APh105c
Homework 6
Due Date: Friday, May 12, 2006

"To do successful research, you don't need to know everything. You just need to know of one thing that isn't known." - Arthur Schawlow

Reading: Read the paper by Srolovitz on surface instabilities posted on the course website.

1. A Feeling for the Numbers: Homogeneous Nucleation.

In class we discussed the free energy competition during the process of homogeneous nucleation. Give a brief recapitulation of those arguments and in particular, a) deduce the critical radius in terms of the relevant materials constants and b) deduce the free energy change when $r = r^*$. Recall that we plotted $\Delta G(r)$, and I want you to find $\Delta G(r^*)$. Use your Morse potential for Cu to estimate the surface energy for Cu(100) - this notation refers to a particular surface found in cubic crystals that is perpendicular to the x-axis. The point here is to get you thinking about the microscopic origins of a quantity such as γ which appears in our expression for r^*. Note that what we really want is the interfacial energy between matrix and precipitate (and not the surface energy, which is what you are calculating). However, this estimate at least gives a sense of the microscopic origins of interfacial energies. Typical structural energy differences between different phases are something like 0.5eV/atom. That is, we are assuming that there is an 0.5eV/atom bulk free energy benefit to forming the precipitate. Use your results for both surface energy and the bulk free energy to estimate the critical radius size. Also, make an estimate of how many Cu atoms would be in such a nucleus. In addition, for fixed bulk energy difference (the 0.5eV/atom I gave you above), make a plot of the critical radius size as a function of the interfacial energy for values ranging from 0.1 to 2 J/m^2. (NOTE: I have NOT done this problem so I am not certain what kind of numbers you will get. I HAVE used the Morse potential you derived in the earlier homework to derive a surface energy, but the nucleation part of the argument I haven't done.)

2. Contact Angle and Heterogeneous Nucleation.

In class and in an earlier problem, we examined nucleation as a competition between surface and bulk energy terms. However, the subject is more subtle than this in the sense that often nucleation takes place *heterogeneously.* This means that nucleation takes place on some site that serves as a seed for the nucleation process. You have probably heard about impurities as the origin of nucleation in supercooled liquids. To that end, this problem addresses heterogeneous nucleation. The basic idea is that a spherical cap (i.e. a part of a sphere) develops on a surface and serves as the critical nucleus.

a) As a preliminary to our investigation of heterogeneous nucleation, we first examine the equilibrium between a drop in contact both with a surface and the surrounding medium. The reason this is pertinent to our discussion of heterogeneous nucleation is that in that case we will consider a nucleus that forms on some surface and we will see that this enhances the nucleation rate. However, to understand this, we first need to understand the interfacial energies. One of the ways of measuring interfacial energies is by examining contact angles. Your job is to deduce the relation between contact angle and the three interfacial energies γ_{sl}, γ_{cl} and γ_{cs}. Basically, this requires you to fill in all of the details of what I did in class. To that end, write an expression for the total interfacial energy of the system assuming that the solid drop is a spherical cap. For an isotropic surface energy we could show that the spherical shape has the lowest energy, but we solve the simpler problem of optimizing the contact angle for fixed volume of solid. Begin by showing that the area of the solid-liquid contact is given by $A_{sl} = 2\pi r^2(1 - cos\theta)$ and that the area of the solid-catalyst contact is given by $A_{sc} = \pi r^2(1 - cos^2\theta)$. Next, show that the volume of the spherical cap is given by

$$V_{cap} = \frac{2}{3}\pi r^3(1 - \frac{3}{2}cos\theta + \frac{1}{2}cos^3\theta). \tag{1}$$

Now imagine that the total area of the catalyst is A_{tot}. Write an expression for the total interfacial energy, make sure that your result features all three of the interfacial terms. Use the volume constraint (i.e. we are trying to find the optimal θ for a given volume of the solid) to eliminate r from your expression for the energy and then minimize the energy with respect to θ

and show that the contact angle is given by

$$\gamma_{cl} = \gamma_{cs} + \gamma_{sl} cos\theta, \tag{2}$$

a result usually known as Young's equation. Note that there is a much simpler way to arrive at this result which is by balancing forces, but the energy argument is relevant to our study of heterogeneous nucleation.

b) We now consider the case in which the droplet being nucleated does so on a surface. The idea is to figure out the total free energy in this case. Using what you learned in part (a) of this problem, write down the relevant free energy for this case (now including the bulk energy term) and work out the critical radius at which nucleation takes place. Note that this result is the same as what we found earlier in the homogeneous case, however, the *volume* (or number of particles) associated with this nucleus is smaller than in the homogeneous case. Plot the number of particles in the critical nucleus as a function of the contact angle θ. Comment on the limits you are examining and in particular, give a qualitative discussion of why the heterogeneous case leads to easier nucleation than the homogenous case. Also, find an expression for the activation energy both for the heterogeneous and homogeneous problems and comment on the relative rates of heterogeneous and homogeneous nucleation. What I am talking about here is examining ΔG_{max} (i.e. the height of the bump in the ΔG vs. r curve) for both the homogeneous and heterogeneous nucleation problems.

3. Mechanics of Thin Films: Part 1.

Another setting within which we will be writing down elastic free energies and using ideas like strain is in the evaluation of thin films and their instabilities. I already mentioned in class that in many circumstances one material is deposited on a second material which is known as the substrate. Often, there is a mismatch in equilibrium lattice parameter (i.e. the spacings between atoms) between the substrate and the deposited material. Consider a substrate with lattice parameter a_{Si}, the lattice constant for Si. For simplicity, assume that the crystal is a cubic crystal and we are adding more atoms onto one of the (001) faces. Now, assume that the *equilibrium* lattice parameter of the deposited atoms is given by $a_{Si_xGe_{1-x}} = xa_{Si} + (1-x)a_{Ge}$, where x reveals the relative proportion of Si and Ge in the deposited atoms. Also, note that the lattice parameters of Si and Ge are $a_{Si} \approx 5.43\AA$ and $a_{Ge} \approx 5.65\AA$. The approximation we have used to find the equilibrium lattice parameter of the SiGe is sometimes referred to as Vegard's law. Compute the strain in the SiGe layer assuming that it is deposited epitaxally on the Si substrate (i.e. the SiGe is unhappy because it does *not* have its equilibrium spacing, but rather that of the underlying Si substrate). Basically, use the strain that I discussed in class. Then, repeat the entirety of the derivation of the strain energy of the homogeneous state that I gave in class. In particular, show that the choice of C_{ijkl} for an isotropic material leads to the strain energy density claimed in class and then plug in your results for the strains and simplify the results so as to obtain the result I derived.

4. Poisson-Boltzmann revisited.

In class I considered the arrangement of charges in solution in the presence of a charged plane. In this problem, you will probe that problem more deeply.

(a) Repeat the entirety of the derivation given in class resulting in the end in expressions for $\phi(x)$, $n_+(x)$ and $n_-(x)$. Make plots of all of these functions for reasonable choices of areal charge density on the plate (i.e. one charge per molecule for tethered molecules or something like that) and for the concentration of salt in solution. Make sure you carefully explain issues such as the signs of quantities appearing in exponentials, the signs in front of the exponentials. Also, when you plot the densities, make sure that you use the linearized version of the theory (i.e. expand the exponentials of the form $e^{-e\phi(x)/kT}$). Note that because the potential itself is exponential, the charge densities will also decay exponentially.

(b) Add up all the charges in solution by integrating $n_+(x)$ and $n_-(x)$ and show that the charges in solution exactly compensate for those on the plane. Make sure you discuss everything you do in obtaining the result and that you interpret it.