

Homework 4 - Solutions

19th October 2004

Problem 1

Since the oscillators are independent total partition function is the product of partition function for each oscillator $Z = Z_1^{3N}$. Then

$$Z_1 = \sum_n e^{-\frac{\hbar\omega n}{\tau}} = \frac{1}{1 - e^{-\frac{\hbar\omega}{\tau}}}$$

$$\log Z = -3N \log(1 - e^{-\frac{\hbar\omega}{\tau}})$$

$$U = \langle E \rangle = \tau^2 \frac{\partial}{\partial \tau} \log Z = 3N \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

$$C_V = \frac{\partial E}{\partial \tau} = \frac{3N(\hbar\omega)^2}{\tau^2} \frac{e^{\frac{\hbar\omega}{\tau}}}{(e^{\frac{\hbar\omega}{\tau}} - 1)^2}$$

For $T \gg \hbar\omega$

$$C_V \rightarrow 3N\tau$$

For $T \ll \hbar\omega$

$$C_V \rightarrow 3N \left(\frac{\hbar\omega}{\tau}\right)^2 e^{-\frac{\hbar\omega}{\tau}}$$

Problem 2

The formulas for entropy and energy are

$$U = \frac{3}{2}N\tau$$

$$\sigma = N \left(\log \frac{n_Q}{n} + \frac{5}{2} \right)$$

$$n_Q = \left(\frac{m\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}}$$

We will differentiate at constant volume and entropy.

$$0 = \frac{d\sigma}{dN} = \log \frac{n_Q}{n} + \frac{5}{2} + N \frac{d \log(\tau^{3/2} V/N)}{dN} = \log \frac{n_Q}{n} + \frac{3}{2} \frac{1}{\tau} \frac{d\tau}{dN} + \frac{3}{2}$$

This gives

$$\begin{aligned} \frac{d\tau}{dN} &= -\tau - \frac{2}{3} \tau \log \frac{n_Q}{n} \\ \mu = \frac{dU}{dN} &= \frac{3}{2} \tau + \frac{3}{2} \frac{d\tau}{dN} N = \tau \log \frac{n}{n_Q} \end{aligned}$$

Problem 3

The particles in the column are independent. Therefore we need to consider just one. It's energy is

$$\epsilon = p^2/2m + mgh$$

Different configurations are parameterized by \vec{x} and \vec{p} . Probability for particle to be in some configuration is $p_\epsilon \sim e^{-\epsilon/\tau}$. Thus the mean potential energy is

$$\begin{aligned} \langle E_p \rangle = mg \langle h \rangle &= mg \frac{\int_0^\infty dh \int_0^L dx \int_0^L dz \int d^3p h e^{-(p^2/2m+mgh)/\tau}}{\int_0^\infty dh \int_0^L dx \int_0^L dz \int d^3p e^{-(p^2/2m+mgh)/\tau}} \\ &= mg \frac{\int_0^\infty dh h e^{-mgh/\tau} \int_0^L dx \int_0^L dz \int d^3p e^{-p^2/2m\tau}}{\int_0^\infty dh e^{-mgh/\tau} \int_0^L dx \int_0^L dz \int d^3p e^{-p^2/2m\tau}} \\ &= mg \frac{\int_0^\infty dh h e^{-mgh/\tau}}{\int_0^\infty dh e^{-mgh/\tau}} \\ &= \tau \frac{\int_0^\infty dx x e^{-x}}{\int_0^\infty dx e^{-x}} \\ &= \tau \end{aligned}$$

Notice that all the integrals canceled except for the one containing h - the variable we are taking mean of. That's because the energy can be written as term containing only this variable plus a term containing only the other variables (this is how you derive the equipartition theorem). Same thing happens when evaluating the mean of kinetic energy. There integrals over positions cancel and the resulting integral is just integral over momenta - and it is the same integral as for an ideal gas not in gravitational field, for which we know the answer:

$$\langle E_k \rangle = \frac{3}{2} \tau$$

The heat capacity is then

$$C_V = \frac{\partial(\langle E_p \rangle + \langle E_k \rangle)}{\partial T} = \frac{5}{2}k$$

Problem 4

For the concentrations we have

$$n_{int} = 10^4 n_{ext}$$

The chemical potential difference is then

$$\mu_{ext} - \mu_{int} = \tau \log \frac{n_{ext}}{n_Q} - \tau \log \frac{n_{int}}{n_Q} = kT \log \frac{n_{ext}}{n_{int}}$$

The chemical potential has units of energy (as you can see from the factor kT in front). Expressing it volts means - what energy do I need to move electron (elementary charge) through some voltage, that is $U = eV$. Thus

$$V = \frac{kT}{e} \log \frac{n_{ext}}{n_{int}} = \frac{(1.38 \times 10^{-23} \frac{J}{K})(300K)}{1.6 \times 10^{-19} J} \log(10^4) \approx 0.24V$$

Problem 5

In this system the hydrogen atoms are independent. That is the electrons can be put onto one atom independently of all the other atoms, and the total energy of the system is the sum of the energies of each atom. Therefore we just need to consider one of them. The probability that the atom is in some configuration is $p \sim e^{(N\mu - \epsilon)/\tau}$ where N is the number of electrons there and ϵ is the energy. Thus

$$\langle N \rangle = \frac{\sum N e^{(N\mu - \epsilon)/\tau}}{\sum e^{(N\mu - \epsilon)/\tau}} = \frac{1e^{(\mu + \Delta/2)/\tau} + 0e^{(\delta/2)/\tau} + 2e^{(2\mu - \delta/2)/\tau} + 1e^{(\mu - \Delta/2)/\tau}}{e^{(\mu + \Delta/2)/\tau} + e^{(\delta/2)/\tau} + e^{(2\mu - \delta/2)/\tau} + e^{(\mu - \Delta/2)/\tau}}$$

Setting this equal to 1 we get

$$\lambda^2 = e^{2\mu} = e^{\delta/\tau}$$

Problem 6

a)

$$\langle N^2 \rangle = \frac{1}{Z} \sum N^2 e^{(N\mu - \epsilon)/\tau} = \frac{\tau^2}{Z} \frac{\partial^2 Z}{\partial \mu^2}$$

b)

$$\begin{aligned}\tau \frac{\partial \langle N \rangle}{\partial \mu} &= \tau \frac{\partial}{\partial \mu} \left(\frac{\tau}{Z} \frac{\partial Z}{\partial \mu} \right) \\ &= -\frac{\tau^2}{Z^2} \left(\frac{\partial Z}{\partial \mu} \right)^2 + \frac{\tau^2}{Z} \frac{\partial^2 Z}{\partial \mu^2} \\ &= -\langle N \rangle^2 + \langle N^2 \rangle \\ &= \langle (\Delta N)^2 \rangle\end{aligned}$$

Problem 7

It seems that the solution the Kittel is asking for, you to take the inside of a tree as a column of gas and equate change in chemical potentials between top at bottom as obtained from ideal gas, to change in potential energy of a molecule. This gives

$$mgh = kT \log \frac{n_h}{n_0} = kT \log \frac{1}{0.9}$$

Taking $m = 18 \times 1.67 \times 10^{-27}$, $T = 300\text{K}$ we get

$$h \approx 1.5\text{km}$$

However this is not how tree looks like. More correct solution is the following.

Imagine the inside of the tree to be filled with sap: water + some molecules (solution). Suppose the roots act as a semipermeable membrane and are in contact with clean water. Semipermeable membrane is a membrane which lets water pass through it but not some of the molecules dissolved in it, say sugar. This causes the pressure on the sugar side to be larger than the pressure on the other side. If the concentration of sugar is low the difference in pressures is $p = n_1 kT$ where n_1 is the number of sugar molecules per volume. Why is this so? It's not so easy to see, but you can imagine what would happen if they were ideal gases. Then they wouldn't see each other. Pressure from water would be same on both sides, and there would be an additional pressure from the sugar on one side, which would give the above formula. However in this case we have liquid and that is definitely not an ideal gas. However you can imagine the following. There is some flow of water molecules from the pure water side. If the pressures were the same, there would be lower flow of molecules from the solution side because once a water

molecule would want to pass and once a sugar molecule, which wouldn't. Thus there would be an overall flow of water from pure side to solution side and that would increase the pressure of the solution.

In any case, let's estimate the height of the tree. On one hand we have osmotic pressure

$$p = \frac{1}{V}n_iRT = \frac{1}{V}\frac{m_i}{M_i}RT = \frac{\rho_i}{M}RT$$

Where i refers to impurity (say sugar) and M is the molar mass. On the other hand this has to be equal to the hydrostatic pressure

$$p = (\rho_w + \rho_i)gh$$

where w refers to water. Thus

$$h = \frac{1}{1 + \rho_w/\rho_s} \frac{RT}{gM}$$

Say the solvent is sugar $C_{12}H_{22}O_{11}$ (I don't know if it is). The molar mass is $M = 148\text{g/mol}$. The solubility of sugar in water at 25C is 215g of sugar per 100g of water. Taking this we get $h = 1150\text{m}$ which is again high. However it is likely that concentration of sugar (or impurities) in sap is not so high (and the formula for osmotic pressure wouldn't work anyway). To get height 20m we would have to take the concentration to be about 0.012.