

Figure 1: Possible microstate configurations for $U = 4hf$ and two oscillators. Note that in this graph, the factor of $\frac{1}{2}$ was dropped.

12 Oscillators and Boltzmann factors

12.1 Model system: quantum oscillators

Consider a molecule like O_2 or N_2 , which comprise the majority of air. These are diatomic molecules, in which the atoms are bound together via a chemical bond. In the section on equipartition, we mentioned that such a gas could have degrees of freedom either 3 (at very low temperatures), 5 (at room temperature), or 7 (at very high temperatures). The 5 were translational and rotational degrees of freedom, and the remaining two of seven were the kinetic and potential energy of vibration. However, we said that due to quantum mechanics the vibrations need a lot of energy to activate. We will explore this effect in this chapter.

A pretty good model for vibrations in molecules and solids is the quantum simple harmonic oscillator. In this system, the energy levels are given by

$$E_n = \left(n + \frac{1}{2}\right)\epsilon, \quad n = 0, 1, 2, 3, \dots, \quad (1)$$

where $\epsilon = hf$, and

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}}, \quad (2)$$

k being the spring constant and m being the mass of the oscillator. Note that in some references, the factor of $\frac{1}{2}$ is dropped and energy is written as $E_n = nhf$. Since any shift in energy does not change the physics, either option will give the same results.

For molecules and solids, typically ϵ is of order a few meV to a few tenths of an eV for light molecules.¹ Recall that 1 eV is about 1.6×10^{-19} J, which sounds like a small amount of energy. However, kT at room temperature is only about 0.025 eV, so the Boltzmann factors for larger values of ϵ can be rather small at room temperature. This is why the vibrations in N_2/O_2 are mostly inactive at room temperature.

12.2 Derivation of Boltzmann factors for collections of oscillators

12.2.1 Two oscillators with fixed energy U

As a thought experiment, consider an **isolated** system of two identical oscillators with $\epsilon = hf$. This could be two N_2 molecules out in space, not interacting with anything else. The most relevant macrostate variable

¹Light because of the mass in f .

is the internal energy U . To compute the entropy, we use

$$S(U) = k \ln \Omega(U). \quad (3)$$

Since the system can only take on integer amounts of energy, we can count the total *quanta* q in the system. That is, for oscillator A and B , we have n_A and n_B that represent the microstate. U is given simply by the sum $n_A + n_B = q$.

As illustrated in Fig 1, for q quanta, there are $q + 1$ possible configurations. Then

$$U = (q + 1)hf \quad (4)$$

$$S = k \ln(q + 1) \quad (5)$$

We would like to find the remaining thermodynamic quantities by taking the derivative; however, since q is an integer, we can only take the finite difference approximation to the derivative:

$$\frac{1}{T} = \frac{\partial S}{\partial U} \simeq \frac{S(q + 1) - S(q)}{U(q + 1) - U(q)} = \frac{k \ln \left(\frac{q+2}{q+1} \right)}{hf}. \quad (6)$$

Solving for T ,

$$kT = \frac{hf}{\ln \left(\frac{q+2}{q+1} \right)}. \quad (7)$$

This is a bit of a strange equation, but one can see that as q increases, then $\frac{q+2}{q+1}$ gets closer to 1, making the logarithm closer to zero, thus increasing the temperature.

12.2.2 N oscillators with q quanta

Now let's consider many oscillators. This is a model of a solid originally formulated by Einstein, which has many atoms that can oscillate.

The claim is that

$$U = \left(q + \frac{N}{2} \right) hf \quad (8)$$

and

$$\Omega(q) = \binom{N - 1 + q}{q} \quad (9)$$

from this, we can compute

$$S(q + 1) - S(q) = k \ln \left(\frac{q + N}{q + 1} \right) \quad (10)$$

We can then get the temperature as a function of q :

$$\frac{1}{T} = \frac{S(q + 1) - S(q)}{U(q + 1) - U(q)} = \frac{k \ln \left(\frac{q + N}{q + 1} \right)}{hf}. \quad (11)$$

12.2.3 Boltzmann factors

Now let's zoom into one of the oscillators. We want to find out what the probability of this oscillator having a given number n_1 of quanta, given that the entire collection has Q quanta. For two total oscillators (one "system" and one "environment"), then given n_1 , we know that $n_2 = Q - n_1$ so there is just one microstate for each value of n_1 . Therefore, the probability is equal for all n_1 up to a maximum of Q . For three total oscillators, given n_1 , we have $q - n_1$ quanta to distribute among two "environment oscillators. This can be done in $Q - n_1 + 1$ ways, as noted previously. So we can see that now the probability of the first oscillator having n_1 quanta decreases as n_1 increases.

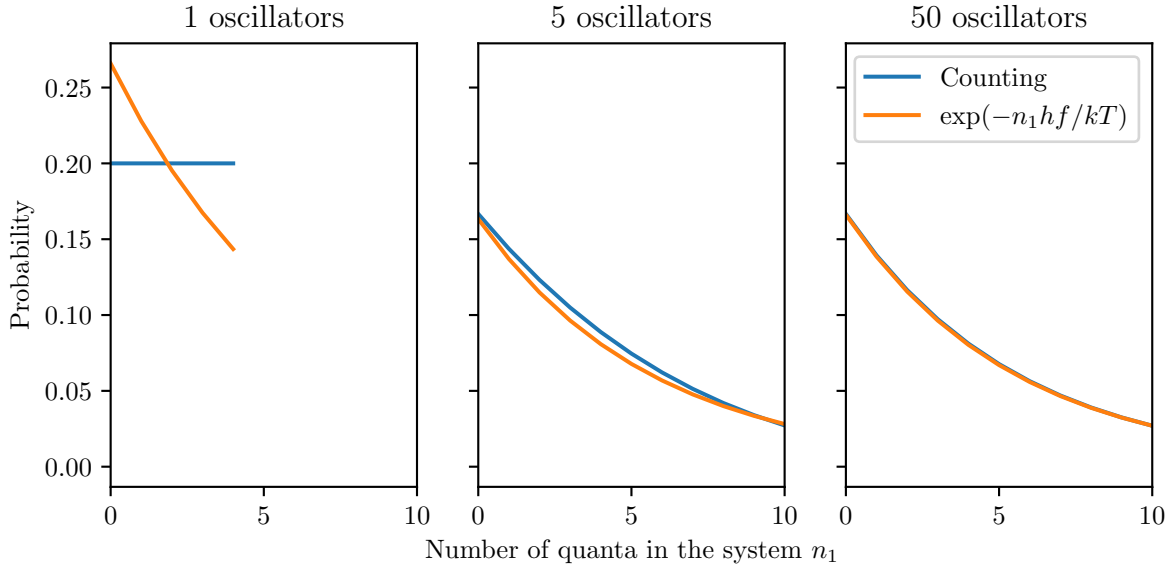


Figure 2: Convergence of the probability distribution of a single oscillator in an environment of other oscillators. The total energy per oscillator is kept constant, and as the environment becomes large compared to the system, the distribution approaches the Boltzmann distribution.

The general formula for N oscillators with q quanta is:

$$\Omega(q, N) = \binom{N-1+q}{q} \quad (12)$$

Substituting $Q - n_1$ for q , we get

$$\Omega(Q, N, n_1) = \binom{N-1+Q-n_1}{Q-n_1}, \quad (13)$$

for $n_1 < Q$.

Given a fixed value of Q and N , we can plot the probability of a given state n_1 as

$$P(n_1, Q, N) = \frac{\Omega(Q, N, n_1)}{\sum_{n_q} \Omega(Q, N, n_q)}. \quad (14)$$

Note that n_1 is a property of the system, while Q and N are properties of the environment. Figure 2 does this plot for increasing N . You can see that as N gets larger, then the probability curve approaches

$$P(n_1, T_{env}) = \frac{\exp(-n_1 hf/kT_{env})}{\sum_{n_1} \exp(-n_1 hf/kT_{env})}, \quad (15)$$

where T_{env} can be computed from Q and N using Eqn 11. Note that here we don't actually care about the total number of oscillators in the environment or the total energy of the environment; all that matters is the *temperature* of the environment. This turns out to be generally true. This is what allows us to abstract away the environment to just having a temperature.

12.3 Heat capacity of oscillators: Einstein's models of solids

Here you get to find out why equipartition sometimes is not applicable.

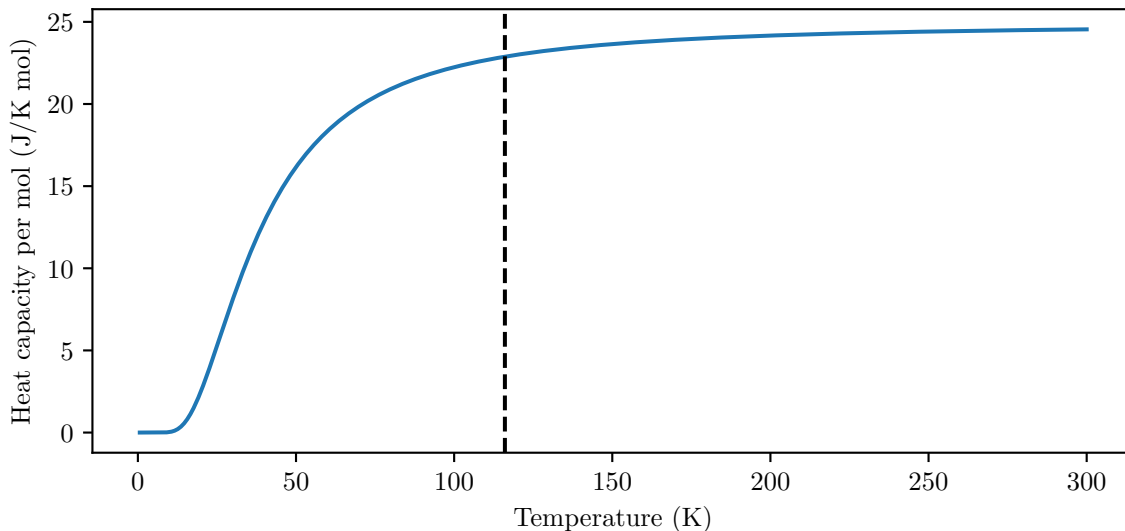


Figure 3: The heat capacity per mol of a collection of quantum oscillators with $hf = .01$ eV. The vertical dotted line is the temperature where $T = hf/k$, and is about where quantum effects are apparent (below this temperature, quantum effects reduce the heat capacity).

First we write down the internal energy as a function of temperature.

$$U = \sum_i E_i P_i(T) \quad (16)$$

At constant volume

$$C_V = \frac{dU}{dT} = \sum_i E_i \frac{dP_i}{dT}. \quad (17)$$

Skipping over quite a few algebraic manipulations and applications of chain rules, etc, we can find that for one oscillator,

$$C_V = k \frac{x^2 e^x}{(e^x - 1)^2}, \quad (18)$$

where $x = \frac{hf}{kT}$. Therefore, for N oscillators in 3 dimensions,

$$C_V = 3kN \frac{x^2 e^x}{(e^x - 1)^2}. \quad (19)$$

Let's consider the limits of this function. It is useful to multiply the numerator and denominator by e^{-x} , and bring it inside the square, which results in

$$C_V = 3kN \frac{x^2}{e^x - 2 + e^{-x}}, \quad (20)$$

As $T \rightarrow \infty$, $x \rightarrow 0$, and $e^x \rightarrow 1$. This would give us $0/0$, but using L'Hopital's rule and differentiating (twice), we get

$$\lim_{T \rightarrow \infty} C_V = \lim_{x \rightarrow 0} 3kN \frac{2}{e^x + e^{-x}} = 3kN. \quad (21)$$

This is the same result we got from equipartition for a collection of N atoms in 3D! So this model has the same high temperature limit as equipartition.

Now let's consider $T \rightarrow 0$. $x \rightarrow \infty$. This is a little easier since we know that e^x increases faster than anything else, so as x becomes very large then it will dominate the other terms. Therefore,

$$\lim_{T \rightarrow 0} C_V = 0. \tag{22}$$

This is very different from the equipartition result, and is a direct result of quantum mechanics! The fact that at low temperatures, the heat capacity goes to zero was one of the first hints that classical mechanics is not the whole story.

We can see the entire function plotted in Fig 3. Note that at room temperature the heat capacity flattens out, but as the temperature is decreased, at around the point of $T = hf/k$, the heat capacity starts to decrease. This is roughly the temperature at which the ratio of the Boltzmann factor between n_1 and $n_1 + 1$ quanta, $\exp(-hf/kT)$, starts to become apparent. Temperatures higher than that don't "see" the discrete energy levels, while for lower temperatures,