Thermodynamics and Statistical Mechanics Homework Assignment 2

Todd Hirtler

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Problem 1

Cold Interstellar molecular clouds often contain the molecule cyanogen (CN) whose first rotational excited states have an energy of $\epsilon_0 = 4.7 \times 10^{-4} eV$ above the ground state. In 1941, studies revealed that starlight passing through these molecular clouds showed that 29 percent of the CN molecules are in the first excited rotational state. To account for this data, astronomers suggested that the CN molecules might be in thermal equilibrium with a reservoir at a well defined temperature.

a) The energy of the rotational state with angular momentum j ($j = 0, 1, 2, \ldots$) is given by $\epsilon(j) = \epsilon_0 j(j+1)/2$, and the degeneracy of the level (i.e. number of states with the same energy) is $g(j) = 2j+1$. Note that the ground state has $j = 0$. Find an expression for the temperature of the thermal reservoir as a function of the fraction x of the excited CN molecules. For simplicity, neglect occupation of states with $j > 1$.

b) Evaluate your answer from part a to find the temperature corresponding to the observed excited fraction. What do you think is the origin of the thermal radiation with which the CN molecule is in equilibrium?

c) Justify the assumption made in part a, that all the molecules are either in the ground or first excited state. (Hint: Using your temperature from part b, compute the fraction of molecules that will be in the second excited state.)

Solution

a) The percentage of CN in the first excited state can be found by using

$$P(E_1) = \frac{3e^{-\beta E_1}}{e^{-\beta E_0} + 3e^{-\beta E_1}} = \frac{3e^{-\beta\epsilon_0}}{3e^{-\beta\epsilon_0} + 1} = \frac{3}{3 + e^{\beta\epsilon_0}} = x$$

The 3 comes from the degeneracy of the first excited state. Rearranging our equation, we get

$$\frac{3}{x} - 3 = e^{\beta\epsilon_0}$$

$$\ln\left(\frac{3}{x} - 3\right) = \beta\epsilon_0 = \frac{\epsilon_0}{kT}$$

$$T = \frac{\epsilon_0}{k\ln\left(\frac{3}{x} - 3\right)}$$

b) Plugging in our given values, we get

$$T = \frac{4.7 \times 10^{-4}}{8.617 \times 10^{-5}\ln\left(\frac{3}{0.29} - 3\right)} = 2.7\text{K}$$

The origin of this thermal radiation is probably related to cosmic background radiation, or some large volume of photons traveling through space.

c) The percentage of CN in the second excited state will be

$$P(E_2) = \frac{5e^{-3\beta\epsilon_0}}{1 + 3e^{-\beta\epsilon_0} + 5e^{-3\beta\epsilon_0}}$$

Plugging in the temperature from the previous part the gives us

$$P(E_2) = 0.008$$

Since this percentage is far less than 1, the second excited state doesn't really contribute much and can be neglected.

Problem 2

Consider a DNA molecule, with N links. If a link is closed, it is of energy 0, and if open, ϵ. However, the DNA requires that the links can open only one at a time from the left end. That is, link s from the left can be open only if links 1 through $s-1$ are all open.

a) Find that partition function.

b) In the limit of $\epsilon \gg T$, find the average number of open links.

Solution

a) Our partition function will be

$$Z = \sum_{s=0}^{N} e^{-\beta E_s} = \sum_{s=0}^{N} e^{-\beta\epsilon s} = \frac{1 - e^{-\beta\epsilon N}}{1 - e^{\beta\epsilon}}$$

b) This part will be pretty messy so let's rewrite the partition function in form easier to work with.

$$Z = \frac{e^{\beta\epsilon} - e^{-\beta\epsilon N}}{e^{\beta\epsilon} - 1}$$

Let's differentiate this in respect to β.

$$\frac{\partial Z}{\partial \beta} = \frac{(\epsilon e^{\beta\epsilon} + \epsilon N e^{-\beta\epsilon N})(e^{\beta\epsilon} - 1) - (\epsilon e^{\beta\epsilon})(e^{\beta\epsilon} - e^{-\beta\epsilon N})}{(e^{\beta\epsilon} - 1)^2}$$

We can now divide by our partition function.

$$\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\epsilon(e^{2\beta\epsilon} - e^{\beta\epsilon} + N e^{-\beta\epsilon(N-1)} - N e^{-\beta\epsilon N} - e^{2\beta\epsilon} + e^{-\beta\epsilon(N-1)})}{(e^{\beta\epsilon} - 1)(e^{\beta\epsilon} - e^{-\beta\epsilon N})}$$

$$= \frac{\epsilon(-e^{\beta\epsilon} - N e^{-\beta\epsilon N} + (N+1)e^{-\beta\epsilon(N-1)})}{(e^{\beta\epsilon} - 1)(e^{\beta\epsilon} - e^{-\beta\epsilon N})}$$

$$= \frac{\epsilon(-e^{\beta\epsilon}e^{\beta\epsilon N} - N + (N+1)e^{\beta\epsilon})}{(e^{\beta\epsilon} - 1)(e^{\beta\epsilon} - e^{-\beta\epsilon N})e^{\beta\epsilon N}}$$

Considering the size of our terms, we can simplify the numerator and denominator making some approximations. The only term to really batter in the numerator is the first term as the other terms are significantly smaller than it. We can use similar logic to ignore the second term in each parentheses in the denominator. This gives us

$$\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-\epsilon e^{\beta\epsilon} e^{\beta\epsilon N}}{e^{\beta\epsilon N} e^{2\beta\epsilon}} = -\frac{\epsilon}{e^{\beta\epsilon}}$$

The expectation value of our energy, which we can use to tell us how many of our links are open is

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\epsilon}{e^{\beta\epsilon}}$$

The average number of links open will then be this divided by ϵ.

$$\langle s \rangle = e^{-\beta\epsilon}$$

Problem 3

Consider a system of N atoms with spin S in a magnetic field $B\hat{z}$, so that the energy of the system is

$$E = -\sum_{i=1}^{N} \mu B S_i^z$$

The $S^z z$ component of the spin can take the $2S+1$ quantized values $-S, -S+1, \ldots, S$, having the magnetic moments $-\mu S, \ldots, \mu S$ respectively.

a) Find the partition function.

b) Find the average magnetization. At high temperatures, compare your result to Curie's law.

c) Find the magnetic susceptibility of the system, χ.

d) Find the average energy.

e) Find the specific heat, C_v.

Solution

a) Since all our spins are independent, we can find the overall partition function by finding a partition function for one particle and exponentiating it by how many particles we have.

$$Z_1 = \sum_{m=-S}^{S} e^{-\beta\mu B m} = \frac{e^{\beta\mu B S} - e^{-\beta\mu B(S+1)}}{1 - e^{-\beta\mu B}} = \frac{e^{\beta\mu B(S+\frac{1}{2})} - e^{-\beta\mu B(S+\frac{1}{2})}}{e^{\frac{\beta\mu B}{2}} - e^{\frac{-\beta\mu B}{2}}}$$

$$= \frac{\sinh\big(\beta\mu B(S+\frac{1}{2})\big)}{\sinh\big(\frac{\beta\mu B}{2}\big)}$$

For N particles, this gives us a partition function of

$$Z_N = \frac{\sinh^N(\beta\mu B(S+\frac{1}{2}))}{\sinh^N(\frac{\beta\mu B}{2})}$$

b) To find the average magnetization, we will first find the Helmholtz Free Energy and then differentiate it with respect to the magnetic field. The Helmholts Free Energy is

$$F = -kT\ln(Z) = -kTN(\ln\Big(\sinh\Big(\beta\mu B(S+\frac{1}{2})\Big)\Big) - \ln\Big(\sinh\Big(\frac{\beta\mu B}{2}\Big)\Big))$$

The Magnetization will then be

$$M = -\Big(\frac{\partial F}{\partial B}\Big)_{T,N}$$

$$= kTN\Big(\frac{\beta\mu(S+\frac{1}{2})\cosh\big(\beta\mu B(S+\frac{1}{2})\big)}{\sinh\big(\beta\mu B(S+\frac{1}{2})\big)} - \frac{\beta\mu}{2}\frac{\cosh\big(\frac{\beta\mu B}{2}\big)}{\sinh\big(\frac{\beta\mu B}{2}\big)}\Big)$$

$$M = N\mu((S+\frac{1}{2})\coth\Bigg(\beta\mu B(S+\frac{1}{2})\Bigg) - \frac{1}{2}\coth\Bigg(\frac{\beta\mu B}{2}\Bigg))$$

Which is our equation for the average magnetization. At high temperatures, this can be simplified by taylor expanding the hyperbolic cotangent functions to second order.

$$\coth(x) = \frac{1+\frac{1}{2}x^2+\dots}{x+\frac{1}{6}x^3+\dots} = \frac{1}{x}(1+\frac{1}{2}x^2)(1+\frac{1}{6}x^2)^{-1}$$

We can taylor expand that last piece to second order to get

$$\frac{1}{x}(1+\frac{1}{2}x^2)(1-\frac{1}{6}x^2) = \frac{1}{x}+\frac{x}{3}$$

Using this for the magnetization, we get

$$M = N\mu((S+\frac{1}{2})\Big(\frac{1}{\beta\mu B(S+\frac{1}{2})} + \frac{\beta\mu B(S+\frac{1}{2})}{3}\Big) - \frac{1}{2}\Big(\frac{2}{\beta\mu B} + \frac{\beta\mu B}{6}\Big))$$

$$= \frac{N\mu^2\beta B}{3}(S^2+S+\frac{1}{4}-\frac{1}{4}) = \frac{N\beta\mu^2 BS(S+1)}{3}$$

This is of the form

$$M = A\frac{B}{T}$$

which is Curie's law.

c) Magnetic susceptibility χ can be found with

$$\chi = \Big(\frac{\partial M}{\partial B}\Big)_T$$

$$\chi = N\mu((S+\frac{1}{2})^2\beta\mu(-\operatorname{csch}^2(\beta\mu B(S+\frac{1}{2})) + \frac{\beta\mu}{4}\operatorname{csch}^2(\frac{\beta\mu B}{2}))$$

$$= N\mu^2\beta(\frac{1}{4}\operatorname{csch}^2(\frac{\beta\mu B}{2}) - (S+\frac{1}{2})^2\operatorname{csch}^2(\beta\mu B(S+\frac{1}{2})))$$

d) We can find the average energy using the partition function using

$$\langle E\rangle = -\frac{\partial\ln(Z)}{\partial\beta}$$

Since we already did this differential earlier, but with some different constants out front, we can use it as a skeleton and just fill the proper coefficients.

$$\langle E\rangle = \frac{-NB\mu}{2}((S+\frac{1}{2})\coth\left(\beta\mu B(S+\frac{1}{2})\right) - \frac{1}{2}\coth\left(\frac{\beta\mu B}{2}\right))$$

e) We can find the specific heat by differentiating our average energy in respect to temperature.

$$C_v = \frac{\partial\langle E\rangle}{\partial T}$$

$$= -\frac{NB\mu}{2}((S+\frac{1}{2})(-\operatorname{csch}^2(\beta\mu B(S+\frac{1}{2})))(-\frac{\mu B(S+\frac{1}{2})}{kT^2}) - \frac{1}{2}(-\operatorname{csch}^2(\frac{\beta\mu B}{2}))(-\frac{\mu B}{2kT^2})))$$

$$C_v = \frac{NB^2\mu^2}{2kT^2}(\frac{1}{4}\operatorname{csch}^2(\frac{\beta\mu B}{2}) - (S+\frac{1}{2})^2\operatorname{csch}^2(\beta\mu B(S+\frac{1}{2})))$$

Problem 4

In this problem we revisit the Einstein solid discussed in the first problem set. The Einstein model of a solid composed of N atoms consists of $3N$ independent quantum harmonic oscillators, all with the same frequency ω ($3N$ oscillators because every atom can oscillate along three independent axes.) Recall that the energy of a single harmonic oscillator in a state with n oscillator quanta is

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega$$

a) Find the partition function of the Einstein solid.
b) Find the average energy.
c) Find the heat capacity C_v.
d) Show that at high temperatures, the Einstein model correctly predicts the Dulong-Petit law for the heat capacity of a solid,

$$C_v = 3Nk_B$$

Where N is the number of oscillators/atoms.

Solution

a)The partition function will be

$$Z = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = e^{\frac{-\hbar\omega\beta}{2}}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{e^{\frac{-\hbar\omega\beta}{2}}}{1-e^{-\beta\hbar\omega}}$$

b) To find the average energy, we will find the logarithm of the partition function and differentiate it with respect to β.

$$\ln(Z) = \frac{-\hbar\beta}{2} - \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$\frac{\partial \ln(Z)}{\partial\beta} = \frac{-\hbar\omega}{2} - \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$\langle E_1 \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Since we have 3N of these oscillators, the average energy will be

$$\langle E \rangle = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\omega\hbar} - 1}\right)$$

c) Now that we have our average energy, we can differentiate it with respect to temperature to find the heat capacity.

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{3N\hbar^2\omega^2}{kT^2}\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

We can let

$$\beta\hbar\omega = \frac{\theta_E}{T}$$

and rewrite this heat capacity equation as

$$C_v = 3Nk\left(\frac{\theta_E}{T}\right)^2\frac{e^{\frac{\theta_E}{T}}}{(e^{\frac{\theta_H}{T}} - 1)^2}$$

d) At high temperatures, we can taylor expand the exponentials and look at the lower order terms.

$$C_v = 3Nk\left(\frac{\theta_H}{T}\right)^2\frac{1 + \dots}{(1 + \frac{\theta_H}{T} + \dots - 1)^2} = 3Nk$$

Which is what we are looking for.

Problem 5

a) Compute the partition function of $3N$ independent classical harmonic Oscillators, i.e.

$$H = \sum_{i=1}^{3N}\left[\frac{p_i^2}{2m} + \frac{1}{2}Kq_i^2\right]$$

b) Compute the heat capacity of the system and compare to the high T limit of the Einstein model.

Solution

a) To find our partition function, since all CHO's are independent of each other, all we need to do is find the partition function for one CHO. To do that we will integrate over phase space.

$$Z_1 = \frac{1}{h}\int dqdpe^{-\beta(\frac{p^2}{2m}+\frac{Kq^2}{2})} = \frac{1}{h}\int e^{-\frac{\beta p^2}{2m}}dp\int e^{-\frac{\beta Kq^2}{2}}dq$$

$$= \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}}\sqrt{\frac{2\pi}{\beta K}} = \frac{1}{\hbar\beta}\sqrt{\frac{m}{k}}$$

Now we have $3N$ of these so our partition function will be

$$Z_{3N} = \left(\frac{1}{\hbar}\sqrt{\frac{m}{K}}\right)^{3N}$$

b) To find th heat capacity, all we need to do is find the logarithm of the partition function and differentiate it with respect to β and then differentiate that with respect to temperature.

$$\ln(Z) = 3N\ln\left(\frac{1}{\hbar\beta}\sqrt{\frac{m}{K}}\right)$$

$$\langle E\rangle = -3N\hbar\beta\sqrt{\frac{m}{K}}\frac{-1}{\hbar}\sqrt{\frac{K}{m}}\frac{1}{\beta^2} = 3Nk_BT$$

$$C_v = \frac{\partial\langle E\rangle}{\partial T} = 3Nk_B$$

Which is what we got for the high temperature limit of the quantum oscillators.