

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.

*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. $N \geq N_A \simeq 6.02 \times 10^{23}$, with 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 these definitions as follows:

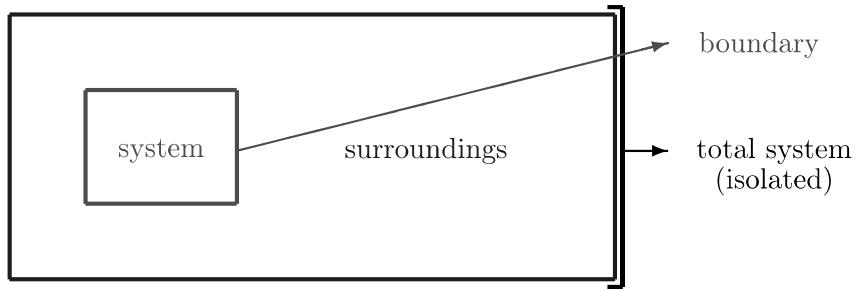


Figure 2.1: Schematic diagram of a thermodynamical system.

- ⓘ 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).

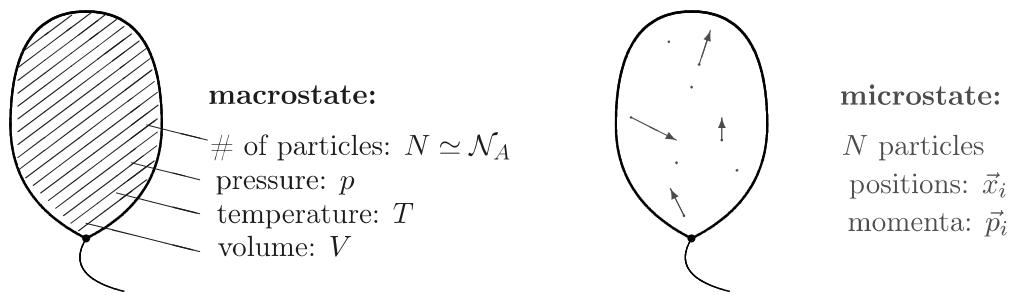


Figure 2.2: Example of macrostates and microstates: inflatable balloon.

We will start these lectures by considering *closed* systems, i.e. systems with $N = \text{C}^{\text{st}}$, 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.

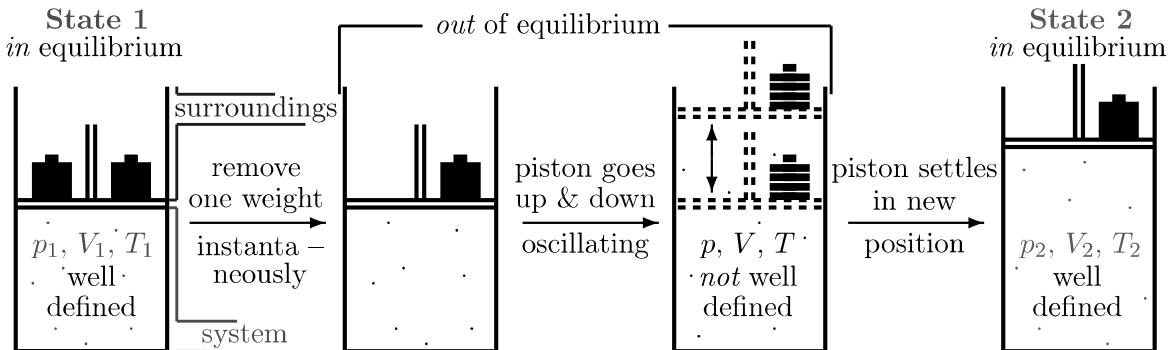


Figure 2.3: Example of a system in and out of equilibrium: gas is enclosed in a container whose top is a piston initially balanced by two identical weights. One of the weights is then removed instantaneously.

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

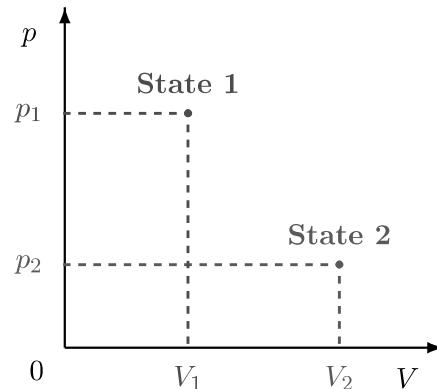


Figure 2.4: $p - V$ diagram for the gas enclosed in the container presented in Fig 2.3. Whilst one can mark the two (well defined) macro states, it is *impossible* to draw the path taken by the system to go from State 1 to State 2!



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 $pV = Nk_B T$ where n is the amount of substance in moles, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ the molar gas constant, and $k_B = R/N_A = 1.381 \times 10^{-23} \text{ J K}^{-1}$ the *Boltzmann constant*. ■



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.

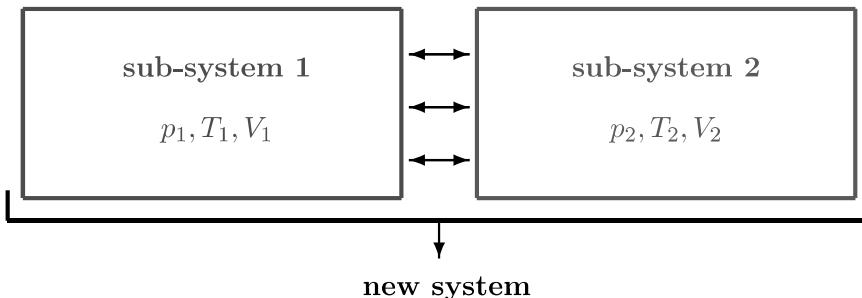


Figure 2.5: Schematic diagram of two thermodynamical sub-systems which are brought into contact (along the double arrows) and interact to form a new thermodynamical system.

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

*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.



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 $pV = Nk_B T$: 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.

*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 *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).



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:

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

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:

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

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, dX is an *exact differential* and functions of state have exact differentials.



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

Mathematical reminder: Let $f_1(x, y) dx + f_2(x, y) dy$ be the change undergone by a function when its variables x and y change to $x + dx$ and $y + dy$. 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 $\bar{d}X$.

■ Example 3.1

- $f(x, y) = xy \rightarrow df = d(xy) = x dy + y dx$
- $\bar{d}g = y dx$

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

$$\Delta f = \int_{(0,0)}^{(1,1)} df = \int_{(0,0)}^{(1,1)} d(xy) = \left[xy \right]_{(0,0)}^{(1,1)} = 1$$

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

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

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:

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

whilst in the second case,

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

since $dx = 0$ in the second integral, as $x = 1$ is fixed. ■

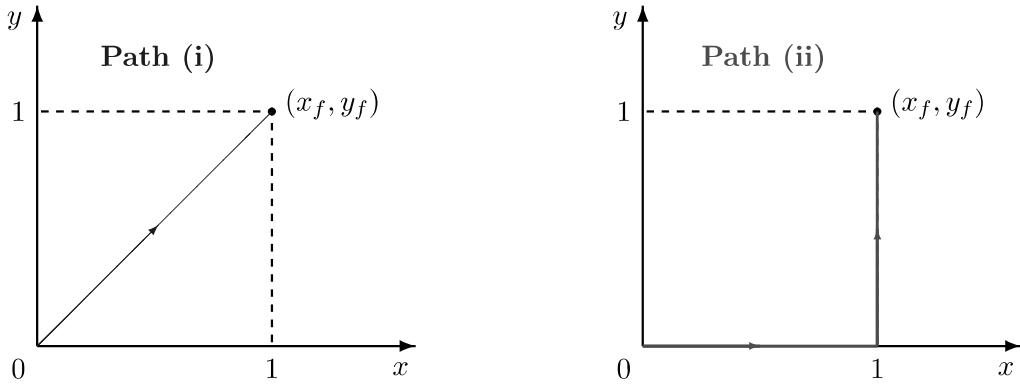


Figure 3.1: Paths (i) and (ii) considered in Example 3.1

R If you replace x by V and y by p in the previous example you get $\mathrm{d}g = p \mathrm{d}V = -\mathrm{d}W$. 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,

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$$

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! $\mathrm{d}Q$ and $\mathrm{d}W$ 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 $\mathrm{d}W = \vec{F} \cdot \vec{dh}$, 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 $\mathrm{d}W = -p_{\text{surr}} \mathrm{d}V$ [‡].

R There exists other kinds of work (electrical, magnetic) where we will have to go back to the previous, more general definition of $\mathrm{d}W = \vec{F} \cdot \vec{dh}$, 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:

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

[‡]Note the sign: $\mathrm{d}W > 0$ 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!



This definition of work means that there are *two* conditions to be met for $p dV$ 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!



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 dT [unit $J K^{-1}$]. Mathematically, we write this definition as $C \equiv dQ/dT$.

[§]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:

$$C = \frac{dU - dW}{dT}$$

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. $dW = 0$, 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 $dW < 0$ 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:

$$C_p = \frac{dU - (-pdV)}{dT} = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p \quad (3.1)$$

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.

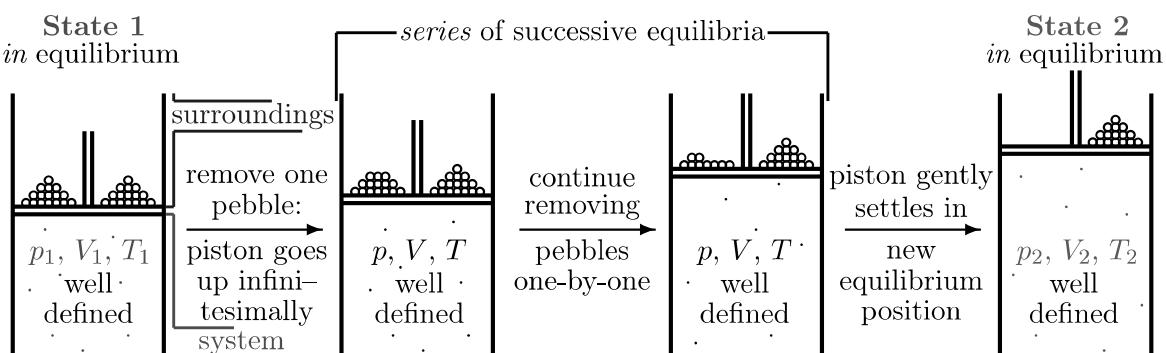


Figure 4.1: Example of a system undergoing a quasi-static process: gas is enclosed in a container whose top is a piston initially balanced by a given weight. Infinitesimal amounts of weight are then removed gradually.



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

*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).

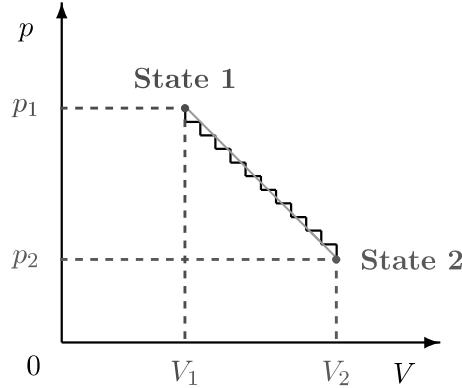


Figure 4.2: $p - V$ diagram for the gas enclosed in the container presented in Fig 4.1. It is now possible to draw the path taken by the system to go from **State 1** to **State 2**, taking infinitesimal steps which ultimately converge to the orange solid line as the step size goes to zero!

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 $dW = -pdV$ 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).

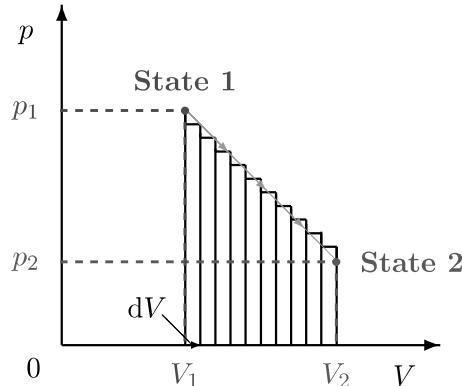


Figure 4.3: Work done by the gas enclosed in the container presented in Fig 4.1 as it expands when the pebbles are removed. The amount of work clearly is the area underneath the orange curve. Note the arrows which mark the direction taken: if the process is reversible, these will point in the other direction 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:

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

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:

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

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).

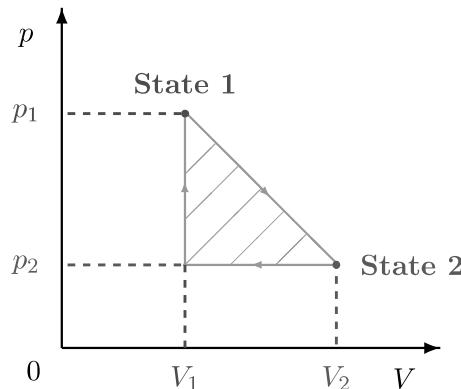


Figure 4.4: Work done (orange hatched area) going from State 1 to State 2 and back to State 1, if two different paths are taken to go back and forth (follow the arrows). This is simply the difference between the areas under the forward path and the reverse path.

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 19th 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.

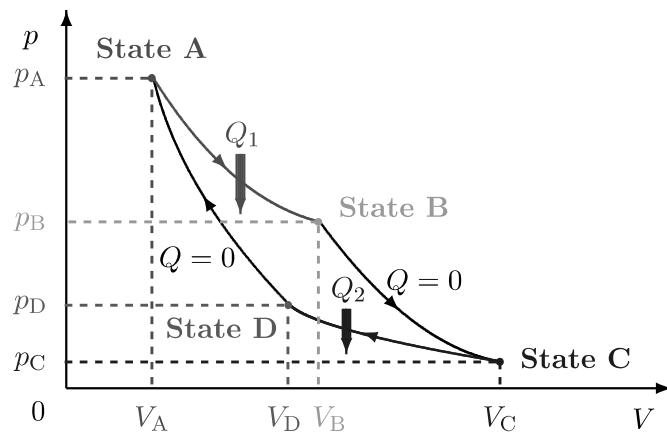
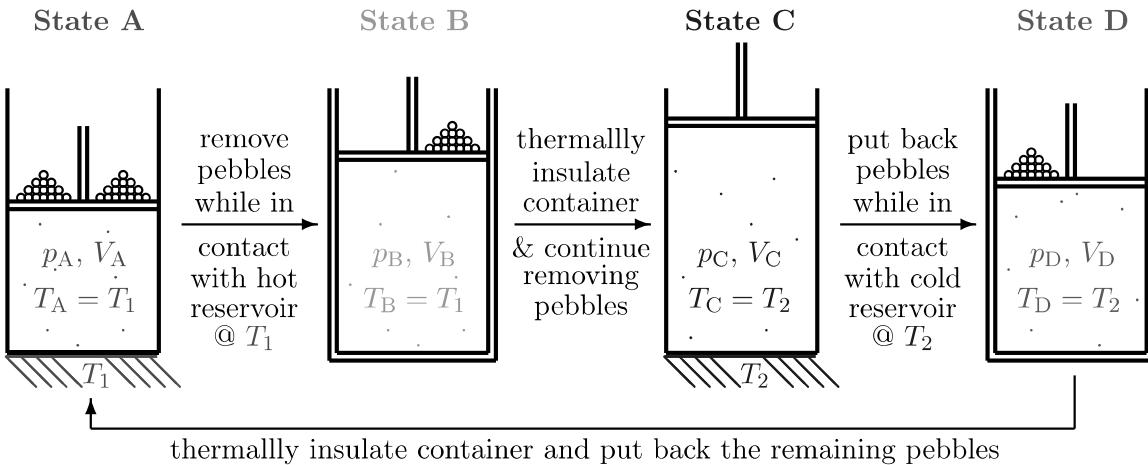


Figure 4.5: Carnot cycle for an ideal gas (top part of the figure) together with its p – V diagram representation (bottom part).

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

[†]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 $B \rightarrow C$ path is non nil), so $V_C > V_B$, $p_C < p_B$ and $W_{BC} < 0$. Applying the first law yields $\Delta U = W_{BC} < 0$ and therefore, as for an ideal gas $U \propto T$, we have $T_C = T_2 < T_1$: 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 $T_2 = T_C$. We then put back some of the pebbles. Reasoning in a similar manner than for the $A \rightarrow B$ path, albeit in the reverse direction as the system is now compressed, we conclude that $T_D = T_2 = T_C$, $V_D < V_C$, $p_D > p_C$ and $W_{CD} > 0$. $\Delta U = 0$ along this isotherm therefore the first law tells us that $Q_2 = -W_{CD} < 0$ (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 $B \rightarrow C$ 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, $V_A < V_D$, $p_A > p_D$, $W_{DA} > 0$. Applying the first law, we deduce $\Delta U = W_{DA} > 0$ and thus $T_A = T_1 > T_2$ for our ideal gas: it has heated.

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

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 $-W_{\text{tot}}$ 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:**

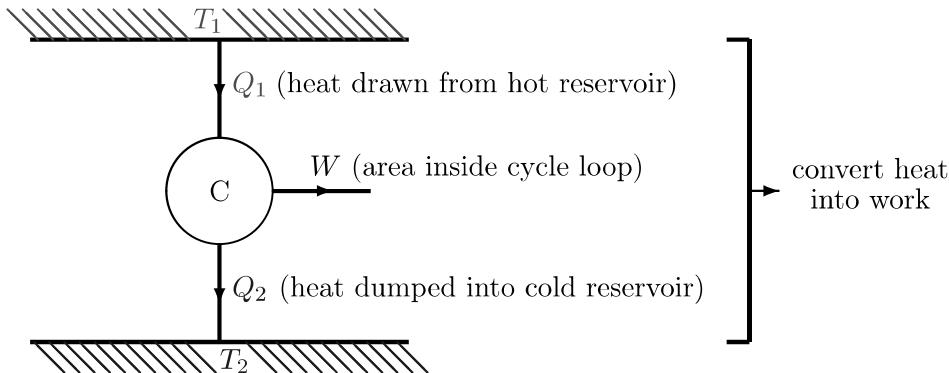


Figure 4.6: Diagram of a (Carnot) engine, C.

[†]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

$$\boxed{\eta = \frac{Q_1 - |Q_2|}{Q_1} = 1 - \frac{|Q_2|}{Q_1}} \quad (4.1)$$

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 $A \rightarrow B$: $T = T_1 = C^{\text{st}}$ so $dU = 0$ and the first law yields $dQ = -dW$. The process is reversible so $p = p_{\text{surr}}$ and $dW = pdV$, so $dQ = pdV$. Integrating:

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

- From $B \rightarrow C$: $dQ = 0$ so the first law (+ reversible process) yields $dU = dW = -pdV$. For a mono-atomic gas $U = 3/2 nRT$, so $dU = 3/2 nRdT$, and using the ideal gas equation of state, one gets $3/2 dT = -TdV/V$, so separating variables and integrating:

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

- R** This adiabatic expansion can be written in the more general form $TV^{\gamma-1} = C^{\text{st}}$, 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 $pV^\gamma = C^{\text{st}}$, 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 $C \rightarrow D$: $Q_2 = nRT_2 \ln(V_D/V_C) < 0$ since $V_D < V_C$
- From $D \rightarrow A$: $T_1/T_2 = (V_D/V_A)^{2/3}$

From $B \rightarrow C$ and $D \rightarrow A$, 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:

$$\eta = 1 - \frac{T_2}{T_1} \quad (4.2)$$



- 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 than 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 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

*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, 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 C_R , as illustrated on the diagram below (Fig. 5.1):

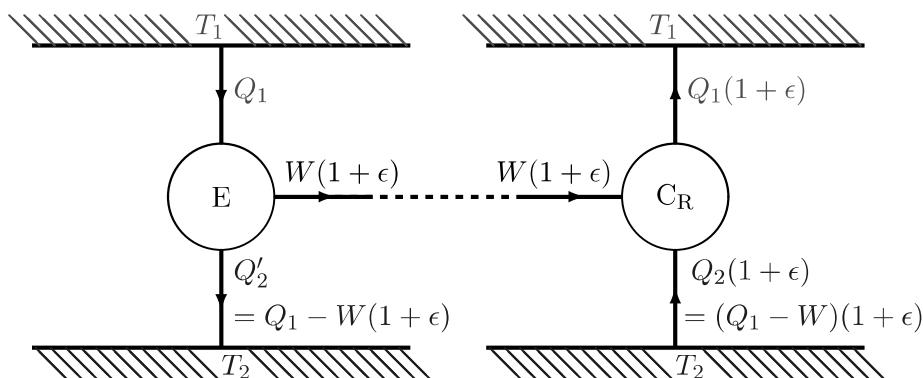


Figure 5.1: Schematic diagram of an engine E driving a reverse Carnot engine C_R .

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

The diagram on Fig. 5.1 simplifies to:

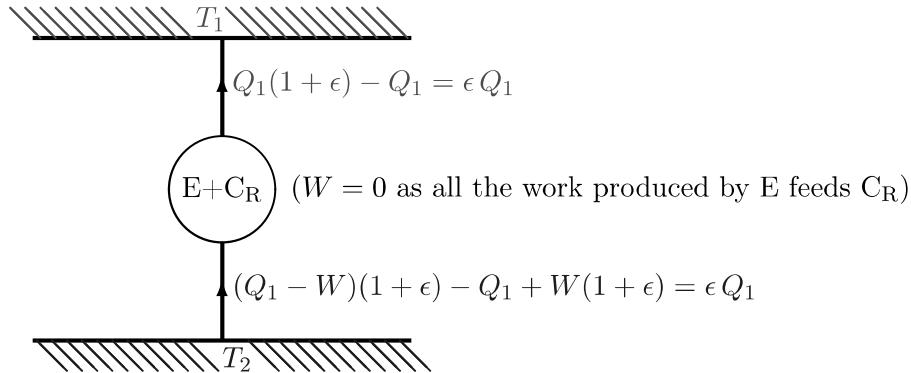


Figure 5.2: Simplified version of diagram on Fig. 5.1.

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:

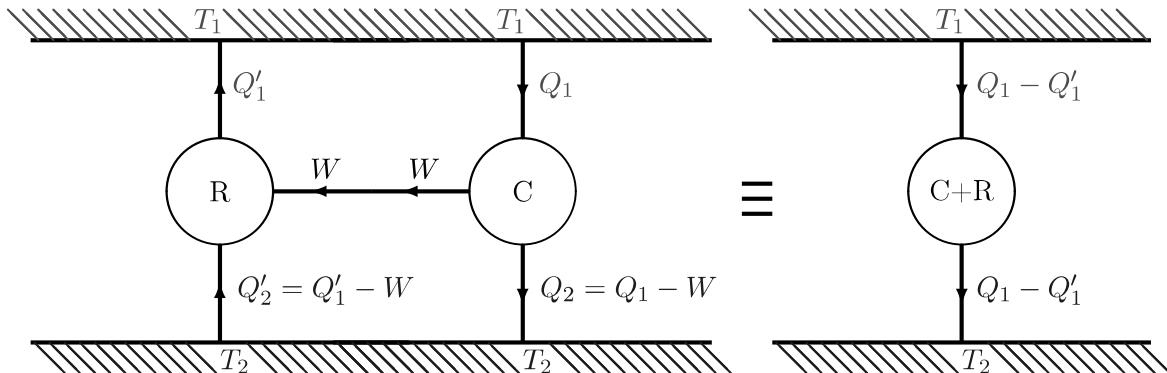


Figure 5.3: Schematic diagram of a Carnot engine C driving a reverse engine R.

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 C_R :

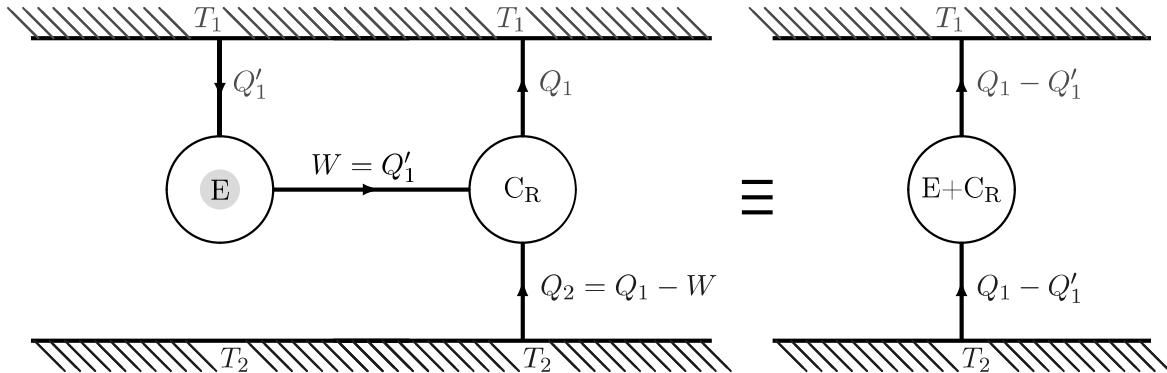


Figure 5.4: Schematic diagram of a hypothetical engine E which violates Kelvin's statement of the second law driving a reverse Carnot engine C_R .

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:

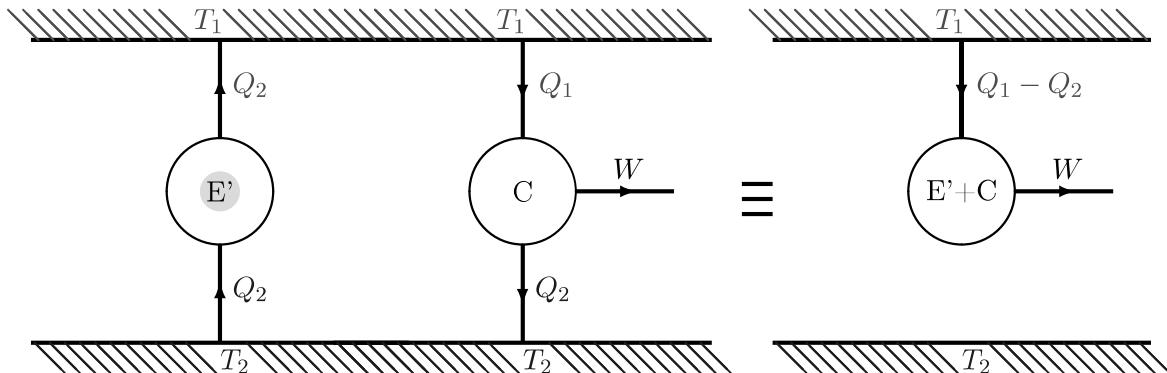


Figure 5.5: Schematic diagram of a hypothetical engine E' which violates Clausius' statement of the second law connected to a Carnot engine C.

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:

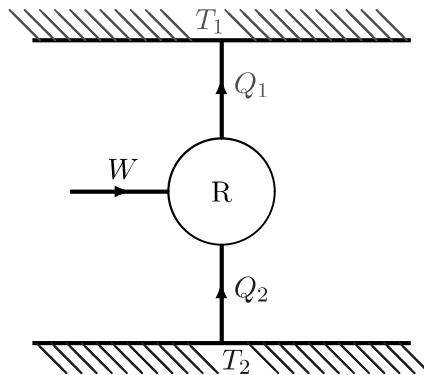


Figure 5.6: Schematic diagram of a refrigerator R.

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:

$$\eta = \frac{Q_2}{W} \quad (5.1)$$

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 !



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:

$$\eta = \frac{Q_1}{W} \quad (5.2)$$

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 $\eta_{CH} = T_1/(T_1 - T_2)$.

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 $T_1 = 373\text{K}$ (boiling point of water) and $T_2 = 320\text{K}$ (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 it 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: $\eta_O = 1 - (V_2/V_1)^{2/5}$. ■

^aWe 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 $\eta_O = 0.56$, the real engine only achieves an efficiency $\eta \sim 25\%$.



- 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:

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

• **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.

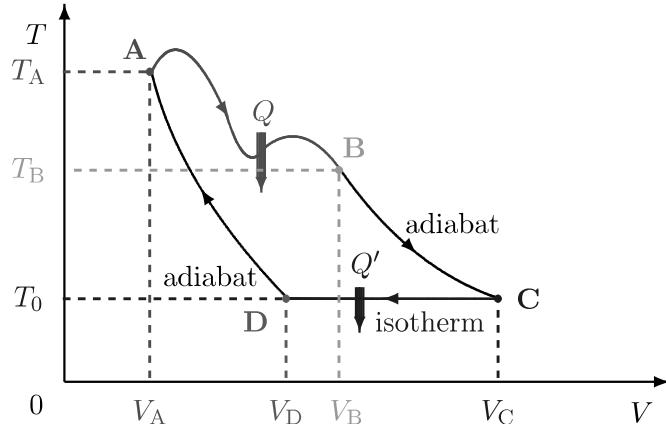


Figure 5.7: $T - V$ diagram of a cycle with a general, albeit quasi-static, process (A → B).

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

[‡]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 dQ'_i the infinitesimal amount of heat dumped into the cold reservoir at temperature T_0 by the very same i^{th} sub-cycle.

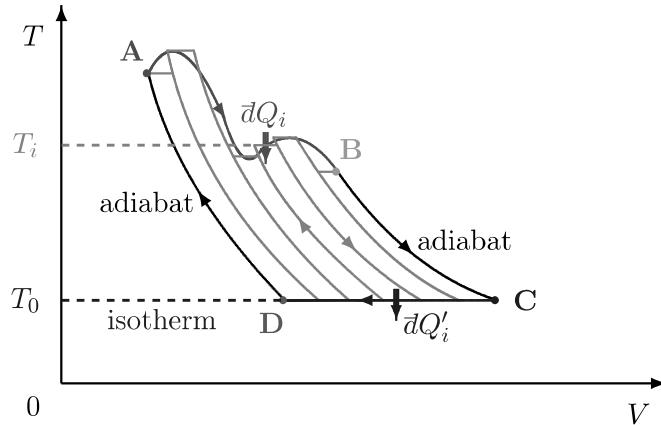


Figure 5.8: $T - V$ diagram of the Fig. 5.7 cycle, divided into infinitesimal elementary Carnot sub-cycles.

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.

$$\left(1 - \frac{|dQ'_i|}{dQ_i}\right) = \left(1 + \frac{dQ'_i}{dQ_i}\right) \leq \left(1 - \frac{|dQ'_i|}{dQ_i}\right)_{\text{rev}} = \left(1 + \frac{dQ'_i}{dQ_i}\right)_{\text{rev}}$$

since $dQ'_i < 0$. We also have demonstrated for an ideal gas (but this result holds for any substance) that $(dQ'_i/dQ_i)_{\text{rev}} = -T_0/T_i$ and therefore, injecting this relation in the previous inequality, we obtain that $dQ_i/T_i \leq -dQ'_i/T_0$ for *any* process A→B. Now for the A→B Carnot sub-processes, $(dQ_i/T_i)_{\text{rev}} = -dQ'_i/T_0$, so we conclude that for any general process A→B, one has $dQ_i/T_i \leq (dQ_i/T_i)_{\text{rev}}$.

Going around the full cycle ABCD on Fig. 5.8 thus yields:

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

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 $\oint (dQ/T)_{\text{rev}} = 0$, we have that $\int_A^B (dQ/T)_{\text{rev}}$ is independent of path. Or in other words, $(dQ/T)_{\text{rev}}$ is an exact differential, and we can therefore write:

$$dS \equiv \left(\frac{dQ}{T} \right)_{\text{rev}} \quad (5.3)$$

which, in turn, implies that $\Delta S = \int_A^B dS = S(B) - S(A)$, 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, $dQ_{\text{rev}} = 0$. Hence $dS = 0$ and $S = C^{\text{st}}$, 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 ($A \rightarrow B$) and a reversible one ($B \rightarrow A$), as indicated on Fig 5.9.

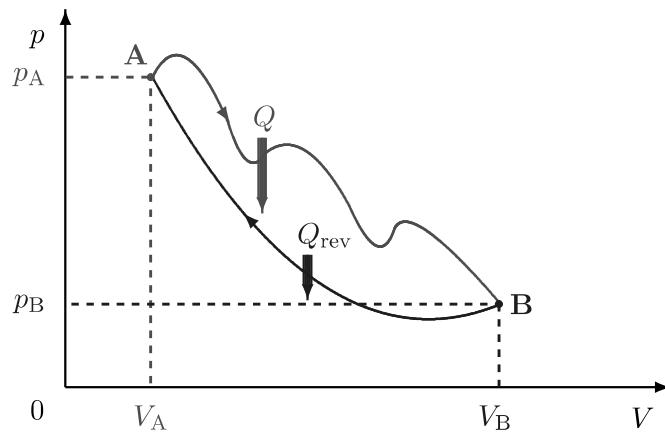


Figure 5.9: $p - V$ diagram of a cycle made of an irreversible process ($A \rightarrow B$) followed by a reversible one ($B \rightarrow A$).

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

$$\boxed{dS \geq 0} \quad (5.4)$$

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 $U_{\text{Univ}} = C^{\text{st}}$ (first law: energy is conserved) and S_{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

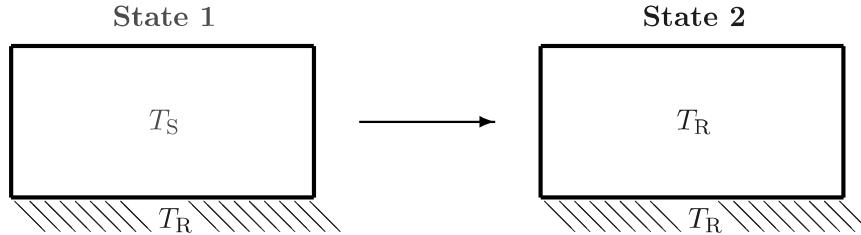


Figure 5.10: Transfer of heat between a system S, initially at temperature T_S (State 1) and a reservoir R at temperature T_R .

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 $\Delta T = T_R - T_S$ 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 $T_S > T_R$, and that we have 2 reservoirs, the first one at temperature T_R , and the second one at $T_S - (T_S - T_R)/2$. Now let us bring the system in contact first with this second reservoir at temperature $T_S - (T_S - T_R)/2$ 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 $T_S - (T_S - T_R)/2$. The temperature T of the system has increased from T_R to $T_S - (T_S - T_R)/2$, 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 $T_S - (T_S - T_R)/2$ is *back to its original state*. Heat exchange with a reservoir is therefore *reversible*.

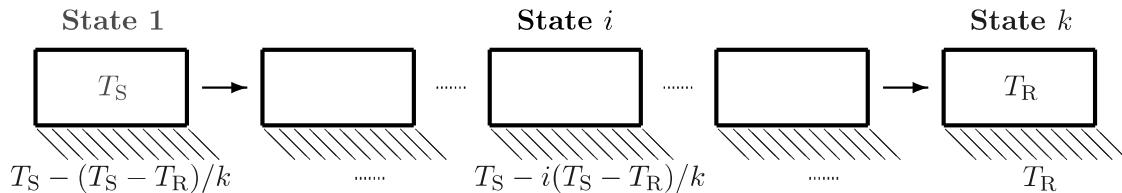


Figure 5.11: Transfer of heat between a system S, initially at temperature T_S (State 1) and k reservoirs regularly spaced in temperature between T_S and T_R .

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 $k \rightarrow \infty$, 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 dT .

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 $dQ_{\text{rev}} = CdT$ and so, if we assume that C is independent of T (true for e.g. an ideal gas), we can write[§]:

$$\begin{aligned}\Delta S_R &= \int_{T_S}^{T_R} \frac{-dQ_{\text{rev}}}{T_R} = \frac{C}{T_R} \int_{T_R}^{T_S} dT = C \frac{T_S - T_R}{T_R} \\ \Delta S_S &= \int_{T_S}^{T_R} \frac{dQ_{\text{rev}}}{T} = C \int_{T_S}^{T_R} \frac{dT}{T} = C \ln\left(\frac{T_R}{T_S}\right)\end{aligned}$$

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 $\Delta S_{\text{Univ}} \geq 0$ no matter what! Let us prove it. We have:

$$\Delta S_{\text{Univ}} = \Delta S_R + \Delta S_S = C \left[\ln\left(\frac{T_R}{T_S}\right) + \frac{T_S}{T_R} - 1 \right]$$

Setting $X = T_S/T_R$ and evaluating the derivative $d(\Delta S_{\text{Univ}})/dX = C(1 - 1/X)$, 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, $d^2(\Delta S_{\text{Univ}})/dX^2 = C/X^2 > 0$ for $X = 1$, this extremum is a minimum. As $\Delta S_{\text{Univ}}(1) = 0$, we therefore conclude that $\Delta S_{\text{Univ}}(X) \geq 0$ 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,

[§]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 $dQ_{\text{rev}} < 0$ as the system has lost heat, but from the point of view of the reservoir, this amount of heat is gained, and therefore $-dQ_{\text{rev}} > 0$ 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!

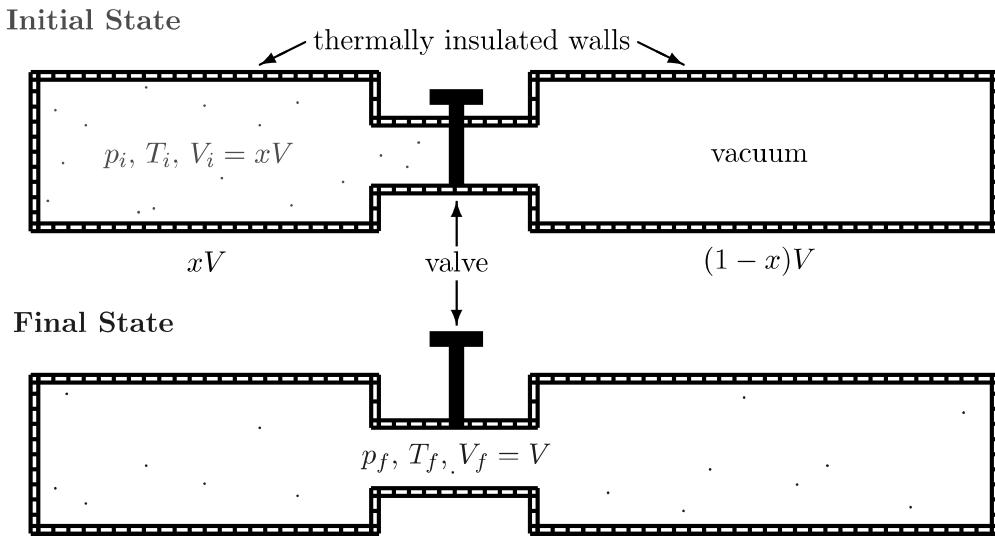


Figure 5.12: Joule expansion of 1 mole of gas initially enclosed in a container of volume xV (with $0 < x < 1$) into a container of volume V .

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 $p_i V_i = RT_i$ and $p_f V_f = RT_f$ (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 $dU = dQ_{\text{rev}} - pdV = 0$, so that $\Delta S \equiv \int dQ_{\text{rev}}/T_i = \int_{V_i}^{V_f} p/T_i dV = \int_{V_i}^{V_f} R/V dV = R \ln(1/x) > 0$. 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_{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

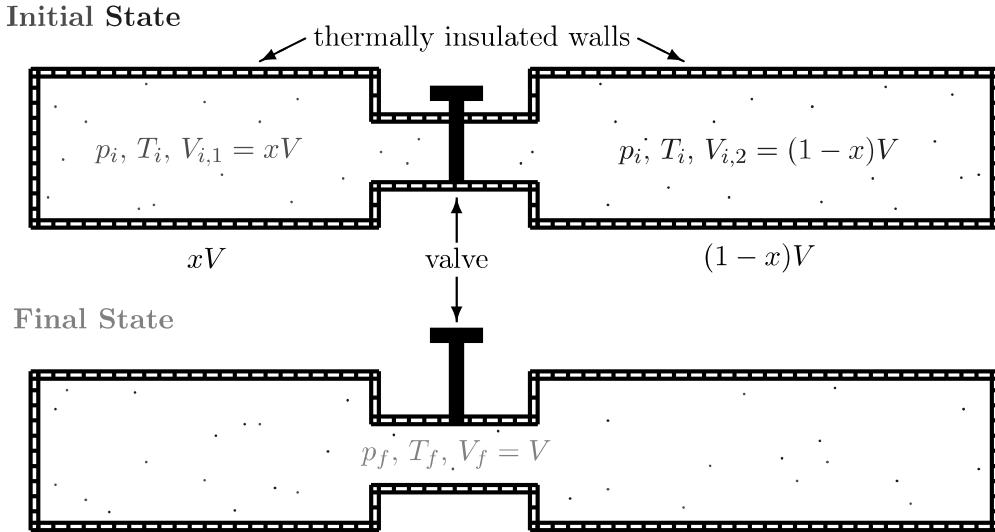


Figure 5.13: Expansion of two different gases initially enclosed in two containers of volume xV and $(1-x)V$ respectively, into a single container of volume V .

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 $dU = 0$, so that $dQ_{\text{rev}} = pdV$ and $dS = pdV/T = Nk_B dV/V$. The total entropy

change is thus:

$$\Delta S = xNk_B \int_{xV}^V \frac{dV_1}{V_1} + (1-x)Nk_B \int_{(1-x)V}^V \frac{dV_2}{V_2} = -Nk_B [x \ln x + (1-x) \ln(1-x)]$$

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

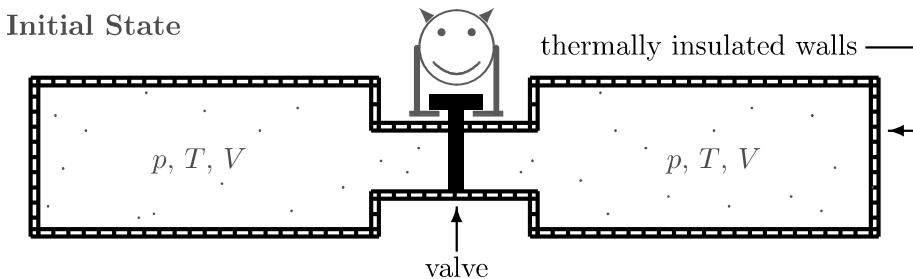


Figure 5.14: Maxwell's intelligent daemon is operating the valve to let specific particles through in order to violate the second law (see text for detail).

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 $dU = dQ + dW$ can be written as:

$$dU = TdS - p dV \quad (6.1)$$

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.

-  For an irreversible process we have $dQ < TdS$ and $dW > -p dV$, but when these infinitesimal heat and work are added together, dU 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:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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 :

$$(S, V) \rightarrow U : \text{Internal energy} \quad (6.2)$$

$$(S, p) \rightarrow H = U + pV : \text{Enthalpy} \quad (6.2)$$

$$(T, V) \rightarrow F = U - TS : \text{Helmholtz free energy} \quad (6.3)$$

$$(T, p) \rightarrow G = U + pV - TS : \text{Gibbs free energy} \quad (6.4)$$

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 $dU = TdS - pdV$ (equation (6.1)), so that $dU = 0$ 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 $dH = 0$. This is verified straightforwardly by taking the differential of equation (6.2): $dH = dU + d(pV) = dU + pdV + Vdp = TdS - pdV + pdV + Vdp$. As we did for U , we can write:

$$dH = \left(\frac{\partial H}{\partial S} \right)_p dS + \left(\frac{\partial H}{\partial p} \right)_S dp$$

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 $dF = dU - d(TS) = dU - TdS - SdT = TdS - pdV - TdS - SdT$, which is nil if its natural variables T and V are fixed. Writing

$$dF = \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV$$

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 $dG = dU + d(pV - TS) = TdS - pdV + pdV + Vdp - TdS - SdT$, which is equal to zero if T and p are fixed. Writing once again:

$$dG = \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp$$

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, $dH = TdS \equiv dQ_{\text{rev}}$ at constant p , i.e. using independent variables T and p , $dH = (\partial H / \partial T)_p dT = C_p dT$ and $\Delta H = \int_{T_i}^{T_f} C_p dT$ 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, $\Delta H = \Delta U + p\Delta V = Q + W + p\Delta V = Q - p\Delta V + W_{\text{other}} + p\Delta V$, with $Q = T\Delta S$ for a reversible process and $Q < T\Delta S$ for an irreversible one. W_{other} stands for any non- pdV 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 $dF = -pdV$ for an isothermal reversible process. Therefore $\Delta F = -\int_{V_i}^{V_f} pdV$ (> 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 pdV 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 $W = pdV$ work + W_{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-pdV* 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, $dG = 0$ for a reversible, isothermal and isobaric process, assuming no other work than pdV . 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, $\Delta G = \Delta U - T\Delta S + p\Delta V = Q + W - T\Delta S + p\Delta V = Q - p\Delta V + W_{\text{other}} - T\Delta S + p\Delta V$ 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 $dU = TdS \equiv dQ_{\text{rev}}$ at constant V , i.e. using independent variables T and V , $dU = (\partial U / \partial T)_V dT = C_V dT$. Thus $\Delta U = \int_{T_i}^{T_f} C_V dT$ 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, $\Delta U = Q + W_{\text{other}}$, 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).

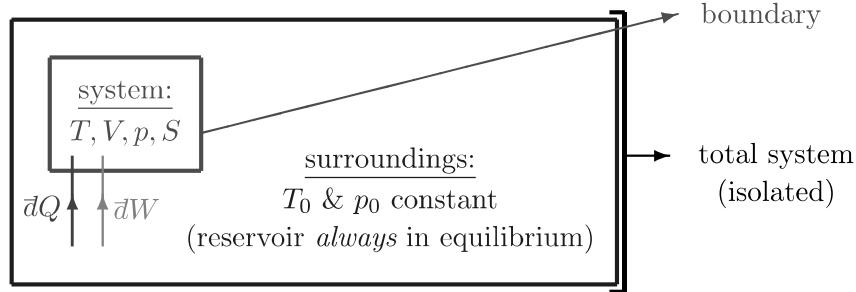


Figure 6.1: Updated schematic diagram of a thermodynamical system.

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 $dU_{\text{tot}} = 0$. In other words, any amount of internal energy gained by the surroundings must be lost by the system and vice-versa, which we write $dU_{\text{surr}} = -dU = T_0 dS_{\text{surr}} - p_0 (-dV)^*$. Rearranging this expression, we obtain $dS_{\text{surr}} = -(dU + p_0 dV)/T_0$.

The second law then tells us that the entropy of the total system, S_{tot} , can only increase. So any infinitesimal change $dS_{\text{tot}} = dS_{\text{surr}} + dS \geq 0$. Multiplying this inequality by T_0 and using the expression for dS_{surr} obtained through the first law then yields: $-(dU + p_0 dV - T_0 dS) \geq 0$. Finally, as p_0 and T_0 are constant, we obtain $dA = d(U + p_0 V - T_0 S) \leq 0$, 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*.



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 $dS = 0$ and $dV = 0$. Therefore $dA = dU \leq 0$ 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 $dS = 0$ and $dp = 0$. Therefore $dA = dU + p_0 dV = dH \leq 0$ 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 dV 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 $dT = 0$ and $dV = 0$. Therefore $dA = dU - T_0 dS = dF \leq 0$ 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 $dT = 0$ and $dp = 0$. Therefore $dA = dU + p_0 dV - T_0 dS = dG \leq 0$ 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

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

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 $dU = TdS - pdV$ with $T = (\partial U / \partial S)_V$, $p = -(\partial U / \partial V)_S$ so that the second derivatives yield the following equality:

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

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

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

For $f = F$, $x = T$ and $y = V$, $dF = -SdT - pdV$ along with $S = -(\partial F / \partial T)_V$, $p = -(\partial F / \partial V)_T$, which yields:

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

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

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

■

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:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \text{ (use } dU = TdS - pdV \text{ divide by } dT \text{ and hold } V \text{ constant)}$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \text{ (use } dH = TdS + Vdp \text{ divide by } dT \text{ and hold } p \text{ constant)}$$

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:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

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: $dT = 0$, so $d(pV) = 0 \rightarrow p dV + V dp = 0$ and $-V dp/dV = p$. Therefore $\kappa_T = 1/p$.
- Adiabatic compressibility: $dS = 0$, so $d(pV^\gamma) = 0 \rightarrow \gamma V^{\gamma-1} p dV + V^\gamma dp = 0$ and $-V dp/dV = \gamma p$. 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 $pV = Nk_B T$, 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*.



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 ($N \sim N_A$), 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

[†]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 $d\Omega = -SdT - p dV - N d\mu$.

generalise our total differentials for the four thermodynamical potentials as:

$$\begin{aligned} U(S, V, N) \rightarrow dU &= TdS - p dV + \mu dN \\ H(S, p, N) \rightarrow dH &= TdS + Vdp + \mu dN \\ F(T, V, N) \rightarrow dF &= -SdT - p dV + \mu dN \\ G(T, p, N) \rightarrow dG &= -SdT + Vdp + \mu dN \end{aligned}$$

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 $p dV$, 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 $dW = \mathcal{F}dh$, 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: $dW = p dV$ with p the pressure and V the volume.
- elastic rod: $dW = t dL$ with t the tension and L the length.
- liquid film: $dW = \gamma dA$ with γ the surface tension and A the area.
- dielectric material: $dW = \vec{E} \cdot d\vec{p}_E$ with \vec{E} the electric field and \vec{p}_E the electric dipole moment.
- magnetic material: $dW = \vec{B} \cdot d\vec{m}$ 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 $dW = -\vec{p}_E \cdot d\vec{E}_{ext}$, where \vec{E}_{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 $dW = -\vec{m} \cdot d\vec{B}_{ext}$ where \vec{B}_{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 dt on it, so that it elongates by an infinitesimal amount dL , as represented on Fig 6.2.

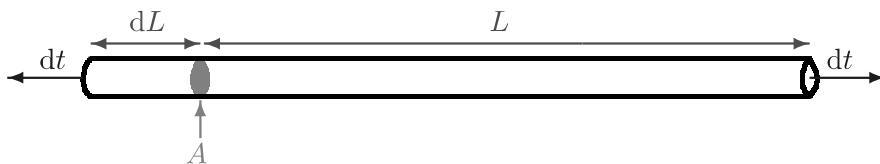


Figure 6.2: Diagram of an elastic rod of initial cross-section A and length L , stretched under infinitesimal tension dt .

First, let us define the physical properties of the system using thermodynamical coefficients. The ratio of the *stress*, $\sigma \equiv dt/A$, to the *strain*, $\epsilon \equiv dL/L$, 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

^{||}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 $dU = SdT + t dL$ and the Helmholtz free energy $dF = -SdT + t dL$, 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 dL is analogous to the isothermal gas expansion in the Carnot cycle: an amount of heat $dQ_{\text{rev}} = TdS = AT E_T \alpha_t dL$ 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 $(\partial U / \partial L)_T = T(\partial S / \partial L)_T + t = AT E_T \alpha_t + t$ which will not be equal to zero in general!