Brief review of thermodynamics

Note: this review is by no means complete. I aim to summarize the main ideas of thermodynamics and some of the results that we need in order to be able to proceed with studying and understanding statistical mechanics. These ideas and notions should be familiar to you from a previous course on thermodynamics, so I will not go into too many details. The first four chapters of the textbook review these things in fairly great detail, and you should have a look at them. Note: in a few sections of the first two chapters, new stat mech notions are introduced – ignore those, for the time being.

1 Generic example of a classical system

Roughly speaking, thermodynamics is attempting to characterize the **macroscopic** properties and behavior of systems with very many degrees of freedom, without making any assumptions about their **microscopic** properties. There are many examples of such systems and we will study quite a few in this course. In order to have a concrete example in mind, to help with understanding the meaning of various definitions, we will take the simplest possible example, shown in Fig. 1: a certain amount of gas enclosed in a given volume.

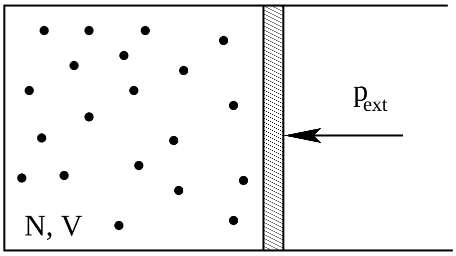

Fig 1. Typical system of interest: atoms or molecules in a gas phase, in an enclosure.

Typically, the number N of atoms in this system is very large, $N \sim 10^{23}$. If we treat the system classically, we know that we need six variables to describe the position and momentum of each atom (its classical degrees of freedom) $\rightarrow$ the total number of *microscopic* degrees of freedom is of order $6 \cdot 10^{23}$. This is a very large number, indeed. If we view this problem as a classical mechanics problem, we would start by writing Newton's 2^{nd} law for each atom. This can be done, but solving these equations is a different matter: there are too many of them! Even if we could solve them, we have no way of measuring the initial conditions (initial positions and momenta of each atom) and so we could not identify unique solutions. For fun, estimate how much memory would be needed to store only the initial conditions – that will tell you why we can't possibly proceed this way.

Thermodynamics was invented/created to deal with such problems. Unlike mechanics, it does not concern itself with ***microscopic*** degrees of freedom, i.e. where is each particle and what is it doing.[1] Instead, thermodynamics tries to find relationships between the ***macroscopic*** quantities characterizing the system, such as the number N of atoms,[2] the volume V of the enclosure, the pressure we apply from the exterior, p_{ext}. Other such quantities of interest are the internal energy U of the system, i.e. how much energy is stored in the system (for our example, it would be the sum of all kinetic and potential energies of all the atoms), or the temperature T of the gas, or the pressure p of the gas, or the chemical potential μ of the gas. One thing to notice is that these are very few quantities, especially when compared to 10^{23}, so we may be able to make some progress now. Another thing to notice is that these are all ***macroscopic*** quantities, totally independent of the microscopic nature of the system. Instead of a gas, we could have a liquid or a solid – this would still have some internal energy and we could still apply pressure and measure its volume and mass and try to find some relationship between them. Another thing to realize is that we can only

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[1] In fact, at the time when thermodynamics was being established, physicists did not believe/know that matter is made of atoms and molecules.

[2] Before physicists knew of atoms, they dealt with the mass m of trapped substance, or equivalently, the number ν of moles. We know that these are proportional to one another, and because it will be convenient later on, we will use the number N of atoms as a variable.

use these few macroscopic quantities to characterize certain types of states of the system, which we call **equilibrium states**. These are very special states, which are reached by the system after a certain amount of time (called relaxation time) following an external perturbation.[3] Once the system is in equilibrium, it will stay in equilibrium (i.e., the values of these macroscopic quantities remain unchanged) until we do something else to it. Some of the quantities mentioned above cannot even be defined if the system is not in equilibrium: for instance, only after equilibrium is reached is the pressure or temperature of the gas the same everywhere, so one could speak of "pressure" or "temperature". In a non-equilibrium state, these quantities are generally not meaningful. In this course, we will only study the formulation of statistical mechanics for equilibrium states. This can be extended to studying non-equilibrium states, although the proper way to do it is still very much a matter of research.

Before looking at some examples of equilibrium states, let me note two more facts: first, not all these macroscopic quantities are independent of each other; there are relationships between them, so once we fix a few, the other ones can only take a certain value each.[4] In fact, it is precisely these relationships that thermodynamics and statistical mechanics are trying to find. Which quantities should be taken as the independent ones and which are dependent on them is a function on how the system is prepared, as described in the examples below. Second, these macroscopic quantities can be divided into two classes: **extensives** and **intensives**. Macroscopic quantities belong to one or the other class depending on whether their values scale proportionally with the amount of matter (for extensives) or not (for intensives). Imagine we have two identical systems in equilibrium, and we join them together by removing the wall separating them. In this case, N, V and U will double, whereas p, T, μ, ρ (the density) will remain unchanged. The former are the extensive quantities, the latter the intensive ones.

Let's see some examples:

(1) **isolated system**: in this case, the walls of the container are such that neither matter (atoms) nor energy (heat) can be exchanged with the "outside world". If we hold the volume of the container fixed then the natural choice of macroscopic variables is the internal energy U, the number of particles N and the volume V (i.e., all the extensives). The reason is that for an isolated system, U and N are conserved, i.e. they keep whatever value they had initially and these values cannot change, so it makes sense to have them as independent variables. To fix V, we fix the position of the piston so that V equals whatever value we want it to have, and then we do not allow it to move. After some time, the system reaches equilibrium – in this case it will arrive at some pressure p and temperature T, which are certain functions of U, N, V. Note that in this case, the value of p_{ext} is of no interest: since the walls cannot move, it makes no difference what is the value of this quantity (we assume that it is not so big as to crush the container; if it was, that would make a difference).

(2) **closed system**: by this we mean that the walls allow the exchange of energy (heat) with the outside, but not of matter. As a result, N is still a good independent variable (it will be equal to whatever number of atoms we chose to put in the system in the beginning), and similarly, if we fix the position of the walls, V is a good independent variable. The energy U, however, is no longer a good choice for an independent variable, since heat will be exchanged with the "outside world" until equilibrium is reached. In such cases of systems in thermal contact, we know that equilibrium is reached when their ***temperatures*** are equal. In other words, we can now fix T_{ext} of the "outside world" and we know that the system will arrive at equilibrium when its own temperature, T, equals T_{ext}. So in this case, we choose T, N, V as independent variables, which we can control and fix to have

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[3] For example, changing the volume of the enclosure or the external pressure.

[4] For example, as you hopefully remember, an ideal gas at equilibrium satisfies the equation of state $pV = Nk_BT$, so if we fix N, V, T, that will automatically determine the value of p.

whatever values we desire, and $U, p, ...$ as dependent ones. However, there is a different possibility: we could allow the piston to move, and fix a certain value of p_{ext} in the "outside world". In this case, we know that the piston will keep moving until $p = p_{\text{ext}}$; only when this holds, can equilibrium be established. As a result, with this setup it makes sense to choose p as the 3^{rd} independent variable (whose value can be set by choosing whatever p_{ext} we want) and leave V as a dependent variable. We will use N, V, T as our independent variable for closed systems in this course, this being the traditional choice in physics. In Chemistry, it is often customary to use the N, p, T option.

Note: you might argue that the discussion above is problematic in the following sense. Let's say that initially the "outside world" is hotter than the system. In this case, when thermal contact is established, heat will flow into the system until its temperature raises to equal that of T_{ext}, and the system reaches equilibrium again. The problem is that since the "outside world" lost some heat to the system, its temperature came down a bit from the initial T_{ext} value, so you might argue that we now do not quite know what this equilibrium temperature is, either. The answer to this is that we assume that the "outside world" (also called a **reservoir**) is so much bigger than the system, that this change in T_{ext} (or p_{ext} in the previous example) is vanishingly small and can be ignored.

(3) **open system**: in this case, the system can exchange both heat and matter with the outside. As before, (again, supposing that we fix the position of the piston), we will take T and V as independent variables. N is no longer good, since atoms will go in and out of the system until so-called chemical equilibrium is established – this happens when the chemical potential μ in the system equals the chemical potential μ_{ext} of the reservoir. I will define the precise meaning of μ in a bit; in the meantime, just think of it as being some quantity somewhat similar to T: if two systems have equal temperatures, then there is no net flow of heat between them, and we say that they are in thermal equilibrium. Similarly, if two systems have equal chemical potentials, then there is no net flow of atoms (matter) between the two (in other words, in average as many atoms leave a system as enter it) and we say that they are in chemical equilibrium.

So in this case, we should choose T, V, μ as independent variables, while $U, p, N, ...$ are the dependent ones. For closed systems we could also have chosen p as the independent variable and V the dependent one, by allowing the piston to move. However, for open systems this choice is not possible, we cannot have T, p, μ as independent variables. The reason is that all these are intensives (independent on the system size) and there must be at least one independent variable which depends on the system size, i.e. is extensive – otherwise we simply do not know how big is the system.

Note that whatever we do, we cannot have p and V *simultaneously* as being both dependent, or both independent variables. If one is dependent, the other one is independent, and viceversa. Pairs of quantities with this property are called **conjugate** to each other. Besides p and V, we also have μ and N as conjugate variables; you might suspect that U and T are conjugate – but this is not true, in fact, as we will see later. It turns out that U is a rather special quantity, as you might assume from the fact that this is the only one of all the mentioned ones that we cannot directly measure. We can measure changes in U, though.

These are not all the possibilities. For instance, if our system was more complicated and could be magnetized, we would have to use the total magnetization $\vec{M}$ as an extensive macroscopic variable; its conjugate is the applied external magnetic field $\vec{B}$ (intensive). Like with p and V, we could either choose to apply a desired external magnetic field $\vec{B}$ (analog to choosing desired p_{ext}), in which case the system will reach an equilibrium state with a certain magnetization $\vec{M}$ (analog to V adjusting itself to its equilibrium value for a given $p = p_{ext}$). Or, we could isolate the system from the outside so that it does not care about this external field (analog of fixing the position of the piston), in which case $\vec{M}$ has whatever value it had initially (analog of V being fixed and independent of p_{ext}). Similarly, if the system is polarizable, its total polarization $\vec{P}$ is a conjugate of the applied electric field $\vec{E}$, and we should choose one of the two as a new independent variable characterizing the equilibrium state of the system, depending on the conditions. What else? In some cases, e.g. a soap bubble, the area A of the surface of the system is a very important macroscopic variable. Its conjugate is the intensive quantity called "surface tension", σ. If the system is a rather one-dimensional object like a polymer, or an elastic rubber band, then its length L is the relevant macroscopic variable, not its volume or area. This is conjugate to the tension T in the rubber band, again in close analogy with the relationship between V and p. And so on and so forth, but we will stop here.

To summarize what we have so far: we are interested only in equilibrium states and ***reversible or equilibrium processes*** – these are processes where we change variables so slowly, that at all times we can assume that the system is in equilibrium. An example would be a process where we want to double the volume of an isolated system. This process is a reversible (or equilibrium) process if we move the position of the piston infinitesimally little, and then wait for equilibrium to be reached again, and then move a bit more, and then wait again ... if this is done slowly enough, the system is practically in equilibrium at all times, although in time the value of V will change, and so will p and T etc. Such a process is reversible, meaning that we can precisely "undo" it by reversing the changes, also slowly. If we start decreasing the volume slowly, we will get back to the initial state through the *inverse sequence* of equilibrium states we went through previously. This is to be contrasted with a non-equilibrium process, where, say, we suddenly double the volume by moving the piston to the new position. Right after this, the gas will be in a highly non-equilibrium state, presumably with most of it rushing into the newly available space. We can't talk of pressure or temperature in these non-equilibrium states. In fact, the only way to fully characterize such non-equilibrium states is to say what each atom is doing – this is what makes them so much more complicated then the equilibrium states, which we can fully characterize by a few macroscopic quantities. Of course, after awhile the system will relax to a new equilibrium state, now with a doubled volume. If we now suddenly compress the volume to half, the system would evolve through a very different set of non-equilibrium states, before reaching a new equilibrium at the initial volume. Generally, the amount of heat and work exchanged with the environment during the reversed process is quite different, resulting in a new equilibrium state (at the initial volume) which is different from the initial equilibrium state we started from. This is why non-equilibrium processes are irreversible – they cannot be "undone". Except for one example, we will not concern ourselves with such irreversible processes in this course.

Keeping only equilibrium states and processes in mind from now on, depending on the nature of the system and on how it is separated from the "outside world" (isolated, open or closed), we can choose a few independent macroscopic variables which fully characterize each equilibrium state - see discussion above. What we would like to do now, is to understand the general rules that tell us what processes are possible, and how we can find equations that will give us the values of the dependent variables as a function of the independent variables.

Here is where the major difference between thermodynamics and statistical mechanics appears. In thermodynamics, there is a set of postulates which tell us how things work in general (we'll come back to these, but for example, the first is that the total energy is conserved). One accepts these postulates or principles as fundamental truth, like axioms in geometry (of course, these postulates were arrived at after much experimental and theoretical trial-and-error work, and we know that they agree with the experimental reality of our world – so if you wish, the proof that they are true is that they have not yet been falsified by any experiments). However, these postulates have to be supplemented by experimental data in order to allow us to derive all the relationships between the various variables. I will show an example below of how this works a bit later. The use of experimentally derived relationships is necessary because thermodynamics makes no attempt to understand the microscopic nature and behavior of the system, which gives rise to these particular relationships. Also, because of this, some quantities (e.g. absolute temperature, or entropy) have somewhat unclear meaning.

In contrast, the goal of statistical mechanics is to use knowledge about the behavior and properties of the microscopical components of the system (the atoms, in our example) to *theoretically derive* all the possible relationships between the macroscopic quantities characterizing the equilibrium states, with no need to use experimental input. This, of course, is a lot more fun. Unlike in thermodynamics, where we can only make statements of the type: if equation (1) is true (because it was measured experimentally) then we can use the fundamental principles to derive and say that equation (2) is true as well – but we have no idea why (1) holds to begin with; by contrast, statistical mechanics provides us with a framework to derive all possible relationships. We can then compare these results against experiments and see if we are right.

A remarkable example of the success of stat mech is the Bose-Einstein Condensation. This is a certain phenomenon that we will study later, theoretically predicted by these two gentlemen in 1924. It takes place in very difficult to achieve conditions (e.g., very low temperatures, on the order of 1 nK) and it was only in 1995 that experimentalists where able to prepare systems in suitable conditions to verify these predictions. If we did not have stat mech, this phenomenon might have gone undiscovered, since within thermodynamics one first needs experiments showing that relationships between variables become rather strange at these low temperatures, to suggest that something new happens there. It is unlikely that in the absence of this prediction for a spectacular new state of matter there would have been much incentive for experimentalists to spend decades trying to reach these low temperatures to see if anything new really happens there. Even if somehow somebody stumbled upon it and showed experimentally that something new is happening, thermodynamics would still not tell us what is the reason for these new strange relationships – it would just allow us to find them based on the experimental data. You must admit that this is much less satisfying than stat mech, which can make theoretical predictions without any need of experimental data, and also provide explanations as to why things work the way they do.

So while the end goals of both thermodynamics and statistical mechanics are basically the same, the means to achieve them are quite different. Let us take a bit more time to remember the principles of thermodynamics and then look at an example of how this all works, after which we will begin to study statistical mechanics in earnest.

2 The principles or laws of thermodynamics

Principle zero: If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C. In other words, the relationship of thermal equilibrium is transitive.

Based on this, one can define a certain property which we call ***temperature***: two thermodynamical systems allowed to exchange energy with each other are in thermal equilibrium when they have the same temperature.[5] The transitivity property then allows us to introduce thermometers and a way to measure temperatures. There are various temperature scales (see chapter 1 for more details). From now on, we will only work with absolute temperatures T: on this scale, at atmospheric pressure, the melting point of ice is 273.15K while the boiling point of water is 373.15K. I assume that you are familiar with all this so I'll stop here.

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[5] Note that we never needed to use such a property in mechanics, or electricity, or magnetism.

We can now proceed with the serious principles. There are 3 of them, and as I said, they basically tell us what kind of processes are allowed to happen in our universe.

2.1 First principle of thermodynamics

This is quite straightforward: it tells us that ***conservation of energy must always hold***. Or, equivalently, that processes in which the energy is not conserved, are impossible. This might seem obvious, but you would be surprised to find out what an incredible amount of human effort has been devoted to finding machines or engines (called perpetuum mobile of first kind) which violate this law, i.e. generate energy out of nothing. There are probably people out there still trying to do it.

The mathematical expression of this law is:

$$dU = \delta W + \delta Q \tag{1}$$

where dU is the infinitesimal change in the internal energy of a system during any small part of a process; δW is the mechanical work *done on the system*, while δQ is the heat exchanged with the outside during this infinitesimal process. We follow the convention in the textbook to use df to denote the differential of a function f: U is a *state* quantity, i.e. one with a well defined value in any state of the system, and dU is its differential which measures the small variation due to some change in other parameters. The work and heat do not characterize the state of the system (we cannot say that in such-and-such a state, the system has this much work or this much heat in it), instead they characterize the process that changes the state; we can say that during a process, this much work/heat has been performed on/exchanged with the system. We use the δ to remind us of this distinction.

For our generic example, the work done during a process is:

$$\delta W = -p_{ext} dV \tag{2}$$

where dV is the infinitesimal change in the volume, during the process. The $-$ sign is very important: when we apply external pressure to shrink the system (i.e., we perform work on the system and increase its internal energy), the volume decreases: $dV < 0 \to \delta W > 0$. If the process is a *reversible process*, then we know that at all times, the pressure of the gas equals the external pressure (else the system would not be in equilibrium), and therefore in this case we have:

$$\delta W_{\text{rev}} = -p dV \tag{3}$$

There are other forms of work. For instance, if we change the number of particles in the system, we expect its internal energy to change as well. The work associated with adding particles to the system is:

$$\delta W = \mu dN \tag{4}$$

where μ is the chemical potential – now we see that its definition is that it equals the change in internal energy when one extra atom is introduced in the system (and all other extensives, such as V, are kept unchanged). For a rubber band, the work is

$$\delta W = T_{\text{ext}} dL \tag{5}$$

where T_{ext} is the applied tension. Again, for reversible processes $T_{\text{ext}} = T$ (please don't confuse with temperature). Similarly, we can define the work associated with changing the surface energy, or magnetizing a system, etc – we will discuss these when we discuss particular examples, later on. Basically in all cases the work is the product of the intensive quantity of a conjugate pair times the differential of the extensive quantity of the pair, with a ± sign chosen so that the contribution is positive when work is done on the system, and negative when the system does the work.

2.2 Second principle of thermodynamics

The first principle is not enough to fully weed out all impossible processes; it turns out that there are processes where energy is conserved, but they still never happen. For a simple example, consider the following. Assume we have a small enclosure of volume v which contains N atoms, which we place in a bigger, isolated enclosure of total volume V, which is otherwise empty. Now imagine that we break the walls of the small enclosure, and take this state (all atoms still inside volume v, but free to move anywhere) as the initial state. We know that this is a highly non-equilibrium state. After some time, the atoms will spread around to occupy all available volume V, and the system reaches a new equilibrium. During this (irreversible) process, there has been no exchange of heat with the exterior (the big volume is isolated) and there has been no work done since expansion against vacuum costs no work: $p_{\text{ext}} = 0 \to \delta W = 0$. So the initial and final internal energies are the same, according to the first principle. Here is the question: why is the inverse process impossible? Why is it that if the atoms are now initially spread out in the entire volume V, they are never observed to all simultaneously congregate inside the small volume v, even for a very short instance of time? According to mechanics, this should be possible since if we reversed all the velocities of all atoms, they would move precisely as if they would go "backwards" in time, towards the state where they are all inside v. Energy would still be conserved and everything would be fine, there's nothing forbidding this from happening from mechanics' point of view. Actually, as we will see later when we discuss statistical mechanics, the "backwards" process is not really forbidden. It is just so extremely unlikely, that we could wait for the entire age of the universe and it might still never happen even once – so the assertion of the second principle of thermodynamics that it is impossible is not too wrong.

Here is how thermodynamics deals with this: it introduces another somewhat mysterious state quantity (i.e., defined for each state of the system, whether equilibrium or non-equilibrium), which is called ***entropy***, S. The second principle of thermodynamics states that ***the entropy of an isolated system* never *decreases***. According to this, the explanation of the previous example is that the entropy of the system with all atoms inside v is smaller than the entropy of the system with all atoms in V. As a result, since the system is isolated, it can evolve from the first state to the second one (energy is conserved, entropy increases, all principles are satisfied) but it is forbidden to evolve from the second state to the initial one, as this would require a decrease of the entropy in an isolated system. Note that it is still possible to collect all atoms inside v, if we intervene from the outside by moving some interior walls. This does not contradict the second principle, as in this case the system itself is no longer isolated (we're interacting with it). Instead, now the isolated system would be bigger, containing the initial system and the person or machine doing whatever is necessary to collect the atoms back; for this total, larger, isolated, system, the total entropy would grow during the process of collecting the atoms, although for the original system, which is now part of this larger system, the entropy would decrease. (Hopefully you remember that entropy is also extensive, as we'll see below. As a result, the entropy of the total system is the sum of entropies of its subsystems).

One direct consequence of this principle is that ***for an isolated system, the state of equilibrium is the state of maximum entropy***. Once the entropy reaches the maximum possible value, it has to stay constant (it cannot decrease) and so the system remains forever in this state of maximum entropy, which therefore must be the same as the equilibrium state. The only way to change the state now is to act from the outside.

This is all fine, but we still need some quantitative way to define/measure the (change in) entropy during a process, so we can know whether the entropy is increasing or decreasing. This is given by the relation:

$$\delta Q_{\text{rev}} = T dS \tag{6}$$

i.e., the heat exchanged during an infinitesimal, *reversible* process equals the temperature of the system times the change in its entropy. (Note: this is not true for irreversible processes. In fact, because in those cases the system evolves through non-equilibrium states for which temperature is not defined, Eq. (6) would make no sense). Since heat (energy) are extensive quantities while T is an intensive, it follows that S is an extensive quantity. This equation allows us to define the entropy of a system, by choosing one state as a reference state with some value of the entropy. To find the entropy of any other state, we need to perform a reversible process to go to that new state, and measure the heat exchanged. We have:

$$dS = \frac{\delta Q_{\text{rev}}}{T} \to \Delta S = S_{\text{final}} - S_{\text{initial}} = \int_i^f \frac{\delta Q_{\text{rev}}}{T}$$

This gives us a way to measure the entropy, although in this thermodynamical framework it is still not clear what it actually is. One beautiful consequence of learning statistical mechanics is that it will give us clear intuition of what entropy is.

Putting together Eqs. (1) – (6), we find that ***for reversible processes*** (of interest to us):

$$dU = TdS - pdV + \mu dN + ... \tag{7}$$

where the dots account for other forms of work performed on the system. This is sometimes called **the fundamental equation of thermodynamics**, and is one of the equations that you *absolutely* have to know. Before going on to explore its consequences, let me quickly state the:

2.3 Third principle of thermodynamics

In the limit $T \to 0$***, the entropy*** $S \to 0$. If you wish, this gives us an absolute scale to define the entropy, by giving us a reference value. This is sometimes called Nernst's principle.

Back to Eq. (7). Let's assume that there are no other macroscopic variables (such as magnetization) and so Eq. (7) has only those three terms on the right hand side. Then this equation shows to us that the internal energy U is a function of the variables S, V, N, since a change in either of these three quantities induces a change in U: $U = U(S, V, N)$. But, by definition, in this case:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

where, e.g. $\left(\frac{\partial U}{\partial S}\right)_{V,N}$ is the partial derivative of $U(S, V, N)$ with respect to S, keeping N and V as constants. This simply says that the total variation of U is the sum of variations due to changing each of its variables. By comparison with Eq. (7), it follows immediately that:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} ; \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} ; \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{8}$$

In other words, if we can somehow figure out the function $U(S, V, N)$, we can take these partial derivatives and find out how the temperature, pressure and chemical potential depend on the variables S, V, N, i.e. find out the relationships: $T = T(S, V, N); p = p(S, V, N); \mu = \mu(S, V, N)$.

We can then also find other relationships between these variables. Because U and all its variables S, V, N are extensive quantities, we can show that in an equilibrium state

$$U = TS - pV + \mu N \tag{9}$$

This is called an Euler equation – let's quickly prove it. The condition that U, S, V, N are all extensive can be written formally as:

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

which simply says that the internal energy of a system that has λ times more entropy, volume and number of particles, is just lambda times as big as the internal energy of the system with S, V, N. Let's take a derivative with respect to λ on both sides, and then set $\lambda = 1$. We need to use straightforward generalizations of the identity

$$\frac{df(\lambda x)}{d\lambda} = \left.\frac{df(y)}{dy}\right|_{y=\lambda x} \frac{d(\lambda x)}{d\lambda} = x \left.\frac{df(y)}{dy}\right|_{y=\lambda x} \overset{\lambda \to 1}{\to} x \frac{df(x)}{dx}$$

We have 3 partial derivatives, but each behaves similarly, so after setting $\lambda = 1$ we find:

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

But these partial derivatives are just $T, -p, \mu$ (see Eq. (8)), so indeed $U = TS - pV + \mu N$.

This allows one then to derive the Gibbs-Duhem equations (see last section of chapter 2; we will not use these in the future so I don't include them here). What we may use occasionally are the so-called *Maxwell relations*, which are the direct generalization of the statement that for a function $f(x, y)$, we must have

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

Since we have three variables, here we have three Maxwell relations. For example, using the pair of variables S, V and making use of Eqs. (8), we find:

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

Similarly (see second from last section of chapter 4), we have

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

These equations allow us to find further relations between various quantities. Taking further derivatives we can identify yet more equations, and we can keep going until we find all possible relationships.

The only problem with all this, is the following: If you go back to the discussion we had about choosing the independent variables describing the system, you'll see that in no case did we find that S would be one of them. In other words, we do not know how to prepare a system experimentally so that its entropy has whatever value we like. However, we found that for an isolated system in equilibrium, we should use U, V, N as the independent variables. Let me then rewrite Eq. (7) to dependent on these variables:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN \tag{10}$$

This shows that $S = S(U, V, N)$. Moreover, remember that the second principle tells us that for an isolated system, the entropy is the quantity which is maximized in equilibrium. As we will see when we start statistical mechanics, this gives us a recipe for finding S: we just have to find what function of U, V, N is maximized in equilibrium, while also being an extensive with the correct units. Once we know $S(U, V, N)$, we can find all possible relationships between dependent and independent variables precisely as we did before. First, the coefficients multiplying dU, dV, dN in Eq. (10) must be partial derivatives of S:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}; \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}; \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{11}$$

This gives us three equations from which we can calculate directly $T = T(U, V, N); p = p(U, V, N); \mu = \mu(U, V, N)$. Notice that it is important to be clear, at all times, which are the independent variables, since the form of the equations will depend very much on that. Second, we can again write 3 sets of Maxwell equations. For instance:

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

and two other similar ones. I hope you realize that you do not need to know these equations by heart. You can derive them very quickly if you know the fundamental equation Eq. (7) and remember that the coefficients of differentials must be the first partial derivatives, and that second order mixed derivatives must be equal to one another.

What if the system is not isolated, but closed? In this case, we decided that T, V, N should be the independent variables. Can we find a state function of these 3 variables? The answer is yes, by performing a Legendre transformation. These are introduced in a very general manner in section 3 of chapter 4, but really, all you need to know is this. Look at Eq. (7). We would like to replace the dS part (showing the S is an independent variable) by a dT, so that T is the independent variable. We can do this using the fact that:

$$TdS = d(TS) - SdT$$

If we put this in Eq. (7) and regroup terms, we find that

$$d(U - TS) = -SdT - pdV + \mu dN$$

so that we have differentials of our desired variables T, V, N on the right-hand side. We define the **free energy** (another state quantity – actually, this, as well as U and S and a few more examples we will discuss, are also called **thermodynamic potentials**):

$$F = U - TS \tag{12}$$

and find that

$$dF = -SdT - pdV + \mu dN \tag{13}$$

So, for a closed system, there is a function $F(T, V, N)$ characterizing its state. If we know this function (and stat mech will tell us how to compute it) we can then find relations between various variables using:

$$S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V,N}; \quad p(T, V, N) = -\left(\frac{\partial F}{\partial V}\right)_{T,N}; \quad \mu(T, V, N) = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{14}$$

and also the corresponding three Maxwell relations (listed in chapter 4). Using definition (12) and Eq. (9), we also find that

$$F = -pV + \mu N \tag{15}$$

In thermodynamics, one usually introduces two more types of thermodynamic potentials, the **enthalpy** $H = U + pV = TS + \mu N$ and the **Gibbs potential or free enthalpy** $G = U - TS + pV = \mu N$. The fundamental equation can be rewritten in terms of these as:

$$dH = TdS + Vdp + \mu dN; \quad dG = -SdT + Vdp + \mu dN$$

showing that $H = H(S, p, N)$ while $G = G(T, p, N)$. We would obviously use the second one for a closed system where we allow the piston to move freely (N, p, T variables). Again, we can write the usual derivatives in each case. Although H and G are very popular in thermodynamics, we will actually not use them in stat mech. Instead, as we will see, we will need the so-called **grand-canonical potential**

$$\Phi = U - TS - \mu N = -pV \tag{16}$$

for which

$$d\Phi = -SdT - pdV - Nd\mu \tag{17}$$

Obviously, $\Phi(T, V, \mu)$ is the appropriate thermodynamic potential when we deal with an open system, since in that case T, V, μ are the independent variables. For completeness sake, let me write now the relations that one can derive from this potential:

$$S(T, V, \mu) = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}; \quad p(T, V, \mu) = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}; \quad N(T, V, \mu) = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \tag{18}$$

The three Maxwell relations are listed in Eq. 4.135 on page 110.

Note: in order to maximally confuse students, the symbols used for these thermodynamic potentials are not unique. Sometimes the internal energy is called E, not U; sometimes the free energy is called A, not F; and sometimes the grand-canonical potential is called Ω, not Φ. I will stick with these names since they are used in the textbook. If you see weird symbols in other textbooks, all you need is a "translation table" to know which symbol stands for what quantity. The general idea, though, should be straightforward: depending on the system of interest and how it is separated from the remaining environment ("outside world" or "reservoir") we decide what are the appropriate independent variables. Using the fundamental equation (7) and the appropriate Legendre transformation, we can find which thermodynamic potential we should deal with (entropy for an isolated system; free energy for a closed system, grand-canonical potential for an open system, etc). Stat mech will give us rules on how to calculate these potentials. Once we know the thermodynamic potential, we can find the values of the dependent variables, as well as any other relationships that we might need, by taking various derivatives from the thermodynamic potential.

As I said before, thermodynamics requires input from experimental observation. In this case, we have no well defined rules on how to theoretically find, for example, the function $S(U, V, N)$ for an isolated system. As discussed when I introduced S, we do have an experimental rule based on the link to the reversible heat exchanged, so in principle one could find this relationship experimentally and then proceed with the derivatives. What happens more often, is that experimentalists measure some other possible relationships between the various parameters, and one has to use those and the various equations listed above to find new ones.

As an example to see how tedious this process could be in thermodynamics, let us study an ideal gas. Assume that experimentalists tell us that for this system, they have found these two relations: $pV = Nk_BT$ and $U = \frac{3}{2}Nk_BT$. We would like to find[6] $F(T, V, N)$. Look at middle Eq. (14):

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V} \rightarrow F(T, V, N) = -Nk_BT \ln \frac{V}{V_0} + F'(T, N)$$

---

[6] We could equally well try to find any other thermodynamical potential instead of F.

where V_0 must be some integration constant with units of volume, to make that argument dimensionless. So now we know the precise dependence of F on V, but not on T, N, since the new function $F'(T, N)$ could be anything. Actually, not really! We know that $F(T, V, N)$ must be an extensive quantity, meaning that $F(T, \lambda V, \lambda N) = \lambda F(T, V, N)$, for any value of λ. This tells us that the most general form allowed for F which is consistent with the last equation, is:

$$F(T, V, N) = -Nk_BT \ln \frac{V}{NV_0} + Nf(T) \tag{19}$$

You can easily check that now, if we double the value of N and V, the total value of F also doubles. So the remaining task is to figure $f(T)$, i.e. a function of only one variable. For this, we need some equation involving $\partial F/\partial T$ – well, this is linked to entropy, see first of Eq. (14):

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \ln \frac{V}{NV_0} - N\frac{df(T)}{dT} \tag{20}$$

Can we calculate S differently? Yes, from Eq. (12):

$$S = \frac{U - F}{T} = \frac{3}{2}Nk_B + Nk_B \ln \frac{V}{NV_0} - \frac{N}{T}f(T)$$

Comparing the last two equations, we find that:

$$\frac{df(T)}{dT} - \frac{f(T)}{T} = -\frac{3}{2}k_B \to T\frac{d}{dT}\left(\frac{f(T)}{T}\right) = -\frac{3}{2}k_B \to \frac{f(T)}{T} = -\frac{3}{2}k_B \ln \frac{T}{T_0}$$

where T_0 is some integration constant with units of temperature (so that the units work out).

Putting this into Eq. (19), we find the desired result:

$$F(T, V, N) = -Nk_BT \ln \left[\frac{V}{NV_0}\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\right] \tag{21}$$

Stat mech will give us this results directly, and will also tell us what the constant $V_0T_0^{\frac{3}{2}}$ is. This example was not too difficult (on purpose) but you see the problem with thermodynamics: we have to take whatever equations we get from experiments, and figure out a way to integrate them to find a thermodynamic potential. There is no universal rule on how to do it – we just have to try all equations until we find a way. And we still have unknown bits at the end of the day (like T_0).

I keep saying that if we know one of the thermodynamic potentials, we have all the information about the system. Before proceeding with an example, let me tell you what other sorts of quantities we will generally want to calculate (because they can be easily measured experimentally, so one can check the results). These are, first, the **specific heats at constant volume/pressure**, defined as:

$$C_V = \left(\frac{\delta Q_{rev}}{dT}\right)_{V,N}; C_p = \left(\frac{\delta Q_{rev}}{dT}\right)_{p,N}; \tag{22}$$

As the definitions above say, these quantities directly characterize how much heat is needed (in a reversible process) to change the temperature of the system by dT, at either constant volume or constant pressure. These definitions are good for the experiments, but not for analytical calculations.

To derive these quantities analytically, we use the fact that $\delta Q_{rev} = TdS$, as discussed for the second principle. So, we have:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N}; C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N}$$

These we can use directly if we know the dependence $S(T, V, N)$ (in the first case) or $S(T, p, N)$, in the second one. Other equivalent forms for these quantities can be obtained using the fact that $TdS = dU + pdV - \mu dN$. We can see that if we keep $V = ct, N = ct \rightarrow dV = 0, dN = 0 \rightarrow (TdS)_{V,N} = dU$ and therefore:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} \tag{23}$$

which we can use directly if we know $U(T, V, N)$. This turns out to be the most useful way to find C_V. Similarly, using $dH = TdS + Vdp + \mu dN \rightarrow (TdS)_{p,N} = dH$:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N} \tag{24}$$

where $H = U + pV$. After doing all sorts of manipulations involving, amongst other things, some Maxwell relations, one can also show that (see Exercise 4.12, page 111):

$$C_p = C_V + TV\frac{\alpha^2}{\kappa}$$

where α and κ are the other two quantities of interest to us, namely **the coefficient of expansion (at constant pressure)**:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{25}$$

which characterizes the percentual change dV/V in the volume if we raise the temperature by dT, while keeping pressure and the number of particles constant; and the **compressibility (at constant temperature)**:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} \tag{26}$$

which measures the percentual change in volume dV/V when pressure is increased by dp, at a constant temperature. The negative sign is there to make this a positive quantity, since an increase in pressure $dp > 0$ leads to a decrease in volume $dV < 0$.

Let us now consider an example, which is typical of the kinds of problems we will solve in this course. Suppose that we have Eq. (21) from somewhere – either the experimentalists gave it to us, or we used stat mech to derive it somehow (deriving this type of equality will be the first part of a typical stat mech problem). What can we do with it?

First, we will use Eq. (14) to find the values of the dependent variables. We find:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \ln\left[\frac{V}{N}\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\right] + \frac{3}{2}Nk_B$$

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

i.e. the equation of state for the ideal gas; and:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_B T \ln\left[\frac{V}{N}\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\right] + k_B T$$

The first and third of this do not look very useful, but we will see soon that we can actually make good use of them. Actually, from the first one, we can see that if the system is closed, $N = ct$, then in an adiabatic process, for which $S = ct$, we must have $VT^{\frac{3}{2}} = ct$. One can use this to compute, for instance, how much work is done during an adiabatic process.

Suppose we want to compute C_V. Since we know $S(T, V, N)$, we can use:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B$$

which is hopefully what you expected to get. How about if we want to use the second formula? In that case, we need $U(T, V, N)$. How can we compute it? Easily:

$$F = U - TS \to U = F + TS$$

Since we have both F and S as functions of T, V, N, a simple substitution will give us the desired $U = \frac{3}{2}Nk_BT$. Actually, let me show you a neat trick. Using Eq. (14) I can write:

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_{V,N} = -T^2\left(\frac{\partial}{\partial T}\frac{F}{T}\right)_{V,N}$$

But

$$-\frac{F}{T} = Nk_B \ln\left[\frac{V}{N}\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\right] = \frac{3}{2}Nk_B \ln T + ...$$

where ... is independent of T. Then,

$$U = -T^2\left(\frac{\partial}{\partial T}\frac{F}{T}\right)_{V,N} = \frac{3}{2}Nk_BT$$

Anyway, using this in the definition of C_V we find, again,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B$$

Let's calculate C_p. For this, we need $S(T, p, N)$. We have $S(T, V, N)$ and we know that $V = Nk_BT/p$, so substituting this in the expression of S, we find:

$$S(T, p, N) = Nk_B \ln\left[\frac{k_B}{p}\frac{T^{\frac{5}{2}}}{T_0^{\frac{3}{2}}}\right] + \frac{3}{2}Nk_B \to C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{5}{2}Nk_B$$

How about if we decided to compute $H(T, p, N)$ and use that to find C_p? Well, we know that

$$H = U + pV = \frac{3}{2}Nk_BT + pV$$

This is not quite good, since this depends on V, whereas we want H as a function of T, p, N only. We use $pV = Nk_BT$ to get rid of V and find:

$$H(T,p,N) = \frac{5}{2}Nk_BT \to C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N} = \frac{5}{2}Nk_B$$

Finally, for the coefficient of expansion we need $(\partial V/\partial T)_{p,N}$, i.e. we need to know $V(T,p,N) = Nk_BT/p$, as we know. Then:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{1}{V}\frac{Nk_B}{p} = \frac{1}{T}$$

For the compressibility, we need to know $(\partial V/\partial p)_{T,N}$, which can be found from $V = Nk_BT/p$ and so:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{1}{V}\frac{Nk_BT}{p^2} = \frac{1}{p}$$

As you can see, for an ideal gas all these quantities are very simple. Of course, in this course we will study some less boring examples, as well.

Finally, let's check that

$$C_p = C_V + TV\frac{\alpha^2}{\kappa} = C_V + TV\frac{p}{T^2} = C_V + Nk_B$$

which is indeed correct.

One last thing: hopefully you remember most of these equations from your thermodynamics course and you're feeling very confident and eager to start learning stat mech. However, if you don't, do not despair – we'll get lots and lots of practice, and you'll become very used to them!