

## MatSci 331 Homework 1

Pair potentials, embedded atom potentials, total energy, and vacancies.

Due Friday, Jan 18 at 5pm in Durand 110.

Evan Reed

### 1 Lennard-Jones potential with a cutoff

Consider the Lennard-Jones potential with a cutoff,

$$V(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] - 4\epsilon \left[ \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^6 \right], & r < r_c \\ 0, & r \geq r_c \end{cases} \quad (1)$$

where  $r_c$  is between the first and second nearest neighbor distances.

1. Calculate the total energy as a function of nearest neighbor distance for a face-centered cubic lattice, body-centered cubic lattice, and diamond lattice.
2. Which of these three phases would you most expect to observe in experiments at atmospheric pressures and low temperatures?
3. Could you describe the relative energies of the silicon diamond lattice and fcc lattice with this potential using an appropriate choice of  $\sigma$  and  $\epsilon$ ?
4. Now consider the full Lennard-Jones potential without a cutoff,  $r_c \rightarrow \infty$ . The total energy for a perfect crystal with  $N$  atoms can be written,

$$E_{tot} = \frac{1}{2}N(4\epsilon) \left[ \sum_j \left( \frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left( \frac{\sigma}{p_{ij}R} \right)^6 \right] \quad (2)$$

where  $p_{ij}R$  is the distance between an atom  $i$  and another atom  $j$  and  $R$  is the nearest neighbor distance. Note that the sum is only over atoms  $j$  rather than pairs.

The summations can be evaluated for a given crystal structure. For the fcc structure,

$$\sum_j p_{ij}^{-12} = 12.13188 \quad (3)$$

$$\sum_j p_{ij}^{-6} = 14.45392 \quad (4)$$

and for the body-centered cubic structure,

$$\sum_j p_{ij}^{-12} = 9.11418 \quad (5)$$

$$\sum_j p_{ij}^{-6} = 12.2533 \quad (6)$$

Using these lattice sums, calculate the equilibrium nearest neighbor distances  $R_0/\sigma$  by setting  $\frac{dE_{tot}}{dR} = 0$ . How does this compare to the nearest neighbor distance for the nearest neighbor potential above?

5. Calculate the ratio of cohesive energies for the fcc and bcc structures. The cohesive energy in this case is the energy per atom required to increase the lattice constant to infinity.
6. What is this ratio using the energies from the nearest-neighbor model above?
7. Based on these comparisons, can you say anything about how important longer range interactions (beyond nearest neighbor) are in van der Waals solids?
8. The experimentally observed low temperature crystal structure of Ne, Ar, Kr, and Xe is face centered cubic. How does this compare with your calculation?

## 2 Morse potential fit

Consider the Morse potential,

$$V(r) = \epsilon \left[ e^{2a(r_e - r)} - 2e^{a(r_e - r)} \right] \quad (7)$$

1. Determine the three empirical parameters:  $a$ ,  $\epsilon$ , and  $r_e$  for fcc Cu. Assuming only nearest-neighbor interactions for simplicity, fit this potential to the cohesive energy  $E_{coh} = 336$  kJ/mol, the fcc Cu equilibrium lattice parameter  $a_0 = 0.361$  nm, and the bulk modulus  $B \equiv V_0 \frac{d^2 E_{tot}}{dV^2} |_{V_0} = 134.2 \times 10^9$  Pa. The equilibrium volume is  $V_0$ . Write your fit parameters using units of eV and Angstroms.

2. Make a plot of the potential. Does it look reasonable? Describe the origin of the dominant features.
3. Suppose that you have some experimental measurements of vibrational frequencies of the fcc crystal. How could you include those numbers into this model potential? What might that do to the model prediction for lattice parameter, cohesive energy, and bulk modulus?

### 3 Environment-dependent pair interactions from EAM potentials

Effective pair potentials can be calculated within the the embedded-atom formalism. The effective pair potentials can be shown to depend on the local atomic environment, e.g. surface atoms, bulk atoms, or atoms around crystal defect. Starting with the embedded atom total energy of the form,

$$E_{tot} = \frac{1}{2} \sum_{i,j} \phi(r_{ij}) + \sum_i F(\rho_i) \quad (8)$$

$$\rho_i = \sum_{j \neq i} \rho_j^a(r_{ij}) \quad (9)$$

1. Taylor expand the functional term by considering density variations  $\delta\rho$  about a reference density  $\rho_0$ . Show that to first order in  $\delta r_{ij}$ , the resulting expression for  $E_{tot}$  takes the form of a pair potential.
2. Now consider what the effective pair potentials are for two different environments: in a perfect crystal and next to a vacancy. Write the effective pair potential for a copper face centered cubic crystal (12-fold coordinated.) Assume the interactions are nearest-neighbor only.
3. Do the same for a copper atom next to a vacancy. For simplicity, assume there is no relaxation around the vacancy.
4. Are these two potentials the same (assume  $F(\rho)$  is nonlinear)? What does this mean?

### 4 1D Coulomb chain energy

Consider the energy of a 1D array of charged atoms interacting through a Coulombic potential,

$$E_{tot}(N) = \sum_{i=1}^N \sum_{j>i}^N \frac{q_i q_j}{r_{ij}} \quad (10)$$

Most materials are charge neutral, or close to charge neutral, so let's assume the charge on the atoms alternates in the array, i.e.  $q_j \equiv (-1)^j \tilde{q}$ .

1. Write a computer program that evaluates  $E_{tot}$  for a given  $N$ . Take the interatomic spacing  $R_0 \equiv 1$  and  $\tilde{q} \equiv 1$ . If you choose to use Matlab, you may find useful tutorials and examples at: [http://www.mathworks.com/academia/student\\_center/tutorials/launchpad.html](http://www.mathworks.com/academia/student_center/tutorials/launchpad.html).
2. What is the interatomic separation that gives the lowest energy in this model? Why?
3. The case of  $N \rightarrow \infty$  is the bulk limit, and the case of finite  $N$  is the nanoparticle or molecular limit. Nanoparticles often have properties that deviate from their bulk counterparts. This 1D problem is a (rare) case where an analytical solution exists for the infinite chain of atoms (bulk case):  $E_{tot}(N \rightarrow \infty)/N = -\frac{\tilde{q}^2}{R_0} \ln 2$ . You can check your code using this information. At what value of  $N$  is  $E_{tot}(N)/N$  converged to two significant figures? How about three significant figures?
4. What do your convergence calculations say about the maximum size of particle likely to exhibit deviation from bulk behavior?