A

STATISTICAL PHYSICS AND THERMODYNAMICS

Statistical physics (or statistical mechanics) is the study of how the properties of bulk materials emerge from the microscopic behavior of their constituent individual units (usually molecules or atoms). As such, it forms the foundation of thermodynamics, which is the phenomenological study of those bulk materials, describing them with only a few parameters like their temperature, pressure, and density. In this appendix, we will recap the main results of thermodynamics and statistical physics that are necessary for the study of soft matter.

A.1 THERMODYNAMICS

Thermodynamics is the study of *heat*, its connection to *energy*, and the static (equilibrium) and dynamic properties of systems that have a thermal component. In a similar fashion as mechanics is based on a few axioms (Newton's laws of motion and the various force laws), thermodynamics is based on a number of laws which are taken as axioms. The zeroth law (so labeled because it was formulated after the first, but more fundamental), deals with the concept of thermodynamic equilibrium; the first law is an extension of the concept of conservation of energy, and the second law tells us about the natural direction of heat flow.

A.1.1 THERMODYNAMIC EQUILIBRIUM

Thermodynamic equilibrium is a state in which several different sub-classes of equilibrium all have to be present. To illustrate them, we will imagine a container that is fully isolated from the outside world, and subdivided into two compartments (figure A.1). The two compartments are in thermodynamic equilibrium with each other if they are in *mechanical*, *thermal* and *chemical* equilibrium.

We will illustrate these three types of equilibria using the properties of an *ideal gas*. An ideal gas consists of point-like atoms that only interact with each other when they collide. Noble gases like helium, neon and argon are good approximations to this ideal. Ideal gases behave according to the ideal gas law, which relates the pressure p, occupied volume V and temperature T of an ideal gas[1]:

$$pV = nRT = Nk_{\text{B}}T. \tag{A.1}$$

In equation (A.1), N is the number of gas atoms, k_{B} is Boltzmann's constant, which converts a temperature into an energy, and is approximately given by $k_{\text{B}} = 1.38 \cdot 10^{-23}\text{J/K}$, and T is the temperature. Since the number of particles in a typical microscopic volume is very large, and k_{B} very small, it is practical to define a reference that is somewhat less unwieldy. To that end, we define *Avogadro's number* $N_{\text{A}} = 6.022 \cdot 10^{23}$, which is the number of carbon-12 atoms in a sample of 12 grams. By definition, a *mole* of material (unit: mol) contains N_{A} atoms of that material. In equation (A.1), n represents the number of moles of gas; the *gas constant* R is then given by $R = N_{\text{A}} \cdot k_{\text{B}} = 8.314\text{J/K}$.

The three types of thermodynamic equilibrium are illustrated in figure A.1. A mechanical object is in equilibrium when both the sum of the forces and the torques acting on it are zero. Suppose the division

[1] Equation A.1 is sometimes referred to as the *equation of state* of the ideal gas. An equation of state is an equation between state variables, which are variables that determine the state of a thermodynamic system - such as its pressure and temperature.

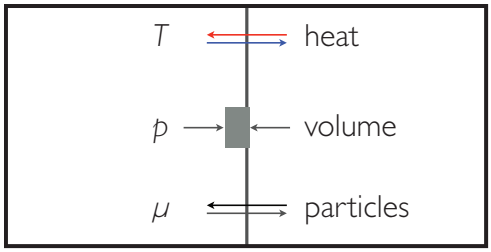

Figure A.1: Illustration of thermodynamic equilibrium: exchange of heat equilibrates temperature, exchange of volume equilibrates pressure, and exchange of particles equilibrates the chemical potential. Note that energy, heat, volume and number of particles scale with the system size (we call them extensive variables), while temperature, pressure and chemical potential (the intensive variables) do not. The equilibrium conditions thus all involve intensive variables, and systems of different size can be in thermodynamic equilibrium with each other.

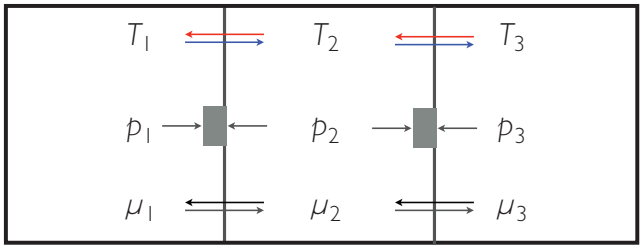

Figure A.2: Illustration of the zeroth law of thermodynamics: when two systems are both in equilibrium with a third, they are in equilibrium with each other.

between the two compartments of our container can move, but the outside walls are rigidly fixed. If the pressure in one (say the left) compartment is larger than in the other, there will be a net force on the wall, which will move it towards the right, reducing the right compartment's volume, and expanding that of the left compartment. This goes on until the *pressure* in both compartments is the same - i.e., they both exert the same force (per unit area) on the wall, at which point there is mechanical equilibrium.

Now suppose that the wall separating the two compartments cannot move, but heat exchange through the wall is possible. Then, if the left compartment is warmer than the right one, heat will flow from the left to the right - a phenomenon you have undoubtedly experienced many times yourself when trying to hold a paper cup of hot coffee. Consequently, the *temperature* of the colder compartment will rise, whereas that of the hotter one will drop, until they are equal and have reached thermal equilibrium. In fact, temperature can be defined by this property: if two systems are in thermal equilibrium (i.e. no net heat flow), then they have the same temperature.

Finally, suppose that particles can be freely exchanged between the two compartments. Clearly if all particles are in one compartment, there is an imbalance that will not be stable, as some particles will move over to the other compartment over time, resulting in a net particle flow. Again, this goes on until the flow of particles from left to right balances that from right to left. The equivalent quantity to pressure and temperature for this type of exchange is called the *chemical potential*, and when there is no more net particle flow between the two compartments, they are said to be in chemical equilibrium.

A.1.2 THE ZEROTH LAW OF THERMODYNAMICS

Suppose we have three systems, as in figure A.2, where system 1 is coupled to system 2, and system 2 to system 3, but there is no direct coupling between systems 1 and 3. Then if there is thermodynamic equilibrium between systems 1 and 2, they have the same temperature, pressure and chemical potential. The same holds for systems 2 and 3. But then we have $T_1 = T_2 = T_3$ (and the same for p and μ), so systems 1 and 3 must also be in equilibrium, which gives us the **zeroth law of thermodynamics**: *If two systems are both in equilibrium with a third system, they are in equilibrium with each other.*

A.1.3 HEAT AND ENERGY

In the example of the previous section, when there is no mechanical equilibrium, it can be reached by doing *work*, by moving the wall:

$$W = \int F \mathrm{d}r = \int \frac{F}{A} A \mathrm{d}r = \int \Delta p \mathrm{d}V. \tag{A.2}$$

In equation (A.2), $\mathrm{d}r$ is the distance over with the wall moves, A the area of the (moving part of the) wall, and $\mathrm{d}V = A\mathrm{d}r$ is the amount of volume added to the compartment with the larger pressure. The net force on the wall equals the difference in pressure, $\Delta p = p_1 - p_2$ times the wall area; the difference in pressure (or net pressure) is usually just denoted p in thermodynamics. Equation (A.2) tells us that a pressure difference can be used to move objects, and thus that work can be extracted. However, if we are interested in the properties of the gas (that is, after all, the system which we are studying here), we should instead calculate the work done on the gas - which is minus the work done by the gas on the wall:

$$W = -\int p \mathrm{d}V. \tag{A.3}$$

Equation (A.3) tells us that when the two compartments move towards mechanical equilibrium, mechanical energy is exchanged between them, until their pressures are equal. Similarly, we've defined thermal equilibrium as the state in which the temperatures of the two compartments are equal, and noted that an imbalance in temperature leads to a flow of heat. The key realization that lays at the foundation of thermodynamics is that this heat is also a form of energy. Microscopically, we can identify temperature as the kinetic energy of the constituent particles of a material, so an exchange in temperature between two systems, i.e. a heat flow, is simply an exchange in kinetic energy - so with that in mind, the fact that heat is a form of energy is not so surprising. The great feat of the early explorers of thermodynamics was to realize this without having microscopic knowledge of the materials[2].

A.1.4 THE FIRST LAW OF THERMODYNAMICS

We will denote a transfer of heat (a heat flow between two systems of unequal temperature) by Q. A transfer of energy in the form of mechanical work is still denoted by W; the total transfer of energy between two systems can then be written as:

$$\Delta \mathscr{E} = Q + W, \tag{A.4}$$

where $\Delta\mathscr{E}$ is the change in *internal energy* of a system[3]. Equation (A.4) is a version of the **first law of thermodynamics**: *The total change in internal energy of a system equals the sum of the net heat transfer to the system and the net work done on the system.* Consequently, for an isolated system, the total internal energy is conserved - just like in classical mechanics.

Quite often, we will want to consider processes in which the heat exchange or work done changes during the process. For those, as we did above when defining the work as the integral over the (varying) force, we need to integrate over the process to find the total change in heat, work or energy. To do so, we use the differential form of the first law:

$$\mathrm{d}\mathscr{E} = \mathrm{d}Q + \mathrm{d}W. \tag{A.5}$$

We already know that $\mathrm{d}W = -p\mathrm{d}V$, which is simply the infinitesimal version of (A.3). As we'll see in section A.1.8, we will find a similar expression for $\mathrm{d}Q$, in terms of the temperature and a quantity called entropy[4]. Before that, however, we will take a macroscopic look at the heat flow Q, starting with the second law.

A.1.5 SECOND LAW OF THERMODYNAMICS

In its simplest form, the **second law of thermodynamics** states an observational fact that will probably not surprise anyone: *Heat cannot spontaneously flow from a cold to a hot reservoir.*

[2] It will probably not surprise you that, given that the number of particles is dimensionless, the chemical potential has dimensions of energy as well, as already is suggested by its name. The chemical potential is the key player in the discussion on solutions in chapter 5.

[3] Some texts do not make the transition from the work done by the system (eq. A.2) to the work done on the system (eq. A.3), and consequently have a minus sign in equation (A.4).

[4] There's a subtle difference between $\mathrm{d}\mathscr{E}$ on the one hand, and $\mathrm{d}Q$ and $\mathrm{d}W$ on the other: $\mathrm{d}E$ is what is known mathematically as a 'perfect differential': if you go around a circular path back to the point where you started, its integral equals zero. For $\mathrm{d}Q$ and $\mathrm{d}W$ this need not be true, which is why people avoid using version (A.5) of the first law. Fortunately, $\mathrm{d}V$ and $\mathrm{d}S$ (with S the entropy) are perfect differentials, and the form people usually use is $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V$ (which by some authors is called the 'combined first and second law' as it includes the concept of entropy). Moreover, if we also allow the number of particles to change, we add a third differential: $\mu\mathrm{d}N$, so $\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$.

Formulated like this, the second law appears almost tautological - but don't be fooled by simplicity, the consequences are quite profound, as we'll see later. Here, we simply note two things. First, the second law is different from the first, in that the first tells you something about the total energy, i.e. the heat plus work, whereas the second tells you something about the flow of heat alone. Second, you might have noticed that the second law is very similar to another commonly known observational fact: water always flows downhill. The flow of water can of course be described by mechanics (and caused by the force of gravity); in close analogy, the flow of heat is described by thermodynamics and caused by a difference in temperature. Moreover, we may say that the flow of water represents a difference in potential energy between a high and a low point - which is well-defined exactly because water will never spontaneously flow uphill. Similarly, we will define a 'thermodynamic potential energy' later based on the flow of heat. This thermodynamic equivalent of the potential energy will be the *entropy*, as we'll see in section A.1.8.

A.1.6 HEAT CAPACITY

Perhaps unsurprisingly, the amount of heat (i.e., thermal energy) you need to add to a sample to increase its temperature by a certain amount ΔT scales with that temperature:

$$Q = C\Delta T, \tag{A.6}$$

where C a proportionality constant known as the *heat capacity*. Equation (A.6) is an observational fact, just like its mechanical analog relating the force and extension of a spring (Hooke's law). Within thermodynamics, we take equation (A.6) as an axiom, as we do the zeroth, first and second law. For macroscopic objects or quantities, one can define a molar or mass *specific heat* by dividing the heat capacity by the mass or the number of moles of gas in a sample.

Although the heat capacity C is a proportionality constant in equation (A.6), its value depends not only on the material in question, but also on the process, where we have multiple choices. Since the total internal energy of a thermodynamic system is the sum of the heat and the work, for measuring C, it matters how we control the sample. The work is the product of a pair of *conjugate variables*: the pressure and the volume. We can experimentally control one of these at a time, but not both - so we could keep either the pressure or the volume constant, while measuring how the heat changes as a function of a change in temperature. Consequently, we get two different ways of determining the heat capacity, which in general results in two different values: the heat capacity at fixed volume, C_V, and the heat capacity at fixed pressure, C_p:

$$C_V = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_V, \qquad C_p = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_p, \tag{A.7}$$

where the subscript indicates which parameter is held fixed.

For an ideal gas, we can relate the values of C_V and C_p to each other by considering two quasi-static processes (processes done so slowly that in each intermediate state the system can be considered to be in thermodynamic equilibrium). In an isovolumetric process (figure A.3), we keep the volume fixed, which means that no work is done; consequently, we get $\Delta\mathscr{E} = \Delta Q = C_V\Delta T$, relating the change in internal energy directly to the change in temperature. Now if we interpret the change in temperature as a change in the kinetic energy of the particles, and recall that for an ideal gas the particles do not interact with each other (so there is no potential energy), the kinetic energy is the only contribution to the energy, and thus the internal energy can depend only on the temperature[5]. Therefore, for an ideal gas, we must have $\Delta\mathscr{E} = C_V\Delta T$ for any quasistatic process. Let's now consider an isobaric process, in which we keep the pressure constant (figure A.3). On the one hand, we still have $\Delta\mathscr{E} = C_V\Delta T$, while on the other, we now have a change in both heat and work: $\Delta Q = C_p\Delta T$ (by definition of C_p) and $\Delta W = -p\Delta V$ (equation A.2). Now using the ideal gas law, we can write $-p\Delta V = -Nk_\text{B}\Delta T$. Combining, we get: $C_p = C_V + Nk_\text{B}$, which gives the desired relation between the two heat capacities. We note that C_p is always greater than C_V, which makes sense: in a constant-volume process, all thermal energy goes into raising the temperature, whereas in a constant-pressure process, the volume of the gas must change, and hence work must be done, so to get the same change in temperature, more energy is required, or in other words, some of the thermal energy is converted to mechanical work.

[5] A straightforward calculation, which can be found in many introductory physics textbooks, shows that for an ideal gas in a box with volume V, you get a pressure on the walls given by $p = \frac{2}{3}(N/V)\left\langle\frac{1}{2}mv^2\right\rangle$, which, combined with the ideal gas law, gives $\left\langle\frac{1}{2}mv^2\right\rangle = \frac{3}{2}k_\text{B}T$, so we can indeed interpret the temperature of an ideal gas as the average kinetic energy of its particles.

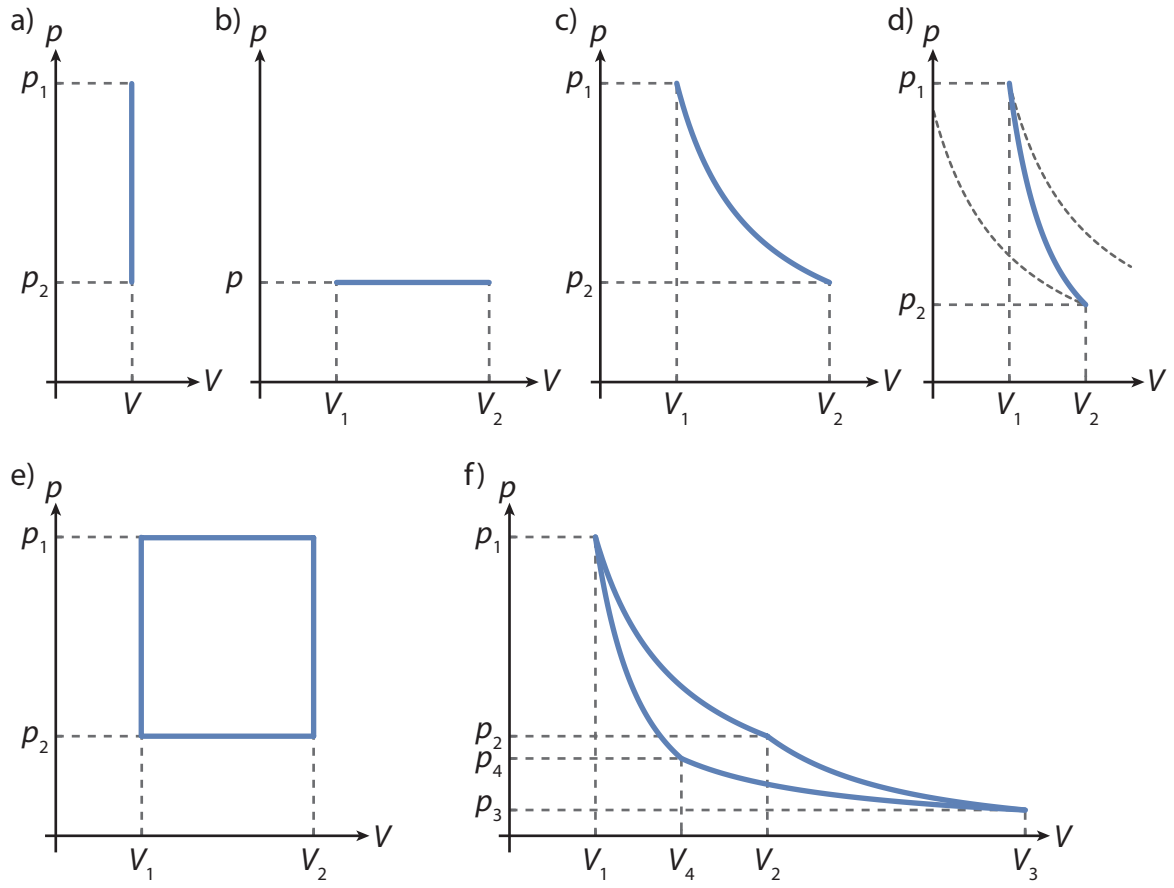

Figure A.3: (p, V)-diagrams for four quasistatic thermodynamic processes and two cycles. (a) Isovolumetric process. (b) Isobaric process. (c) Isothermal process, with $pV = Nk_B T$ = const. (d) Adiabatic process (no heat flow). Dashed lines indicate isotherms, showing that the line describing an adiabat, pV^γ = const is steeper than that of an isotherm. (e) Simple heat engine combining two isovolumetric and two isobaric processes. The amount of work extracted from the system equals the area enclosed by the cycle. (f) Carnot cycle, consisting of two isothermal and two adiabatic processes.

A.1.7 HEAT ENGINES

The fact that we can convert thermal energy to mechanical work can be exploited by building a *heat engine*. We simply set up a cyclic process in which we extract more work from the system than we put into it, in effect converting heat to mechanical work. Using the isovolumetric and isobaric process, we can do so easily, see figure A.3e: we first expand at constant pressure, then reduce pressure at constant volume (by cooling), compress at constant pressure, and increase pressure at constant volume (by heating). Since compressing a cooler gas requires less work, we get a net conversion of heat to work, which is the basic idea behind the steam engine and most combustion engines.

Note that not all the heat that we put into the heat engine is converted to work. For a practical heat engine, we need both a hot reservoir, at temperature T_h, from which we extract an amount of heat Q_h, and a cold reservoir (usually the environment), at temperature T_c, into which we 'dump' a (smaller) amount of heat Q_c, see figure A.4a. We define the *efficiency* of the engine as the ratio between the extracted work and the input heat: $\eta \equiv W/Q_h$.

If we make sure that all the processes in the cycle of our heat engine proceed in a quasistatic manner, i.e., going from one equilibrium state smoothly into one another, our engine is *reversible*: we can go through the cycle in the opposite direction, using work to transfer heat from the cold to the hot reservoir (this is how a refrigerator works). For a reversible engine, its cycle will at some point return to its original state, at which point its internal energy will be the same as at the start (as the internal energy depends only on the internal state). The first law of thermodynamics then tells us that the extracted work equals the difference between the extracted and dumped heat: $W = Q_h - Q_c$, and the efficiency equals

$$\eta \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}. \tag{A.8}$$

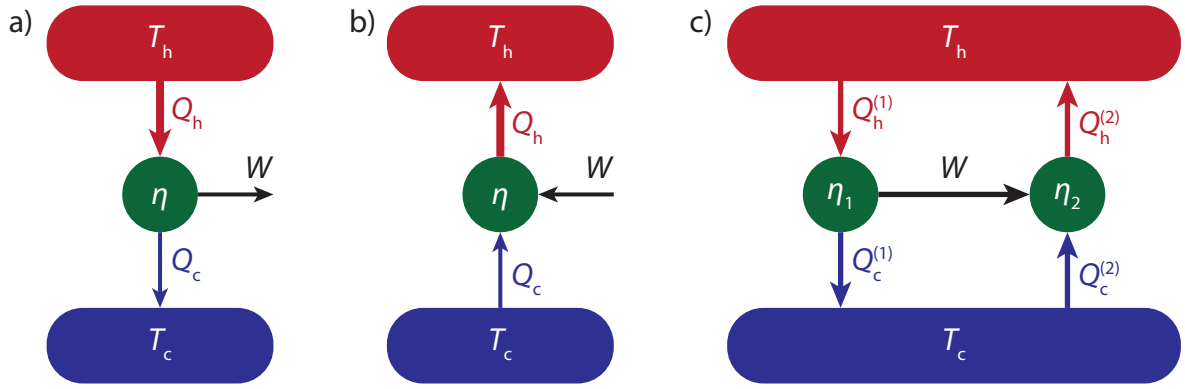

Figure A.4: (a) A heat engine takes an amount of heat Q_h from a hot heat bath at temperature T_h, and converts this into an amount of work W, as well as a remaining amount of heat Q_c which is dumped into a cold bath at temperature T_c (usually the environment). (b) A heat engine run in reverse is a refrigerator, extracting heat from a cold bath and dumping it in a hot bath. (c) Schematic in which two reversible heat engines with different efficiencies are coupled. The work from the left engine is used to run the right engine in reverse. The result is a net heat flow from the cold to the hot heat bath, violating the second law of thermodynamics.

You might think that the efficiency of a reversible engine depends on its design, but this turns out not to be the case; it depends only on the temperatures of the two heat baths. This result is known as *Carnot's theorem*, and to see why it works, consider the opposite case. Suppose we have two reversible heat engines with different efficiencies, η and $\eta^* < \eta$. We then use the work extracted from the engine with the highest efficiency to run the one with the lowest efficiency in reverse, see figure A.4b. If the second engine uses all the work produced by the first, we get:

$$\eta^* < \eta \quad \Leftrightarrow \frac{W}{Q_h^*} < \frac{W}{Q_h} \quad \Rightarrow Q_h < Q_h^*, \tag{A.9}$$

so the amount of heat extracted from the hot bath by the more efficient engine is lower than the amount of heat added (to the hot bath!) by the less efficient engine. As no net work is put into the system, this heat has to come from the cold bath. This setup thus leads to a net spontaneous flow of heat from the cold to the hot bath, in direct violation of the second law of thermodynamics. Therefore, the efficiencies of the two reversible engines have to be identical.

The fact that the efficiency of all reversible heat engines is the same means that we only need to calculate it once to get a universally valid expression for it. Moreover, we can do the calculation for a case that is designed to make that calculation easy. To that end, we'll use the Carnot cycle (figure A.3f), which consists of two isothermal (figure A.3c) and two adiabatic (A.3d) processes. An isothermal process is one in which temperature is kept fixed. By the ideal gas law, the resulting curve in the pV plane is given by $p = Nk_B T/V$, and because the change in internal energy depends only on the change in temperature, for an isothermal process the internal energy is constant ($d\mathscr{E} = 0$, so $dQ = -dW$). For an adiabatic process, there is no heat flow ($dQ = 0$), which gives $d\mathscr{E} = C_V dT = dW = -p dV$. Using the differential form of the ideal gas law, $Nk_B dT = d(pV) = p dV + V dp$, we can re-write this relation to

$$\frac{dp}{p} + \frac{C_p}{C_V}\frac{dV}{V} = 0, \tag{A.10}$$

or $pV^\gamma = \text{const}$, where $\gamma = C_p/C_V$. Since $\gamma > 1$, the line describing an adiabat in the pV plane is steeper than that describing an isotherm.

Calculating the amount of work done and amounts of heat absorbed and extracted in a Carnot cycle is now a simple exercise. For the isothermal process from (p_1, V_1) to (p_2, V_2), we get (combining the ideal gas law, the expression for work in equation A.3, and the isothermal property that $dQ = -dW$)

$$Q_h = -W = \int_{V_1}^{V_2} \frac{Nk_B T_h}{V} dV = Nk_B T_h \log\left(\frac{V_2}{V_1}\right). \tag{A.11}$$

Likewise, we find that the amount of heat dumped in the isothermal process from (p_3, V_3) to (p_4, V_4) is given by $Q_c = Nk_B T_c \log(V_3/V_4)$. Since the two adiabatic processes occur (by construction) without absorbing or

dumping any heat, we can write for the efficiency:

$$\eta_{\text{Carnot}} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c \log(V_3/V_4)}{T_h \log(V_2/V_1)}. \tag{A.12}$$

Now V_2 and V_3 (and V_4 and V_1) are related by adiabatic processes, which obey $pV^\gamma = \text{const}$, or, again by application of the ideal gas law, $TV^{\gamma-1} = \text{const}$, so we have $T_h V_2^{\gamma-1} = T_c V_3^{\gamma-1}$ and $T_h V_1^{\gamma-1} = T_c V_4^{\gamma-1}$. If we divide these two equations by each other, we find that $V_2/V_1 = V_3/V_4$, which means that the two log terms in equation (A.12) are equal, and thus

$$\eta_{\text{reversible}} = 1 - \frac{T_c}{T_h}. \tag{A.13}$$

A.1.8 ENTROPY

The calculation of the efficiency of a reversible engine may not seem to be that spectacular at first, but it provides us with a very useful relation. Comparing equations (A.8) and (A.13), we can read off that $Q_c/Q_h = T_c/T_h$, or, after rearranging,

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c}. \tag{A.14}$$

Remember that Q_h is the heat that flows into the engine from the hot bath at T_h, whereas Q_c is the heat that flows out of the engine to the cold bath at T_c. Equation (A.14) tells us that in a complete cycle, the difference between the 'heat per temperature' influx and outflux is zero. Therefore, next to the internal energy of the system, this 'heat per temperature' gives us a second quantity that is unchanged when we've gone through a full reversible cycle. This second quantity is known as the *entropy*.

You may object that, even though we've proven that the efficiency of any reversible engine must be the same, we used the specific setup of the Carnot engine to derive equation (A.13). For any other system (e.g., the isovolumetric/isobaric engine in figure A.3e), heat does not flow in at a constant temperature, as the internal temperature of the engine changes under compression or expansion. You would of course be right, so we need a little care to make our expression for the entropy universally valid. The trick is to consider infinitesimal steps: let us add reversibly an infinitesimal amount of heat, δQ, from a reservoir at temperature T. The added 'heat per temperature', or entropy, to the system is then given by

$$\mathrm{d}S = \frac{\delta Q}{T}. \tag{A.15}$$

Adding heat to a system increases its entropy, removing heat (i.e., flipping the sign of δQ), removes it. For a complete Carnot cycle, we can integrate equation (A.15) to get

$$\Delta S_{\text{Carnot}} = \oint \frac{\mathrm{d}Q}{T} = \frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0, \tag{A.16}$$

by equation (A.14).

We can always construct a Carnot cycle between any two points (p_1, V_1) and (p_2, V_2) in the p, V state space of an engine. By equation (A.16), the entropy change if we go around that cycle is zero, so we can define an entropy difference between the two points as

$$\Delta S_{12} = \int_1^2 \frac{\mathrm{d}Q}{T}, \tag{A.17}$$

where '1' and '2' refer to the points in the state space.

Equations (A.16) and (A.17) still wouldn't be much use if the change in entropy would depend on the path taken. That however is not the case: the entropy, like the energy, is a *state function*: it depends only on the thermodynamic variables[6]. You can easily see that this is true as you can describe any cycle as the limit of a large number of Carnot cycles, and as equation (A.16) holds for each of those Carnot cycles, it also holds for their sum, i.e., the arbitrary cycle. Therefore, the change in entropy over any closed path is zero, and the entropy difference between two points is well-defined.

[6] Thermodynamic variables describe the state of the system - e.g., the volume, pressure, temperature, and number of particles. As these are also related to each other by one or more equations of state, the energy and entropy are in practice given as functions of fewer variables. For instance, for an ideal gas, the state is fixed when setting the temperature, volume and number of particles, as we can then calculate the pressure using the ideal gas law.

You may have noted that equations (A.16) and (A.17) strongly resemble those of the definition of the potential energy of a conservative force in mechanics. There, we have that the amount of work around any closed cycle is zero, so (for a one-dimensional force $F(x)$, the three-dimensional case goes analogously):

$$0 = \oint F(x)\mathrm{d}x, \qquad \Delta V_{12} \equiv -\int_1^2 F(x)\mathrm{d}x, \tag{A.18}$$

where '1' and '2' now simply refer to positions. The potential energy difference between two points is thus minus the work you need to do to get a particle there, or equal the amount of work you can get out of the system. The entropy is exactly the same, *except for the sign*: the increase in entropy of a system equals the net work extracted from it. This observation gives us the interpretation of the thermodynamic entropy: from a system with lower entropy, you can extract more work, or, entropy is minus the 'heat potential energy' of a system.

When left to its own devices, a mechanical system, through friction and drag (non-conservative forces) will generally tend to find a local minimum of its potential energy. Likewise, thermal systems, by dissipating energy to their environment, will gradually tend to maximize their entropy. The equilibrium point (the equivalent to the minimum of the potential energy) is thus the state of maximum entropy.

We already noted that entropy, like energy, is a state function. Moreover, also like energy, it is extensive: if we double the system size and the number of particles in the system (thus keeping the density the same), we also double the entropy. As both energy and entropy are extensive, we may expect that changes in energy and entropy are related by an intensive variable, just like changes in volume and energy are related by the (intensive) pressure. To see how this works, consider a system with fixed volume V and number of particles N. We then add an infinitesimal amount of heat δQ to this system. As the volume and number of particles are held fixed, there is no net work done, so by the first law, $\mathrm{d}\mathscr{E} = \delta Q$, and by combining this relation with equation (A.17), we get

$$\left(\frac{\mathrm{d}S}{\mathrm{d}\mathscr{E}}\right)_{V,N} = \frac{1}{T}. \tag{A.19}$$

Perhaps unsurprisingly, the intensive variable relating energy and entropy is the temperature. Equation (A.19), in combination with (A.3), allows us to re-write the first law in terms of entropy, volume, and number of particles:

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N. \tag{A.20}$$

Equation (A.20) is the form of the first law[7] that is most used. We introduced the third term, $\mu\mathrm{d}N$, to allow for a change in the number of particles as well. N is a dimensionless extensive variable, so μ, known as the *chemical potential* must be an intensive variable with the dimension of energy: it is simply the energy cost of adding one more particle at fixed volume and entropy.

A.1.9 FREE ENERGY

We've seen in sections A.1.7 and A.1.8 that not all internal energy of a system is available to do work. In particular for a heat engine, some of the available energy in the hot reservoir will inevitably be used to raise the temperature of the cold reservoir, and thus the total entropy of the system consisting of the engine and whatever it is working on. This principle holds generally, as a direct consequence of the second law of thermodynamics. In many practical cases, knowing the internal energy of your system is therefore not very useful. Instead, you want to know how much energy is available to do work. This quantity is known as the (Helmholz) *free energy*[8], which is given by[9]

$$F = E - TS, \tag{A.22}$$

[7] Sometimes called the 'combined first and second law'.

[8] Free energies are sometimes called *thermodynamic potentials*. Transformations of the type given by equations (A.22), (A.24), (A.26), and (A.28) are examples of *Legendre transforms*. For a 'nice' (i.e., smooth) enough function $f(x)$, the Legendre transform g(x) is defined such that, up to an additive constant, the derivatives of f and g are each other's inverse. Working back from this definition, we get

$$g(x) = x\frac{\mathrm{d}f}{\mathrm{d}x} - f(x). \tag{A.21}$$

Treating the energy as a function of entropy, and using equation (A.19) to relate the derivative of the energy to the temperature, we find that the free energy in equation (A.22) is indeed the Legendre transform of the internal energy.

[9] Sadly the symbols used for the various free energies are not universally agreed upon. In particular, you will frequently find A for the Helmholz free energy. To be sure, always check of which variables the given free energy is a function.

and its differential can be easily calculated to be

$$\mathrm{d}F = \mathrm{d}E - \mathrm{d}(TS) = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N - T\mathrm{d}S - S\mathrm{d}T = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N. \tag{A.23}$$

The Helmholz free energy is a function of the system's temperature, volume, and number of particles. Like the internal energy, it is extensive, meaning that it scales with the system size. We will use it in various applications in chapters 2, 4, 5, and 7. There are however cases for which it is not the handiest choice, for instance when studying gases (rather than liquids, which is what we almost exclusively do in this book). In that case, rather than controlling the volume, it may be easier to control the pressure of your system. Fortunately, there is also free energy that is a function of temperature, pressure, and number of particles, known as the *Gibbs free energy*, given by

$$G = F + pV = E - TS + pV, \tag{A.24}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N. \tag{A.25}$$

Alternatively, you might have a system that, in addition to a reservoir of heat, has a reservoir of particles (a grand-canonical system) at a given chemical potential. In that case, the free energy of choice would be a function of temperature, volume, and chemical potential, known as the *grand canonical free energy*

$$\Phi = F - \mu N = E - TS - \mu N, \tag{A.26}$$

$$\mathrm{d}\Phi = -S\mathrm{d}T - p\mathrm{d}V + N\mathrm{d}\mu. \tag{A.27}$$

Finally, in chemistry you may encounter reactions which produce or absorb heat (so temperature is not fixed), for which you'd want a free energy that is a function of entropy, pressure, and number of particles: the *enthalpy*:

$$H = E + pV, \tag{A.28}$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}N. \tag{A.29}$$

All the free energies defined above are extensive. Note that you cannot define a free energy that is a function of the temperature, pressure, and chemical potential: it would be a function of intensive variables alone, and thus no longer extensive, and therefore be the same for all system sizes.

A.1.10 THE GIBBS-DUHEM RELATION

Although we've split the concept of 'thermodynamic equilibrium' into three constitutive parts, in practice you can't separate them fully. That turns out not to be due to lack of experimental skill, but due to a fundamental constraint in thermodynamics: a relation between the intensive variables of a system that fixes one of them as a function of the others. For example, in a single-component system, once you've set the temperature and pressure, the chemical potential is also set. To see how this comes about, we'll start from the Gibbs free energy, generalizing equation (A.25) to a system with multiple components:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \mathrm{d}N_i, \tag{A.30}$$

from which we can read off that the Gibbs free energy is a function of temperature T, pressure p, and the number of particles of the various components N_i. Also, to calculate any of the chemical potentials, we can simply take derivatives of the Gibbs free energy:

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}, \tag{A.31}$$

where $j \neq i$ means all components except the one labeled with i. Defining $N = \sum_i N_i$ as the total number of particles in the system, we can calculate the Gibbs free energy per particle:

$$\mathrm{d}g = -s\mathrm{d}T + v\mathrm{d}p + \sum_i \mu_i \mathrm{d}n_i, \tag{A.32}$$

where $g = G/N$, $s = S/N$, $v = V/N$, and $n_i = N_i/N$. Substituting $G = Ng$ in equation (A.31), we get

$$\mu_i = g + \frac{\partial g}{\partial n_i} - \sum_j n_j \frac{\partial g}{\partial n_j}. \tag{A.33}$$

If we now sum n_i times equation (A.33) over all components, we get an explicit (and perhaps surprisingly simple) expression for g:

$$g = \sum_i \mu_i n_i, \tag{A.34}$$

where we used that $\sum_i n_i = 1$. By multiplying equation (A.34) with N, we also find an explicit expression[10] for G:

$$G = \sum_i \mu_i N_i. \tag{A.35}$$

The total differential of the Gibbs free energy as given by equation (A.35) is

$$\mathrm{d}G = \sum_i \mu_i \mathrm{d}N_i + \sum_i N_i \mathrm{d}\mu_i. \tag{A.36}$$

As equations (A.30) and (A.36) are the total differential of the same quantity, they must be the same, and we can read off that

$$S\mathrm{d}T - V\mathrm{d}p + \sum_i N_i \mathrm{d}\mu_i = 0. \tag{A.37}$$

Equation (A.37) is known as the *Gibbs-Duhem relation*. We can simplify it to a single component to get the relation between temperature, pressure and chemical potential mentioned at the top of the section. We can also formalize the discussion one step further, and replace all extensive variables except the entropy with an abstract extensive variable X_i (sometimes called a 'flux'), paired with an intensive 'force' f_i. In that case, the (internal) energy is a function of S and the X_j's, the temperature is still $(\partial U/\partial S)_{X_i}$, and the forces are the other derivatives, $f_i = (\partial U/\partial X_i)_{T,X_{j\neq i}}$. The Gibbs-Duhem relation then reads:

$$S\mathrm{d}T + \sum_i X_i \mathrm{d}f_i = 0. \tag{A.38}$$

We'll use the Gibbs-Duhem relation in section 5.1 to derive the Gibbs phase rule, which gives the maximum number of coexisting phases in a thermodynamic system. Further formalizations like in equation (A.38) are useful when extending the theory to systems with magnetic, nematic, or active components, which contain additional contributions to the energy beyond the ones we've discussed here.

[10] Equation (A.35) is often simply stated as a direct consequence of (A.30), and if you see why it's true from there feel free to forget about the steps in between, but for me that only works in retrospect.