Week Six PHY-480

Lewis

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Question 1

Outline how you would structure a python code to carry out MD simulations of equilibrium dynamics at fixed temperature of N Argon atoms in a periodic box of volume V using the velocity Verlet algorithm.

Pseudo-code Solution

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1. Initialize system parameters:
   - Number of atoms N
   - Box volume V and box length L = V^(1/3)
   - Time step dt, total simulation time, temperature T
   - Lennard-Jones parameters (epsilon, sigma)

2. Set up initial positions:
   - Arrange atoms in an fcc lattice inside the box

3. Set up initial velocities:
   - Assign velocities from Maxwell-Boltzmann distribution at temperature T
   - Subtract center of mass velocity to ensure total momentum = 0

4. Apply periodic boundary conditions (PBC):
   - Ensure all positions are mapped into the simulation box
   - When calculating distances, use the minimum image convention

5. Compute forces:
   - For each pair of atoms, compute Lennard-Jones force:
     F(r) = -dV(r)/dr with V(r) = 4*epsilon*((sigma/r)^12 - (sigma/r)^6)
   - Store forces on each atom

6. Velocity Verlet integration loop:
   For each timestep:
      (a) Update positions:
          r_i(t+dt) = r_i(t) + v_i(t)*dt + 0.5*F_i(t)/m * dt^2
      (b) Apply periodic boundary conditions to new positions
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      (c) Compute new forces F_i(t+dt)
      (d) Update velocities:
          v_i(t+dt) = v_i(t) + 0.5*(F_i(t) + F_i(t+dt))/m * dt

7. Temperature control:
   - Calculate kinetic energy from velocities
   - Rescale velocities by a factor to match target temperature T

8. Output and analysis:
   - Record energies (kinetic, potential, total)
   - Record temperature and pressure
   - Save configurations for structural analysis

9. End simulation when final time is reached
```

Question 2

Describe how to treat an atom that moves out of the simulation box.

Answer

When an atom moves out of the primary simulation box we apply periodic boundary conditions which essentially means the atom is "wrapping" back into the box from the opposite side like folding the ends of a piece of paper. For example, if an atom crosses the right side boundary of the box, it will reenter from the left side at the corresponding position similar to a globe.

Question 3

Describe how to treat shortest distance interactions with atoms in periodically repeated cells surrounding the primary simulation box.

Answer

To compute interactions, the minimum image convention is used. When there are two atoms, the distance is calculated not only within the primary box but also considering the nearest periodic images of each atom. The effective distance between two particles is the shortest possible distance between them in all repeated cells.

Question 4

Describe how you would calculate the pair distribution function of the Argon simulation model that you set up in class 11.

Answer

The pair distribution function $g(r)$ is calculated by measuring how particle density varies as a function of distance from a reference atom. Beginning with computing all interatomic distances using periodic boundary conditions. Then bin the distances into a histogram with bin width Δr. Normalize by the expected number of atoms in each spherical shell $4\pi r^2 \Delta r \rho$, where $\rho = N/V$ is the number density. Average over many timesteps to improve statistics and plot.

Question 5

Describe how you would use results from MD simulations to calculate the pressure of your model system.

Answer

The pressure can be obtained using the virial theorem:

$$PV = Nk_BT + \frac{1}{3}\sum_{i<j} \vec{r}_{ij} \cdot \vec{F}_{ij}$$

where $\vec{r}_{ij}$ is the displacement vector between atoms i and j, and $\vec{F}_{ij}$ is the force between them. The first term represents the ideal gas contribution, while the second term comes from interatomic interactions.

Question 6

Describe how you would calculate the specific heat of the system.

Answer

The specific heat C_V can be obtained from energy fluctuations at equilibrium using:

$$C_V = \frac{\langle E^2 \rangle - \langle E \rangle^2}{Nk_BT^2}$$

Alternatively, one can use kinetic energy fluctuations with the Lebowitz formula:

$$\frac{\langle K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N}\left(1 - \frac{3N}{2C_V}\right)$$

where K is the kinetic energy. Recording energies during the simulation allows computation of C_V.

Question 7

If you cool the system below the melting temperature describe what you expect the atomic structure to look like. What would happen to the atom diffusion rate?

Answer

Below the melting temperature, the Argon atoms would freeze into a crystalline solid structure. The pair distribution function would show sharp peaks corresponding to long range order. The atomic diffusion rate would decrease drastically, approaching zero in the solid phase since atoms are localized near lattice sites and only vibrate around equilibrium positions.