APh105c
Homework 3
Due Date: Friday, April 21, 2006

"To arrive at the truth it is necessary, at least once in life, to rid oneself of all the opinions one has received, and to construct anew, and from the fundamentals, all the systems of one's knowledge." - Descartes, 1637

Reading: Read chaps. 8, 13 and 28 of Dill and Bromberg.

A. Taking Stock 1

This problem must be submitted by email to me, Frosso and Dave - no hand-written copies will be permitted. What I want you to do here is to rank the three most important things you have learned so far and to explain why they are on your list. Your explanations must be well thought out and cogently argued.

1. The Hemoglobin Story

We have adopted hemoglobin as our molecule of interest to discuss the statistical mechanics of binding reactions. In this problem, you will work out the characteristics of hemoglobin binding from a number of different perspectives.

(a') A feeling for the numbers: in class I made a rough estimate of the number of red blood cells and the number of Hemoglobin molecules in each red blood cell. In this part of the problem, I want you to take it a little further. Figure out roughly how many O_2 molecules you bring in with each breath and how many Hemoglobin molecules it would take to use each and every one of those oxygens. How does this compare with the total number of Hemoglobins in your body?

(a) In class, I derived the fractional occupancy of hemoglobin in a model in which the equilibrium constant for each stage in the reaction is different. Work out the *special* case of what I did in class in which the equilibrium constant is the same whether there is already oxygen bound or not. Show that the resulting expression is of the form

$$\theta([O_2]) = 4\frac{[O_2]/K}{1+[O_2]/K}. \tag{1}$$

(b) Repeat the derivation given in class in terms of equilibrium constants and then make a plot of the result for parts (a) and (b) using the parameters:

$$K_1 = 0.0188 mmHg^{-1} \tag{2}$$

$$K_2 = 0.0566 mmHg^{-1} \tag{3}$$

$$K_3 = 0.407 mmHg^{-1} \tag{4}$$

$$K_4 = 4.28 mmHg^{-1} \tag{5}$$

for the full problem. Beware: these constants are equilibrium constants and I used dissociation constants in my derivation. As a result, you need to invert these numbers to use them in the formula we derived. See what choice of K in part (a) gives a "best fit" to the data from part (b) (I am not expecting a very good fit!).

(c) Now formulate the problem as a statistical mechanics problem using the grand canonical distribution the way we did in class. Like with the treatment in class assume that there are three body interactions characterized by an energy K and four-body interactions characterized by an energy L. Write the total grand partition function and derive the occupancy by taking a derivative of the log of the partition function following the prescription given in class. Then, find a relation between the parameters used here and those used in part (b) - that is, in this part of the problem you have the parameters ϵ, J, K and L and in part (b) you have $K_1 - K_4$. The idea is to use the K_is to determine the parameters used in the statistical mechanics model.

(d) One of the favorite tools for dealing with cooperative interactions is the use of the so-called Hill function. In this problem, you will derive the Hill equation and then see to what extent it is possible to use it for thinking about hemoglobin. For a reaction $nA + R \rightleftharpoons nAR$, we need n copies of the ligand A in order to form the complex nAR. In this case, imitate the treatment of binding given in class to find an expression for the fraction of receptors that are in the complexed state by using the definition of the dissociation constant

$$K_d = \frac{[A]^n[R]}{[nAR]}. \tag{6}$$

In particular, show that

$$\theta([A]) = \frac{[A]^n/K_d}{1 + [A]^n/K_d}. \tag{7}$$

The number n is called the Hill coefficient. Make a plot of the binding probability for the cases $n = 1, 2$ and 4 using a sensible value of K from the earlier problems. Here too, using the data provided on the HW website, see if you can find a best fit to the Hb data using a Hill function.

Note: the data that is the basis of working out the binding is included as an excel spreadsheet for the homework. For those wanting extra credit, work out a best fit for your results from part (c) by fitting to the data.

2. Elasticity, Hydrodynamics and Indicial Notation.

Indicial notation is not central to thermodynamics, though it makes the business of thinking about elasticity and hydrodynamics much easier. Nevertheless, this problem aims to give you practice in thinking about indicial notation and gives you a chance to think further about the ideas concerning elasticity and hydrodynamics that we covered in class.

A key notational convenience that will be afforded us is the use of the summation convention. The basic injunction is: *sum over all repeated indices*. So as to gain familiarity with this convention, work out the following examples.

(a) $a_i b_i$ (also write this in vectorial notation).

(b) Write out the three components of the vector $v_i = \epsilon_{ijk} a_j b_k$ (note that the Levi-Cevita symbol is 1 for even permutations of ϵ_{123}, -1 for odd permutations and zero for all other cases. Note that this is another way of writing the cross product between two vectors.

(c) $\frac{\partial v_i}{\partial x_i}$ (write this in direct notation also).

(d) Given a matrix $\mathbf{M}$, what is M_{ii}? What is another way of writing this? Consider the matrices $\mathbf{A}$ and $\mathbf{B}$. Write the ij^{th} element of the matrix $\mathbf{AB}$ in terms of the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ individually. Use indicial notation.

(e) In the Navier-Stokes equations one encounters terms like $\mathbf{v} \cdot \nabla \mathbf{v}$. Rewrite this in indicial notation, using the summation convention.

(f) In linear elasticity, the stress tensor is of the form $\sigma_{ij} = C_{ijkl}\epsilon_{kl}$. Write out the components of σ_{11} and σ_{12} of the stress tensor by exploiting the summation convention.

(g) The equilibrium equations for elasticity are written as

$$\frac{\partial \sigma_{ij}}{\partial x_j} + b_i = 0. \tag{8}$$

This is three equations corresponding to $i = 1, 2, 3$. Write all three equations by using the summation convention.

(h) For the particular case of an isotropic, linear elastic solid, the elastic modulus tensor is of the form

$$C_{ijkl} = \lambda \delta_{ij}\delta_{kl} + \mu(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl}). \tag{9}$$

In this case, find an expression for the stress $\sigma_{ij} = C_{ijkl}\epsilon_{kl}$ and the stored energy of the solid, $W(\{\epsilon_{ij}\}) = \frac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl}$. Write your expression for the stress in both indicial and vector notation. Also, use this form for the elastic modulus tensor to obtain the equilibrium equations (the so-called Navier equations) by plugging your result for σ_{ij} into

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0. \tag{10}$$

Note that we are looking at the particular case in which the body force has been set to zero.

(i) The Navier-Stokes equations are of the form

$$\rho(\frac{\partial v_i}{\partial t} + v_k \frac{\partial v_i}{\partial x_k}) = \mu \frac{\partial^2 v_i}{\partial x_k \partial x_k} - \frac{\partial p}{\partial x_i}. \tag{11}$$

Write all three equations by exploiting what you know about the summation convention. Also, write these equations in direct (vectorial) form.

3. Energy to Create Point Defects and Precipitates.

In this problem, we are going to examine the energetics of crystalline solids that contain one of two types of internal structures. One class of internal structures is the presence of point defects such as vacancies (i.e. missing atoms in the crystal lattice) and interstitials (i.e. extra atoms in tetrahedral or octahedral vacant regions within the crystal. The second class of internal structure is known as a precipitate and refers to the idea that within the host material (Al, for example) there are second phase particles known as precipitates. For example, one might have Al_2Cu precipitates within an Al matrix. The goal of this problem is to see the way some of the ideas we have been discussing in class (such as pV work) apply to real world problems concerning microstructures in materials.

a) In this first part of the problem you will use statistical mechanics to derive an expression for the concentration of point defects in a crystal. The basic idea is to imagine a three-dimensional crystalline lattice with a total of N sites. Next, consider the case in which N_{vac} of those sites are not occupied by atoms - these are the so-called vacancies. The bottom line is that such defects are a fact of life, even in that pretty gold wedding ring that some of you might be wearing. What we want to do is construct the free energy $F(T, N_{vac}; N) = U(N_{vac}) - TS(N_{vac}; N)$. First, write an expression for the energy $U(N_{vac})$ in terms of the energy ϵ_{vac} which is the energy *cost* to put a single point defect in the material. Note that as we discussed in class, this kind of model is predicated on the assumption that there are NO interactions between point defects. Next, construct the entropy by counting up the number of ways of arranging the N_{vac} vacancies on the N lattice sites. Write an explicit expression for your free energy and simplify it by invoking the Stirling approximation. Our goal is to compute the equilibrium number of vacancies as a function of the temperature. To determine N_{vac}, minimize your free energy with respect to N_{vac} and show that in the low concentration limit that the concentration of vacancies is given by

$$c_{vac} = \frac{N_{vac}}{N} = e^{-\epsilon_{vac}/kT}. \tag{12}$$

If a typical vacancy formation energy is 0.5eV, find the equilibrium concentration of vacancies. Note: you will have a chance to estimate the vacancy formation energy in the remainder of the problem.

b) When a point defect or a precipitate is present in a material, it results in an overall volume change of the material. This volume change occurs at fixed external pressure (i.e. the hunk of material is sitting there in the lab at atmospheric pressure). As a result of this volume change, there is a contribution to the total energy cost of creating the defect in the form of pV work. Consider a single interstitial and assume that the volume change that it imposes on the crystal is $\Delta V = 0.6 V_{atomic}$. That is, when we put an interstitial in the lattice, it swells that whole crystal by a fraction of the volume per lattice site. Use the lattice parameter for Al in the fcc crystal structure and then compute the pV work associated with the presence of such a point defect at atmospheric pressure. Report your result in joules, eV and in $k_B T$ units. Is this a big or small effect on the scale of the cohesive energy/atom for the crystal?

c) A second interesting feature caused by the presence of a spherical inclusion (or inclusions of any shape for that matter) is that the solid is deformed and there is strain energy stored in the stretched atomic bonds surrounding the inclusion. In this part of the problem, we will use the theory of elasticity to estimate the size of this relaxation. The Navier equations that serve as the equilibrium equations (i.e. sum of all forces on a little material volume element equals zero) for an isotropic linear elastic solid may be written in direct notation as,

$$(\lambda + \mu)\nabla(\nabla \cdot \mathbf{u}) + \mu \nabla^2 \mathbf{u} + \mathbf{f} = 0. \tag{13}$$

Show that for a problem with spherical symmetry (like the point defects or precipitates that we are thinking of here) that the Navier equations can be written as

$$r^2 \frac{d^2 u_r}{dr^2} + 2r \frac{du_r}{dr} - 2u_r = 0. \tag{14}$$

Solve this differential equation for the displacements (strictly radial) of the crystal surrounding our defect of interest. You will need to fix two unknown constants. Use the fact that the displacements have to decay to zero at infinite distance from the inclusion to fix one of these constants. To fix the other constant, assume that the displacement at the boundary of the inclusion (which we take to have radius a) is given by a parameter δ. Using the radial displacement that you have computed, now compute the strain tensor and use the strain to compute the strain energy. If we assume that the spherically symmetric defect induces a displacement of $0.3\mathring{A}$ around the defect, what is the energy scale associated with the elastic relaxation?

In thinking about point defects such as interstitials and vacancies, one of several contributions to the energy of such defects is given by the changes in the bond energy of the various atoms in the vicinity of that point defect. Consider a crystal that is characterized by an energy function of the form $E_{tot} = \frac{1}{2}\sum_{ij} V(R_{ij})$, where $V(R)$ is a pair potential and R is the distance between the two atoms of interest.

(d) The Morse potential is given by $V(r) = V_0(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)})$, where V_0, a and r_0 are parameters to be determined by fitting to experimental data. Using the experimental data for the cohesive energy of fcc Cu ($E_{coh} = 336$kJ/mole), the fcc Cu equilibrium lattice parameter ($a_0 = 3.61\mathring{A}$) and the bulk modulus ($B = \Omega\frac{\partial^2 E_{coh}}{\partial\Omega^2}$ =134.3GPa($\Omega \equiv$ volume)), determine the parameters V_0 (in eV), a (in $\mathring{A}^{-1}$) and r_0 (in $\mathring{A}$) under the assumption that only near neighbor atoms interact.

Hint: Note that the cohesive energy is given by

$$E_{coh} = \frac{1}{2}\sum_{ij} V(R_{ij}), \tag{15}$$

where $\mathbf{R}_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$. Use translational invariance to realize that the sum for every i is equivalent, so the expression above can be rewritten as

$$E_{coh} = \frac{N}{2}\sum_{j} V(R_{0j}), \tag{16}$$

where R_{0j} is the distance of the j^{th} atom from the atom at the origin. Also, remember that we are only considering near neighbor interactions, so this sum will run over the 12 neighbors of a given atom within the fcc crystal.

e) Consider a single vacancy in an fcc crystal and compute the change in the total energy of the system when an atom is taken out of the crystal. More precisely, use your Morse potential to estimate the vacancy formation energy which is defined as

$$\epsilon^f_{vac} = E_{tot}(N-1; vac) - (N-1)E_{tot}(N; perfect)/N. \tag{17}$$

Our notation here is defined as: $E_{tot}(N-1; vac)$ is the energy of an N-atom crystal in which one atom has been removed. You will obtain this energy using the Morse potential, $E_{tot}(N; perfect)$ is the energy of the perfect crystal that contains N atoms and we divide this by N to find the energy per atom. Make sure you understand the *definition* of the vacancy formation energy before you actually make the calculation. Explain the definition and then compute the vacancy formation energy. Report your vacancy formation energy in eV and comment on the numerical value of this energy relative to the cohesive energy of the crystal. I can tell you that the rough value of the observed vacancy formation energy for Cu (and other metals) is something like 1eV. The pairwise interaction model is not an entirely satisfactory description of the energetics of metals, and the situation is even more complicated for semiconductors.

f) Recall that in the earlier part of this problem we began a calculation of the elastic relaxation energy associated with point defects and precipitates. Note that this is an *additional* contribution which is above and beyond the bond breaking terms computed above. In particular, recall that you assumed that these defects produce a spherically symmetric distortion field and you computed the radial displacements associated with such defects. Now we finish that calculation by actually finding out how much energy is associated with these relaxations. The relaxation energy is evaluated using

$$E_{strain} = \int_\Omega W(\epsilon) dV, \tag{18}$$

where Ω is the volume extending from the surface $r = a_0$ to infinity, and $W(\epsilon)$ is the strain energy density. To make contact with two familiar elastic moduli, namely Young's modulus E and Poisson's ratio ν, we write the strain energy density as

$$W = \frac{E}{2(1+\nu)}[\epsilon_{ij}\epsilon_{ij} + \frac{\nu}{1-2\nu}tr(\epsilon)^2]. \tag{19}$$

Note that the Einstein summation convention is in effect here. Convince yourself that the strains in spherical co-ordinates are simply equal to the ones in a rotated cartesian frame, so that $\epsilon_{rr} = \epsilon_{33}$ etc. Show using the displacements you computed in the previous homework that the strains are given by

$$\epsilon_{rr} = -\frac{2b}{r^3} = -\frac{2\delta a_0^2}{r^3} \tag{20}$$

$$\epsilon_{\theta\theta} = \epsilon_{\phi\phi} = \frac{b}{r^3} = \frac{\delta a_0^2}{r^3}. \tag{21}$$

We have used a_0 to represent the radius of the hole left by the vacancy and δ as the displacement of the surface of the hole induced by relaxation. You will want to know that in spherical coordinates for a displacement field which is purely radial, the strains are given by $\epsilon_{rr} = \partial u_r/\partial r$, $\epsilon_{\phi\phi} = \epsilon_{\theta\theta} = u_r/r$. For further details, see Landau and Lifshitz, **Theory of Elasticity**, pg. 3. Show, in turn, that this implies

$$W = \frac{E}{2(1+\nu)}\frac{6\delta^2 a_0^4}{r^6}. \tag{22}$$

Performing the integration suggested in eqn. 18 results in

$$E_{strain} = \frac{4\pi E\delta^2 a_0}{(1+\nu)}, \tag{23}$$

which is an estimate for the point defect formation energy for this particular choice of boundary conditions.

For the choice of parameters relevant to a typical metal like Cu, we may estimate this energy as follows. Consider a relaxation due to the point defect of $\delta = 0.1\mathring{A}$. Assume that the spherical hole has radius $a_0 = 4.0\mathring{A}$ and elastic moduli $\nu = 1/3$ and $E = 0.8eV/\mathring{A}^3$ (i.e. roughly 125GPa). If we use these numbers in eqn. 23, find the resulting energy and compare this number to typical point defect formation energies. Comment on your sense of the relative importance of the bond breaking and elastic relaxation terms to the enthalpy of formation.