Problem 1. Einstein Model of Solid

A solid consists of an array of atoms in a crystal structure shown below. In a simple model (used by Einstein at the advent of quantum mechanics) each atom is assumed to oscillate independently of every other atom[1].

Thus, in one dimension a "solid" of N atoms consists of N independent harmonic oscillators. The Hamiltonian of each oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{1}$$

where m is the mass of the atom. In two dimensions each atom can oscillate in the x direction and the y direction. Thus, the solid of N atoms consists of $2N$ independent quantum oscillators. The Hamiltonian of each atom is

$$\begin{aligned} H =& H_x + H_y & (2)\\ =& \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) & (3)\end{aligned}$$

Finally in three dimensions (shown below) the solid of N atoms consists of $3N$ independent oscillators

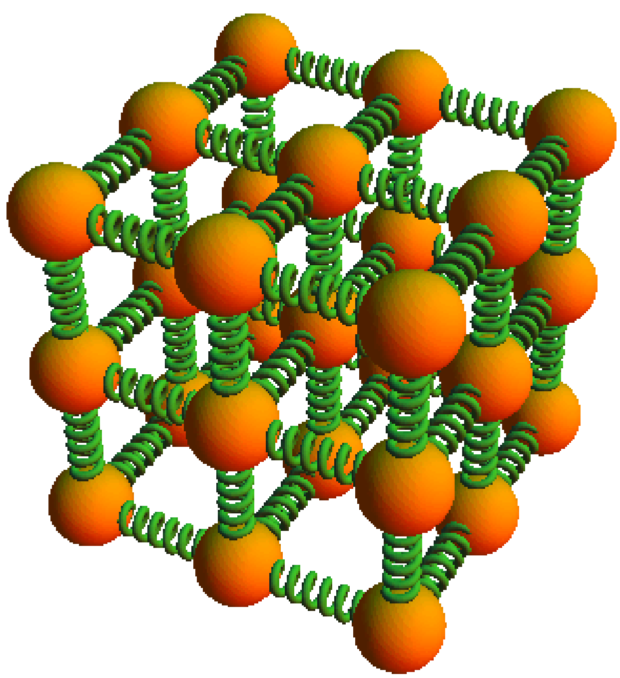


Figure 1:

[1] In reality the motions of the atoms are coupled to each other, and the oscillation pattern of the solid, may be found by breaking it up into normal modes.

(a) By appealing to the equi-partition theorem, argue that the mean energy of the solid at temperature T is

$$E = 3Nk_BT\,, \tag{4}$$

if the solid is treated as $3N$ independent classical oscillators. Determine the specific heat C_V in this case.

(b) (Optional: But please read and review past problems) When each the solid is treated as $3N$ quantum harmonic oscillators, show that the mean total energy is

$$E = 3N\langle\epsilon\rangle = 3N\frac{\hbar\omega_0}{e^{\beta\hbar\omega_0}-1} \tag{5}$$

where $\langle\epsilon\rangle$ is the mean energy of one oscillator. Thus that the mean vibrational quantum number of an oscillator is

$$\frac{E}{3N\hbar\omega_0} \equiv \frac{\langle\epsilon\rangle}{\hbar\omega_0} \equiv \bar{n} = \frac{1}{e^{\beta\hbar\omega_0}-1} \tag{6}$$

(c) Show that the specific heat C_V for one mole of solid is

$$C_V^{1\,\mathrm{ml}} = 3R\frac{(\beta\hbar\omega_0)^2\exp(-\beta\hbar\omega_0)}{(1-\exp(-\beta\hbar\omega_0))^2}\,. \tag{7}$$

What is the specific heat in the high temperature limit?

(d) Download a text file with the experimental data on the specific heat of silver[2], see here. Make a graph of the data, and the Einstein prediction for $C_V^{1\,\mathrm{ml}}$ for $\hbar\omega_0 = 4E_0, 2E_0, E_0, E_0/2, E_0/4$ with $E_0 = 0.013\,\mathrm{eV}$. E_0 was a free parameter in the Einstein model. Also show on your graph the classical prediction for the specific heat[3].

(e) Show that the entropy of one mole of solid ($3N_A$ harmonic oscillators) is

$$S = 3N_Ak_B\left(\frac{\beta\hbar\omega_0}{e^{\beta\hbar\omega_0}-1} - \log(1-e^{-\beta\hbar\omega_0})\right) \tag{8}$$

(f) Show that the inverse temperature of the system is related to the mean vibrational quantum number via

$$\beta \equiv \frac{1}{k_BT} = \frac{1}{\hbar\omega_0}\log\left(\frac{1+\bar{n}}{\bar{n}}\right) \tag{9}$$

and that the entropy of the system is related to $\bar{n}$ via:

$$S = 3N_Ak_B\left[(1+\bar{n})\log(1+\bar{n}) - \bar{n}\log\bar{n}\right] \tag{10}$$

[2] The file contains two columns, the first is the temperature in Kelvin, the second is the specific heat in units of $J/(\mathrm{mol}\,K)$

[3] The fact that the specific heats drop with temperature, was a major success of the early quantum mechanical theory. In the classical case you should find that $C_V^{1\,\mathrm{ml}} = 3R$ is constant

Problem 2. Ways to partition energy amongst N quantum harmonic oscillators

Recall that the entropy (divided by k_B) is the the number of ways a system can partition the total available energy into states (or configurations in a classical context). We have computed the entropy for an ideal gas by directly counting the number of possible configurations.

We will now give another example where we can explicitly count the number of states. The example is that of N quantum harmonic oscillators sharing total energy E. The total energy consists of q vibrational quanta of energy $E \equiv q\hbar\omega_0$ (q is an integer).

(a) For four atoms and three quanta of energy ($N = 4$ and $q = 3$) show that there are 20 ways for the oscillators to share the energy. For instance, the first atom could have the three quanta and the rest none. That is one possible state.

(b) If each of the ways is to partition the total energy in part(a) is equally likely (this is the microcanoncial ensemble), what is the probability that one of the atoms will have all the energy? What is the probability that the first atom has two quanta?

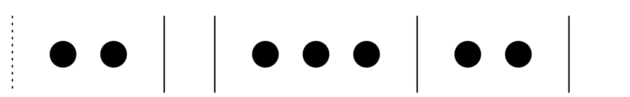
(c) Show in general that there are

$$\Omega(q) = \frac{(N+q-1)!}{q!(N-1)!} \tag{11}$$

ways to distribute q units of energy amongst the N atoms.

Hint: Consider each oscillator to be a bin, and each bit of energy to be a ball. We are asking for the number of ways to put q balls in N bins.

Take seven balls (units of energy) and five bins (oscillators), $N = 5$ and $q = 7$. Lay out the 7 energy units (balls) between the dashed lines.



To partition the 7 energy energy units (balls) amongst the five oscillators (bins), I need four dividers, shown by the solid lines. In the figure below, I have paced the four dividers in one possible way, partitioning the energy so that the first bin has 2 units, the second bin has none, the third bin has 3, the fourth has two, and the fifth has none. The total number of objects (ball or divider) is $q + (N - 1) = 11$. Use this logic and the number of ways of choosing q of these objects to be balls to explain Eq. (11).

(d) Show that for $N = 400$ oscillators and $q = 400$ quanta the number of states is approximately

$$e^{2N \ln 2} = 10^{240} \tag{12}$$

I quoted this number in lecture.

(e) Show more generally that for N oscillators and q quanta that

$$\Omega(E) = e^{N[(1+\bar{n})\ln(1+\bar{n}) - \bar{n}\ln\bar{n}]} \tag{13}$$

where $\bar{n} = q/N = E/(N\hbar\omega_0)$. Show the entropy of the system agrees with the previous problem (Problem 1).

Do not *use* the results of the first problem in any way – just compare the result.

(f) Starting from your results for $S(E)$ show that

$$\frac{1}{T} = \frac{k_B}{\hbar\omega_0}\log\left(\frac{1+\bar{n}}{\bar{n}}\right) \tag{14}$$

This is the same expression as in problem one. Rearranging Eq. (14) we see that $\bar{n}$ is related to the temperature as before:

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega_0} - 1}\,. \tag{15}$$

Do not *use* the results of the first problem in any way – just compare the result.

Discussion: We have computed properties of the solid in two ways. The first method, uses the partition functions at a fixed temeprature. It works with a subsystem wich have probability

$$P_m^{\rm sub} = \frac{1}{Z}e^{-\beta\epsilon_m}\,. \tag{16}$$

to be in microstate m of the subsystem. This probability distribution is known as the canonical ensemble. It is technically easier.

The second method, directly counts the number of states of the total system to find the total entropy at a fixed energy. The probability to be in a microstate of the full system is

$$P_m^{\rm full} = \text{const. indep of } m = \frac{1}{\Omega(E)} \tag{17}$$

This probability distribution is known as the micro-canonical ensemble. It is conceptually important. The two ensembles are equivalent.