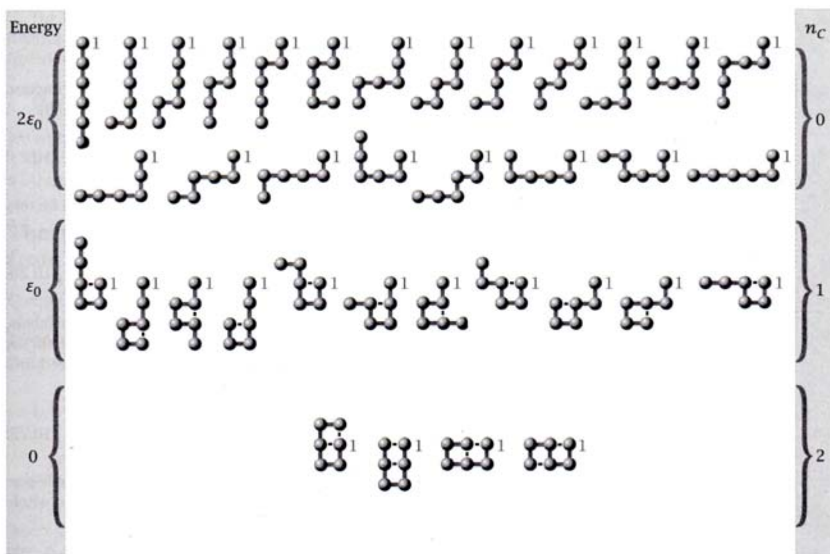
University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Homework Assignment 5

Due at midnight on Tuesday 2/17/15. Show calculations as well as answers.

1) Lattice models are simple graphical methods for constructing partition functions for complex systems. Here is a lattice model for an order-disorder transition in a polymer. We model a polymer as a string of beads held together by "bonds". Structured polymers are chains of beads that wrap back on themselves causing non-bonded beads to be adjacent or "in-contact". The more 'contacts" that are formed the more the polymer is structured and the lower is the polymer's energy. Consider the structures of polymers composed of six beads. Highly structured polymers have two contacts (n_C=2) and have energy ε=0. Polymers with single contacts (n_C=1) have energy $\varepsilon=\varepsilon_0$. Unstructured polymers have no contacts (n_C=0) and their energy is $\varepsilon=2\varepsilon_0$.



a) The figure at the above right shows all the microstates for six-bead polymers with 0, 1, and 2 contacts. Write out the form of the partition function for this polymer system and evaluate the partition function for ε_0=5.00 x10^{-21} J and T=300K.

b) Calculate the probabilities that a polymer has n_C=2, n_C=1, or n_C=0. Assume the same conditions as in part a. Note: In your calculation you have to include the number of microstates in each energy.

c) Using your result from part b, calculate the average number of contacts $\langle n_C \rangle$ per polymer, the molar internal energy and the molar entropy.

d) Repeat the calculations in part a-c only assume T=50K. Calculate the change in the average number of contacts, and the molar ΔU and ΔS when the temperature of the polymer is raised from T=50K to T=300K.

2) The data below show the binding of oxygen to squid hemocyanin.

$[O_2]$	f_B x100	$[O_2]$	f_B x100
1.13	0.30	136.7	55.7
5.55	1.33	166.8	67.3
7.72	1.92	203.2	73.4
10.72	3.51	262.2	79.4
31.71	8.37	327.0	83.4
71.87	18.96	452.8	87.5
100.5	32.90	566.9	89.2
123.3	47.80	736.7	91.3

Determine from a Hill plot whether the binding of oxygen to squid hemocyanin is non-cooperative, fully cooperative or partially cooperative. Determine the minimum number of binding sites consistent with the data.

3) This problem explores when you do and do not have to quantize translational motions. Assume argon atoms in the gas phase translate in one dimension and behave ideally

a) What is the AVERAGE translational kinetic energy per argon atom? Assume T=1000K

b) Assume you can model the energy of translation of an argon atom using the particle in a one dimensional box model. Assume the box is 1 m in length. For what value of the quantum number n is the particle in the box energy equal to the average energy calculated in part a? Calculate the partition function and determine the probability that an argon atom is in this energy state.

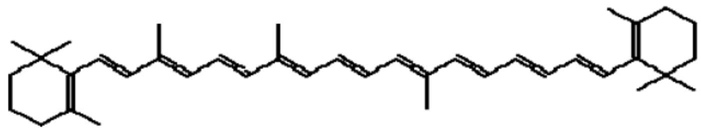
c) Based on your answers in parts a and b, how important are quantum effects in the translation of argon at T=1000K?

d) Suppose the box within which argon translates is 10.0 nm in length. For this box size calculate the n for the energy that is equal to $k_BT/2$. Also, determine the partition function and calculate the probability that an atom has this energy.

e) Based on your answer in part d, how do quantum effects vary with the size of the box a? Do quantum effect increase or decrease with box size?.

f) Based on your answers to parts a-e, discuss why the vibrational heat capacity is almost zero at T=100K, but the translational heat capacity is 3R/2. Hint: atomic vibrations have amplitudes of about 0.01 Angstroms.

4) β-carotene, a precursor of retinal, a visual pigment found in the retina of the eye, has the formula given below. β-carotene contains 11 conjugated double bonds which contribute 22 π electrons that are delocalized along the length of the molecular chain. Suppose we can model the energies of these electrons with the particle-in-the-box model.



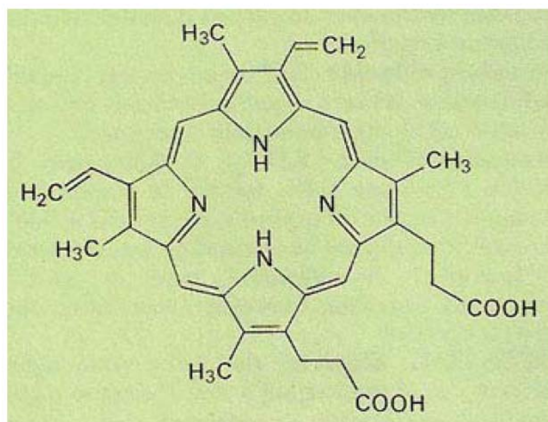
a) Assuming each particle-in-the-box energy level is occupied by at most two electrons, what is the quantum number n associated with the highest occupied energy state?

b) For the highest occupied energy state what is the wave function? If the length of the carotene molecule is L, what is the probability of finding an electron in the region from x=L/3 to x=2L/3.

c) If β-carotene absorbs radiation with a wavelength of λ=480 nm, calculate the energy change ΔE .

d) When the electrons in the highest occupied energy state adsorb energy at λ=480 nm they make a transition from the highest occupied energy state to the lowest unoccupied energy state. From your results in parts a-c, calculate the length L of the carotene molecule.

5) Porphyrin rings like the one in the figure at the right appear in myoglobin and chlorophyll. A porphyrin ring contains 26 π electrons which may be treated as particles in a thin square box



a) What is the expression for the energies of a particle in a two dimensional square box as a function of the quantum numbers n_X, n_Y, the electron mass m, and the dimensions of the box a?

b) Assume for the purpose of this calculation that the square box has sides a=1nm. Assume also that at most two electrons can occupy a single energy microstate. Order the 13 occupied energy levels from the lowest energy to the highest energy. Designate each energy level by its quantum numbers (n_x,n_y). Note any degeneracies.

c) Calculate the energy change ΔE that results when a porphyrin absorbs a photon and promotes and electron from the highest occupied energy state to the lowest unoccupied energy state.

d) Calculate the frequency and wavelength of radiation absorbed by this porphyrin ring. Give your answer for wavelength in units of nm

e) For the highest occupied energy level calculate the probability of finding an electron in the region $0 < x < a/2$ and $0 < y < a/2$.