HOMEWORK 5: LATTICE STATICS
Due electronically April 4 at midnight

In this homework, you will build on the lattice sums code that you developed in Group Exercise 3-0 to explore the properties of FCC crystals and how they depend on simulation parameters. For this assignment, you will need:

- **statics.py**: python file where you will implement the lattice statics code
- **GE3-0.py**: python file from Group Exercise 3-0
- **fcc1.npy, fcc2.npy, fcc3.npy, fcc4.npy, fcc5.npy**: numpy files containing lists of atomic positions (xyz triplets) for NxNxN FCC unit cells (e.g. **fcc2.npy** is for 2x2x2 unit cells). Note that the atomic positions are normalized so that the system size is always 1x1x1 in dimensionless length units.
- For general clarification questions, please ask publicly on Piazza. For private questions about the specifics of your code, please email your code to the TA's.

0. (4 pts) Turn in the tables you filled out for Group Exercise 3-0.

1. (4 pts) Implement the Lennard-Jones interatomic potential and the lattice sums from the Group Exercise as directed in the prompts in **statics.py**. Use the Lennard-Jones equation of the form

$$\phi_{LJ}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

Turn in your completed **statics.py** file with your solutions filled in.

- You may verify your code for a 2x2x2 unit cell system, using $\varepsilon = 0.9$, $\sigma = 1.1$, $a = 1.70$, and $r_c = 1.01a$. The non-periodic lattice sum should return potential energy $U = -105.9984$, and the periodic lattice sum should return $U = -179.3014$. (Note: used minimum image convention here, even though $r_c > aN_{cell}/2$.)

2. (4 pts) The difference between the non-periodic and periodic lattice sums represents the energy of the unfulfilled atomic bonds at the free surfaces of the non-periodic system, i.e. the surface energy. For a 3x3x3 unit cell system using $\varepsilon = \sigma = 1$, $a = 1.41$, and $r_c = 1.01a$, calculate and report the average surface energy per unit area, γ. Does the sign of the surface energy make sense?

3. (4 pts) Now we will use lattice statics (a.k.a. molecular statics) to calculate the equilibrium thermodynamic properties of a Lennard-Jones crystal. Again, we will use parameters $\varepsilon = \sigma = 1$ and a cutoff radius $r_c = 1.01a$, where a is the lattice parameter. For a periodic 3 x 3 x 3 lattice of FCC unit cells, starting from a lattice parameter $a = 1.4$, systematically vary the lattice parameter in increments of $\Delta a = 0.01$, and calculate the internal energy. Report the T = 0K equilibrium lattice parameter a_0 and the internal energy U_0. (U_0 will be the minimum internal energy, and a_0 will be the lattice parameter corresponding with the minimum internal energy.) Note: You do not need to turn in your lattice statics code.

- You may verify your code for a periodic 2x2x2 unit cell system, using $\varepsilon = 0.9$, $\sigma = 1.1$, $a = 1.4$, and $r_c = 1.01a$. You should find $a_0 = 1.74$ and $U_0 = -183.0477$. (Note: used minimum image convention here, even though $r_c > aN_{cell}/2$.)

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4. Both the potential energy cutoff radius r_c and the system size (number of atoms, N_{atom}) can alter the results of atomistic simulations, so in this problem we will use lattice statics to explore those effects.

(a) (4 pts) For a 3 x 3 x 3 FCC Lennard-Jones crystal with $\varepsilon=\sigma=1$, determine the T = 0K equilibrium properties as a function of r_c. Use cutoff radii corresponding to the first, second, third, fourth, and fifth neighbor distances. Use lattice statics to calculate and plot the equilibrium lattice parameter a_0 and the cohesive energy per atom $u = U_0/N_{atom}$ as a function of r_c. Do the values seem to be converging? Recommend a minimum cutoff distance r_c to ensure accurate property determination.

(b) (4 pts) Now set the cutoff distance r_c to your recommended value, and vary the system size from $N = 1$ to 5 unit cells per side. Plot the equilibrium lattice parameter a_0 and the cohesive energy per atom $u = U_0/N_{atom}$ as a function of system size. Do the values seem to be converging? Recommend a minimum system size $NxNxN$ unit cells to ensure accurate property determination.

5. Now we will exercise the lattice statics framework to investigate defect energies. Based on the results of question 4, we will use a periodic 3x3x3 lattice of FCC unit cells with four neighbor shells ($r_c = 1.01*a*\sqrt{2}$). The equilibrium lattice constant of the perfect crystal $a_0 = 1.55$ and the potential energy $U_0(N_{atom}) = -850.9422$.

(a) (4 pts) Create a vacancy by removing a single atom from your system. (It can be any atom; they are all the same.) Recalculate and report the equilibrium lattice parameter a_0 and potential energy $U_0(N_{atom} - 1)$. Does creating a vacancy increase or decrease the total system energy? Why?

(b) (2 pts) Report the vacancy formation energy, which is the difference between the potential energy of the perfect and imperfect crystals, appropriately scaled:

$$U_{VF} = U_0(N_{atom} - 1) - \left(\frac{N_{atom} - 1}{N_{atom}}\right) U_0(N_{atom})$$

In question 4, you calculated the potential energy per atom in the perfect crystal u. Explain the magnitude of the vacancy formation energy in terms of u.

(c) (2 pts) You should have discovered that a_0 does not change when a vacancy is created. Explain.

(d) (3 pts) I have some bad news for you. The vacancy energy you calculated doesn't match the experimentally measured value. Give three reasons why this doesn't surprise you.

(e) (4 pts) Starting again from the perfect crystal, create an interstitial by inserting an atom at an octahedral site [e.g. the body center site (0.5,0.5,0.5)]. Recalculate and report the equilibrium lattice parameter a_0, the potential energy $U_0(N_{atom} + 1)$, and the interstitial formation energy U_{IF} (defined similarly to U_{VF} above). Does creating an interstitial increase or decrease the total system energy? How does the magnitude of the interstitial formation energy compare to the vacancy formation energy? Does that make sense physically?

(f) (2 pts) You should have discovered that a_0 changes when an interstitial is created. Explain.