## Discussion Section # 5 – February 21, 2014

1. In class, we learned that the partition function, q, can generally be written as

$$q = \sum_i e^{-\beta\varepsilon_i}$$

(i) Let's derive the average energy in terms of the partition function. Starting from the expression

$$\langle\varepsilon\rangle = \sum_i \varepsilon_i p_i(\varepsilon_i) = \sum_i \varepsilon_i \frac{e^{-\beta\varepsilon_i}}{q}$$

where $\varepsilon_i$ is the energy of the quantum state *i* and $p_i(\varepsilon_i)$ is the probability of occupying that state, derive, with guidance from your class notes

$$\langle\varepsilon\rangle = -\frac{1}{q}\frac{\partial q}{\partial\beta} = -\frac{\partial \ln q}{\partial\beta}$$

2. 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?

3. Let's derive the vibrational partition function for this diatomic molecule. Starting with the definition of the partition function given in Question 1, show that

$$Q = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

(Hint: Refer to class notes for help)

4. Show that the average vibrational energy for the diatomic molecule is

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

5. As temperature T→ 0, what value does <ε> converge to?

How about as T→∞? Taylor series expand the exponential terms to first order in <ε> to estimate this *classical* limit of <ε>.

Can you graphically show how <ε> varies with T?