Problem 1.   Variance in Energy from Partition Functions

Recall that the partition function is

$$Z(\beta) = \sum_s e^{-\beta\epsilon_s} \tag{1}$$

and that the probability of being in state s is

$$P_s = \frac{e^{-\beta\epsilon_s}}{Z(\beta)} \tag{2}$$

(a) Show that the mean energy and $\langle\epsilon^2\rangle$ can be found if you know $Z(\beta)$ via the formula:

$$\langle\epsilon\rangle = -\frac{1}{Z(\beta)}\frac{\partial Z}{\partial\beta} \tag{3}$$

$$= -\frac{\partial}{\partial\beta}\log Z(\beta) \tag{4}$$

$$\langle\epsilon^2\rangle = \frac{1}{Z(\beta)}\frac{\partial^2 Z}{\partial\beta^2} \tag{5}$$

(b) Show that variance in the energy is

$$\sigma_\epsilon^2 \equiv \langle(\delta\epsilon)^2\rangle = \langle\epsilon^2\rangle - \langle\epsilon\rangle^2 = \frac{\partial^2}{\partial\beta^2}(\log Z) \tag{6}$$

and that

$$\sigma_\epsilon^2 = -\frac{\partial\langle\epsilon\rangle}{\partial\beta} \tag{7}$$

(c) Return to the quantum harmonic oscillator of discussed previously. Show that the variance in the energy is

$$\langle(\delta\epsilon)^2\rangle = (\hbar\omega_0)^2\frac{e^{-\beta\hbar\omega_0}}{(1-e^{-\beta\hbar\omega_0})^2} \tag{8}$$

(d) Find the leading approximate expression for the variance $\langle\delta\epsilon^2\rangle$ in the low temperature limit $k_BT \ll \hbar\omega_0$.

(e) Consider the probabilities P_n for the simple harmonic oscillator to be in the n-th state, which you worked out in a previous homework.

  (i) Show by Taylor expansion that in the limit $k_BT \ll \hbar\omega_0$ there are effectively only two states – the ground state with probability $P_0 \simeq 1-e^{-\beta\hbar\omega_0}$, and the first excited state, with small probability, $P_1 \simeq e^{-\beta\hbar\omega_0}$. Show that the higher excited states, $P_2, P_3, \ldots$, have probability of order $O(e^{-2\beta\hbar\omega_0})$ or smaller, which is negligble to order $e^{-\beta\hbar\omega_0}$.

  (ii) Calculate the mean energy $\langle\epsilon\rangle$ and the variance $\langle(\delta\epsilon)^2\rangle$ with P_0 and P_1 only with these approximations. Show that the variance agrees with part (d).

Problem 2.   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]. The model has one free parameter ω_0 and predicts the general properties of specific heats of solids.

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

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{9}$$

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 (or energy) of each atom is a sum of two harmonic oscillators:

$$H = H_x + H_y \tag{10}$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) \tag{11}$$

Finally in three dimensions (shown below) the solid of N atoms consists of $3N$ independent oscillators as shown below, and each atom can oscillate in the x, y, or z directions. The Hamiltonian of each atom shown in Fig. 1 consists of three harmonic oscillators:

$$H = H_x + H_y + H_z \tag{12}$$

$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) + \left(\frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2 z^2\right) \tag{13}$$

The total Hamiltonian is a sum of the Hamiltonians of each atom.

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

$$E = 3Nk_BT\,, \tag{14}$$

if the solid is treated as $3N$ independent classical oscillators. Determine the specific heat C_V^{1ml} for one mole of substance in this case.

(b) When each the solid is treated as $3N$ quantum harmonic oscillators, the energy of the solid is $E = 3N\langle\epsilon\rangle$, where the $\langle\epsilon\rangle$ is the average energy of the a single harmonic oscillator. By reviewing the results of previous homework, write down the total energy of the solid at temperature T, and record the mean vibrational quantum number $\bar{n}$ of a single oscillator.

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[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.
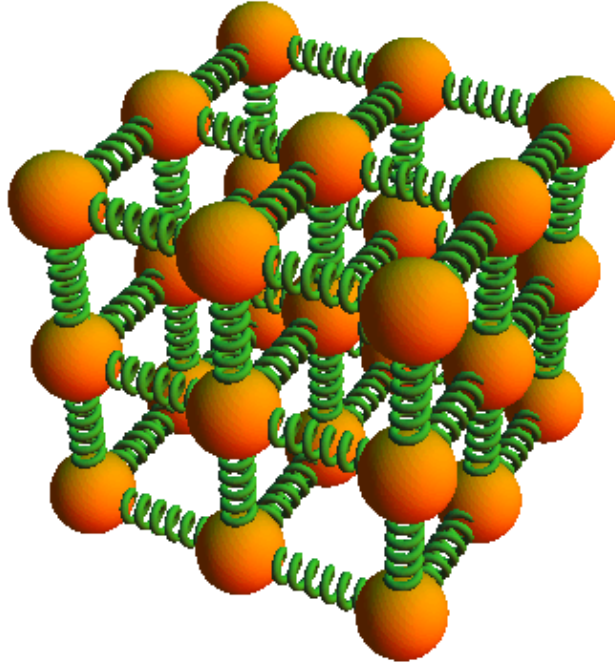
Figure 1:

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

$$\beta \equiv \frac{1}{k_B T} = \frac{1}{\hbar \omega_0} \log\left(\frac{1 + \bar{n}}{\bar{n}}\right) \tag{15}$$

(d) Show that the specific heat C_V for one mole of solid is[2]

$$C_V^{1\,\text{ml}} = 3R \frac{(\beta \hbar \omega_0)^2 \exp(-\beta \hbar \omega_0)}{(1 - \exp(-\beta \hbar \omega_0))^2}. \tag{17}$$

Make a Taylor series expansion of $C_V^{1\,\text{ml}}$ at high temperature, including the just leading term. What is the specific heat in the ultimate high temperature limit? Your result should be consistent with part (a). Why?
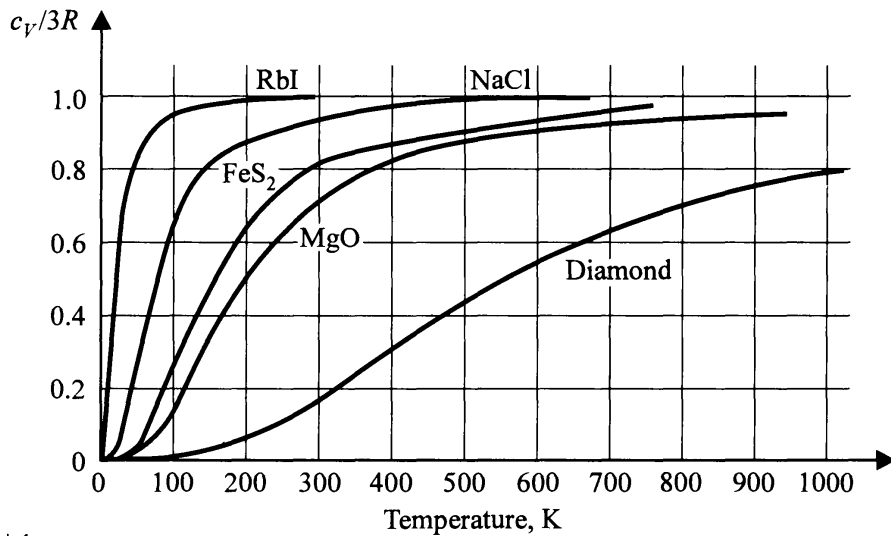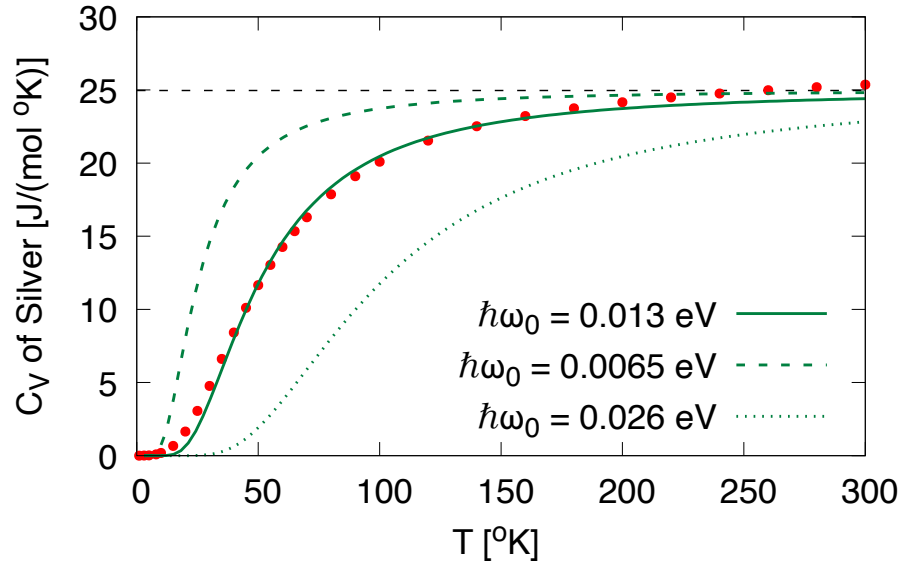
(e) Download a text file with the experimental data on the specific heat of silver[3], see here. Make a graph of the data, and the Einstein prediction for $C_V^{1\,\text{ml}}$ for $\hbar \omega_0 = 4E_0, 2E_0, E_0, E_0/2, E_0/4$ with $E_0 = 0.013\,\text{eV}$. E_0 was a free parameter in the Einstein model. The graph I get for silver is shown below as well as the C_V for other substances:

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[2]It is generally when computing C_V to recognize that

$$T \frac{\partial}{\partial T} = -\beta \frac{\partial}{\partial \beta} \tag{16}$$

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

(i) Diamond is known to be a very hard substance. Loosely explain how this fact is reflected in the data on C_V presented in the figure below? *Hint*: What does the graph of C_V for different substances tell you about the relative strengths of the spring constants of the material?

Approaches 3R at high temperature where the dynamics is classical

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Problem 3. Ways to partition energy amongst N quantum harmonic oscillators

Recall that the entropy (divided by k_B) is the logarithm of the number of ways a system can partition the total available energy into states 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) (Optional: Review) 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) (Optional: Review) 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) (Optional: Review) Show that that there are

$$\Omega(q) = \frac{(N+q-1)!}{q!(N-1)!} \tag{18}$$

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. (18).

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

$$e^{2N \ln 2} = e^{555} \tag{19}$$

I quoted this number in lecture.

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

$$\Omega(E) = e^{N[(1+\bar{n})\ln(1+\bar{n}) - \bar{n}\ln\bar{n}]} \tag{20}$$

where $\bar{n} = q/N = E/(N\hbar\omega_0)$. Show the entropy of the system is

$$S = Nk_B\left[(1+\bar{n})\log(1+\bar{n}) - \bar{n}\log\bar{n}\right] \tag{21}$$

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

$$\frac{1}{T} = \frac{k_B}{\hbar\omega_0}\log\left(\frac{1+\bar{n}}{\bar{n}}\right) \tag{22}$$

This is the same expression as in the previous problem. Compute $\beta\hbar\omega_0$ for the special case discussed in class where $N = q = 400$.

(g) Rearrange Eq. (22) to show that $\bar{n}$ is related to the temperature as before:

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega_0} - 1}. \tag{23}$$

Do not *use* the results of the previous 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 an independent subsystem wich have probability

$$P_m^{\text{sub}} = \frac{1}{Z}e^{-\beta\epsilon_m}. \tag{24}$$

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 total energy. The probability to be in a microstate of the full system is

$$P_m^{\text{full}} = \text{const.} = \frac{1}{\Omega(E)} \tag{25}$$

This probability distribution is known as the micro-canonical ensemble. It is conceptually important. The two ensembles are equivalent. They should be. We derived the Boltzman factor and the canonical distribution from the entropy of the microcanonical ensemble.