Homework #2

due: Thursday, 10/15/09

1. For the two 10-particle two-state systems described in lecture, suppose the total energy to be shared between the two objects is $E = E_A + E_B = 4$. What is the distribution of energies that gives the highest multiplicity?

2. For a simple one-component system, the 1st Law of Thermodynamics can be written

$$dE = TdS - pdV$$

using what you know from thermodynamics (i.e. what you learned in PChem class) show

$$\left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V = -p$$

3. One can obtain an analogous expression from statistical mechanics

$$\left(\frac{\partial \langle E\rangle}{\partial V}\right)_\beta - \beta\left(\frac{\partial \langle p\rangle}{\partial \beta}\right)_V = -\langle p\rangle$$

where $\langle E\rangle$ is the average energy and $\langle p\rangle$ is the average pressure using the probability distribution function $P_i = e^{-\beta E_i}/Q$ and $Q = \sum_j e^{-\beta E_j}$. To derive the above expression first obtain expressions for $\langle E\rangle$ and $\langle p\rangle$. Note that for each state j

$$p_j = -\left(\frac{\partial E_j}{\partial V}\right)_T$$

Differentiate the expression for $\langle E\rangle$ with respect to V (keeping β fixed) to obtain

$$\left(\frac{\partial \langle E\rangle}{\partial V}\right)_\beta = -\langle p\rangle + \beta\langle Ep\rangle - \beta\langle E\rangle\langle p\rangle$$

Similarly, one can differentiate $\langle p\rangle$ with respect to β (keeping V fixed) to obtain

$$\left(\frac{\partial \langle p\rangle}{\partial \beta}\right)_V = \langle E\rangle\langle p\rangle - \langle Ep\rangle$$

Verify these last two expressions and combine them to obtain the top expression.

4. Explain how one can use the results of problems 1 and 2 to show that $\beta \propto 1/T$.

5. Show that the Boltzmann distribution can be used to determine the relative population (to the ground state population n_0) such that

$$\frac{n_i}{n_0} = e^{-\beta E_i}$$

6. One can derive the Gibbs entropy formula using the Boltzmann entropy formula, the average energy obtained from the Boltzmann distribution function and both equations for the Helmholtz free energy (i.e. A = E – TS and A = - kT lnQ). Derive the formula

$$S = -k \sum_i P_i ln P_i$$