Problem 1. Variance in Energy From Partition Functions

Last week you showed that

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \tag{1}$$

(a) Generalize the methodology of that problem to show that

$$\left\langle E^2\right\rangle = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} \tag{2}$$

What is the analogous expression for

$$\langle E^n\rangle \tag{3}$$

where n is a positive integer?

(b) Show that variance in the energy is

$$\sigma_E^2 \equiv \left\langle (\delta E)^2\right\rangle = \left\langle E^2\right\rangle - \langle E\rangle^2 = \frac{\partial^2}{\partial \beta^2}(\log Z) \tag{4}$$

and that

$$\sigma_E^2 = -\frac{\partial \langle E\rangle}{\partial \beta} \tag{5}$$

(c) Consider the two state system of HW3.P1. Use the methods of this problem to compute the variance in the energy of a two state atom $\langle(\delta E)^2\rangle$ interacting with the thermal environment. Do you get the same answer as previously?

(d) Return to the quantum harmonic oscillator of discussed in HW4.P3, HW5.P3, HW6.P2. Show that the variance in the energy is

$$\left\langle (\delta E)^2\right\rangle = (\hbar\omega_0)^2 \frac{e^{-\beta\hbar\omega_0}}{(1-e^{-\beta\hbar\omega_0})^2} \tag{6}$$

(e) Find the leading approximate expression for the variance $\langle \delta E^2\rangle$ in the low temperature limit $k_B T \ll \hbar\omega_0$.

(f) Consider the probabilities P_n for the simple harmonic oscillator to be in the n-th state, which you worked out in HW4.P2. Show that in the limit $k_B T \ll \hbar\omega_0$ 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, $P_1 \simeq e^{-\beta\hbar\omega_0}$, while the higher excited states, $P_2, P_3, \ldots$, have negligible probability. Calculate the mean energy $\langle E\rangle$ and the variance $\langle(\delta E)^2\rangle$ with P_0 and P_1 only with these approximations. Show that the variance agrees with part (e).

(g) Determine the leading approximate expression for the variance of $\langle(\delta E)^2\rangle$ of the SHO in the high temperature limit $k_BT \gg \hbar\omega_0$ by Taylor expanding Eq. (6) appropriately. You should find that the leading term is independent of $\hbar$.

Discussion: The result is independent of $\hbar$, indicating that the dynamics is classical. It is a good exercise to compute $\langle \delta E^2\rangle$ using the classical probability distribution of HW5.P1. If you do all the integrals correctly you should get the same as in part (g). This is recommended as as an exercise.

Problem 2. Estimates of Entropy

Take the Sackur-Tetrode equation which determines the entropy of an ideal mono-atomic gas:

$$S = Nk_B \left[\log\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{7}$$

(a) Use the Sackur-Tetrode equation to show that

$$\frac{1}{T} = \frac{3}{2}\frac{Nk_B}{E} \qquad p = \frac{Nk_BT}{V} \tag{8}$$

(b) (Optional) Show that the Sackur-Tetrode equation can be written

$$S = Nk_B\left[\log\left(\frac{v}{\lambda_{\rm th}^3}\right) + \frac{5}{2}\right] \tag{9}$$

where $v = V/N$ and $\lambda_{\rm th}$ is the thermal de Broglie wavelength given in Eq. (11).

(c) Take an ideal gas of Helium at Standard Temperature Pressure (STP) – the volume per particle is $v = V/N$, and the interparticle spacing is ℓ_0, with $\ell_0 = v^{1/3}$. Determine the inter particle spacing in nm.

(d) The thermal de Broglie wavelength is of order

$$\lambda_{\rm th} \sim \frac{h}{p} \sim \frac{h}{\sqrt{mk_BT}} \tag{10}$$

In evaluating the formula for the entropy of the ideal gas, the thermal de Broglie wavelength is defined as

$$\lambda_{\rm th} \equiv \frac{h}{\sqrt{2\pi m k_BT}} \tag{11}$$

Determine the thermal de Broglie wavelength of Helium at STP in nm.

How can you do this without looking up numbers? Well, I do it like this – the proton mass is approximately $m_pc^2 \simeq 1000\,\text{MeV}$, or 2000 times the electron mass[1], $m_ec^2 \simeq 0.5\,\text{MeV}$. These are good numbers to remeber. Insert a factor of c^2 to make estimates

$$\frac{h}{\sqrt{m_pk_BT}} = \frac{hc}{\sqrt{(m_pc^2)(k_BT)}} \tag{12}$$

[1] More precisely $m_pc^2 \simeq 938\,\text{MeV}$, while $m_e \simeq 0.511\,\text{MeV}$.

From there you should remember $\hbar c$ (or hc) and $k_B T$. Recall that the Helium nucleus consists of two protons and two neutrons.

Another (possibly better) strategy might be to recall that the Bohr radius is $a_0 = 0.53\,\text{Å}$, and that the binding energy of an electron to a proton in hydrogen is given by

$$\frac{\hbar^2}{2m_e a_0^2} = 13.6\,\text{eV} \tag{13}$$

in the Bohr model. Note this is the *electron mass*, not the proton mass.

So to estimate the thermal debroglie wavelength of a proton, instead of inserting the speed of light you can insert the Bohr radius and the electron mass.

$$\frac{\hbar^2}{\sqrt{2m_p k_B T}} = a_0\sqrt{\frac{\hbar^2}{(2m_e a_0^2)}\frac{1}{k_B T}}\sqrt{\frac{m_e}{m_p}} = 0.5\,\text{Å}\sqrt{\frac{13.6\,\text{eV}}{k_B T}}\sqrt{\frac{1}{2000}} \tag{14}$$

(e) Sackur-Tetrode equation says

$$S = Nk_B\left[\log\left(\frac{v}{\lambda_{\text{th}}^3}\right) + \frac{5}{2}\right] \tag{15}$$

Thus, up to a logarithm (which is never very large), the entropy is of order Nk_B. This gives a simple way to estimate entropy of any substance. It is of order the number of particles (times k_B).

Determine $S/(Nk_B)$ for Helium gas at STP.

(f) Determine S in $J/{}^\circ$K for one mole Helium gas and $\Omega(E)$ for one mole of Helium gas at STP. You should not have to look up numbers here, but simply remember that $R = N_A k_B$.

Problem 3. Entropy of mixing

Read section 14.6 and derive equation 14.40

Problem 4. Entropy of during an adiabatic expansion

Consider the expression for the number of states in a mono-atomic ideal gas

$$\Omega = CV^N E^{3N/2} \tag{16}$$

and

$$S = Nk_B\log(V) + \frac{3}{2}Nk_B\log(E) + \text{const} \tag{17}$$

Recall that in an adiabatic expansion of an ideal gas $TV^{\gamma-1} = \text{const}$, which we derived from demanding that the heat inflow was zero, and that entropy was constant. Work in reverse: show that if $TV^{\gamma-1} = \text{const}$, then the entropy defined in Eq. (17) is constant during an adiabatic expansion. Describe qualitatively, using notions of phase space volume, why the entropy remains fixed as the system expands.