Lab 1: Empirical energy methods

Due date 2/24/2005

Problem 1 (15 points): Lattice constants and energies.

In this problem, we look at relaxation and total energies.

In experiments, a crystal structure in equilibrium is automatically at its correct lattice parameter, which is also the lowest energy configuration. In calculations, we know neither the equilibrium lattice parameter nor the lowest energy configuration beforehand. In calculations, we pick an initial configuration (unit cell, atom positions), and then find the equilibrium (lowest energy) configuration. This is called "relaxation". There are two types of relaxations. The first type is unit cell relaxations; the second type is atomic positions relaxations. To find the lowest energy geometry, both unit cell and atomic positions must be fully "relaxed".

A. Calculate the lattice constant and total energy (in eV) for FCC Au. This calculation will be done with the supplied Lennard-Jones potential (input file gulp1a.in). Determine the result in two different ways.

1) By using the minimizer in GULP, which performs relaxations automatically. Make sure the **opti** flag is set in the first line of the gulp file.

2) By plotting the energy for a few lattice parameters near the equilibrium lattice parameter. Edit the gulp input file so that **opti** is replaced by **single**. Then, you will need to manually edit the unit cell parameters in the gulp input file (after the keyword **cell**).

B. Repeat this calculation using the supplied EAM potential (input file gulp1b.in).

C. How do the EAM and LJ lattice constants compare with experiments (the experimental lattice parameter for Au is 4.08? Is this expected? Why or why not? The energies for the two calculations (1a and 1b) will be different. Comment on this.

Problem 2 (30 points): Compute the vacancy formation energy in FCC Au.

In this problem, we will look at many of the issues involved in total-energy calculations. We will look at supercell convergence, effect of relaxations, and shortcomings of potentials.

The vacancy formation energy of a crystal, $E_{f,vacancy}$, is given by the cost of removing an atom and putting it in the bulk.

$$E_{f,vacancy} = E_{cell\,with\,(n-1)\,atoms\,on\,n\,sites} - \frac{n-1}{n} * E_{perfect}$$

where n is the number of sites in the supercell.

A.   Compute the vacancy formation energy for Au using the Lennard-Jones potential provided.

Compute the vacancy formation energy as a function of different supercell sizes (you can pick which ones). Use the supercell builder provided (called **buildcell**). Do not relax your cell after you take out the atom (make sure **single**, not **opti**, is at the top of your gulp input file). What is the ratio of the vacancy formation energy to the cohesive energy? Is this what you would expect?

B.   Repeat these calculations, but this time relax the cell after removing the vacancy (make sure **opti**, not **single**, is set in your gulp input file). How does the vacancy formation energy change compared with nonrelaxed calculations?

C.   Compute the vacancy formation energy using the EAM potentials provided. Do it as accurately as you can. Use what you learned in parts A and B. You can do it any way you like, but show work.

D.   How do the "final" answers from part A and part B compare? The experimental vacancy formation energy for Au is 0.9 eV. Comment on your results, in light of the agreement in problem 1.

Problem 3 (45 points):

A. Compute the surface energy of a solid (100) surface of FCC Au using the LJ potential. How you do this is up to you, but remember the issues of supercell size and relaxations. In your answer, make sure to write down the formula you use. Hint 1: Think hard about what dimension supercell you use, keeping in mind periodic boundary conditions. Do not make your calculations take longer than required. Hint 2: There are two size convergence issues to think about. Again, think about periodic boundary conditions. Give your answer in eV/Angstroms^2.

B. Compute the surface energy of a solid (100) surface of FCC Au using the EAM potential. How you do this is up to you, but remember the issues of supercell size. In the interests of time, you can skip relaxations.

Problem 4   Short answer (5 points):

When using potentials, the choice of potential is important. In this problem set, we used the Lennard-Jones and EAM energy methods. For what other types of problems would you use Lennard-Jones potentials? When would you use EAM? When would neither be appropriate?

Problem 5   Short answer (5 points):

Given the incredibly simple form of the Lennard-Jones potential, why use computers to solve what at first glance appears to be a pencil-and-paper type problem? The following exercise should clarify the issue as well as provide some insight as to why central-force pair potentials usually show outward surface relaxations.

Calculate the distance where the Lennard-Jones potential,

$$U_{I,J} = \frac{A}{r^{12}} - \frac{B}{r^6} \quad .$$

reaches the minimum value (i.e. express r_0 in terms of A and B). Plug in the values of A and B given for the Au Lennard-Jones potential and compare the result with your answer in Problem 1. Explain any discrepancies.

Extra credit question (but longer and harder, OPTIONAL!) (10 points):

For FCC Au, calculate C11, C12, and C44 using the EAM method. To do this, you will need to compute the energetics of deformation, and fit the resulting energy curves.