

# MatSci 331 Homework 2

## Lennard-Jones vacancy concentration: Total energy calculations with periodic boundary conditions

Due Jan. 30 at the beginning of class.

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In this problem, you will write a computer program to calculate the energy of a vacancy in a Lennard-Jones face-centered cubic crystal. You will calculate forces on the atoms, establish an energy minimization algorithm, and explore the effect of computational cell size on the vacancy energy. Feel free to use a programming language that you are comfortable with. Matlab might be a good option if you are new to programming. You can access Matlab on Stanford's corn server (to log in from a unix prompt: `ssh -Xl <your suid> corn.stanford.edu`). See the additional information on the course website regarding the use of Matlab on corn. There are Matlab programs distributed on the class website that may help you get started. Sections of chapters 3 and 4 of Frenkel and Smit (available electronically) may be of use if you are looking for some additional guidance with this homework.

### 1 Set up computational cell

Following the example in class, write a code to set up a computational cell supercell consisting of  $L \times M \times N$  periodic copies of the fcc crystal. Use the cubic fcc unit cell as the primitive cell. The basis atoms for the cubic cell are located at (0,0,0), (0.5,0.5,0), (0,0.5,0.5), and (0.5,0,0.5) where relative coordinates are utilized. To get real space coordinates, multiply by the lattice constant,  $a$ . We will use the Lennard-Jones potential with a cutoff,

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

Note there is a discontinuity which is typically not desirable, leading to discontinuous forces. We'll use this form for simplicity in testing the code. We will use distance units of  $\sigma$  and energy units of  $\epsilon$ .

Assuming the cutoff  $r_c$  is set so that it only considers nearest neighbor interactions, what is the lattice constant  $a$  of the cubic fcc unit cell at minimum energy? Use this value throughout the remainder of your calculations.

## 2 Calculate total energy

Write code to calculate the total energy of the computational cell with periodic boundary conditions. For simplicity, loop over all atoms within the computational cell (1 to N)  $i$  and  $j$ , and  $x$ ,  $y$ , and  $z$  periodic copies of the computational cell  $\ell$ ,  $m$ , and  $n$ .

$$E_{tot} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{\ell=\ell_{min}}^{\ell_{max}} \sum_{m=m_{min}}^{m_{max}} \sum_{n=n_{min}}^{n_{max}} V(|\vec{r}_i - \vec{r}_j + \ell La\hat{x} + mMa\hat{y} + nNa\hat{z}|) \quad (2)$$

The values of  $\ell_{max}$ ,  $m_{max}$  and  $n_{max}$  should be large enough that  $\ell_{max}La > r_c$ ,  $m_{max}Ma > r_c$ ,  $n_{max}Na > r_c$ . You may want to write some code that sets  $\ell$ ,  $m$  and  $n$  to satisfy this condition so you don't have to think about it. Set  $\ell_{min} = -\ell_{max}$ , etc. The expression for  $E_{tot}$  above includes unphysical atomic self-interaction terms which need to be omitted when using a LJ potential - you will need to write some code to accomplish this.

Tip: There are more efficient ways to evaluate the total energy summation, but you may find it most useful to write the code in a fashion that is the most simple and least likely to contain errors, i.e. a brute-force evaluation of the sums above. Such an approach is likely to lead to slow, inefficient code, but you can speed it up later once you get it working.

1. To check your total energy calculation code, evaluate the total energy per atom for the fcc crystal with  $r_c$  chosen such that only nearest neighbor interactions are considered, e.g.  $r_c = 1.3$ . Is this value what you expect? Test this calculation for multiple values of L, M, and N.
2. Now increase  $r_c$  to 3. What is the total energy in this case? Why is it different?

## 3 Calculate forces

1. Calculate the analytical expression for the forces on the atoms for the LJ potential above. Note that the force is ill defined at  $r_c$ . This is problematic for MD simulations but will be ok for our purposes here.
2. Write some code to calculate the force on each atom. It may be computationally least expensive to put this code within your energy loop since some of the terms used to calculate the energy are similar to those used to calculate the forces. However, do what is organizationally most simple and easy to track down errors.
3. Calculate the forces on the atoms with  $r_c = 1.3$ . Are these what you should expect?
4. What happens to the forces when you change the lattice constant? Why?

## 4 Make a vacancy

1. Remove an atom from the crystal to create a vacancy. Calculate the total energy with  $r_c = 1.3$ .
2. Convince yourself that the vacancy energy is given by,

$$E_{vac} = E_{tot}(N - 1) - \left( \frac{N - 1}{N} \right) E_{tot}(N) \quad (3)$$

Here  $E_{tot}(N)$  is the energy of the perfect crystal with  $N$  atoms,  $E_{tot}(N - 1)$  is the energy of the  $N - 1$  atom crystal with vacancy.

3. What is the vacancy energy for  $r_c = 1.3$ ?
4. How does the vacancy energy compare with the perfect crystal energy per atom you calculated above for this cutoff value? Is this consistent with the ratio of cohesive energy to vacancy energy we calculated for a pair potential in class?
5. Calculate the forces on the atoms in the vacancy case. Is this what you expect? What would happen if you minimize the energy with respect to atom positions around the vacancy?
6. Calculate the vacancy energy with  $r_c = 3.0$  for a series of  $L$ ,  $M$ , and  $N$  values from 1 and up to determine the converged value. If we want to calculate the energy of an isolated vacancy, it is necessary to do this for a computational cell size sufficiently large that the vacancies don't interact with each other.
7. With  $r_c = 3.0$ , how are the forces qualitatively different from the case of  $r_c = 1.3$ ? Why?

## 5 Minimize the energy with respect to atom positions

1. Now allow the atoms to move in response to the forces. Write a code that implements a steepest descent algorithm to minimize the energy of the system with respect to atomic positions. Use the looping approach discussed in class. Initially, use a value of  $\alpha = 1E - 3$  and a force tolerance of  $1E - 2$ .

Tip: As a check on the veracity of your forces, the total energy should go down on each iteration in the limit of small  $\alpha$ . If your total energy goes up, try decreasing  $\alpha$  and check that your forces are correct.

2. As in the previous problem, compute the vacancy energy as a function of computational cell size. How big does the cell need to be for the energy to be converged?

3. Run the same calculation with a 5% decrease in the lattice vector length, e.g. use  $0.95a$  as the lattice vector. This corresponds to a new volume of  $0.95^3 V_0$  where the material is under pressure. How big does the computational cell need to be now to get a converged vacancy energy *without* atomic relaxation?
4. How much does the vacancy energy change when the atoms are allowed to relax under pressure? How do these results differ from the unstrained computational cell case?
5. Compute the ratio of the converged vacancy energy to the cohesive energy and compare to the values of around 0.3 that are observed for metals.
6. Do you think that relaxation of the atoms can account for the discrepancy in this ratio between pair potentials and metals discussed in class?

## 6 Calculate the vacancy concentration

For Argon, Lennard Jones parameters are  $\epsilon = 1.67 \times 10^{-14}$  ergs and  $\sigma = 3.4 \times 10^{-8}$  cm. Take the concentration of vacancies per site in the crystal to be approximated by

$$n \approx e^{\frac{-E_{vac}}{kT}} \quad (4)$$

1. For Argon at  $T = 20$  K, what do you expect the vacancy concentration to be for the case of the compressed lattice above?
2. What is the approximate minimum size of such a crystal in which you would expect to see a single vacancy?
3. How big is the impact of atomic relaxation on the equilibrium vacancy concentration?

## 7 Appropriate choice of $\alpha$

1. Experiment with the value of  $\alpha$ . What happens if you make it too big? What happens if it is too small?
2. Put an interstitial into your computational cell by placing an extra atom at, e.g. position (0.5,0.5,0.5) in one of the conventional cubic unit cells (octahedral interstice). Does the optimal value of  $\alpha$  depend on the initial arrangement of atoms?