Hints for Exam #1 for CCB 422/522, Spring 2021

Note: this was a difficult exam! This not an answer key, but rather a set of hints to help you learn. (I have been known to ask the same question again on subsequent exams.)

1. Many scientists have repeatedly hit on the idea of using MD simulations to estimate $\langle \exp(+\beta V)\rangle$, where V is the potential energy, and the average is over the Boltzmann distribution.

   Key here is to expand out the $\langle \rangle$, which indicate an average. Remember that $\langle f(x)\rangle = (1/Q) \int f(x) \exp(-\beta V) dx$.

2. Maximizing entropy is a very important procedure in statistical mechanics and in many types of modeling. Generally, one wants to maximize the entropy of a distribution subject to certain constraints. Show that the Boltzmann distribution arises from a maximum entropy principle subject to a constraint; what is this constraint?

   Please see pp. 171-173 in your text.

3. Starting from $A = -RT \ln Q$, derive an expression for the constant-volume heat capacity C_V in terms of Q. Of course, you can look up the answer somewhere! Here, you must show the derivation.

   Please see pp. 50-51 in Slater.

4. Consider a particle of mass m, that can move in one dimension with a harmonic oscillator potential $V(x) = \frac{1}{2}k(x-x_0)^2$: ....

   Please see pp. 201-203 in MDF.

5. Consider a sphere of radius R. Assume there is a point charge of magnitude q at it origin, plus a uniform surface charge density ρ on the surface.

   Use Gauss' law both inside and outside the sphere. Inside, the charge enclosed by a sphere of radius $r < R$ is q; the charge enclosed by a sphere of radius $r > R$ is the sum of q and the charge on the surface.

6. Suppose you have a solution of monomers, X, than can form polymers by the following equilibria:

   $$X + X \leftrightarrows X_2; \quad X_2 + X \leftrightarrows X_3; \quad ... \quad X_n + X \leftrightarrows X_{n+1}$$
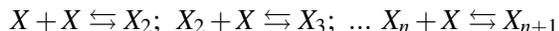
   where each of the above reactions has the same equilibrium constant K.

   This was a hard problem. Let $x = [X]$; then $[X_2] = Kx^2$, $[X_3] = K^2x^3$, etc. So

   $$Q = x + Kx^2 + K^2x^3 + \ldots = x[1 + Kx + (Kx)^2 + (Kx)^3 + \ldots] = x/(1-Kx)$$

   The average number of monomers is

   $$<n> = (1/Q)\{[X] + 2[X_2] + 3[X_3] + \ldots\} = (x/Q)[1 + 2Kx + 3(Kx)^2 + \ldots]$$

   This is a bit tricky to simplify, and was not required. But, one can see that $<n>$ looks like a derivative of Q:

   $$<n> = (x/Q)\left(\frac{\partial(Q/x)}{\partial(Kx)}\right) = \frac{1}{(1-Kx)}$$

7. Consider the very simple protein dimer problem we considered in class:

(c) Now, let $[M] = 0$. The Hill coefficient n_H is a measure of the cooperativity of binding. It describes the rate of change of fractional occupation *vs* ligand concentration at half saturation, and is defined as:

$$n_H = \left(\frac{\partial \ln[f/(1-f)]}{\partial \ln[L]} \right)_{f=1/2}$$

This was the part that was a bit complex. First, determine that $f/(1-f) = K\lambda$ where $\lambda = [L]$; then

$$n_H = \left(\frac{\lambda}{K\lambda} \right) \left(\frac{\partial [K\lambda]}{\partial \lambda} \right) = 1$$

A Hill coefficient of 1 indicates non-cooperative binding, which is indeed what we have in this simple example. Make sure that you can do calculations like one shown here.