

## 11 Microscopic probabilities of systems connected to a bath: Boltzmann factors

We will end the course by coming full circle. Remember that in Unit 3 we talked about microstates and how they lead to the second law of thermodynamics and thus maximizing entropy to find equilibration. Then in Unit 8 we studied free energy, which when minimized, maximizes entropy of the combined system and reservoir. It is useful to understand what happens to the microstates of a system in this situation—when the system is connected to a reservoir. Here we will study the probability of microstates of a system connected to a reservoir at a given temperature  $T$ . We will first just start with the answer and some examples, and then explain why the Boltzmann factors are correct in a later unit.

### 11.1 Boltzmann factors

**For a system in constant with a reservoir at temperature  $T$ ,** the probability of a microstate with energy  $E$  is proportional to  $e^{-\frac{E}{kT}}$ .

### 11.2 Example: Boltzmann atmosphere

Consider an idealization of our atmosphere in which the system is in complete thermal equilibrium at temperature  $T$ . Both of these approximations are quite large actually! In reality the temperature varies with location and altitude because the atmosphere is typically an out of equilibrium system. However, here we will study the equilibrium expectation for an atmosphere of gas.

We are going to be interested in the pressure as a function of altitude ( $h$ ). We will do this by computing the *ratio* of pressures at different altitudes  $h_2, h_1$ . Assuming that the atmosphere is an ideal gas,

$$\frac{p(h_1)}{p(h_2)} = \frac{N(h_1)/V(h_1)}{N(h_2)/V(h_2)}, \quad (1)$$

where we have assumed that the temperature is the same at both altitudes. The important insight here is that  $N(h_1)/V(h_1)$  is the density of atoms at height  $h_1$ , which is also proportional to the probability that any given atom appears at height  $h_1$ . So the ratio of pressures is the ratio of probabilities:

$$\frac{p(h_1)}{p(h_2)} = \frac{P(h_1)}{P(h_2)}, \quad (2)$$

where  $P$  is the probability of an atom appearing at  $h_1$  or  $h_2$ . Note the difference in case. The Boltzmann factors allow us to compute that ratio.

Consider a single atom connected to a bath at temperature  $T$ . The microstate is given by its position,  $\mathbf{r}$ , and its velocity  $\mathbf{v}$ . The Boltzmann factor is then

$$P(h) \propto \exp\left(-\frac{\frac{1}{2}m\mathbf{v}^2 + mgh}{kT}\right), \quad (3)$$

where  $g$  is the force of gravity and  $h$  is the height. Then,

$$\frac{P(h_1)}{P(h_2)} = \frac{\exp\left(-\frac{\frac{1}{2}m\mathbf{v}(h_1)^2 + mgh_1}{kT}\right)}{\exp\left(-\frac{\frac{1}{2}m\mathbf{v}(h_2)^2 + mgh_2}{kT}\right)}. \quad (4)$$

The trick here is to realize that the velocity is completely independent of the altitude, so the velocity parts cancel.

$$\frac{P(h_1)}{P(h_2)} = \frac{\exp\left(-\frac{mgh_1}{kT}\right)}{\exp\left(-\frac{mgh_2}{kT}\right)} = \exp\left(-\frac{mg}{kT}(h_1 - h_2)\right) = \frac{p(h_1)}{p(h_2)}. \quad (5)$$

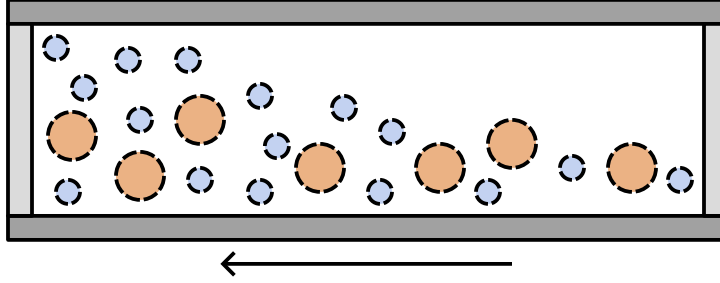


Figure 1: A centrifuge (or an atmosphere). The arrow indicates the direction of acceleration. The orange dots represent molecules with a larger mass, while the blue dots represent a higher mass type of molecule. The “height” increases to the right. There are relatively more blue dots at larger height than orange dots.

Now suppose we set  $h_2$  to be sea level. Then the pressure (and density) of gas decreases exponentially as  $h_1$  (the altitude) increases. Note that how much the pressure decreases depends on the mass of the atom. So atoms that are light like He end up being much more plentiful (relatively speaking) high in the atmosphere than heavy atoms.

### 11.3 Centrifuge

Consider a centrifuge, as you might have used in a chemistry lab. Such a device is used to separate particles of different mass by spinning them in a tube. Here’s the setup—suppose there are two different types of molecules in the centrifuge, call them  $A$  and  $B$ . They have different masses  $m_A$  and  $m_B$ . For the sake of discussion, let’s assume that  $m_A > m_B$ . We expect that the heavier molecules will be pushed to the bottom of the tube and the lighter ones pushed to the top. We can understand this approximately using Boltzmann factors. Note that here we are considering centrifuging gases; in chemistry often liquids are used which have a bit more of a complicated analysis. We will be interested in the ratio

$$\frac{n_A(h)}{n_B(h)}, \quad (6)$$

where  $n_A(h)$  is  $N_A/V$ , the molecular density.

By spinning the centrifuge such that the centrifugal acceleration is  $a$ ,

$$\frac{n_A(h_1)}{n_A(h_2)} = \exp\left(-\frac{ma}{kT}(h_1 - h_2)\right). \quad (7)$$

Now we can compute the ratio of the densities at height  $h$  to another reference height  $h_{ref}$ .

$$\frac{n_A(h)}{n_B(h)} = \frac{n_A(h)}{n_A(h_{ref})} \frac{n_B(h_{ref})}{n_B(h)} \frac{n_A(h_{ref})}{n_B(h_{ref})} \quad (8)$$

$$= \frac{\exp\left(-\frac{m_A a}{kT}(h - h_{ref})\right) n_A(h_{ref})}{\exp\left(-\frac{m_B a}{kT}(h - h_{ref})\right) n_B(h_{ref})} \quad (9)$$

$$= \exp\left(-\frac{a}{kT}(m_A - m_B)(h - h_{ref})\right) \frac{n_A(h_{ref})}{n_B(h_{ref})}. \quad (10)$$

### 11.4 Quantum mechanics: a minimum of what you need to know

Boltzmann factors are particularly useful in analyzing very small systems. These systems are typically best described by quantum mechanics. But do not fear! You don’t need to know too much about quantum mechanics to understand this.

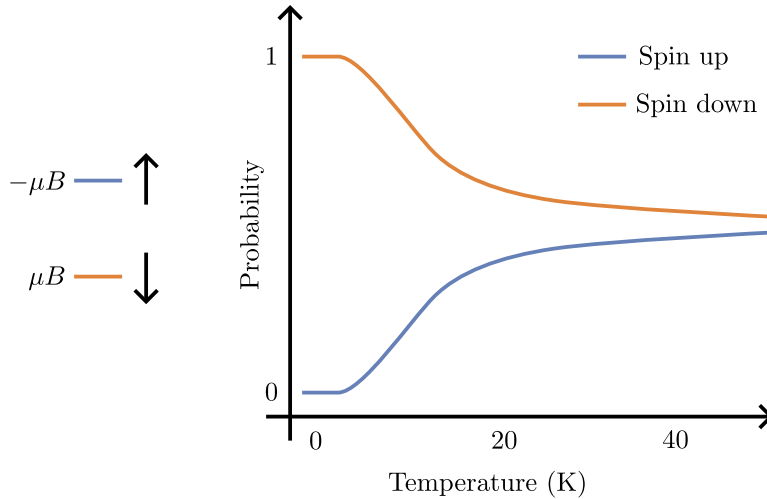


Figure 2: (left) The energy level diagram for a two-state system of an electron in a magnetic field. (right) The probability of each state as a function of temperature.

You simply need to know that unlike classical mechanics, in quantum mechanics under certain conditions (such as electrons in an atom or molecule, or vibrations in solids), energy is quantized. This means that only particular energies are allowed. Typically this is charted using *energy level diagrams* as a guide.

In quantum mechanics, the system is in a state, which we will label  $i = 1, 2, 3, \dots$ . The energy of that state is  $E_i$ . Often these energies will be measured in the unit eV, which is approximately equal to  $1.6 \times 10^{-19}$  J. For that reason we often use the Boltzmann constant in eV/K units for problems like this.

## 11.5 Computing average energy with Boltzmann probabilities

Define the Boltzmann factor for state  $i$  as

$$f_i = e^{-E_i/kT}. \quad (11)$$

The partition function is the sum of all the Boltzmann factors:

$$Z = \sum_i f_i. \quad (12)$$

Then the probability of a state is given by

$$P_i = \frac{f_i}{Z}. \quad (13)$$

To compute the internal energy, we simply take the average over all possible states:

$$U = \langle E \rangle = \sum_i P_i E_i(T) \quad (14)$$

## 11.6 An electron in a magnetic field

For example, consider an electron in a magnetic field. Electrons have magnetic moments  $\mu$  that due to quantum mechanics can only either point up or down. The energy of these two states in a magnetic field pointing in the  $z$  direction is  $E_\uparrow = -\mu B$ , and  $E_\downarrow = \mu B$ .<sup>1</sup> Confusing the matter slightly is that  $\mu$  is actually

<sup>1</sup>We are glossing over some details; if you want to know exactly how this can be computed/derived, you can find that in a quantum mechanics class! In this class we will always assume that a quantum mechanic has computed the energy values for us!

**negative.** These magnetic moments (often called spins) line up in ferromagnets, but for the moment let's just consider a single electron connected to a reservoir at temperature  $T$ .

The Boltzmann factors are

$$f_{\uparrow} = \exp(\mu B/kT) \quad (15)$$

and

$$f_{\downarrow} = \exp(-\mu B/kT). \quad (16)$$

The partition function is

$$Z = f_{\uparrow} + f_{\downarrow} = \exp(\mu B/kT) + \exp(-\mu B/kT). \quad (17)$$

Using the above facts, the probability of the magnetic moment pointing up is

$$p_{\uparrow} = \frac{\exp(\mu B/kT)}{\exp(\mu B/kT) + \exp(-\mu B/kT)}. \quad (18)$$

Multiplying the top and bottom by  $\exp(-\mu B/kT)$ , we get

$$p_{\uparrow} = \frac{1}{1 + \exp(-2\mu B/kT)}. \quad (19)$$

Doing the same thing for the  $\downarrow$  state,

$$p_{\downarrow} = \frac{1}{1 + \exp(2\mu B/kT)}. \quad (20)$$

The internal energy is

$$U = -\mu B p_{\uparrow} + \mu B p_{\downarrow} \quad (21)$$

We now have completely understood the microstate physics of the two state system. We now can compute the macrostate variables from the microstate variables. As the temperature goes to zero,  $p_{\downarrow} \rightarrow 1$  and  $p_{\uparrow} \rightarrow 0$ , remembering that  $\mu$  is negative. This minimizes the internal energy, just as we saw in the free energy section. In fact, the Boltzmann factors are just the microscopic probabilities that correspond to a system connected to a bath at temperature  $T$ , so the value of  $U$  that minimizes the free energy must be the same as the value of  $U$  computed using Boltzmann factors.

On the other hand, as the temperature goes to infinity,  $p_{\uparrow} \rightarrow 0.5$  and  $p_{\downarrow} \rightarrow 0.5$ . The average internal energy thus increases from  $\mu B$  (which is negative) to 0 as the temperature increases, as you can see in Fig 3

There is no volume to speak of for an electron, so the heat capacity is given by the derivative of the internal energy with respect to the temperature:

$$C = \frac{dU}{dT}. \quad (22)$$

The exact form is complicated and not particularly enlightening; we will just discuss the qualitative features here. The heat capacity has an odd shape, in which it is near zero at zero temperature, then jumps suddenly as the higher energy state starts to have non-zero probability, and then once both states are equally occupied and the internal energy no longer increases with temperature, the heat capacity goes back to zero. This is very different from what we saw in equipartition (which had a constant heat capacity), and in fact was one of the ways in which quantum mechanics was confirmed experimentally.

We can also compute the entropy as

$$S = \int_0^T \frac{C(T')}{T'} dT'. \quad (23)$$

The entropy  $S$  starts at zero and approaches a constant. That constant is exactly equal to  $S = k \ln 2$ . Why is this? At high temperature, both states are equally occupied, and so  $\Omega = 2$ ! The reason that we cannot use the original  $S = k \ln \Omega$  formula is that the probability of the states is not exactly equal unless the temperature is very high. Next time, we will sort out this apparent tension.

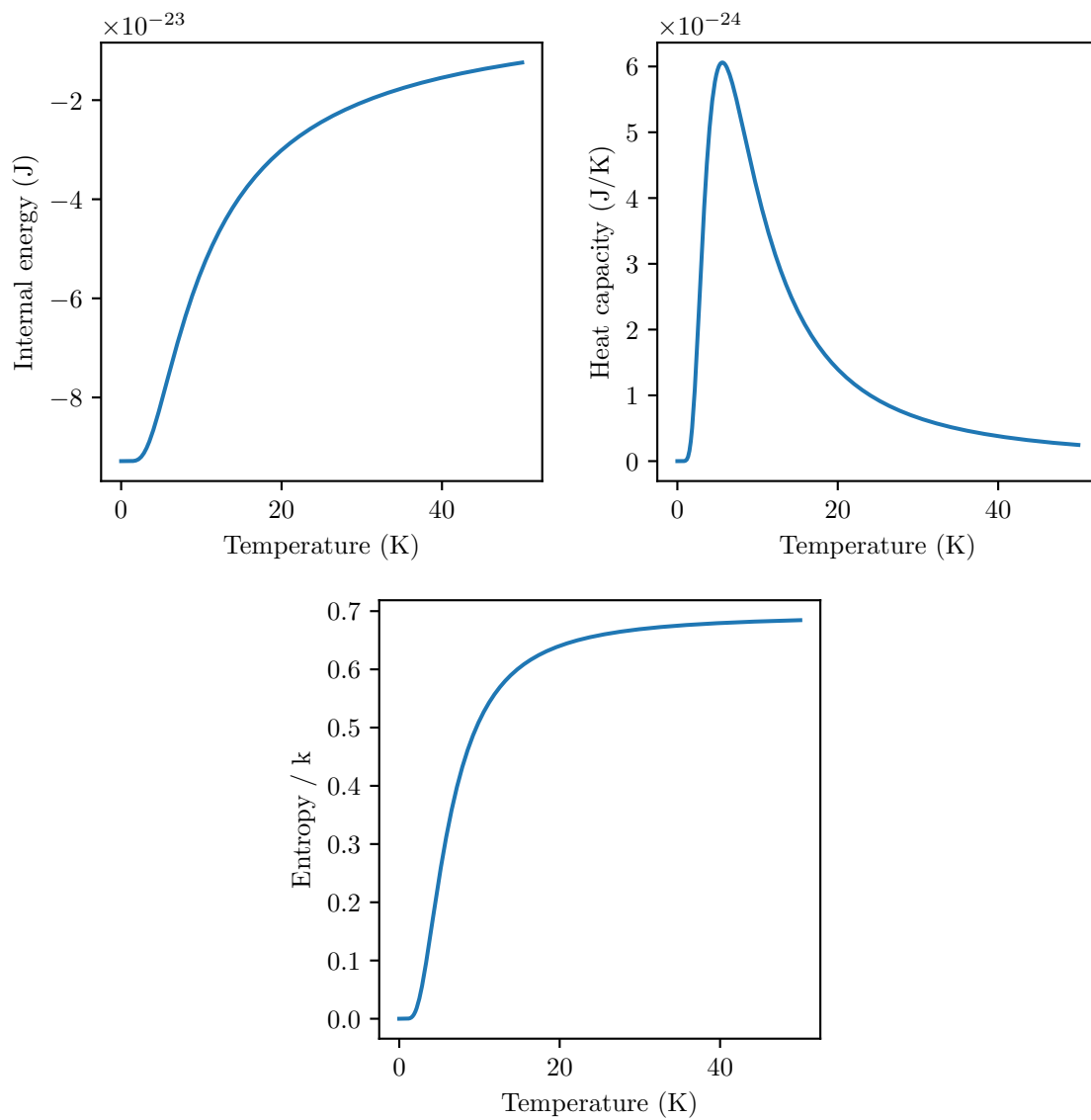


Figure 3: Macrostate variables for an electron in a magnetic field of 10 Tesla.