Question 2: Molecular dynamics simulations of a Lennard-Jones fluid

Consider a set of particles that interact via a Lennard-Jones potential. This system, referred to as a *Lennard-Jones fluid*, captures the behavior of simple solvents. Develop a simulation model for a Lennard-Jones fluid in which $N = 125$ particles are placed in a 3D, periodic, cubic simulation box. Assume particles only interact via a Lennard-Jones potential with characteristic energy ϵ and length σ which set the energy and length scales of the simulations, respectively.

Other recommended parameters include:

- Use a dimensionless timestep of $\Delta t = 0.001$.
- Assume the mass of each particle is $m = 1.0$.
- Set the Boltzmann constant to $k_B = 1.0$.
- Sample and save system properties every 100 timesteps.
- For your final simulations, run for at least 100,000 timesteps (this should take < 15 mins).

Note: these simulations will take substantially longer than the Monte Carlo simulations, so I recommend reducing the number of particles and simulation timesteps while you are testing code. I also recommend saving your trajectories (positions and velocities), to prevent running the code more times. See Python tutorial 3 for instructions on automatically saving data in Python.

(a) Simulate a Lennard-Jones fluid initialized at a temperature $T = 1.2\ \epsilon/k_B$ and a density $\rho = 0.85$ particles/σ^3 using Molecular Dynamics with a velocity Verlet integrator and no thermostat. Plot the kinetic energy, potential energy, and total energy per particle as a function of the simulation time and comment on their relative values. Indicate the approximate number of timesteps necessary for the system to reach equilibrium.

(b) Using an Andersen thermostat, rerun the molecular dynamics simulation of the same system with the temperature maintained at $T = 1.2\ \epsilon/k_B$ using a coupling constant $\eta = 1$. Plot the kinetic energy, potential energy, and total energy per particle as a function of the simulation time, and indicate the number of timesteps necessary for the system to reach thermal equilibrium. Compare features of these plots to the results from part **a**.

(c) Plot the equilibrium distribution of particle **speeds** for the simulations from part **a** and part **b**. Specify the time interval used for the calculation. Compare these results to the Maxwell-Boltzmann distribution and calculate the ensemble-average temperature for the thermostatted simulation. Explain if your results match your expectations. I recommend using a histogram size of 0.2σ/unit time.

(d) Perform MD simulations of Lennard-Jones fluids at $T = 1.5\ \epsilon/k_B$ and at densities of $\rho = 0.01$, $\rho = 0.10$, and $\rho = 0.85$ particles/σ^3 and compare the corresponding radial distribution functions. Specify the time interval used for the calculation and report the length scale in units of σ. Comment on key features of the plot. I recommend using a histogram size of $0.02\ \sigma$. Explain system phase behavior based on your results. Simulation visualization is also recommended.

(e) Calculate the chemical potential of a Lennard-Jones particle for each of the systems considered in part **d**. Recall that the chemical potential is the change in the free energy of the system upon addition or subtraction of a single particle. Explain the method that you use for this calculation. Hint: you do not need to perform any additional simulations if you have saved your trajectories.