

# PSet 2: Lattice Sums, Part 1

## Solutions

Attached is the following code that was used in this problem set

1. `make_latt.py`: make FCC and BCC lattice
2. `lat_sum.py`: lattice sum routines, modifications 1-5
3. `PS2-*.py`: code for generating plots corresponding to homework problems

### 1 Exercise 1: Simulate lattice sum of FCC cell with Lennard-Jones Potential

This is already implemented in the code given. Relevant lattice sum codes include are `lat_sum#` for  $\# = 1, 2, 3, 4, 5$ .

1. `lat_sum1`  $\rightarrow$  naive implementation of lattice sum with double counting
2. `lat_sum2`  $\rightarrow$  more efficient indexing without double counting
3. `lat_sum3`  $\rightarrow$  implementation with cutoff interaction
4. `lat_sum4`  $\rightarrow$  alternate with periodic boundary conditions
5. `lat_sum5`  $\rightarrow$  periodic boundary conditions using cutoff (e.g., for minimum image convention)

Running these codes, one finds that all implementations of the lattice sums result in the same numerical answer. For small cells, the gain in efficiency is negligible. We use `latsum5.m` and assume the minimum image convention.

### 2 Exercise 2: Equilibrium parameters for FCC

To find the minimum equilibrium energy and lattice parameter, we vary the lattice parameter for a fixed cutoff energy. Figure 1 shows the energy calculated for a relatively small cell consisting of 3 repeating units in the three cartesian directions. For the purposes of these simulations,  $\epsilon = \sigma = 1$ .

These parameters correspond to a minimum energy/atom: -7.8802 and equilibrium lattice constant: 1.553

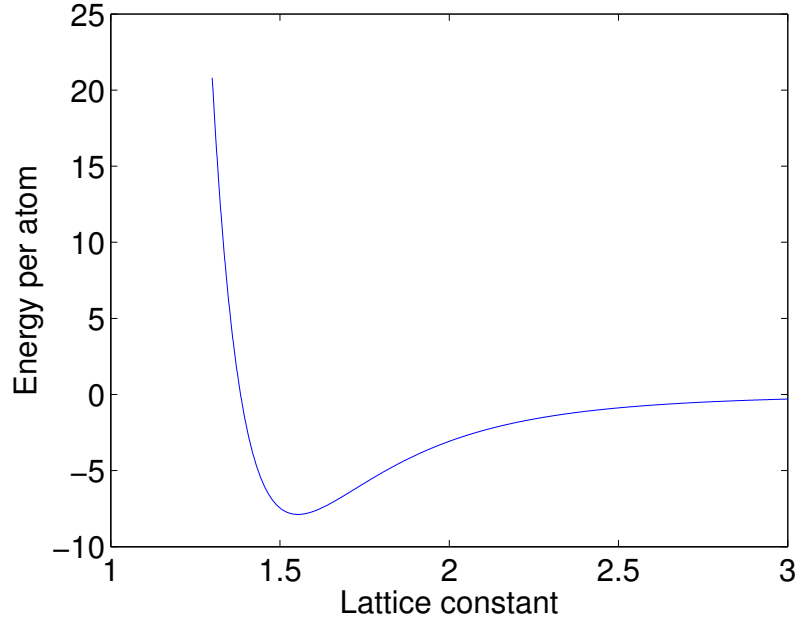


Figure 1: Energy landscape as a function of lattice parameter for lattice sum of FCC lattice;  $n = 3$  repeating units in each cartesian direction.

### 3 Exercise 3: Convergence with cutoff for FCC

We test the accuracy of our choice of simulation by testing the radius cutoff used. The convention used is the minimum image convention with periodic boundary conditions, in which the cutoff distance is taken to be less than or equal to half the size of the simulation cell. For convenience, we take the cutoff distance to be half the size of simulation cell and modulate the size of the simulation cell.

We plot the change in energy with respect to cutoff for a fixed lattice size. This is demonstrated in Figure 2, which plots the convergence of energy per atom with respect to the number of nearest neighbors. For the FCC lattice, the nearest neighbor distance is  $\frac{a_0}{\sqrt{2}}$ . The effective nearest neighbors taken into consideration for the interaction cutoff radius is found from the quotient of the cutoff with nearest neighbor distance.

As seen in Figure 2, it requires on the order of 5 repeating FCC unit cells (i.e., around 4 neighbor shells) to sufficiently begin to capture the long range interactions between all atoms, though larger simulation cells would be needed to capture the correct minimum energies.

Table 1 illustrates the numerical convergence of lattice parameter and energy per atom for different cutoffs. Though the equilibrium lattice constant converges quickly within tens of unit cells, simulations cells on the order of 150 unit cells are needed for proper convergence for the equilibrium energy.

The infinite lattice sum for the FCC lattice has been computed, and is a useful reference for the error in interaction cutoff. In assuming  $\epsilon = \sigma = 1$ , the Lennard-Jones potential takes the form

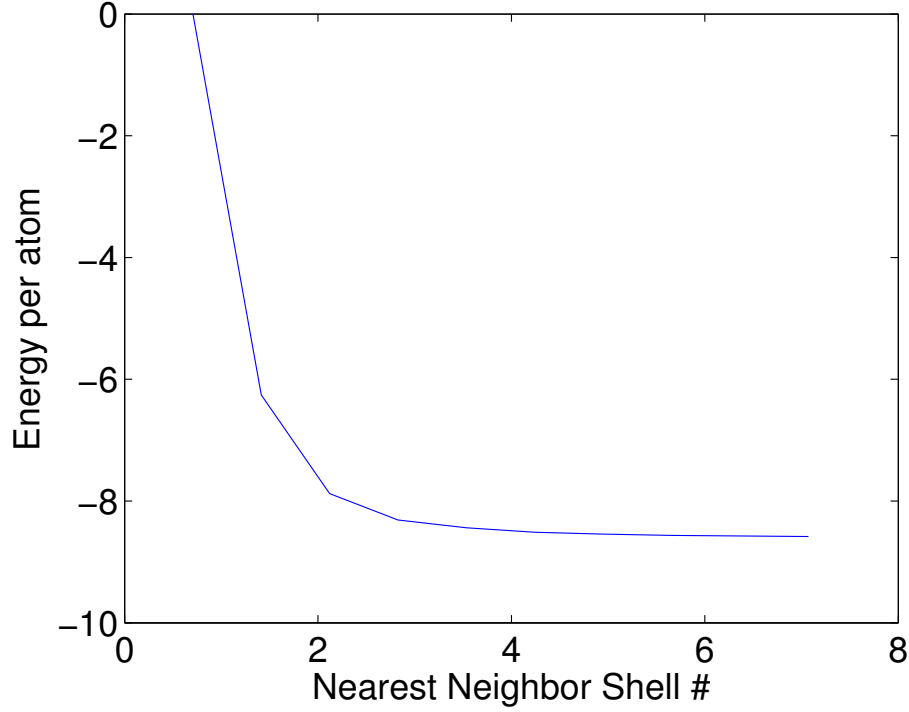


Figure 2: Convergence of energy per atom for LJ potential in FCC lattice with respect to nearest neighbor shells, using  $a_0 = 1.55$

$$U_{cell}(r) = 4\left(\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^6\right). \quad (1)$$

For an infinite lattice, the lattice sum comes to be

$$u_{atom}(r) = \frac{U(r)}{N_{atom}} = 2\left(A_{12}\left(\frac{1}{r_{nn}}\right)^{12} - A_6\left(\frac{1}{r_{nn}}\right)^6\right). \quad (2)$$

For an FCC lattice,  $A_{12} = 12.1318$  and  $A_6 = 14.4539$ . With the calculated equilibrium lattice constant  $a_0 = 1.54$  (i.e.  $r_{nn} \approx 1.0903$ ),  $u_{atom} \approx -8.6362$ . This is approximately an error of 0.0382 when compared to the largest cutoff tested; a larger simulation cell would be needed for better precision.

Table 1: Convergence of lattice parameter and energy per atom for FCC atom using LJ potential; all cutoffs are half the simulation cell size;  $\infty$  cutoff is theoretical value

Cutoff (rcs, in units of $a_0$ )	Equil. Lattice constant	Equil. Energy per atom	$\Delta$ Energy
1	1.587	-1.4999	—
1.5	1.553	-7.8802	-6.3803
2.5	1.544	-8.4424	-0.5522
3.5	1.543	-8.5492	-0.1068
5	1.542	-8.5905	-0.0413
6	1.542	-8.5980	-0.0075
$\infty$	—	-8.6362	error $\approx$ -0.0382

## 4 Exercise 4: Comparison with BCC lattice

We next simulate the LJ potential using the BCC lattice. A similar summary to the FCC lattice for the BCC lattice is presented below.

For 3 repeated unit cells in the three cartesian directions, we obtain a minimum energy of -6.8472 and corresponding equilibrium lattice constant of 1.253, as seen in Figure 3.

It takes around 7 repeated units cells (i.e., 7 x 7 x 7 simulation cell) or around 4 nearest neighbor shells to begin to converge in energy.

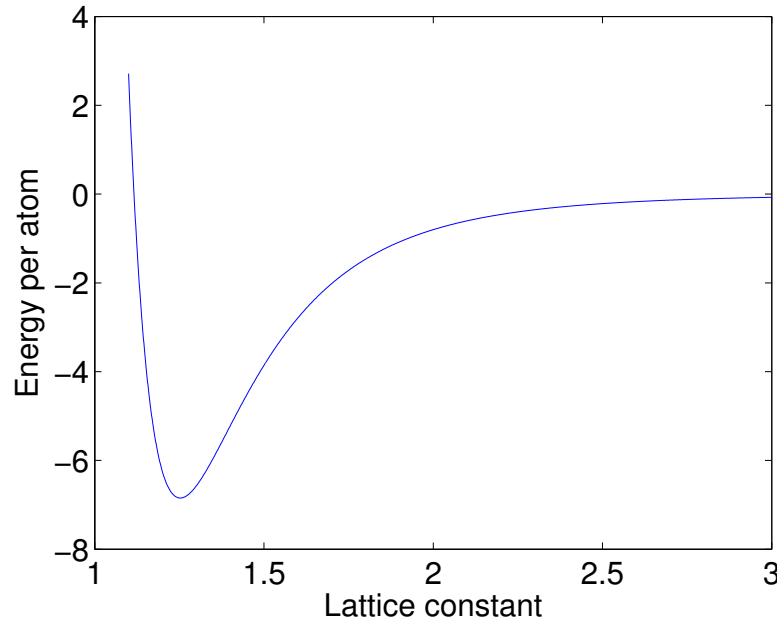


Figure 3: Energy landscape as a function of lattice parameter for lattice sum of BCC lattice;  $n = 3$  repeating units in each cartesian direction.

As the equilibrium energy for BCC more positive than that of FCC, it is less stable.

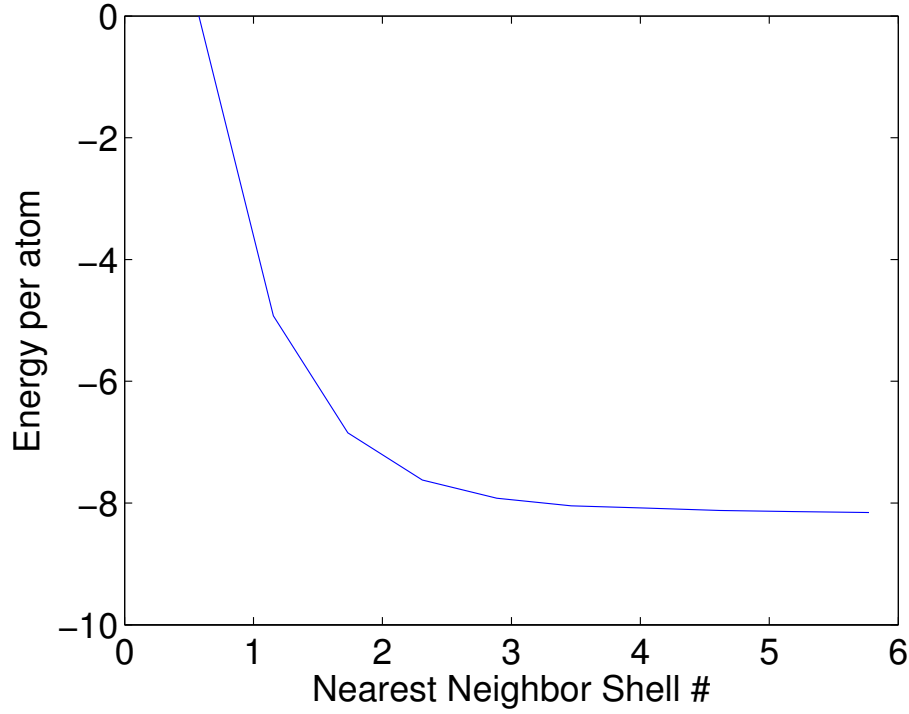


Figure 4: Convergence of energy per atom for LJ potential in BCC lattice with respect to nearest neighbor shells, using  $a_0 = 1.25$

For an infinite lattice, the lattice sum comes to be

$$u_{atom}(r) = \frac{U(r)}{N_{atom}} = 2(A_{12}(\frac{1}{r_{nn}})^{12} - A_6(\frac{1}{r_{nn}})^6). \quad (3)$$

For a BCC lattice,  $A_{12} = 9.1142$  and  $A_6 = 12.2533$ ,  $r_{nn} = \frac{\sqrt{3}a_0}{2} = 1.082$ ,  $u_{atom} \approx -8.1896$ . This corresponds to an error of 0.0102 for the largest simulation cell tested. Larger simulation cells are needed for better accuracies, but are not worth the time (at least without parallelization of some sort).

Table 2: Convergence of lattice parameter and energy per atom for BCC atom using LJ potential; all cutoffs are half the simulation cell size; infinite cutoff is theoretical value

Cutoff (rcs, in units of $a_0$ )	Equil. Lattice constant	Equil. Energy per atom	$\Delta$ Energy
1	1.296	-0.5000	—
1.5	1.253	-6.8472	-6.3472
2.5	1.237	-7.9497	-1.1025
3.5	1.235	-8.1212	-0.1715
5	1.234	-8.1998	-0.0786
$\infty$	—	-8.1896	error $\approx$ -0.0102

## 5 Exercise 5: Thermodynamic parameters for FCC

It is possible to calculate some thermodynamic quantities of relevance at 0K. At 0K (and constant temperature and volume), the Helmholtz free energy  $A$  is equivalent to the internal energy  $U$ . Thus, the pressure  $P$

$$P = \left. \frac{\partial A}{\partial V} \right|_{T,V} = \left. \frac{\partial U}{\partial V} \right|_{T=0K,V}. \quad (4)$$

Additionally, the Gibbs free energy is  $G = U + PV$ .

We plot the energy as a function of volume in Figure 5, which bears resemblance to the original Lennard-Jones potential. The volume as a function of pressure is subsequently shown in Figure 6, illustrating that with increasing pressure, the volume per unit cell is decreases; similarly, at no pressure, the simulation cell simply remains at its equilibrium volume. Figure 7 plots the Gibbs free energy as a function of pressure.

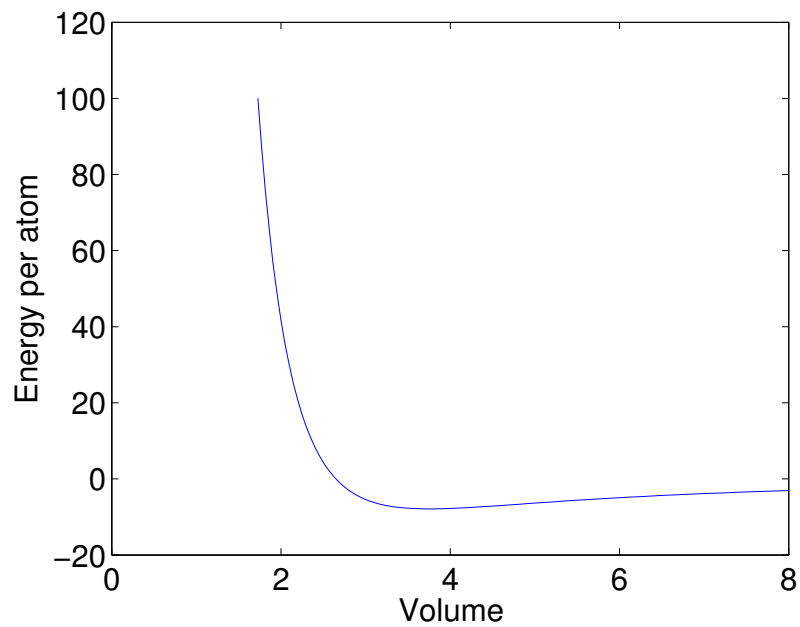


Figure 5: Energy per atom versus volume of unit cell for 3 x 3 x 3 simulation supercell

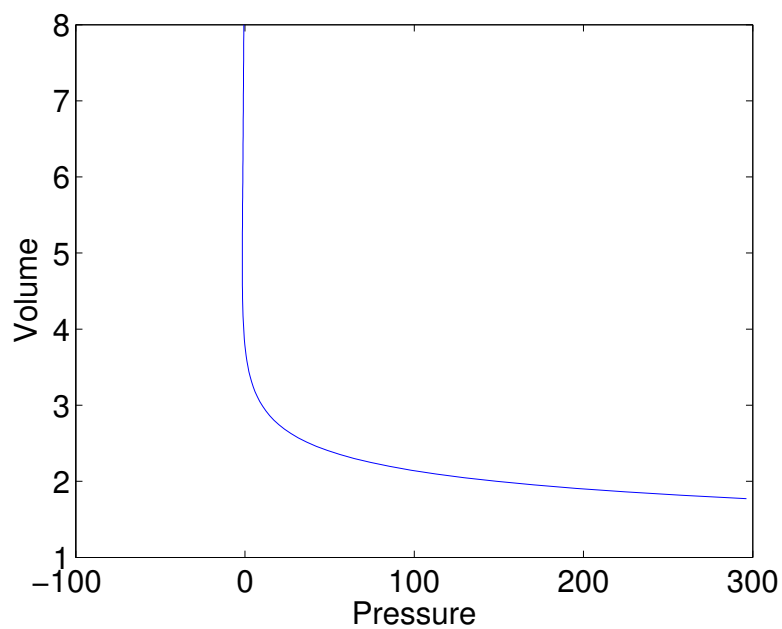


Figure 6: Volume of unit cell versus pressure for 3 x 3 x 3 simulation supercell

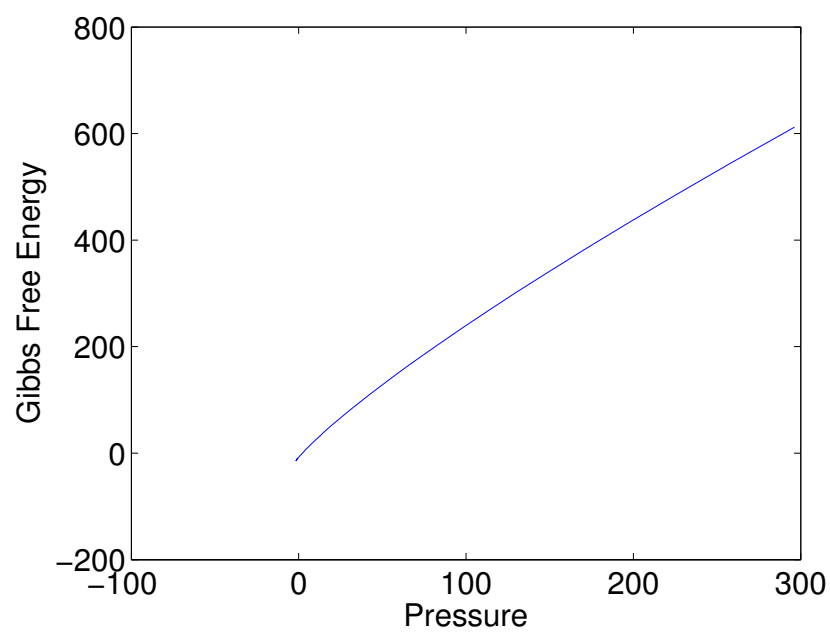


Figure 7: Gibbs free energy versus pressure for 3 x 3 x 3 simulation supercell