

Lab 1: Assignment

Empirical energy methods

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 position relaxations. To find the lowest energy structure, both unit cell and atomic positions must be fully “relaxed”.

- A. Calculate the lattice constant and total energy (in eV) for FCC Cu. 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 `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**).

$$a_0 = 3.616817 \quad E = -0.92970444 \text{ eV}$$

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

$$a_0 = 3.619070 \quad E = -13.68463759 \text{ eV}$$

- C. How do the EAM and LJ lattice constants compare with experiments (the experimental lattice parameter for Cu is 3.61)? Is this expected? Why or why not? The energies for the two calculations (1A and 1B) will be different. Comment on this.

The lattice constants both agree well with experiments. This is expected, as both potentials are fitted to experiments. The energies are very different. This is fine – different energy methods will give different energies. The important thing is *differences* between structures within a single energy method.

Problem 2 (40 points): Compute the vacancy formation energy in FCC Cu.

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_{vacancy} , is given by the cost of removing an atom and putting it in the bulk.

$$E_{\text{vacancy}} = E_{\text{cell with } n-1 \text{ atoms and } n \text{ sites}} - (n-1)/n * E_{\text{perfect}}$$

where n is the number of sites in the supercell.

A. Compute the vacancy formation energy for Cu 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 your `gulp` input file). What is the ratio of the vacancy formation energy to the cohesive energy? Is this what you would expect?

6x6x6:

$$E_{\text{vacancy}} = -200.35130683 - (863/864) * -200.81615837 = 0.232425 \text{ eV}$$

The ratio is 1:1, as you'd expect from LJ potentials. This is a limitation of pair potentials and can be rationalized by counting the broken-pair bonds.

- 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?

1x1x1:

$$E_{\text{vacancy}} = -0.49676348 - (3/4) * -0.92970444 = 0.200515 \text{ eV}$$

3x3x3:

$$E_{\text{vacancy}} = -24.63721344 - (107/108) * -25.10201980 = 0.23238 \text{ eV}$$

6x6x6:

$$E_{\text{vacancy}} = -200.35130683 - (863/864) * -200.81615837 = 0.232425 \text{ eV}$$

In this case, there is no difference between relaxed and unrelaxed calculations. However, most of the time relaxations are very important! You should always include relaxations in your 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.

1x1x1:

$$E_{\text{vacancy}} = -9.45046689 - (3/4) * -13.68463759 = 0.813011 \text{ eV}$$

3x3x3:

$$E_{\text{vacancy}} = -365.16769438 - (107/108) * -369.48521484 = 0.896361 \text{ eV}$$

5x5x5:

$$E_{\text{vacancy}} = -1706.29083089 - (499/500) * -1710.57969832 = 0.867708 \text{ eV}$$

6x6x6:

$$E_{\text{vacancy}} = -2951.59285415 - (863/864) * -2955.88171869 = 0.867705 \text{ eV}$$

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

The answers are different, even though lattice constants agree. The answer from the EAM potential agrees much better with experiments. The failure of the LJ potentials is expected : the Lennard-Jones potentials were fit to lattice constants but not anything else.

This problem shows you have to be careful: If you try to use your potential for something it is not fitted for, you can get into trouble!

Problem 3 (40 points):

- A. Compute the surface energy of a solid (100) surface of FCC Cu using the LJ potential. How you do this is up to you, but remember the issues of supercell size and relaxations. Hint 1: Think hard about which dimension supercell you use, keeping in mind periodic boundary conditions. Do not make your calculations take longer than is required. Hint 2: There are two size convergence issues to think about. Again, think about periodic boundary conditions.

Surface energy = (energy of slab with vacuum- energy of bulk slab, normalized to size of slab with vacuum)/surface area/2

(factor of 2 for 2 surfaces created)

The two size convergence issues are the size of the vacuum, and the size of the slab (bulk). You have to make sure the slab does not “see” the other slab, and that deep inside the slab, the atoms are the same as the bulk. Both can be taken care of by using big supercells, with big vacuum layers.

All cells are taken as Nx1x1, to best test the convergence with respect to vacuum size and slab size. Taking NxYxZ (where Y and Z are larger than 1) would take a lot more computing time.

All supercells are 50x1x1

RELAXED:

$$\begin{aligned} \text{E}_{\text{surface, 5 layers removed (2.5 cell)}} &= \\ & (-43.75366967 - (190/200) * -46.4852218) / (3.61 * 3.61 * 2) = \\ & \mathbf{0.0156265 \text{ eV/\AA}^2} \end{aligned}$$

$$\begin{aligned} \text{E}_{\text{surface, 10 layers removed (5 cell)}} &= \\ & (-41.42584049 - (180/200) * -46.4852218) / (3.61 * 3.61 * 2) = \\ & \mathbf{0.0157634 \text{ eV/\AA}^2} \end{aligned}$$

$$\begin{aligned} \text{E}_{\text{surface, 12 layers removed (6 cell)}} &= \\ & (-40.96082194 - (178/200) * -46.4852218) / (3.61 * 3.61 * 2) = \\ & \mathbf{0.0157634 \text{ eV/\AA}^2 = 0.0157697 \text{ eV/\AA}^2} \end{aligned}$$

- B. Compute the surface energy of a solid (100) surface of FCC Cu 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.

Relaxed:

$$\begin{aligned} \text{E}_{\text{surface, 5 layers removed (2.5 cell)}} &= \\ &= \frac{(-641.44628198 - (188/200) * -684.23187933)}{(3.61 * 3.61 * 2)} = \\ &= 0.0664392 \text{ eV/\AA}^2 \end{aligned}$$

$$\begin{aligned} \text{E}_{\text{surface, 10 layers removed (5 cell)}} &= \\ &= \frac{(-614.07719064 - (180/200) * -684.23187933)}{(3.61 * 3.61 * 2)} = \\ &= 0.0664321 \text{ eV/\AA}^2 \end{aligned}$$

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 the EAM? What would neither be appropriate?

(Answers may vary)

Lennard-Jones potentials are best used in systems with fluctuating dipoles (because of the $1/r^6$ term) and fluctuating dipoles *only*. Thus, they are often used to simulate noble gases (such as Ar or Ne). They can also be used to make very rough qualitative studies. In addition, the terms in the LJ potential have simple physical interpretations. By changing the potential parameters, you can study a model system as a function of atomic “size”, or bond strength. EAM potentials are generally used in metallic systems. Neither is appropriate for oxides or semiconductors. Neither is appropriate if you need electronic information (such as a band structure).

Extra credit question (but longer and harder, OPTIONAL!) (40 points):

For FCC Cu, 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.