24-623/12-623 2017 HW#3

Total points: 50
Assigned: September 27, 2017.
Due: October 12, 2017, midnight to Canvas. Please use the Canvas discussion board to ask questions of the instructor, the course assistant, or the other students.

1. (10 points) In HW#1, you calculated (i) how many water molecules are in spherical droplets with diameters of 1 nm, 10 nm, and 100 nm, and (ii) the number of distinct pair interactions in each of the droplets assuming that a water molecule could be modeled as three non-interacting rigidly-connected point masses.

Now, estimate the number of distinct pair interactions in each droplet for cutoff radii of (a) 1 nm, (b) 2 nm, and (c) 5 nm. Base your calculation on the center of mass of each molecule (i.e., if the center of masses of two molecules fall within the cutoff radius, then all the point masses on each molecule interact). Make sure that you have the correct number of molecules to start (see HW#1 solutions). Present your final results in a table.

2. (25 points) In this exercise, you will extend the functionality of your MD code. The end task is to model an LJ fluid in the NVE ensemble. Initial dimensionless coordinates for a 256-atom liquid system in a cubic simulation cell of dimensionless side length $L = 6.8$ are available in the file liquid256.txt on Blackboard. Modify your MD code so that it:

- Randomly initializes the particle velocities in a manner that gives the system zero total momentum.
- Incorporates the continuous force, continuous energy cutoff scheme with a dimensionless cutoff of 2.5.
- Calculates the instantaneous temperature and pressure.
- Applies periodic boundary conditions and the nearest image convention so that you can model bulk systems (you will need to define the simulation cell side length as a variable in your code).

You will implement the NVT ensemble in HW#4. Don't do it now.

Submit your code electronically and provide plots and written explanations showing the following for the 256-atom liquid LJ phase with $L = 6.8$ at a steady-state argon temperature of 100 K:

- How you determined when your system is equilibrated.
- Time variation of kinetic energy, potential energy, total energy, temperature, and pressure for 200 units of LJ time (i.e., 100,000 time steps). **The total energy should be conserved.**
- Conservation of momentum in the x, y, and z directions.

3. (15 points) Plot the average pressure as a function of density, ρ, for 950 kg/m^3 $< \rho <$1,150 kg/m^3 at an argon temperature of 100 K using NVE simulations. Estimate the density that gives zero pressure.

BONUS (10 points)

By writing the equations of motion as

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{v}_i \\ \dot{\mathbf{v}}_i &= \mathbf{F}_i/m_i - \eta \mathbf{v}_i, \end{aligned}$$

and taking η to be a constant, positive number we can slowly remove kinetic energy from the system (i.e, a quench). In the Verlet scheme, the integration for the x-direction will proceed as:

1. $v_{i,x}(t + \Delta t/2) = v_{i,x}(t) + [F_{i,x}(t)/m_i - \eta v_{i,x}(t)]\Delta t/2$
2. $r_{i,x}(t + \Delta t) = r_{i,x}(t) + v_{i,x}(t + \Delta t/2)\Delta t$
3. $v_{i,x}(t + \Delta t) = [v_{i,x}(t + \Delta t/2) + F_{i,x}(t + \Delta t)\Delta t/(2m_i)]/(1 + \eta\Delta t/2)$

Implement this scheme in your MD code. Quench the LJ liquid structure to a solid at zero temperature using different values of η for $L = 6.8$. Under what conditions do you get (i) a crystalline phase or (ii) an amorphous (i.e., disordered) phase? Compare these two solid phases and the liquid phase qualitatively and quantitatively.