Discussion 6

Name and section: ______________________________

1. The partition function, q, can generally be written as

$$q = \sum_i \mathrm{e}^{-\beta \epsilon_i} \tag{1}$$

where ϵ_i is the energy of the state i and $\beta = 1/(k_B T)$.

   (a) Derive the average energy in terms of the partition function. Starting from the expression

$$\langle \epsilon \rangle = \sum_i \epsilon_i p(\epsilon_i) = \sum_i \frac{\epsilon_i \mathrm{e}^{-\beta \epsilon_i}}{q} \tag{2}$$

   where $p(\epsilon_i)$ is the probability of occupying state i. Derive

$$\langle \epsilon \rangle = -\frac{1}{q}\frac{\partial q}{\partial \beta} = -\frac{\partial \ln q}{\partial \beta} \tag{3}$$

   using eqs. (1) and (2).

   (b) Now let's study the temperature dependence of the average vibrational energy of a diatomic molecule. We learned from CH351 that the vibrational motion of a diatomic molecule can be described as a one-dimensional harmonic oscillator problem. If the molecule vibrates with frequency ω, what are the quantized vibrational energy levels?

(c) Let's derive the vibrational partition function for this diatomic molecule. Starting with the definition of the partition function given in eq. (1), show that

$$q = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1 - \mathrm{e}^{-\beta\hbar\omega}}. \tag{4}$$

(d) Show that the average vibrational energy for the diatomic molecule is

$$\langle\epsilon\rangle = \frac{1}{2}\hbar\omega\left(\frac{1 + \mathrm{e}^{-\beta\hbar\omega}}{1 - \mathrm{e}^{-\beta\hbar\omega}}\right). \tag{5}$$

(e) In the limit as $T \to 0$, to what value does $\langle \epsilon \rangle$ converge?

(f) What about the limit of $T \to \infty$? Taylor series expand the exponential terms to first order in $\beta\hbar\omega$ to estimate the *classical* limit of $\langle \epsilon \rangle$.

(g) Graphically show how $\langle \epsilon \rangle$ varies with T.