In this project, we will write and use a simple molecular dynamics code to simulate noble gas atoms interacting via a Lennard-Jones potential

\[ U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

It is typical to ignore interactions beyond some cutoff, which we can reasonably choose to be \( r_{\text{cut}} = 3.0\sigma \) (see Fig. 9.1 in Giordano). This speeds up the calculation quite substantially especially as we go to larger and larger systems. However, we then have the issue of a discontinuous potential and also discontinuous derivatives (Giordano doesn’t really explore these issues). The potential can be slightly altered so that \( U(r) \) and its derivative are continuous at \( r = r_{\text{cut}} \). We can use,

\[ U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] - 4\epsilon \left[ \left( \frac{\sigma}{r_{\text{cut}}} \right)^{12} - \left( \frac{\sigma}{r_{\text{cut}}} \right)^6 \right] + \frac{24\epsilon}{r_{\text{cut}}} \left[ 2 \left( \frac{\sigma}{r_{\text{cut}}} \right)^{12} - \left( \frac{\sigma}{r_{\text{cut}}} \right)^6 \right] (r - r_{\text{cut}}) \]

for \( r \leq r_{\text{cut}} \). For \( r > r_{\text{cut}} \), the potential and forces are all zero. Verify that this potential and the forces are continuous at \( r = r_{\text{cut}} \). Note that there are a lot of constant terms that we can calculate once at the beginning of the program to make the code efficient.

The equations of motion are integrated using the Verlet algorithm (see Eq. 9.4 to 9.5 in Giordano), which for each atom is given by

\[ \vec{r}_{n+1} = 2\vec{r}_n - \vec{r}_{n-1} + \frac{\Delta t^2}{m}\vec{F}_n \]

where \( \vec{r}_n \) is the position vector of an atom at time step \( n \), \( \Delta t \) is the discrete time step, \( m \) is the atom mass, and \( \vec{F}_n \) is the force on the atom due, in this case, to the Lennard-Jones interactions.

Here is a general outline of your code:

1. Place all atoms in a box on fcc lattice sites. Do not bother to add random displacements as Giordano suggests.

2. Determine previous positions for atoms based on an initial random velocity.
3. Add a constant displacement to the previous position of the atoms so that the net momentum is zero.

4. Compute the potential and force at $r = r_{cut}$ for the Lennard-Jones potential. Use to correct potential later on as given by equation above.

5. Loop on a total number of molecular-dynamics (MD) time steps nsteps.

6. At each MD step, loop over all atoms and possible interacting neighbors.

7. Compute potentials and forces. Use Newton’s 3rd law to save effort. Consider periodic boundary conditions.

8. Advance positions of atoms according to the Verlet algorithm.

9. Compute total kinetic and potential energy and effective temperature.

10. Compute any quantities desired for thermal averages.

11. Return to step 4 to advance to the next MD step.

We will use the MD code to study a dilute gas of Argon atoms. The length scale here is given by $\sigma$. We will define $\sigma = 1$ in our code, but assume we are studying Argon atoms which has $\sigma = 3.4\,\text{Å}$. Thus, all lengths in our calculation will be measured in units of $3.4\,\text{Å}$. For the other parameter $\epsilon$ in the code, we will take $\epsilon = 1$. However, for Ar, $\frac{\epsilon}{k_B} = 120^\circ K$, which sets the energy scale. For the mass of the atoms, define $m = 1$. Take the cutoff to be $r_{cut} = 3\sigma$. (Note: Read page 274 in Giordano to understand what we are doing)

1. Start with $N = 32$ atoms in a $10\sigma \times 10\sigma \times 10\sigma$ box. The total volume of the box is then $\Omega = 10^3\sigma^3$. Convince yourself that this density can correspond to a dilute gas since the average separation between the atoms is much greater than $\sigma$. Adjust the variable $v_0$ to get a temperature of about $T = 10^6 K$. You will have to determine the temperature by averaging the kinetic energy over time and using the equipartition theorem. After equilibrating the system (i.e. running for a long time), compute the speed distribution and compare to the Maxwell-Boltzmann distribution. Compute the heat capacity from fluctuations in the total energy, as discussed in lecture. How does the heat capacity compare to what you expect for an ideal gas? Also, compute the radial distribution function as discussed in class. From the radial distribution function, you should see some evidence of the interatomic interactions.

2. Place $N = 256$ atoms on an fcc lattice in a box with dimensions $2^\frac{3}{2}\sigma \times 2^\frac{3}{2}\sigma \times 2^\frac{3}{2}\sigma$. Run the simulation at about $T = 50^\circ K$. Again compute the heat capacity and radial
distribution functions. Finally, use the virial theorem to compute the pressure. Does the system want to expand or contract?