as long as the size of the box L is much larger than the particle de Broglie wavelength, $\lambda_B \equiv h/p$, where p is the momentum of the particles, they will not affect the behaviour of the system.

[¶] This calculation is very similar to the one you have already seen for the wave function of an ideal gas in a box. Note that the eigenmode $n_x = n_y = n_z = 0$, i.e. $\vec{k} = \vec{0}$ and $\omega = 0$ must, in general, be set aside. It exists whatever the size of the cavity and corresponds to a constant electro-magnetic field, but given our specific choice of boundary conditions its amplitude is equal to zero.

in $[0, +\infty]$. In reality, the energy of the electro-magnetic field, as that of a material system is quantified.

More precisely, to an electro-magnetic wave with wave vector $\vec{k}$ and angular frequency ω, we can associate particles called photons whose momentum $\vec{p}$ and energy ϵ are given by the Planck-Einstein relations $\vec{p} = \hbar\vec{k}$ and $\epsilon = \hbar\omega$[‖]. From $k = \omega/c$, we thus get that $\epsilon = \|\vec{p}\|c \equiv pc$ for photons. If one compares this relation between energy and momentum to that of a particle of mass m given by special relativity, $\epsilon = \sqrt{p^2c^2 + m^2c^4}$, one deduces that photons must be massless particles. The two possible polarization states of the electro-magnetic wave with wave vector $\vec{k}$ translate into two independent spin states[**] for the corresponding photons with momentum $\vec{p} = \hbar\vec{k}$. So a classical eigenmode characterized by $\vec{k}$ and a polarization state appears as a possible individual state for photons trapped in the cavity[††].

From the classical spectral density of eigenmodes (11.1) (and using $\omega = \epsilon/\hbar$ and $\mathrm{d}\omega = \mathrm{d}\epsilon/\hbar$), we therefore deduce the following individual density of state for photons:

$$g(\epsilon) = \frac{V\epsilon^2}{\pi^2\hbar^3c^3} \tag{11.2}$$

11.3 Statistical properties of photons

11.3.1 Peculiarities of photons

- As their spin is an integer, they are bosons.
- They do not interact with one another, but only with the cavity walls which is how the system reaches thermal equilibrium, so they constitute an ideal gas.

> R Truly speaking, this last statement is not correct, as you will see when you study Quantum Electro Dynamics (the theory of quantification of the electro-magnetic field which accounts for its coupling to charged particles). Pairs of photons can interact to momentarily produce an e^-e^+ pair for instance. However this effect scales like α^2 times the coupling between matter and radiation which thermalises, where $\alpha \equiv 1/137$ is the fine structure constant, so it is negligible for our blackbody study.

- Their number is *not* conserved. This is a new situation. To better understand what it means, let us look more closely at how the electro-magnetic field, i.e. the photon gas, arises in the cavity and reaches thermal equilibrium. As the walls are kept at constant temperature T, thermal agitation sets the charged particles they contain (essentially the e^-) in motion. These random motions create (classically) random electro-magnetic fields which propagate freely inside the cavity and in turn induce motions of the charged particles in its walls. So a (quite) weak coupling (for a macroscopic cavity) exists between the photon gas and the matter that makes the walls. This drives the system to thermal equilibrium.

> R One could think that since walls are made of atoms, emission lines specific to these atoms would preferentially appear in the blackbody radiation spectrum, which would

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[‖] This means that the energy of the wave with angular frequency ω is $N_\omega\,\hbar\omega$ where N_ω is the number of photons the wave is made of.

[**] This does not mean, however that the photon is a fermion with spin $s = 1/2$. A more careful study shows that photons are bosons with spin $s = 1$, and the reason why the spin can only be ±1 and not 0 is that for massless particles, the momentum $\vec{p}$ can never be $\vec{0}$ since their speed must remain equal to c no matter the reference frame chosen. Choosing $\vec{p}$ as the quantification axis, the only two possible states are therefore $\pm\, s\hbar$ for the projected value of the spin along this axis. These correspond to the left and right circular polarization of the corresponding electro-magnetic wave.

[††] Note that we naturally excluded the classical mode $\vec{k} = \vec{0}$ in this quantification.

then be expected to depend on the nature of the walls. However, this does not happen: the structure of the walls is sufficiently rich that *all* frequencies are coupled to the thermostat (vibration of atoms, impurities, defects, etc ...). So at equilibrium, the number of photons of a given frequency solely depends on the temperature T of the thermostat.

The coupling thus described looks similar to what happens with paramagnets or molecules: the photons exchange energy with the thermostat to reach thermal equilibrium and the total energy is conserved in these exchanges. However, the fundamental difference with these other systems is that the interaction between matter and radiation occurs through the absorption or emission of photons, so that their total number does not remain constant. This is *not* a situation where the number of particles can fluctuate by exchanging some with a reservoir, so that the total number of particles (gas + reservoir) remains constant either. This is a *completely* different physical problem in which the total number of particles is *not* conserved.

11.3.2 Photon distribution function

So how do we resolve this issue? In the same way you derived the Bose-Einstein statistics, but realizing that the constraint of fixed mean number of particles does not apply, so that the Lagrange multiplier $-\beta\mu$, or equivalently the chemical potential of the photons, μ (since $-\beta = -1/(k_B T)$ is fixed), must be *nil* [‡‡]. This immediately yields the following mean occupation number of a single-particle state i for photons:

$$\bar{n}_i = \frac{1}{\exp\big(\epsilon_i/(k_B T)\big) - 1} \tag{11.3}$$

R
- $\epsilon_i = 0$ is naturally excluded as it corresponds to $\vec{k} = \vec{0}$, which, as we have seen, is impossible for photons. So the divergence of $\bar{n}_i$ when $\epsilon_i \to 0$ is irrelevant.
- Bose-Einstein condensation *cannot* happen for photons: one cannot fix the total number of particles, it is μ which stays constant instead!

[‡‡] In other words, the grand canonical ensemble is the natural choice here as the number of particles varies, but the mean number of particles, $\bar{N}$, is *not* constrained, so its associated Lagrange multiplier must be nil.

12. Blackbody radiation laws

12.1 Planck's law

This is the fundamental law from which one can deduce all the others. It concerns the spectral electro-magnetic energy density $u(\omega, T)$ of the blackbody. Max Planck discovered it empirically before demonstrating it from the notion of quantification[*].

Within a cavity of macroscopic volume V as defined in the previous chapter, individual possible energies for photons can practically be considered as continuous, and when thermal equilibrium with the thermostat at temperature T is reached, the mean occupation number $\bar{n}$ of an individual state with energy ϵ[†] thus reads:

$$\bar{n}(\epsilon, T) = \frac{1}{\exp\big(\epsilon/(k_B T)\big) - 1} \tag{12.1}$$

Assume that the system considered is sufficiently large so that one can neglect fluctuations (i.e. we are in the thermodynamical limit). The number of photons $\mathrm{d}N(\epsilon, T)$ which have individual energy in the range $[\epsilon, \epsilon + \mathrm{d}\epsilon]$ at temperature T is obtained by multiplying the number of photons occupying each of the individual states (12.1) by the number of such states, $g(\epsilon)\,\mathrm{d}\epsilon$:

$$\mathrm{d}N(\epsilon, T) = \bar{n}(\epsilon, T) g(\epsilon)\,\mathrm{d}\epsilon \tag{12.2}$$

As each of them has energy ϵ (with error $\mathrm{d}\epsilon$), plugging in equation (11.2) for $g(\epsilon)$, the total energy $\mathrm{d}U(\epsilon, T)$ of this system of photons is:

$$\mathrm{d}U(\epsilon, T) = \epsilon\,\mathrm{d}N(\epsilon, T) = \frac{\epsilon}{\exp\big(\epsilon/(k_B T)\big) - 1}\left(\frac{V\epsilon^2}{\pi^2\hbar^3 c^3}\right)\mathrm{d}\epsilon \tag{12.3}$$

and since $\epsilon = \hbar\omega$ for a photon, we get $\mathrm{d}U(\epsilon, T) = V u(\omega, T)\,\mathrm{d}\omega$, with

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[*] We will discuss more in detail later in this chapter why the mathematical form of u for the blackbody contradicts the classical theory of electromagnetism.

[†] Note that we have dropped the subscripts i for $\bar{n}$ and ϵ in equation (11.3) in order to simplify notation.

Law 8 — Planck's law.

$$u(\omega,T)=\frac{\hbar\omega^3}{\pi^2c^3}\,\frac{1}{\exp\big(\hbar\omega/(k_BT)\big)-1} \tag{12.4}$$

R The Planck law is *only* valid in the case where the radiation is in thermal equilibrium with a thermostat. This constitute an important restriction, as in practice most emission/absorption of photons takes place *out of* equilibrium. Arguably the most common example is lighting by an electric lamp which *irreversibly* transforms electric energy into radiation.

12.2 How does it look like?

Let us draw u as a function of ω for a fixed T. As usual, we identify the function main features (asymptotic behaviour, extrema) to do so:

- At low frequencies, when $\hbar\omega \ll k_BT$, we can expand the exponential term to obtain $u(\omega,T)\simeq k_BT\omega^2/(\pi^2c^3)$, which is called the *Rayleigh-Jeans formula*. So the spectral energy density is a parabola when $\omega\to 0$.
- At high frequencies, when $\hbar\omega \gg k_BT$, we get $u(\omega,T)\simeq \hbar\omega^3\exp\big(-\hbar\omega/(k_BT)\big)/(\pi^2c^3)$, which is the so-called *Wien's law*. So the spectral energy density decreases exponentially when $\omega\to+\infty$.
- The maximum of u, $\omega_{\max}$, can be derived from the calculation of the logarithmic derivative $u^{-1}(\partial u/\partial\omega)_T$, which yields a simple transcendental equation which one can easily solve numerically. We leave it as an exercise to show that this procedure yields to *Wien's displacement law* $\omega_{\max}=2.821\,k_BT/\hbar$, where the maximum angular frequency is proportional to the temperature, T.

These considerations lead to the graph below (Fig. 12.1).

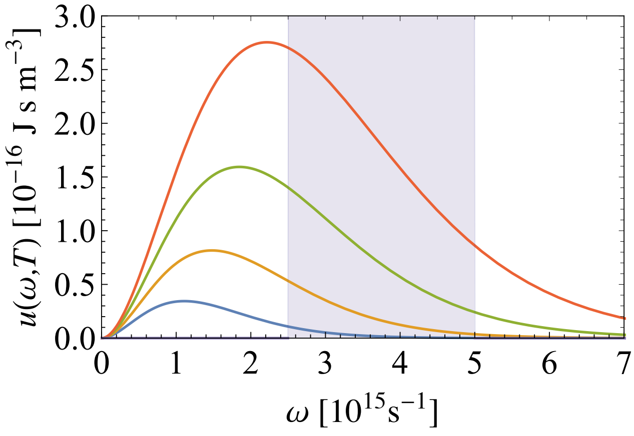

Figure 12.1: Planck's law (equation (12.4)) plot for several temperatures: 3000K in blue, 4000K in orange, 5000K in green and 6000K (approximate temperature of the Sun surface) in red. The band shaded in light purple indicates the visible light frequency range.

R • While the peak in frequency, $\omega_{\max}$ shifts to higher frequencies proportionally to T as T increases, the total energy (area under the u curve in Fig. 12.1) grows like T^4.
• Also note that the number of photons $N(\omega,T)$ has a similar shape to $u(\omega,T)$ with

only the power law index of ω reduced by one. This means that the photon number increases dramatically with T!

12.3 Why classical theory fails

In the classical wave theory of electro-magnetism, each of the eigenmodes of the cavity behaves like a simple harmonic oscillator with the same angular frequency. Indeed, taking the curl of Maxwell's curl equations for the electric and magnetic fields and eliminating $\vec{B}$ from the equation for $\vec{E}$ yields the standard wave equation:

$$\nabla^2 \vec{E}(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2 \vec{E}(\vec{r},t)}{\partial t^2} = \vec{0} \tag{12.5}$$

As previously discussed, we can write the electric field as a linear combination of all the eigenmodes of the cavity, which upon explicitly separating the time and spatial dependence of the progressive monochromatic plane waves reads[‡]:

$$\vec{E}(\vec{r},t) = \sum_{\vec{k},\sigma} A_{\vec{k},\sigma}(t)\, \vec{\mathcal{E}}_{\vec{k},\sigma}(\vec{r})$$

Injecting this in the wave equation (12.5) gives:

$$\sum_{\vec{k},\sigma} \left(\frac{\mathrm{d}^2 A_{\vec{k},\sigma}(t)}{\mathrm{d}t^2} + c^2 k^2 A_{\vec{k},\sigma}(t) \right) \vec{\mathcal{E}}_{\vec{k},\sigma}(\vec{r}) = \vec{0} \tag{12.6}$$

where the term in between brackets must vanish for each combination of $(\vec{k},\sigma)$ in order for a non-nil $\vec{E}$ to obey Maxwell's equations. This term has the well-known form of a sum of one dimensional simple harmonic oscillators, and we know from the classical equipartition of energy theorem (see 9.1.1) that when they are in contact with a thermostat at temperature T, the mean energy of each one of these is $k_B T$. So classical theory predicts a spectral energy density, using the spectral density of eigenmodes (11.1):

$$u_{\text{class}}(\omega,T) = k_B T g(\omega)/V = k_B T \omega^2/(\pi^2 c^3) \tag{12.7}$$

which dramatically fails to reproduce Wien's experimental results (high frequency exponential decrease and maximum which shifts linearly with temperature). Furthermore, upon integrating $u_{\text{class}}(\omega,T)$ over the whole range of frequency $\omega \in [0,+\infty[$, one finds that the total energy density $u_{\text{class}}(T)$ diverges! This is the so-called "ultra-violet" catastrophe as the energy divergence comes from short wavelengths, i.e. large ω.

12.4 Thermodynamical quantities

12.4.1 Total energy: towards Stefan-Boltzmann's law

On the other hand, integrating equation (12.4) over the entire range of possible frequencies $\omega \in [0,+\infty[$ and multiplying by the volume, V, one obtains the total energy

$$U(T,V) = \frac{V\hbar}{\pi^2 c^3} \int_0^{+\infty} \frac{\omega^3}{\exp\big(\hbar\omega/(k_B T)\big) - 1}\, \mathrm{d}\omega \tag{12.8}$$

[‡] The summation over σ includes the possible different polarization states.

which, contrary to the classical result, does converge[§]! Let us calculate it. A change of variable $x = \hbar\omega/(k_B T)$ gives

$$\begin{aligned} U(T,V) &= \frac{V\hbar}{\pi^2 c^3}\left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^{+\infty} \frac{x^3}{\exp(x)-1}\,\mathrm{d}x} \\ &= \frac{V\hbar}{\pi^2 c^3}\left(\frac{k_B T}{\hbar}\right)^4 \qquad \frac{\pi^4}{15} \end{aligned} \tag{12.9}$$

as the integral in the first equality is a known combination of Gamma functions which equals to $\pi^4/15$. So we finally get:

$$U(T,V) = Vu(T) = V\frac{\pi^2\, k_B^4}{15\,\hbar^3 c^3}T^4 \equiv aVT^4 \tag{12.10}$$

where the constant $a = \pi^2 k_B^4/(15\,\hbar^3 c^3)$ is *not* the Stefan-Boltzmann constant, σ, which appears in front of the power emitted per unit surface rather than the energy. We will derive it in the next chapter. However, the scaling of the total energy in T^4 is identical to that of the power emitted per unit surface, which hints that Stefan-Boltzmann's law, as we will see later, is a consequence of Planck's.

12.4.2 Grand potential, pressure and entropy

The grand potential of the photon system, by definition is:

$$\begin{aligned} \Phi &= -k_B T \sum_i \ln(1+\bar{n}_i) \\ &= -k_B T \int_0^{+\infty} g(\epsilon)\ln(1+\bar{n}(\epsilon,T))\,\mathrm{d}\epsilon \\ &= -k_B T \frac{V}{\pi^2\hbar^3 c^3}\int_0^{+\infty} \epsilon^2 \ln\left(1+\frac{1}{\exp\left(\epsilon/(k_B T)\right)-1}\right)\mathrm{d}\epsilon \\ &= -\frac{V}{\pi^2\hbar^3 c^3}\int_0^{+\infty} \frac{\epsilon^3}{3}\,\frac{1}{\exp\left(\epsilon/(k_B T)\right)-1}\,\mathrm{d}\epsilon \\ &= -\frac{1}{3}U(T,V) \end{aligned} \tag{12.11}$$

where the intermediate step of calculating the integral over the logarithm function is performed using an integration by parts. This naturally yields the equation of state of the

---

[§] Strictly speaking, we are faced with a consistency problem: we should be able to derive the total energy of the photon gas from a purely quantised point of view, rather than the semi-classical approach we have followed in these notes. In other words, we should be able to use the average energy of a simple quantum harmonic oscillator (equation (9.8) divided by N and with $U_0^{(1D)} = 0$), representing a particular field eigenmode, to write:

$$U(T,V) = \int_0^{+\infty} g(\omega)\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(\hbar\omega/(k_B T)\right)-1}\right)\mathrm{d}\omega = \frac{V}{\pi^2 c^3}\int_0^{+\infty}\left(\frac{\hbar\omega^3}{2} + \frac{\hbar\omega^3}{\exp\left(\hbar\omega/(k_B T)\right)-1}\right)\mathrm{d}\omega$$

However, whilst the second term in the integral does yield the same result as equation (12.8) there also appears a first term $\hbar\omega^3/2$ which diverges when integrated over the whole range of possible ω values. This term arises because the energy of the fundamental level of a quantum harmonic oscillator is not zero (as can be seen by setting the quantum number n, interpreted here as the number of photons in the field eigenmode (earlier defined as N_ω), to $n = 0$ in equation (9.4)). This energy of the quantised electro-magnetic field which is present even in the absence of photons is referred to as *vacuum energy* or zero-point energy and (more or less) happily renormalised away, but this is another (long and very involved) story!

photon gas by calculating the pressure:

$$\boxed{p = -\left(\frac{\partial \Phi}{\partial V}\right)_T = \frac{1}{3}\,u(T)} \tag{12.12}$$

which is the classical radiation pressure traditionally derived for isotropic radiation.

R

- As $\mu = 0$ for the photon gas, there are only two variables, T & V.
- As the number of photons N is not fixed, the equation of state cannot be a function of the volume because V is the only extensive variable left! So this "extensiveness" cannot be compensated to make the pressure intensive, as is the case for an ideal gas where one can multiply by N to get the intensive factor N/V in front of the temperature dependence. As a consequence, the photon gas pressure is a function of temperature *alone*.

As for the entropy, we have

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_V = \frac{4}{3}\,\frac{U(T,V)}{T} \tag{12.13}$$

which goes to zero when $T \to 0$ in the same way that fermions and massive bosons do.

13. Absorption & emission of radiation

Experiment shows that a sufficiently heated body emits light, e.g. the filament of a lamp, hot iron etc ... This thermal radiation emission is the subject of this section and we will show that it is intrinsically linked to the ability of the body to absorb radiation externally emitted.

13.1 Definitions

Let the power radiated by an infinitesimal surface element $\mathrm{d}S$, centred on point M of a body $\mathcal{B}$, in an infinitesimal solid angle $\mathrm{d}\Omega$ around the direction defined by unit vector $\hat{k}$ and in an infinitesimal band of angular frequency $[\omega, \omega + \mathrm{d}\omega]$ be:

$$\mathrm{d}P \equiv \eta(\omega, \hat{k}, M, T)\,\mathrm{d}\omega\,\mathrm{d}\Omega\,\mathrm{d}S \tag{13.1}$$

This relation defines the *emissivity*, η, of the body $\mathcal{B}$. It has the dimension of an energy per unit surface $[\mathrm{J\ m}^{-2}]$ and depends on the nature of the body $\mathcal{B}$, the point M chosen on its surface, the temperature T at which the body is heated, the angular frequency ω at which the emitted radiation is observed as well as the direction $\hat{k}$ along which this latter propagates[*]. If we call ϑ and φ $(0 \leq \vartheta \leq \pi\,;\ 0 \leq \varphi \leq 2\pi)$ the angles which mark the direction of $\hat{k}$ with respect to the normal to $\mathrm{d}S$ in M and an axis perpendicular to this normal which serves as origin for φ, we then have, as usual for a spherical coordinate system, $\mathrm{d}\Omega = \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi$.

Suppose now that $\mathcal{B}$ receives electro-magnetic radiation emitted by external sources. By analogy with what we just did for emission, let us write the power received at the same point M by the same surface element $\mathrm{d}S$, but in the angular frequency range $[\omega', \omega' + \mathrm{d}\omega']$ and which arrives within the solid angle $\mathrm{d}\Omega'$ around the direction defined by the unit vector $\hat{k}'$ as:

$$\mathrm{d}P \equiv \varpi(\omega', \hat{k}', M)\,\mathrm{d}\omega'\,\mathrm{d}\Omega'\,\mathrm{d}S \tag{13.2}$$

---

[*] To be complete, in some cases it also depends on the polarization state of the emitted radiation, but we will neglect this in these lectures.

Quite clearly, the quantity ϖ has the same dimension as the emissivity η. In the most general case, part of this power $\mathrm{d}P$ is absorbed by $\mathcal{B}$, and the rest is sent back, whether by reflection or diffusion[†]. We then define the *absorptivity*, α of the body $\mathcal{B}$ at point M as the fraction of the received power that is absorbed. This is a *dimensionless* number that depends on the nature of the body $\mathcal{B}$, the point M chosen on its surface, the temperature T at which the body is heated, but also on the angular frequency ω' and the direction $\hat{k}'$ of the incident radiation. In other words, $\alpha = \alpha(\omega', \hat{k}', M, T)$.

13.2 The case of the blackbody

We (would like to) call "blackbody" , a body $\mathcal{B}$ whose absorptivity verifies:

$$\alpha(\omega', \hat{k}', M, T) = 1\,, \quad \forall(\omega', \hat{k}')$$

That is to say, a *blackbody* is a body which absorbs *all* the power of the incident radiation it receives at point M, regardless of its wavelength and direction. It is called that way because if you illuminate it with any radiation, it does not reflect or diffuse any component of this radiation, which makes it look black.

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- It is possible for a body to be a blackbody only in a certain range of temperature.
- As we have already seen, a black body emits radiation, so it will only appear black to the eye if its temperature is not too high, because in that case its emission at visible wavelengths is negligible. If you shine visible light on it, it will absorb it entirely and therefore does not send back any colour!

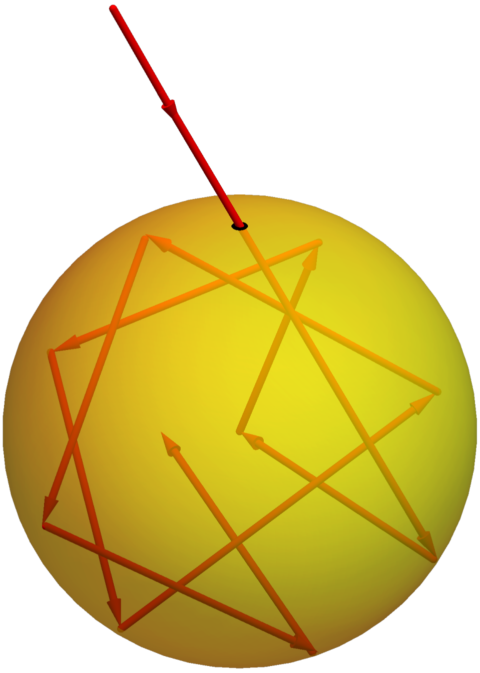

Figure 13.1: Schematics of the closest practical realisation of a true blackbody. A light ray (red line with arrows) is trapped inside a spherical cavity.

A surface plastered with soot is an approximative blackbody (at least for radiation at visible and near-visible wavelengths), but the practical realisation that is closest to a true

---

[†] We assume that $\mathcal{B}$ is sufficiently thick and opaque that no radiation can go through it.

blackbody consists in poking a small hole in a closed container (see Fig. 13.1). Indeed, any radiation directed towards this hole under any angle will be trapped in the cavity with almost no chance of coming out of it. It is because we always refer to this prototype that we say *the* blackbody.

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- The link with the previous chapter definition of the blackbody as a gas of photons in thermal equilibrium in a cavity should be straightforward: if you poke a hole in the said cavity, you find yourself in the same situation as in Fig. 13.1!
- Sometimes you will hear people talk about "white body" for a body with $\alpha = 0$, or "grey body" for intermediate cases.

13.3 Kirschoff's law

13.3.1 Statistical equilibrium

Let us put a body $\mathcal{B}$ in thermal equilibrium with a photon gas at temperature T, i.e. let us place $\mathcal{B}$ in a closed container in contact with a thermostat at temperature T and wait for the equilibrium to be established. In such an equilibrium situation, the total power emitted and absorbed by $\mathcal{B}$ are equal.

Having picked a unit vector $\hat{k}$, we consider the radiation emitted in that direction and the radiation received in the same direction, i.e. along a unit vector $-\hat{k}$, to mathematically write this equilibrium condition as:

$$\int \Big[\eta(\omega,\hat{k},M,T) - \alpha(\omega,-\hat{k},M,T)\,\varpi(\omega,-\hat{k},M,T)\Big]\,\mathrm{d}\omega\,\mathrm{d}\Omega\,\mathrm{d}S = 0 \tag{13.3}$$

However, this cancellation is not only global, it must also happen locally at each point of $\mathcal{B}$ and for each ω and $\hat{k}$. Indeed, should there exist a contribution $(\eta - \alpha\varpi) > 0$ over a small domain $\delta_1(\omega,\vartheta,\varphi,M)$ of the body $\mathcal{B}$, it should then be compensated by a negative contribution on another domain $\delta_2(\omega',\vartheta',\varphi',M')$ since the integral must vanish. As we can change η and α for δ_2 without altering δ_1, by e.g. sticking a piece of opaque screen on the surface element $\mathrm{d}S_2$ to prevent exchanges between this surface element and the gas of photons in the container, this would destroy the global cancellation without affecting the equilibrium between $\mathcal{B}$ and the radiation. We must therefore conclude that:

$$\eta(\omega,\hat{k},M,T) = \alpha(\omega,-\hat{k},M,T)\,\varpi(\omega,-\hat{k},M,T) \tag{13.4}$$

Now we can calculate $\varpi(\omega,-\hat{k},M,T)$ in this situation, because we know that the photon gas at equilibrium must follow the Planck law derived in the previous chapter! The number of photons $\mathrm{d}N(\vec{k'},T)$ with wave vectors in the range $[\vec{k'},\vec{k'}+\mathrm{d}\vec{k'}]$ at temperature T therefore is:

$$\mathrm{d}N(\vec{k'},T) = 2\frac{V}{(2\pi)^3}\frac{\mathrm{d}^3k'}{\exp\big(\hbar\omega'/(k_BT)\big)-1} \tag{13.5}$$

All these photons have a speed c in the direction $\vec{k'}$ and an energy $\hbar\omega' = \hbar ck'$. Those which hit the surface element, $\mathrm{d}S$, of $\mathcal{B}$, centred at M, during the time interval $[t, t+\mathrm{d}t]$, are contained in a cylinder of base $\mathrm{d}S$ and axis of length $c\,\mathrm{d}t$ parallel to $\vec{k'}$. This allows us to write the energy received by $\mathrm{d}S$ during $\mathrm{d}t$ as:

$$\varpi(\omega',\hat{k}',M,T)\,\mathrm{d}t\,\mathrm{d}S\,\mathrm{d}\Omega'\,\mathrm{d}\omega' = \hbar\omega'\,\mathrm{d}N(\vec{k'},T)\frac{c\cos\vartheta\,\mathrm{d}t\,\mathrm{d}S}{V} \tag{13.6}$$

where ϑ is the angle between $-\vec{k'}$ and the normal to $\mathrm{d}S$ at M (see Fig. 13.2).

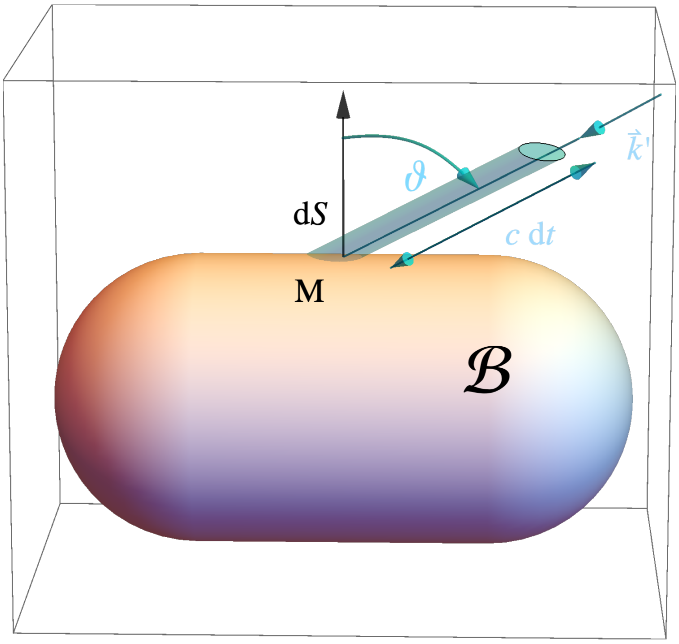

Figure 13.2: Geometrical view of photons in the cavity hitting the body $\mathcal{B}$.

Given that $\mathrm{d}^3k' = k'^2\mathrm{d}k'\,\mathrm{d}\Omega' = \omega'^2/c^3\mathrm{d}\omega'\,\mathrm{d}\Omega'$, we can inject equation (13.5) into (13.6) to get:

$$\varpi(\omega',\hat{k}',M,T) = \frac{\hbar\omega'^3}{4\pi^3c^2}\,\frac{\cos\vartheta}{\exp\big(\hbar\omega'/(k_BT)\big)-1} = \frac{c}{4\pi}u(\omega',T)\cos\vartheta \tag{13.7}$$

where, as expected, the spectral energy density of Planck's law, $u(\omega',T)$, given by equation (12.4), appears. Going back to our cancellation equation (13.4), we are thus able to derive:

Law 9 — Kirschoff's law.

$$\frac{\eta(\omega,\hat{k},M,T)}{\alpha(\omega,-\hat{k},M,T)} = \frac{c}{4\pi}u(\omega,T)\cos\vartheta \tag{13.8}$$

• The left hand side term in Kirschoff's law only involves *intrinsic* properties of the body studied, i.e., both η and α are independent of the conditions in which $\mathcal{B}$ is placed: they remain the same even when the body emits/absorbs radiation in a *non*-equilibrium situation!
• The right hand side term, on the contrary, is a *universal* function of T, ω and direction *only*.

In other words, Kirschoff's law states that the ratio between emissivity and absorptivity is *independent* of the body considered and of the point chosen on its surface. Another way to state this is that "good absorbers are good emitters" and vice-versa.

13.3.2 Application to the blackbody: Stefan-Boltzmann's law

In the case of the blackbody, as we have seen, the absorptivity is by definition $\alpha_B(\omega,-\hat{k},M,T) = 1$ and so its emissivity, $\eta_B(\omega,\hat{k},M,T) = c/(4\pi)\,u(\omega,T)\cos\vartheta$, is *independent of its nature.*

It thus serves as a reference, as it is simply proportional to $\cos\vartheta$, where ϑ is the angle between the direction of observation and the normal to the surface of the blackbody. This dependence on direction is referred to as *Lambert's law.* Integrating over all directions we obtain the power emitted in the angular frequency band $[\omega, \omega + \mathrm{d}\omega]$ by the surface element $\mathrm{d}S$:

$$\begin{aligned} P_B(\omega, T)\,\mathrm{d}\omega\,\mathrm{d}S &= \mathrm{d}\omega\,\mathrm{d}S \int \eta_B(\omega, \hat{k}, M, T)\,\mathrm{d}\Omega \\ &= \mathrm{d}\omega\,\mathrm{d}S\,\frac{c}{4\pi} u(\omega, T) \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi/2} \cos\vartheta \sin\vartheta\,\mathrm{d}\vartheta \end{aligned} \tag{13.9}$$

where the last integral over ϑ only goes to $\pi/2$ because radiation is only emitted outside of the body. We thus deduce that $P_B(\omega, T) = cu(\omega, T)/4$. That is to say, a measure of the power emitted per unit surface of the blackbody directly yields the energy density of a photon gas in thermal equilibrium! This explains why Planck's law, initially destined to describe blackbody radiation, was deduced from the properties of the photon gas.

Finally, the total power per unit surface of the blackbody obeys:

Law 10 — Stefan-Boltzmann's law.

$$P_B(T) = \int_0^{+\infty} P_B(\omega, T)\,\mathrm{d}\omega = \frac{\pi^2 k^4}{60 c^2 \hbar^3} T^4 \equiv \sigma T^4 \tag{13.10}$$

where σ is called *Stefan-Boltzmann's constant.*

IV

Thermodynamics of Real Gases

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14. Statistical study of a fluid

In a gas, the potential energy of interactions between molecules is small compared to their kinetic energy. At high temperatures and low densities, the regime where the ideal gas approximation is valid, it is even negligible. However as the temperature decreases and/or the density increases the contribution of the interaction energy to the total energy becomes more important and the properties of the gas start to deviate from that of an ideal gas. Finally, when the interaction energy becomes comparable to the kinetic energy, the gas condenses and becomes a liquid.

The Van der Waals model allows to understand this transition from gas to liquid, even though it relies on a rather crude mean field theory and should only be expected to yield qualitative results. This is because it possesses the necessary properties to describe the physical phenomena at play in real gases and liquid-gas phase transitions.

14.1 General case

Consider a mono-atomic[*] fluid made of $N \ggg 1$ identical particles of mass m, contained in a recipient of volume V and kept at temperature T. We can calculate the macroscopic properties of this system using classical mechanics and the partition function:

$$\mathcal{Z} = \frac{1}{N!}\frac{1}{h^{3N}} \int \cdots \int \mathrm{d}^3 p_1 \cdots \mathrm{d}^3 p_N \, \mathrm{d}^3 r_1 \cdots \mathrm{d}^3 r_N \, \exp\left(-\frac{\mathcal{H}}{k_B T}\right) \tag{14.1}$$

where

$$\mathcal{H} = \frac{1}{2m}\sum_{i=1}^{N} \vec{p_i}^2 + \mathcal{U}(\vec{r_1}, \cdots, \vec{r_N})$$

---

[*] Strictly speaking, the mono-atomic hypothesis is not necessary to derive the EOS of real gases but will simplify our life considerably as it allows us to ignore the internal degrees of freedom and non-spherical shape of molecules that we have previously discussed in the lectures devoted to the statistical mechanics of simple systems.

is the Hamiltonian of the system, complete with its kinetic (first term) and potential (second term) energy parts. The integration over all momenta $\vec{p_i}$, i.e. the kinetic part of $\mathcal{Z}$, is the same as for the ideal gas, so

$$\mathcal{Z} = \frac{1}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2} \int\cdots\int \mathrm{d}^3r_1 \cdots \mathrm{d}^3r_N \exp\left(-\frac{\mathcal{U}(\vec{r_1},\cdots,\vec{r_N})}{k_BT}\right) \tag{14.2}$$

i.e. when the potential energy $\mathcal{U}$ is negligible in front of k_BT, $\int\cdots\int \mathrm{d}^3r_1 \cdots \mathrm{d}^3r_N = V^N$ and $\mathcal{Z}$ is the partition function of the ideal gas. If we want to do better and take into account the interaction between gas particles, we thus have to determine $\mathcal{U}$.

Suppose that the total interaction energy is the sum of the pairwise interaction energies between particles[†], $u(\|\vec{r_i}-\vec{r_j}\|)$, i.e. that

$$\mathcal{U}(\vec{r_1},\cdots,\vec{r_N}) = \frac{1}{2}\sum_{i,j}^{i\neq j} u(\|\vec{r_i}-\vec{r_j}\|)$$

where the $1/2$ factor arises from the need *not* to double count the interaction energy between particles i and j. Having made this approximation, we still have to determine $u(r)$. In principle one could calculate it from Quantum Mechanics, but in practice it is a very difficult proposition, especially if the molecules involved are complex. However, one can show that at large distances, r, the interaction energy between particles varies like r^{-6}, which corresponds to an attractive "Van der Waals" force that scales like r^{-7}.

> The physical origin of these Van der Waals forces is the following: a charge fluctuation in a molecule creates an electric dipole (or more generally multipole) which polarizes a neighbouring molecule. In turn, the dipole (or multipole) induced on this second molecule acts on the polarization of the first. Note that even though we talk about large distances for r, these forces are short-range interactions between neighbouring molecules.

At short distances (when r becomes of the order of the size of the molecules themselves), the molecules exert intense repelling forces upon one another. Essentially this is because the Pauli exclusion principle which rules their electrons prevent molecules from inter-penetrating. This behaviour at short and large distances can be captured by a potential $u(r)$ of the shape given by Fig.14.1, which has two important characteristics: the position r_0 of its minimum, and the value at this minimum $-u_0 < 0$. Their order of magnitude is ~ 1 Å for r_0 and a few 10^{-2} eV for u_0 (i.e. a few 100 K for u_0/k_B).

Practically, one uses empirical analytic forms with the correct shape of $u(r)$. Arguably the most famous one, which we plot in Fig.14.1 is called the *Lennard-Jones* potential:

$$u_{LJ}(r) = u_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right] \tag{14.3}$$

which has only two parameters, u_0 and r_0 and intercepts the x-axis (i.e. $u_{LJ} = 0$) at $r_1 = r_0/2^{1/6} \simeq 0.89\, r_0$.

[†] Such an approximation may look natural enough to make, but the main interaction between molecules is caused by the electron motion they induce within one another when they are close, so this could easily be influenced by the presence of a third molecule in the vicinity. In other words, the approximation assumes that three body interactions are weak which is fine for a gas but much less so for a liquid ...

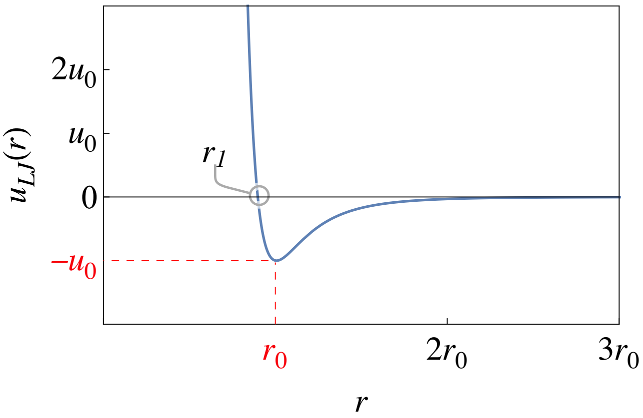

Figure 14.1: The Lennard-Jones potential describing the behaviour of the Van der Waals forces between molecules in a real gas.

14.2 The Van der Waals model

Even with the approximation previously made for the interaction energy, evaluating the volume integral present in the partition function of the system (equation (14.2)) is extremely difficult. So we are going to use a still cruder approximation, albeit one that we have already met before when discussing the statistical mechanics of solid crystals: the mean field approximation.

14.2.1 Mean field approximation

Consider a given molecule. One can say that, at a zeroth order approximation, the $N-1 \ggg 1$ other molecules which are almost uniformly distributed in the volume V, are felt by this molecule, as an almost continuous cloud. Neglecting the perturbation of this cloud caused by the presence and motion of the molecule, this latter will have a potential energy $u_{\text{eff}}(\vec{r})$ which will depend only on its position and *not* on the positions of the other $N-1$ particles anymore. In other words, in this approximation, each particle moves in a mean field created by all the other particles, and the system behaves as an ensemble of *independent* particles, just as the vibrations of atoms in a crystal were turned into an ensemble of independent oscillators.

The total potential energy of the system thus becomes a sum of terms[‡], each of which involves the coordinates of a single particle, i.e.

$$\mathcal{U}(\vec{r_1},\cdots,\vec{r_N}) = \frac{1}{2}\sum_{i=1}^{N} u_{\text{eff}}(\vec{r_i})$$

and the partition function given by equation (14.2) becomes

$$\mathcal{Z} = \frac{1}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2}\left[\int \mathrm{d}^3r \, \exp\left(-\frac{u_{\text{eff}}(\vec{r})}{2k_BT}\right)\right]^N \tag{14.4}$$

[‡] $u_{\text{eff}}(\vec{r})$ is obtained by averaging $\sum_{i=2}^{N} u(\|\vec{r}-\vec{r_i}\|)$ over the positions $\vec{r_2},\cdots,\vec{r_N}$ of the $N-1$ other molecules, so $u(\|\vec{r_i}-\vec{r_j}\|)$ is present in both $u_{\text{eff}}(\vec{r_i})$ *and* $u_{\text{eff}}(\vec{r_j})$, hence the factor of $1/2$ in the following formula for $\mathcal{U}(\vec{r_1},\cdots,\vec{r_N})$.

14.2.2 Effective potential

The mean field approximation neglects the correlations between molecules, i.e. it considers that the molecules are uniformly distributed in the recipient volume. In these conditions, the effective potential $u_{\text{eff}}(\vec{r}) = u_{\text{eff},0}$ ought to be constant over the entire volume V. However, we have seen that this approximation breaks down when the distance between molecules approaches the molecule size, r_1 (see Fig.14.1). On these small distances, individual molecules do not feel an average attractive force created by an homogeneous cloud, but a very strong repulsive force from their immediate neighbour. To crudely account for this effect, we will simply consider that a fraction V_0/V of the recipient volume is forbidden to any given molecule, due to the presence of the others. This allows us to calculate the integral in the formula (14.4) as:

$$\int \mathrm{d}^3r \, \exp\left(-\frac{u_{\text{eff}}(\vec{r})}{2k_BT}\right) = (V - V_0) \, \exp\left(-\frac{u_{\text{eff},0}}{2k_BT}\right)$$

Our task now boils down to evaluating the constants V_0 and $u_{\text{eff},0}$.

Let us start by the excluded volume, V_0. The minimum allowed distance between two particles is almost equal to r_1, as the interaction potential is extremely steep at smaller distances (for the Lennard-Jones potential it diverges in r^{-12}, see Fig.14.1). So when two molecules approach one another, the volume forbidden to one of them due to the presence of the other is $4\pi r_1^3/3$. As there are $N(N-1)/2$ possible pairs of molecules, the total volume excluded simply is $N(N-1)/2 \times 4\pi r_1^3/3 \simeq 2\pi N^2 r_1^3/3$, if we assume that $V_0 \ll V$ so that the spheres of exclusion of any pair of molecules almost never intersect. The excluded volume *per particle*, is therefore $V_0 = 2\pi r_1^3/3 \times N \equiv bN$, i.e. V_0 is proportional to N, with a proportionality constant, b, which only depends on the nature of the gas and is of the order of four times the *proper volume*, $v_0 \equiv 4\pi/3 \times (r_1/2)^3$, of a molecule.

Let us now turn to $u_{\text{eff},0}$ and take for origin of our coordinate system the position of a given particle. As previously mentioned, the others are uniformly distributed in space, except that they cannot get closer to the origin than r_1. The number $n(\vec{r})\,\mathrm{d}^3r$ of particles contained in an infinitesimal volume d^3r around $\vec{r}$ is therefore:

$$n(\vec{r}) = \begin{cases} 0 & \text{if } r < r_1 \\ \frac{N-1}{V-V_0} \simeq \frac{N}{V} & \text{if } r > r_1 \end{cases}$$

The potential energy of the particle located at the origin of the coordinate system is thus:

$$u_{\text{eff},0} = \int u(\vec{r}) n(\vec{r}) \, \mathrm{d}^3r = \frac{N}{V} \int_{r_1}^{+\infty} 4\pi r^2 u(r) \, \mathrm{d}r$$

with $u(r) < 0$ over the entire integration domain (see Fig. 14.1). In other words, $u_{\text{eff},0} < 0$ and independent of $\vec{r}$, as expected. An order of magnitude for $u_{\text{eff},0}$ is the number of particles times the minimal value of the potential between two particles, $N \times (-u_0)$, times the ratio of the *interaction volume*[§] and the total volume, V. This ratio is of the order of a few v_0/V where "few" depends on the exact model used for $u(r)$. In a general manner, one therefore writes $u_{\text{eff},0} = -2aN/V$ where $a > 0$ is a constant of order a few $u_0 v_0$ which depends on the nature of the fluid.

R The important point in this calculation is that $u(r) \xrightarrow{r\to\infty} 0$ fast enough for $\int 4\pi r^2 u(r)\,\mathrm{d}r$ to converge. This is obviously true for Van der Waals forces, where $u(r) \propto r^{-6}$ at large distances, but *not* for charged particles where $u(r) \propto r^{-1}$.

[§] This is the volume of a sphere whose radius is equal to the range of the potential $u(r)$.

Exercise 14.1 Calculate $u_{\text{eff},0}$, a and b as a function of u_0 and v_0 in the specific case of the Lennard-Jones potential given by equation (14.3).
Ans: $u_{\text{eff},0} = -64Nu_0v_0/(3V)$, $a = 32u_0v_0/3$ and $b = 4v_0$. ■

Plugging the general expressions obtained for V_0 and $u_{\text{eff},0}$ in the formula (14.4) for the partition function we finally obtain

$$\boxed{\mathcal{Z} = \frac{V^N}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2}\left[\left(1-\frac{bN}{V}\right)\exp\left(\frac{aN}{k_BTV}\right)\right]^N} \tag{14.5}$$

which is the partition function of the system in the Van der Waals approximation. Note that is is equal to the partition function of the ideal gas, multiplied by a corrective term (in between square brackets and raised to the power N).

14.3 Thermodynamical quantities

Now that we have derived the partition function of the system in the Van der Waals approximation, we can use it to obtain thermodynamical quantities of interest, and in particular the famous Van der Waals equation of state. We therefore start with the calculation of the Helmholtz free energy of the system, F, as we know this is the one which provides the most direct route to the EOS. We have, using expression (14.5) for $\mathcal{Z}$ and Stirling's formula:

$$\begin{aligned} F &= -k_BT\ln\mathcal{Z} \\ &= -Nk_BT\left[\frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right)+1\right] - Nk_BT\ln\left(\frac{V-bN}{N}\right) - \frac{aN^2}{V} \end{aligned} \tag{14.6}$$

where the first term on the right hand side and the $-Nk_BT\ln(V/N)$ part of the second term combine to give the Helmholtz free energy of a mono-atomic ideal gas, and the $-bN$ part of the second term and the third term are Van der Waals corrections. Note that, as required, F is extensive, F/N only depends on the ratio N/V, not on N and V separately.

To get the EOS, we then calculate the system pressure:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V-bN} - \frac{aN^2}{V^2}$$

which is known as the *Van der Waals equation of state*, and more commonly written as:

$$\boxed{\left(p+\frac{aN^2}{V^2}\right)(V-bN) = Nk_BT} \tag{14.7}$$

Once again this EOS is similar to that of the ideal gas, with a smaller volume available $(V-bN)$ instead of V to account for the finite size of the molecules, and a reduced pressure (by an amount aN^2/V^2) because of the attraction between molecules at large distances.

The internal energy, is

$$U = -\frac{\partial\ln\mathcal{Z}}{\partial\beta} = \frac{3}{2}Nk_BT - \frac{aN^2}{V} \tag{14.8}$$

which is, once again, the internal energy of a mono-atomic ideal gas with a correction term (second term on the right hand side) that accounts for the potential energy of the particles in a real gas ($N \times u_{\text{eff},0}/2$). On the other hand, the heat capacity at constant volume, $C_V = (\partial U/\partial T)_{V,N} = 3Nk_B/2$, is the *same* as that of an ideal gas.

R • Note that the second term in the internal energy for a Van der Waals gas depends on V and *not* on T. It is therefore *not correct* to say that the internal energy of a real gas is a function of T alone, this statement only applies to ideal gases.
• What is true for C_V, i.e. it is the same for a Van der Waals gas than for an ideal gas, is *not* true for C_p (see exercise 14.2)

Exercise 14.2 Calculate C_p for a Van der Waals gas as the sum of C_p for a mono-atomic ideal gas and a corrective term which is a function of T and V.
Ans: $C_p = 5Nk_B/2 + 2aN^2k_B(V-bN)^2/(k_BTV^3 - 2aN(V-bN)^2)$. ■

The entropy of the gas reads:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B\left[\frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + \frac{5}{2}\right] + Nk_B\ln\left(\frac{V-bN}{N}\right) \tag{14.9}$$

which can also be split into the entropy of a classical ideal gas with a correction, $-bN$ in the second right hand side term, which accounts for the reduced volume due to the finite size of the particles. In order words, the entropy of a Van der Waals gas is smaller than that of an ideal gas because the volume really accessible to the particles is smaller.

Finally, the chemical potential of the Van der Waals gas can be calculated from:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_BT\left[\frac{3}{2}\ln\left(\frac{mk_BT}{2\pi\hbar^2}\right) + 1\right] - k_BT\ln\left(\frac{V-bN}{N}\right) + \frac{k_BTV}{V-bN} - \frac{2aN}{V} \tag{14.10}$$

which differs from that of an ideal gas by the $-bN$ part in the second and third terms on the right hand side, as well as the presence of the last term. We can easily rewrite this expression for μ as:

$$\mu = \frac{F}{N} + \frac{k_BTV}{V-bN} - \frac{aN}{V} = \frac{1}{N}(F+pV) \equiv \frac{G}{N} \tag{14.11}$$

where we have used the equation of state (14.7) to obtain the last equality, and ultimately the definition of the Gibbs free energy, G. This relation between μ and G is a general result for a fluid characterised by three external parameters, i.e. it holds for real and ideal gases.

15. Gas-liquid phase transition

Even though the Van der Waals model for real gases derived in the previous chapter involves rather crude approximations, it still proves very useful as it contains the basic physical ingredients necessary to understand the phase transition between liquid and vapour observed to take place in real fluids. This will be the subject of this chapter.

15.1 Van der Waals isotherms

Isotherms for an ideal gas are monotonic hyperbolae. That is to say, for a given value of T, $p \propto 1/V$. Van der Waals isotherms generally have a similar shape, except that for some values of T, the extra terms contributing to the pressure and volume become significant and extrema appear. Indeed, differentiating the Van der Waals equation of state (14.7), one obtains:

$$\left(\frac{\partial p}{\partial V}\right)_{T,N} = -\frac{N k_B T}{(V-bN)^2} + 2a\frac{N^2}{V^3} \tag{15.1}$$

This expression is equal to zero when:

$$V - bN = \left(\frac{k_B T}{2aN}\right)^{1/2} V^{3/2} \tag{15.2}$$

Plotting both left-hand ($y_0 = V - bN$) and right-hand ($y_i = \sqrt{k_B T_i/(2aN)}V^{3/2}$, with $i \in \mathbb{N}^+$ and $T_1 < T_2 < \cdots < T_n$) side terms of the previous equation onto a single graph in Fig.15.1 for various temperatures T_i, one realises that either these two curves intersect in two places (at low temperatures), or not at all (high temperatures). Moreover, from the same figure, it is quite clear that there must exist a *critical temperature*, $T_i \equiv T_c$, for which the two curves are tangent to one another, i.e.

$$\left(\frac{\partial y_0}{\partial V}\right)_{T,N} = \left(\frac{\partial y_i}{\partial V}\right)_{T_i,N} \quad \Leftrightarrow \quad 1 = \left(\frac{9 k_B T_c}{8aN}\right)^{1/2} V^{1/2} \tag{15.3}$$

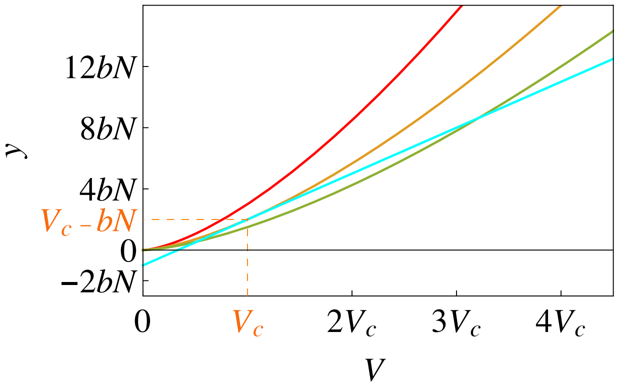

Figure 15.1: Graphical solution of equation (15.2). The cyan solid line represents $y_0 = V - bN$ whereas the orange curve indicates $y_2 = y_c$, for which $T_2 = T_c$ and y_0 is a tangent in V_c. y_1 (green curve) and y_3 (red curve) correspond to temperatures $T_1 = 3T_c/4$ and $T_3 = 3T_c/2$ respectively lower and higher than T_c. Note that the only curves to intersect y_0 twice are those with $T_i < T_c$.

This yields an expression for the *critical volume*, $V_c = 8aN/(9k_BT_c)$, which, when injected into $y_0 = y_i$ at the point of tangency gives $T_c = 8a/(27k_Bb)$, and thus $V_c = 3bN$. Finally, plugging these expressions into the Van der Waals equation of state, one obtains the *critical pressure*, $p_c = a/(27b^2)$. Also note that $(\partial p/\partial V)_{T,N}$ is always negative (the first term in equation (15.1) always dominates), except between the two extrema when they exist, and that these extrema are located further and further apart as the temperature of the isotherm decreases. All these considerations lead to the isotherms for a Van der Waals gas plotted on Fig. 15.2.

Let us pick a specific isotherm with temperature T. For high values of the volume V, pressure is a slowly decreasing function of V which corresponds to a high compressibility (a small increase of pressure changes the volume considerably) typical of a gas. On the other hand, for low values of V the pressure is a rapidly decreasing function of V. In other words, one needs a large change of pressure to reduce the volume by a small amount so the fluid is almost incompressible: it is a liquid.

R In this latter domain (small values of V) the Van der Waals approximation is poorly justified, but it qualitatively captures the behaviour of the liquid because it takes into account the main characteristic of the interaction between molecules, namely that their potential energy becomes comparable to their kinetic energy.

For intermediate values of $V \sim V_c$ things are more complicated. Looking at the isotherm graph (Fig.15.2) there clearly exist two domains of temperature:

- At high temperature ($T > T_c$), p remains a decreasing function of V for all values of the volume. When one follows such an isotherm, i.e. when one increases V at constant T, one *continuously* moves from a weak compressibility regime (liquid) to a high compressibility regime (gas). The system remains *homogeneous* during the transformation, and we call the fluid *supercritical.*
- At low temperature ($T < T_c$), there exists a range of values of V where $(\partial p/\partial V)_{T,N} > 0$, i.e. a range of *negative* compressibility. This means that the system becomes *unstable* in these conditions (the fluid wants to expand as one compresses it) and the isotherm *cannot* be an equilibrium state for the fluid. A more detailed analysis of

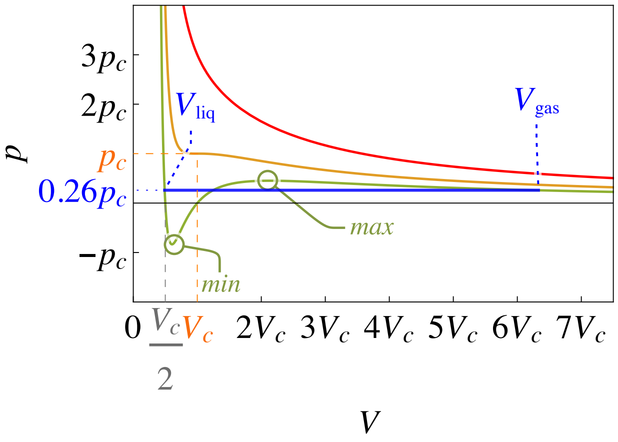

Figure 15.2: Examples of Van der Waals isotherms in the three different temperature regimes, $T_3(=3T_c/2) > T_c$ (red curve), $T_2 = T_c$ (orange curve) and $T_1(=3T_c/4) < T_c$ (green curve). Note that the green curve intersects the $x-$axis, $p = 0$, at $V_c/2$ and V_c, and possesses both a minimum and a maximum, as indicated on the figure. The horizontal blue line corresponds to the equilibrium pressure of the system when it splits into two phases, liquid and gas (see example 15.2 for detail on how it is calculated).

what happens to the system is required and we will devote the rest of this chapter to it.

For low enough values of the temperature (e.g. $T_i = 3/4T_c$ in Fig.15.2), p itself becomes negative, a sure sign that everything is going to hell in a handbasket!

The isotherm corresponding to $T_i = T_c$, which separates the two temperature domains previously described is called the *critical isotherm*. The ratio $p_cV_c/(Nk_BT_c)$, sometimes called "compression factor at the critical point", is a dimensionless quantity and is independent of the parameters a and b used in the Van der Waals approximation, i.e. it has the same value for *all* fluids ($p_cV_c/(Nk_BT_c) = 3/8 = 0.375$). Typical experimental values for real fluids show that this is indeed the case, but with values closer to 0.3, and even lower for so-called polar fluids like water.

■ **Example 15.1 — Experimental values for real fluids.** Helium (He) has $T_c = 5.2$ K, $V_c = 57.8$ cm^{3}mol^{-1}, $p_c = 2.26$ atm and $p_cV_c/(Nk_BT_c) = 0.3$; Nitrogen (N_2) has $T_c = 126.1$ K, $V_c = 90.1$ cm^{3}mol^{-1}, $p_c = 33.5$ atm and $p_cV_c/(Nk_BT_c) = 0.29$; Water (H_2O) has $T_c = 647.4$ K, $V_c = 56.3$ cm^{3}mol^{-1}, $p_c = 218.3$ atm and $p_cV_c/(Nk_BT_c) = 0.23$. ■

Another approximation than Van der Waals for real gases, the Dietericci approximation that you will encounter in one of the problem sheets, yields a value of this ratio of 0.29, in better agreement with the experimental measures.

15.2 The law of corresponding states

This property of the compression factor at the critical point lead us to go further and define *reduced coordinates* as the following dimensionless quantities: $\tilde{T} \equiv T/T_c$, $\tilde{V} \equiv V/V_c$ and

$\tilde{p} \equiv p/p_c$. We can then rewrite the Van der Waals equation of state as:

$$\boxed{\left(\tilde{p} + \frac{3}{\tilde{V}^2}\right)\left(3\tilde{V} - 1\right) = 8\tilde{T}} \qquad (15.4)$$

This reduced equation is independent of the Van der Waals parameters a and b, i.e. it is the same for all Van der Waals fluids! One thus says that two different fluids (as in fluids with different values of T_c, V_c and p_c) verify the law of "corresponding states". This means that if we fix their $\tilde{T}$ and $\tilde{V}$ at the same values, then their value for $\tilde{p}$ is also the same.

15.3 Helmholtz free energy

To gain some insight into the unstable region previously uncovered by looking at the Van der Waals isotherms, let us examine how the Helmholtz free energy of the system, F, varies as a function of V, at constant T.

> R Although this is a natural choice since we have seen in the lecture on availability that a system at fixed T and V will spontaneously evolve towards an equilibrium for which F is a minimum, most other textbooks prefer to use the Gibbs free energy, G, which is minimal for a system in equilibrium at fixed T and p, to discuss phase transitions. As repeatedly mentioned in these lectures, F is more directly linked to the equation of state of thermodynamical systems than G, so we will stick to it.

Speaking in general terms, as p must remain a positive quantity, $(\partial F/\partial V)_{T,N} = -p$ should always be negative. In other words, at fixed T, F should be a decreasing function of V. Furthermore, we expect this decrease to be fast at small V (high pressure) and slow at large V (low pressure). As we have seen previously, when $T > T_c$, p itself, as for an ideal gas, is everywhere a decreasing function of V, so that $(\partial p/\partial V)_{T,N} < 0$ and $(\partial^2 F/\partial V^2)_{T,N} = -(\partial p/\partial V)_{T,N} > 0$. Mathematically, this last statement means that for F to be a true, stable minimum for the system, $F(V)$ needs to be *convex* (i.e. at each point V of $F(V)$, the tangent is below the curve).

Let us now consider the case of a Van der Waals isotherm with $T < T_c$ (see Fig.15.2). We realise that $F(V)$ will then present two inflection points (change of concavity) corresponding to the two extrema of the isotherm, since $(\partial p/\partial V)_{T,N}$ — and thus $(\partial^2 F/\partial V^2)_{T,N}$ — changes sign at these extrema. Given that F is convex both at very small and very large V, it will be *concave* between the extrema, and the stability condition $(\partial p/\partial V)_{T,N} < 0$ will not be satisfied. As a consequence, $F(V)$ as sketched in Fig.15.3 *cannot* represent the Helmholtz free energy of a system in equilibrium in this volume range.

So what went wrong? Why can't there exist an equilibrium solution for the system in this volume range? Well, we have only considered *homogeneous* systems so far, and we know that two fluid states (liquid and gas) exist *separately* from one another. So, in principle, nothing prevents our system from spontaneously separating into two sub-systems, each of them homogeneous, but corresponding to these two different macroscopic states. When such a separation occurs, we say that the system is composed of two *phases* in equilibrium.

> R Nothing guarantees a priori that the two phases can co-exist. We know from the previous lectures on basic thermodynamics that two systems are in mechanical and thermal equilibrium if they have the same pressure and temperature respectively, but this is already the case here because the two phases are located on the same isotherm and we consider a unique value of p on that isotherm. So we are left with only one requirement, which arises because our two sub-systems can exchange particles: they

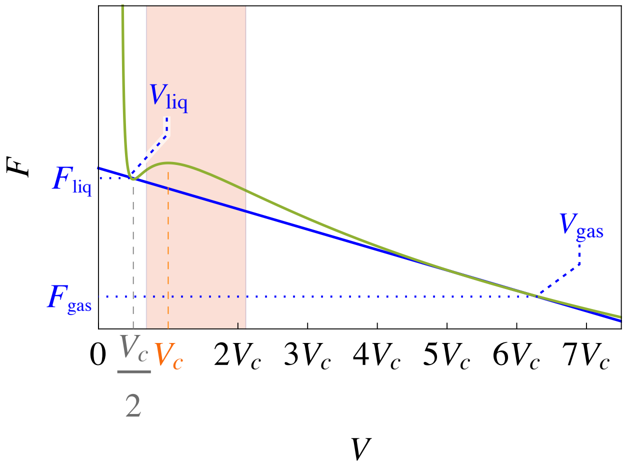

Figure 15.3: Sketch of the Helmholtz free energy (green solid curve) corresponding to the Van der Waals isotherm $T = 3T_c/4$ plotted in Fig.15.2. The blue line represents the bi-tangent to F derived in equation (15.5), with V_{liq} and V_{gas} calculated in example 15.2. The pink shaded region indicates the range of volume values where F is concave and therefore *cannot* be the free energy of a system in equilibrium. This latter must split into two phases and follow the bi-tangent instead.

must be in *diffusive* (also called "chemical" sometimes) equilibrium, i.e. their chemical potential must be the same ($\mu_{\text{gas}} = \mu_{\text{liq}}$). We will prove this latter equality later on, but for the moment note that the three equilibrium conditions involve *intensive* variables.

How do we decide how many particles are in the liquid and gas phases? Well, we know that at fixed T and V, the equilibrium state of a system must minimise the Helmholtz free energy. This means that our two phase solution will only be preferred by the system if its resulting Helmholtz free energy, which is the sum of the Helmholtz free energy of the two phases (F is additive), is smaller than the Helmholtz free energy of the homogeneous system. Pushing this argument a bit further, we conclude that of *all* possible separations in two phases, the one with the lowest Helmholtz free energy will constitute the equilibrium state of the system.

We now turn to the task of calculating this minimal Helmholtz free energy. Let us call $F_{\text{liq}} \equiv F(V_{\text{liq}}, T, N)$, the Helmholtz free energy of the homogeneous system of N molecules at temperature T when it is in the liquid phase, and $F_{\text{gas}} \equiv F(V_{\text{gas}}, T, N)$, the Helmholtz free energy of the homogeneous system when it is in the gas phase. If we build a two phase system with N_{liq} molecules in the liquid phase and $N_{\text{gas}} = N - N_{\text{liq}}$ molecules in the gas phase, the volume occupied by this system will simply be $V_{\text{2ph}} \equiv V = V_{\text{liq}} \times N_{\text{liq}}/N + V_{\text{gas}} \times N_{\text{gas}}/N$, and its Helmholtz free energy $F_{\text{2ph}} = F_{\text{liq}} \times N_{\text{liq}}/N + F_{\text{gas}} \times N_{\text{gas}}/N$. Eliminating $N_{\text{liq}}/N = 1 - N_{\text{gas}}/N$ from this latter expression, we can rewrite F as:

$$F_{\text{2ph}} = F_{\text{liq}} + \frac{V - V_{\text{liq}}}{V_{\text{gas}} - V_{\text{liq}}} \times (F_{\text{gas}} - F_{\text{liq}}) \tag{15.5}$$

where V is a volume point located between V_{liq} and V_{gas}. This is the equation of the straight line joining the points (V_{liq}, F_{liq}) and (V_{gas}, F_{gas}) in Fig.15.3.

> R When $T > T_c$, $F_{\text{2ph}}(V) > F(V)$, as F is always convex in that case. In other words, the straight line (chord) $F_{\text{2ph}}(V)$ is always above the curve $F(V)$ and the system remains homogenous in a single phase over all the volume range since this corresponds to a smaller F.

To obtain the values of V_{liq} and V_{gas} geometrically, i.e. to determine which of all the possible straight lines F_{2ph} follows, we require the equilibrium condition $p(V_{\text{liq}}) = p(V_{\text{gas}})$ on the isotherm, that is to say we require that the pressure be the same for the two homogeneous phases which mark the beginning and the end of the system phase transition. This is a "natural limit" requirement since the two phases must constitute an equilibrium for the system when they co-exist, no matter how many particles are in which phase. Mathematically, this means that $(\partial F/\partial V)_{T,N}(V_{\text{liq}}) = (\partial F/\partial V)_{T,N}(V_{\text{gas}})$, i.e. $F_{\text{2ph}}(V)$ must be tangent to $F(V)$ at both volume values V_{liq} and V_{gas}.

■ **Example 15.2 — Calculation of V_{liq} and V_{gas} for the Van der Waals isotherm $T = 3/4\,T_c$.** For this isotherm, $T = 2a/(9k_B b)$. Together with $p(V_{\text{liq}}) = p(V_{\text{gas}})$, $\mu(V_{\text{liq}}) = \mu(V_{\text{gas}})$ yields a system of transcendental equations, as can easily be seen from the expression of the chemical potential in the Van der Waals model (equation 14.10). In general such a system must be solved numerically, but one can assume $V_{\text{gas}} \gg V_{\text{liq}}$ for this particular isotherm and $V_{\text{liq}} \approx 3bN/2$[*] to eliminate the V_{liq} terms and obtain a simplified transcendental equation: $-\ln(X/2) + 7X - 4 = 0$, which is accurate to first order in $X \equiv bN/V_{\text{gas}}$. Solving this equation yields $V_{\text{gas}} \simeq 19bN \gg V_{\text{liq}}$, as initially assumed. Plugging this value of V_{gas} into the pressure equilibrium constraint, we get $p(V_{\text{liq}}) = p(V_{\text{gas}}) \simeq a/(104b^2)$, so that the Van der Waals EOS turns into the following cubic equation for V_{liq}: $V_{\text{liq}}^3 - (217/9)bNV_{\text{liq}}^2 + 104b^2N^2V_{\text{liq}} - 104b^3N^3 = 0$, whose root $V_{\text{liq}} \simeq 1.47bN$ is the one compatible with our initial assumption for V_{liq}[†]. ■

> R Note that F_{2ph} is also a function of the temperature T, both *explicitly* because of the expressions of F_{liq} and F_{gas} we derived in the previous chapter (see equation 14.6) but also *implicitly* as the values of V_{liq} and V_{gas} depend on the Van der Waals isotherm considered.

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[*] We know that for the two phases to be able to achieve pressure equilibrium, the exact value of V_{liq} must be very close to that which cancels the pressure as p is a very steep function of V for a liquid, see Fig.15.2.

[†] Normally one would need to iterate the procedure, i.e. inject this new value of V_{liq} back into the diffuse equilibrium constraint to get a new value of V_{gas}, and so on and so forth until convergence of both V_{liq} and V_{gas} to a pre-defined level of accuracy is achieved, but our initial guess is already accurate to the level of a few percent, so we stop here.

15.4 Liquid-vapour equilibrium

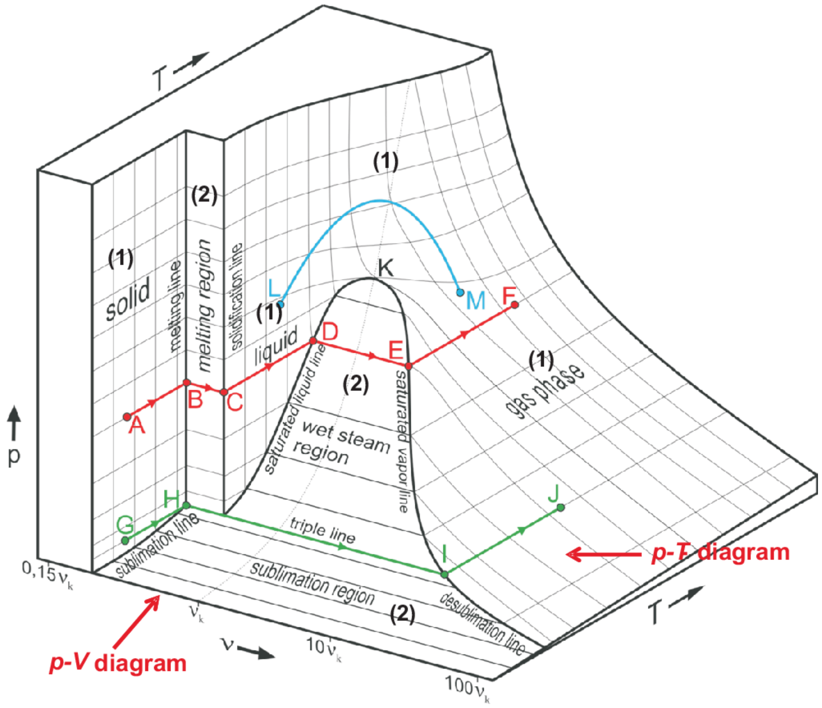

Figure 15.4: Typical three dimensional phase diagram representing surfaces of equilibrium of a pure substance which contracts upon freezing (contrary to e.g. water), borrowed from J. Carstensen (University of Kiel). Bold numbers in between brackets indicate the number of phases of the substance which co-exist in the region. Note that the liquid-vapour *co-existence* curve which joins together all the values of $V_{\rm liq}(T)$ and $V_{\rm gas}(T)$ (and is labelled ‘saturated liquid line’ and ’saturated vapor line’ on the diagram) is *not* planar. The critical point is denoted by the letter ‘K’. Note that even though the solid phase (and its interface with the liquid and gas phases) is missing from our analysis because the Van der Waals model is a poor one for solids, you can intuitively understand what is happening in the different regions of the diagram. For instance, the ‘sublimation line’ and ‘sublimation region’ where solid and vapour co-exist, the ‘melting line’ and ‘melting region’ where solid and liquid co-exist and the ‘triple line’ (in green) where all three phases co-exist. Two interesting isobaric paths are marked on the figure (A to F in red, and G to J in green). On both of these paths you heat the system to go progressively from the pure solid to the pure gas phase, following the arrows, and see how the (specific) volume of the system changes. Notice that from B to C (in the ‘melting region’), even though you continue heating the system, its temperature does not change: the heat simply converts the solid into a liquid, and similarly from D to E in the ‘wet steam region’, heat turns the liquid into vapour. We will come back to this concept of *latent heat* later in this chapter, but it should not surprise you: if the two phases co-exist in thermal equilibrium, their temperature must stay the same as long as they co-exist. The same reasoning applies on the ‘triple line’ (from H to I), where the three phases co-exist in equilibrium. Note that the specific volume increases sharply (discontinuity) when such phase transitions occur, but that otherwise it varies very little (especially in the pure solid and liquid phases, from A to B or C to D or G to H).

Looking back at Fig.15.2, it is now easy to describe the behaviour of the system at equilibrium for $T < T_c$. Let us consider an isotherm at temperature T below the critical temperature and increase the volume slowly enough so that the system goes through a series of equilibrium states. As long as $V < V_{\text{liq}}(T)$, the system is an homogeneous liquid phase. When V becomes greater than V_{liq} and until it reaches a value of V_{gas}, the system splits into two phases: a liquid phase with the characteristics of an homogenous system occupying a volume of V_{liq}/N per molecule, and a gaseous phase (also called *vapour*) with the characteristics of an homogenous system occupying a volume of V_{gas}/N per molecule. The number of particles in the liquid phase is $N_{\text{liq}} = N(V_{\text{gas}} - V)/(V_{\text{gas}} - V_{\text{liq}})$, and the number of particles in the vapour phase is $N_{\text{gas}} = N(V - V_{\text{liq}})/(V_{\text{gas}} - V_{\text{liq}})$.

R The ratio $N_{\text{liq}}/N_{\text{gas}} = (V_{\text{gas}} - V)/(V - V_{\text{liq}})$ can be read directly on the isotherm (Figure 15.2): the number of particles in a phase is inversely proportional to the distance which separates the volume V of the system from the volume of the homogeneous phase in question (V_{liq} or V_{gas}). This is the so-called “lever rule”.

The Helmholtz free energy of the system is then $F_{2\text{ph}}(V)$, which is a linear function of V (see equation (15.5)), so that the pressure $p = -(\partial F_{2\text{ph}}/\partial V)_{T,N}$ is a constant as long as the two phases are present. It is called the *saturation vapour pressure*, and is a function of T *only*. In other words, between volumes V_{liq} and V_{gas} on Fig.15.2, the system does not follow the green Van der Waals isotherm, but the horizontal blue segment. For $V > V_{\text{gas}}(T)$, the system becomes homogeneous again, but in a gas phase this time around. Finally, as T increases, the volumes V_{liq} and V_{gas} get closer together, until they superimpose at a value of V_c for $T = T_c$. For temperatures above T_c, the distinction between liquid and vapour does not make much sense anymore. All this information can be summarised in a three dimensional *phase diagram*, an example of which is plotted in Fig.15.4.

As indicated by the front red arrow on Fig.15.4, the equilibrium surfaces of this three dimensional phase diagram can be projected onto the (p, V) plane that we have used to study the Van der Waals isotherms.

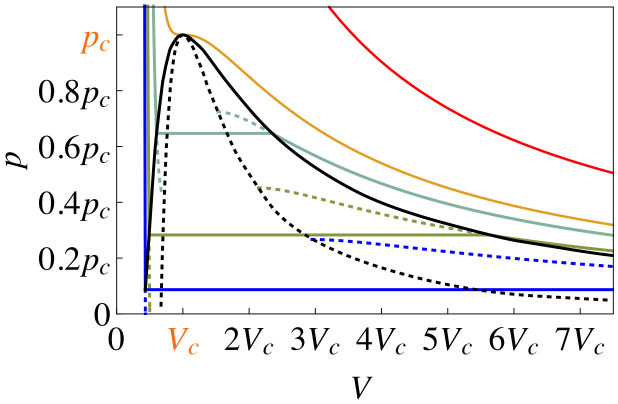

Figure 15.5: Two dimensional phase diagram representing projected surfaces of equilibrium of the Van der Waals fluid onto the (p, V) plane (corresponding to, from top to bottom, isotherms with $T = 1.5T_c$ (red), $T = T_c$ (orange), $T = 0.9T_c$ (blueish-green), $T = 0.75T_c$ (green) and $T = 0.6T_c$ (blue)). Note the existence of *meta-stable* states of the system sandwiched between the co-existence curve (solid black line) and the *spinodial* curve (dotted black line) which links together all the pressure extrema of the Van der Waals isotherms (see Fig. 15.2). We will discuss their meaning shortly.

Alternatively, one can project these surfaces onto the (p, T) plane as indicated by the right hand side red arrow on Fig.15.4:

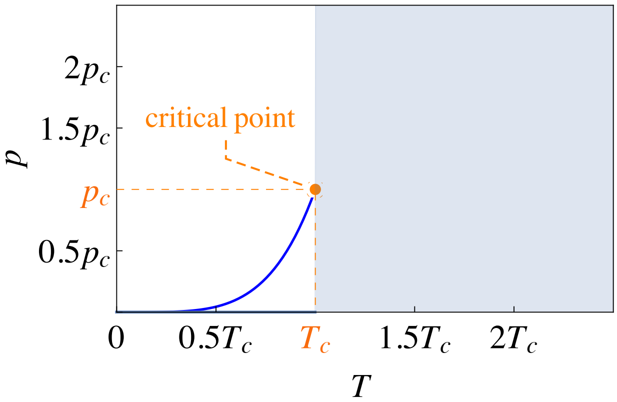

Figure 15.6: Two dimensional phase diagram representing projected surfaces of equilibrium of the Van der Waals fluid onto the (p, T) plane. The solid blue curve which separates the homogeneous liquid phase (blank region above the curve) from its gaseous counterpart (blank region below the curve) is called the *vaporization curve*. The two phases only co-exist along that curve, which is bounded by the critical point at the top, and the *triple point* at the bottom. This latter is not represented on the diagram as it corresponds to the existence of a *solid* phase at low T (see Fig.15.4), that the Van der Waals approximation fails to account for. The shaded light blue region marks the domain where the distinction between liquid and vapour makes little sense and one only talks about a Van der Waals fluid.

15.5 Characteristics of the transition

The liquid-vapour transition we have just studied presents three fundamental properties which pertain to a whole class of phase transitions called *first order* phase transitions.

15.5.1 Co-existence of the two phases

If $T < T_c$, we have seen that the liquid and vapour phases co-exist in thermal and mechanical equilibrium for all values of V between $V_{\rm liq}$ and $V_{\rm gas}$. This means that if the vaporization (or liquefaction) happens at fixed pressure (temperature), the temperature (pressure) remains constant all along the process. We will now demonstrate that the associated thermodynamics potential, namely the Gibbs free energy, G, stays constant as well during the process[‡]. Indeed, during the co-existence regime, we have $G_{\rm 2ph} = F_{\rm 2ph} + pV$, where $F_{\rm 2ph}$ is given by equation (15.5) and $p = -(\partial F_{\rm 2ph}/\partial V)_{T,N}$ so that:

$$\begin{aligned} G_{\rm 2ph} &= F_{\rm liq} + \frac{V - V_{\rm liq}}{V_{\rm gas} - V_{\rm liq}} \times (F_{\rm gas} - F_{\rm liq}) - V\frac{F_{\rm gas} - F_{\rm liq}}{V_{\rm gas} - V_{\rm liq}} \\ &= \frac{F_{\rm liq}V_{\rm gas} - F_{\rm gas}V_{\rm liq}}{V_{\rm gas} - V_{\rm liq}} \qquad (15.6) \end{aligned}$$

and since, as we have seen previously, $V_{\rm liq}$ and $V_{\rm gas}$ are functions of temperature alone and so are $F_{\rm liq}$ and $F_{\rm gas}$ and by extension $G_{\rm 2ph}$. As the temperature is constant during the phase transition process, $G_{\rm 2ph}$ is therefore a constant. From this result, one deduces that at equilibrium between the phases, the Gibbs energy per particle of each homogeneous phase,

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[‡] We have already used this result to calculate $V_{\rm liq}$ and $V_{\rm gas}$ on the specific isotherm $T = 3T_c/4$ in a previous example, but here we establish why this was a legitimate thing to do.

a.k.a. the chemical potentials of the two phases, $\mu_{\text{liq}} \equiv G_{\text{liq}}/N$ and $\mu_{\text{gas}} \equiv G_{\text{gas}}/N$, are *equal*. Indeed, proceeding as we previously did for F, we can call $G_{\text{liq}}(p,T,N)$ and $G_{\text{gas}}(p,T,N)$ the Gibbs free energies of the homogeneous system when *all* its N particles are in the liquid and vapour phases respectively. We then have $G_{\text{2ph}} = G_{\text{liq}} \times N_{\text{liq}}/N + G_{\text{gas}} \times N_{\text{gas}}/N$. As we have just demonstrated that G_{2ph} is a constant and given that p, T and N are fixed, we can differentiate this expression to obtain $\mathrm{d}G_{\text{2ph}} = G_{\text{liq}}/N \times \mathrm{d}N_{\text{liq}} + G_{\text{gas}}/N \times \mathrm{d}N_{\text{gas}} = 0$ so that $(\mu_{\text{liq}} - \mu_{\text{gas}})\mathrm{d}N_{\text{liq}} = 0$ and the equality between chemical potentials immediately follows. As previously mentioned, this form $\mu_{\text{liq}} = \mu_{\text{gas}}$ is often used to characterise the diffusive equilibrium between two phases, in direct analogy with $p_{\text{liq}} = p_{\text{gas}}$ and $T_{\text{liq}} = T_{\text{gas}}$ for the mechanical and thermal equilibria respectively.

15.5.2 Entropy variation during the phase transition

When n molecules out of N go (at constant T and p) from the liquid state to the vapour state, the entropy of the system, S, increases by:

$$\Delta S \equiv \frac{n}{N}(S_{\text{gas}} - S_{\text{liq}}) = nk_B \ln\left(\frac{V_{\text{gas}} - bN}{V_{\text{liq}} - bN}\right) \tag{15.7}$$

given equation (14.9) and using the same notation for the entropies S_{liq} and S_{gas} as previously used for the Helmholtz and Gibbs free energies. This increase is positive since $V_{\text{gas}} > V_{\text{liq}} > bN$ and proportional to the number of particles vaporized, n. This entropy variation must be accompanied by a heat exchange of the system with its surroundings. Indeed, since $G = U - TS + pV$ stays constant during the vaporization, as do T and p, we must have $\Delta G = \Delta U - T\Delta S + p\Delta V = 0$. Defining W and Q as the work and heat given *to* the system during the vaporization process, the first law of thermodynamics yields $\Delta U = W + Q$, and since the transformation is *reversible* (the system stays in thermal, mechanical and diffusive equilibrium throughout), $W = -p\Delta V$ and $Q = T\Delta S$. We thus conclude that $Q > 0$, i.e. heat must be given to the system for ΔG to cancel: this is an *endothermic* process. This heat needed to change the state of the system from the liquid to the vapour phase is called *latent heat* of vaporization and is usually defined per mole:

$$\boxed{L = \frac{\mathcal{N}_A}{n} T\Delta S = RT \ln\left(\frac{V_{\text{gas}} - bN}{V_{\text{liq}} - bN}\right)} \tag{15.8}$$

Note that this is completely intuitive: you have to keep on heating liquid water when it starts boiling to turn all of it into water vapour at the same temperature! As the simple exercise given below shows, this latent heat is large when compared to the amount of heat required to raise the temperature of each different homogeneous phase by tens of degrees.

Exercise 15.1 Take a litre of water at 10°C and vaporize it to 160°C at constant standard pressure $p = 10^5$ Pa. How much heat Q, do you need?
[The specific heat capacities of water in its liquid and vapour phases are $c_p^{\text{liq}} = 4200$ J kg^{-1}K^{-1} and $c_p^{\text{gas}} = 1900$ J kg^{-1}K^{-1} respectively, and its specific latent heat of vaporization at 100°C $L_V = 2.3 \times 10^6$ J kg^{-1}.]
Ans: $Q = 2.8 \times 10^6$ J. ■

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- As V_{liq} and V_{gas} are functions of T alone, so is L.
- $L = 0$ when $T = T_c$ as $V_{\text{liq}} = V_{\text{gas}}$ for that particular isotherm.
- $S(T)$ will exhibit a discontinuity when the phase transition occurs, as $\Delta S > 0$ but

the temperature does not change. This jump in the value of S will be of order L/T.
• The reverse process also exists: vapour can condense into a liquid. This is an *exothermic* process where the latent heat is given to the surroundings of the system.

15.5.3 Meta-stable states

Let us come back to the Van der Waals isotherms in Fig.15.2. Between point $p(V_{\text{liq}})$ and the minimum of p as well as between the maximum of p and $p(V_{\text{gas}})$, p still is a decreasing function of V, and thus the compressibility of the system is positive. Of course we have shown that the true equilibrium state of the system does not follow the Van der Waals isotherms between $p(V_{\text{liq}})$ and $p(V_{\text{gas}})$, but the points in the two regions previously defined can still be reached by the system: they are called *meta-stable* states.

Indeed, considering our $F_{2\text{ph}}$ formulation as a linear function of V (equation (15.5)), one clearly sees that any "local" straight line connecting two points located either between point F_{liq} and the first inflection point of $F(V)$ or between its second inflection point and point F_{gas} will be *above* $F(V)$ (see Fig.15.3). Conversely, only straight lines joining a point between point F_{liq} and the first inflection point of $F(V)$ to another point between its second inflection point and point F_{gas} are *below* $F(V)$. This tells us that if somehow the system manages, one way of another, to find itself trapped between F_{liq} and the first inflection point of $F(V)$ or between its second inflection point and F_{gas}, fluctuations of small amplitude will *not* be able to move it away from this point: the system is *locally* stable. However, a fluctuation with a large enough amplitude will "see" that there exists a possibility of realizing a more stable state by separating into two phases. As the probability of fluctuations goes down rapidly when their amplitude increases, a meta-stable state can therefore be maintained for quite a long time.

In practice, when we slowly increase the volume available to the liquid at constant T, the system can remain homogeneous beyond point F_{liq}, in a state called *superheated liquid*, but not beyond the first inflection point of $F(V)$ when it becomes violently unstable (negative compressibility). In a similar manner, if we slowly reduce the volume available to the vapour at fixed T, we will be able to keep it in a homogeneous phase beyond point F_{gas} (but not beyond the second inflection point of $F(V)$), in a meta-stable state called *supercooled vapour*. Important perturbations (like a drop of liquid in supercooled vapour, or a vapour bubble in a superheated liquid, impurities, or a simple shock) will trigger an evolution of the system towards its true equilibrium: the two-phase state. The meta-stable domain is bounded by the two phase co-existence curve on one side, and the curve linking the extrema of the different Van der Waals isotherms (or equivalently the inflection points of the different corresponding $F(V)$) as T varies. Such a curve is called a *spinodial curve* and is represented on Fig.15.5.

15.6 The Clausius-Clapeyron equation

Let us now examine the other two dimensional phase diagram, the one obtained when projecting in the (p, T) plane (see Fig.15.6). The line in this diagram defines the region where the two phases co-exist.In other words, if we are in the homogeneous gas phase on the line (i.e. $T < T_c$) and p increases slightly, we will jump to the homogeneous liquid phase immediately. This will appear as a volume discontinuity and is a characteristic of the liquid-vapour phase transition.

On either side of the line, *all* N particles are either in the gas or the liquid phase. As we have previously shown, the Gibbs free energy (at fixed p and T) of these two phases are equal: $G_{\text{liq}} = G_{\text{gas}}$. This means that G is continuous as we cross the phase transition line.

Let us then sit on this line and move upwards along it by an infinitesimal amount. As the total number of particles, N, is constant, the change in G caused by this displacement for each phase is given by:

$$\begin{aligned} \mathrm{d}G_{\mathrm{liq}} &= -S_{\mathrm{liq}}\mathrm{d}T + V_{\mathrm{liq}}\mathrm{d}p \\ \mathrm{d}G_{\mathrm{gas}} &= -S_{\mathrm{gas}}\mathrm{d}T + V_{\mathrm{gas}}\mathrm{d}p \end{aligned} \tag{15.9}$$

Equating these two expressions to enforce the continuity of G across the phase transition line at the new position yields:

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_{\mathrm{gas}} - S_{\mathrm{liq}}}{V_{\mathrm{gas}} - V_{\mathrm{liq}}} = \frac{L}{T(V_{\mathrm{gas}} - V_{\mathrm{liq}})}} \tag{15.10}$$

where the last equality arises from the definition of latent heat ($L = T\Delta S$). This relation which defines the slope of the phase transition line as the ratio of the latent heat released by the phase transition and the discontinuity in volume between the phases is known as the *Clausius-Clapeyron equation*.

Exercise 15.2 Find an approximated solution, $p(T)$, to the Clausius-Clapeyron equation. [Assume that L is independent of T, $V_{\mathrm{gas}} \gg V_{\mathrm{liq}}$ and that the gas EOS is that of an ideal gas.]
Ans: $p = p_0 \exp(-L/(k_B T))$. ■

15.7 Classification of phase transitions

The liquid-gas phase transition that we have just studied is not the only kind of phase transition that exists in nature. Ehrenfest thus proposed to classify phase transitions based on whether the derivatives of the thermodynamical potential (usually F or G) of a system are continuous. This means that if the n^{th} derivative of this potential is discontinuous, we will say that we have a n^{th} order phase transition. In the case of the liquid-gas phase transition, as we have seen, latent heat is released/absorbed, so $S = -(\partial F/\partial T)_{V,N}$ is discontinuous, as is $V = (\partial G/\partial p)_{T,N}$. So we are dealing with a first order phase transition.

In practice, phase transitions of order greater than two are rare, and the thermodynamical limit tends to break down at phase transition (fluctuations are large), so the thermodynamic potentials are not well defined. For these reasons, the modern classification is more simple than that originally advocated by Ehrenfest: if latent heat is present, the phase transition is first order; if not, the phase transition is called *continuous*.

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- Note that when $T \to T_c$, the amplitude of the discontinuity diminishes as $S_{\mathrm{liq}} \to S_{\mathrm{gas}}$, and that for $T \geq T_c$ we do get a *continuous* phase transition.
- For most simple materials, the liquid-gas phase transition is part of a larger phase transition which includes a solid phase at smaller T or higher p, as illustrated on Fig.15.4.

16. Cooling of real gases

The purpose of these final lectures is to close the loop. Recall the Basic Thermodynamics part of the course at the beginning of the year, where we studied the thermal behaviour of ideal gas under certain practical transformations (adiabatic, isothermal expansions, etc ...). We will now see how real gases behave during similar transformations and what practical consequences this has.

16.1 Joule expansion revisited

Remember the Joule expansion for ideal gases (section 5.6.2). No heat enters or leaves the system as the containers are thermally insulated, no work is done either by or on the gas as it expands in a vacuum, so its internal energy, U, is unchanged according to the first law. For an ideal gas, U is a function of T alone, so $\Delta U = 0 \implies \Delta T = 0$.

We can reformulate this statement using the *Joule coefficient*, $\mu_J \equiv (\partial T/\partial V)_U$, i.e. the change of temperature induced by a change in volume at constant internal energy, which is the relevant constraint in the case of a Joule expansion. Using the reciprocity and reciprocal theorems, we can re-write the Joule coefficient as $\mu_J = -(\partial T/\partial U)_V(\partial U/\partial V)_T = -1/C_V(\partial U/\partial V)_T$. From the first law of Thermodynamics, $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, so that $(\partial U/\partial V)_T = T(\partial S/\partial V)_T - p$, and using the Maxwell relation for F (equation (6.7)), one gets $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$, therefore

$$\boxed{\mu_J = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]} \tag{16.1}$$

As we have just recalled, for a mole of an ideal gas with EOS $p = RT/V$, $\mu_J = 0$. Now for a real gas, we have seen than the pressure is always lower than for an ideal gas because of the presence of an attractive long-range force between molecules. This means that since $C_V > 0$, $\mu_J < 0$ for a real gas. Indeed, as U is *not* changing in a Joule expansion ($Q = W = 0$), and the potential energy of the gas becomes less negative as it expands (the distance between gas molecules increases and the intermolecular attraction becomes weaker), then the kinetic energy of the gas must also decrease and the real gas must thus cool.

Let us calculate by how much. That is where μ_J becomes handy. Indeed, during a Joule expansion, the change of T is simply:

$$\Delta T = \int_{V_i}^{V_f} \mu_J \, \mathrm{d}V = -\int_{V_i}^{V_f} \frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]\mathrm{d}V \tag{16.2}$$

Take the Van der Waals EOS. For one mole of gas, it yields* $p = RT/(V-b) - a/V^2$ so $(\partial p/\partial T)_V = R/(V-b)$ and $\mu_J = -a/(C_V V^2)$. As $V_i < V_f$, we deduce that $\Delta T = -a/C_V \times (1/V_i - 1/V_f) < 0$ for a Van der Waals gas: as expected, it cools.

Exercise 16.1 What is the temperature change when one Joule expands 1 mole of Helium enclosed in a $(0.1\text{ m})^3$ container into a $(0.2\text{ m})^3$ container?
[Use the Van der Waals EOS with $a = 0.00346$ J m^3 mol^2 and the *molar heat capacity*[a] of Helium, $C_V = 12.48$ J K^{-1} mol^{-1}.]
Ans: $\Delta T = -0.243$ K. ■

[a] This is the specific heat of Helium times its molar mass (4g).

16.2 Joule-Kelvin expansion

The Joule expansion is interesting conceptually, but of little practical use. As we have seen, the gas cools a bit when it expands but then “so what”? What you would want in practice is a kind of “cooling machine” where you feed in warm gas and get out cold liquid! As it turns out, James Joule and William Thomson (a.k.a. Lord Kelvin) discovered the process such a machine could be based on. Note that this process, similarly to the Joule expansion, is inherently *irreversible.*

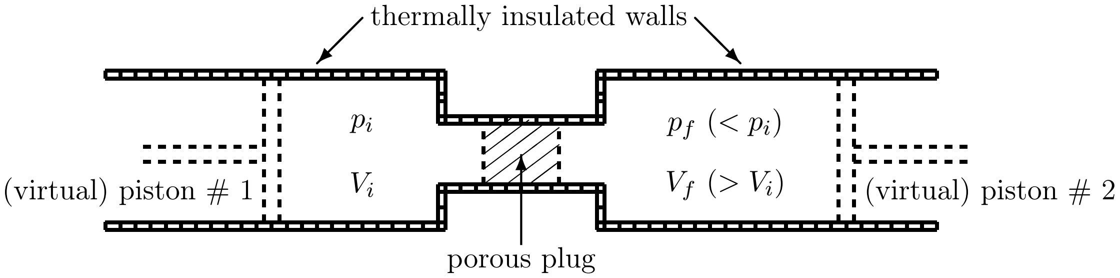

Figure 16.1: Schematic diagram of a Joule-Kelvin expansion.

Consider a highly pressurized gas at pressure p_i enclosed in a thermally insulated container of volume V_i, which is forced through a porous plug (see Fig. 16.1). It might be helpful to pretend it is pushed by a piston†. The internal energy of this gas is U_i and the work done by the piston is $p_i V_i$. This gas expands as it goes through the plug and occupies another thermally insulated container of volume $V_f > V_i$. It also has to do work to push

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*Strictly speaking, the constants a and b in this molar form of the equation are not the same as those in equation (14.7): they differ by a factor of $\mathcal{N}_A^2$ and $\mathcal{N}_A$ respectively, as they are defined per mole rather than per molecule.

†In reality, this piston could be “virtual” and it would then be the inflowing gas behind the gas that is enclosed in volume V_i that is doing the pushing.

another piston which exerts a lower pressure $p_f < p_i$ at the back of the container[‡]. This work is $p_f V_f$. The temperature of the gas may change in the process, so we will denote its internal energy by U_f.

The first law tells us that since there is no heat exchange, the change of energy $\Delta U = U_f - U_i$ must be equal to the amount of work done *on* the gas to get it through the plug, minus the amount of work done *by* the gas as it comes out of it. Mathematically, $\Delta U = p_i V_i - p_f V_f$, i.e $U_i + p_i V_i = U_f + p_f V_f$ or $H_i = H_f$, that is to say the process conserves the enthalpy of the gas. As in the Joule expansion we want to know how much the temperature of the gas has changed during the process, so we define the *Joule-Kelvin coefficient*, $\mu_{JK} \equiv (\partial T/\partial p)_H$, which measures the temperature change of the gas as we reduce its pressure at constant enthalpy. In a similar fashion as what we did for μ_J, we can use the reciprocity and reciprocal theorems, coupled to the definition of C_p[§] to re-write this coefficient as $\mu_{JK} = -(\partial T/\partial H)_p (\partial H/\partial p)_T = -1/C_p (\partial H/\partial p)_T$. Again from the first law of Thermodynamics, $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, so that $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$ and $(\partial H/\partial p)_T = T(\partial S/\partial p)_T + V$, and using the Maxwell relation for G (equation (6.8)), one gets $(\partial H/\partial p)_T = -T(\partial V/\partial T)_p + V$, therefore

$$\boxed{\mu_{JK} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]} \tag{16.3}$$

As for μ_J, for a mole of an ideal gas with EOS $V = RT/p$, $\mu_{JK} = 0$, and thus the change in temperature during a Joule-Kelvin expansion,

$$\Delta T = \int_{p_i}^{p_f} \mu_{JK}\ \mathrm{d}p = \int_{p_i}^{p_f} \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]\mathrm{d}p \tag{16.4}$$

is also nil. But what about a real gas? Will ΔT be positive or negative? Well, it depends on the sign of μ_{JK}, which can, contrary to μ_J, be positive or negative; and since $C_p > 0$, it ultimately depends on the sign of $T(\partial V/\partial T)_p - V$.

> R The change in entropy during a Joule-Kelvin expansion can be calculated quite straightforwardly. As the enthalpy is constant, we have $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p = 0$, so that $\mathrm{d}S = -V/T\mathrm{d}p$, and thus
>
> $$\Delta S = -\int_{p_i}^{p_f} \frac{V}{T}\ \mathrm{d}p$$
>
> which for a mole of ideal gas with EOS $V/T = R/p$ yields $\Delta S = R\ln(p_i/p_f) > 0$, in line with what we expect for an irreversible process.

Therefore, the equation

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}} \tag{16.5}$$

defines the so called *inversion curve* in the $T - p$ plane, i.e. the locus where the Joule-Kelvin expansion switches from cooling the gas to heating it (see Fig.16.2).

[‡] Again, in reality, the expanding gas could be pushing the lower pressure gas in front of it instead of the piston, as long as any change in the bulk kinetic energy of the gas flow can be considered negligible throughout the process.

[§] At constant p we have $\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V$, as we used in equation (3.1).

■ **Example 16.1 — Calculation of the inversion curve for a Van der Waals gas.** Starting from the Van der Waals EOS in the form $p = Nk_BT/(V-bN) - aN^2/V^2$, we calculate $(\partial T/\partial V)_p$, take its inverse, multiply it by T and substract V from the result to obtain equation (16.5) in the form $(V-bN)/(1-\xi) - V = 0$, with $\xi = 2aN(V-bN)^2/(k_BTV^3)$. This yields $\xi = bN/V \iff (V-bN)^2 = bk_bTV^2/(2a)$[¶]. As V, $(V-bN)$, T, a and b are all positive, we can take the square root of this last equation to get $V = bN/(1-\sqrt{bk_BT/2a})$. Injecting this expression for V in the Van der Waals EOS then yields the following explicit form of the inversion curve:

$$p = \frac{1}{b^2}\left(-\frac{3bk_B}{2}T + \sqrt{8abk_B}T^{1/2} - a\right)$$

The (quadratic) equation $p = 0$ has two roots, $T_+ = 2a/(bk_B) = 27T_c/4$ and $T_- = 2a/(9bk_B) = 3T_c/4$, and a maximum pressure $p_{\max} = 9p_c$, achieved when $\mathrm{d}p/\mathrm{d}T = 0$, i.e. for $T = 8a/(9bk_B) = 3T_c$. This curve is plotted in Fig.16.2. ■

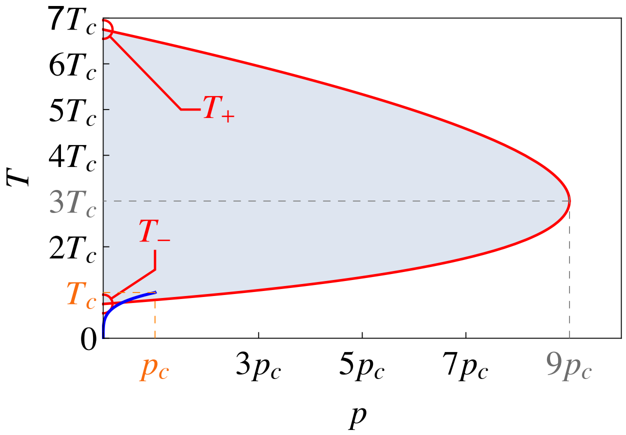

Figure 16.2: Joule-Kelvin expansion inversion curve (in solid red) for a Van der Waals gas, as calculated in example 16.1. The inversion curve separates a light blue shaded domain where $\mu_{JK} < 0$ which means that the Joule-Kelvin expansion is cooling the gas, from a blank region where $\mu_{JK} > 0$ and the Joule-Kelvin expansion heats the gas. Note that the inversion curve also crosses the co-existence curve (in solid blue), which makes it very interesting a process to liquefy gases!

T_+, as calculated in example 16.1 for the Van der Waals gas, is called the *maximum inversion temperature*, as it is clear that above this temperature the Joule-Kelvin expansion can only heat the gas, regardless of its pressure. Note that this maximum temperature can be quite low. For instance, ^{4}He has $T_+ = 43$ K. This means that to cool Helium using the Joule-Kelvin process, one needs to cool it below 43 K first! Finally, let us mention that the Joule-Kelvin process is very useful to liquefy gases (intersection with the co-existence curve: see Fig.16.2), and one can show that a liquefier needs to work on the inversion curve for maximal efficiency.

[¶] Rigorously speaking, this solution is only valid for $\xi \neq 1$, but in the case $\xi = 1$, we have $(\partial T/\partial V)_p = 0$ so T independent of V and the solution to the inversion curve equation is $V = 0$, which we can rightfully discard.