3. Molecular dynamics

Each pair of particles in a Lennard-Jones fluid interacts via the potential

$$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

where r is the distance between the two particles, σ is the interaction range and ϵ is the interaction strength. This potential contains an attractive tail leading to particle clustering. Another variant is to cut this, remaining with the following, purely repulsive, Weeks-Chandler-Anderson potential,

$$\begin{aligned} U_{WCA}(r) &= 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon \qquad \text{if} \qquad r \leq 2^{1/6}\sigma \\ U_{WCA}(r) &= 0 \qquad\qquad \text{otherwise.} \end{aligned} \tag{2}$$

We refer to an ensemble of particles interacting according to $U_{WCA}(r)$ as the Weeks-Chandler-Anderson potential.

Given a potential U, the particles obey Newton's equations of motion

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -\sum_{j\neq i} \nabla_i U(|\mathbf{r}_i - \mathbf{r}_j|) \tag{3}$$

where m_i is the mass of particle i, $\mathbf{r}_i = (x_i, y_i, z_i)$ is the position of particle i in 3-dimensional space, $\nabla_i = (\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i})$

1. Write down an expression for $\mathbf{f}_{ij}(t)$, the force on particle i due to the presence of particle j in terms of $\mathbf{r}_i(t)$, $\mathbf{r}_j(t)$ and $r = |\mathbf{r}_i - \mathbf{r}_j|$.

2. One way to integrate Newtons equations of motion is to use the Verlet algorithm. In the absence of any external forces, the position of particle i at time $t + \delta t$, $\mathbf{r}_i(t + \delta t)$ is given by

$$\mathbf{r}_i(t + \delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \delta t) + \frac{\delta t^2}{m_i}\sum_{j\neq i} \mathbf{f}_{ij}(t) \tag{4}$$

   in terms of previously defined quantities. How many sets of particle positions need to be stored when using this algorithm? How should you initialise the system?

3. An alternative way to implement one step of the Verlet algorithm is to maintain a set of positions $\mathbf{r}_i$ and velocities $\mathbf{v}_i$. Given their values at time t, in addition to the set of forces acting on the particles at time t, the corresponding quantities at time $t + \delta t$ are obtained by executing the following steps in sequence:

   - Update the velocities so that $\mathbf{v}_i$ is replaced with the result of the expression $\mathbf{v}_i + \frac{\delta t}{2m_i}\mathbf{f}_i$.

- Update the positions so that $\mathbf{r}_i$ is replaced with the result of the expression $\mathbf{r}_i + \mathbf{v}_i \delta t$.
- Update the forces $\mathbf{f}_i$ taking into account the particle positions that have just been calculated.
- Update the velocities a second time so that $\mathbf{v}_i$ is replaced with the result of the expression $\mathbf{v}_i + \frac{\delta t}{2m_i}\mathbf{f}_i$.

Show that this velocity Verlet algorithm is exactly equivalent to version involving only positions. Are there any advantages in working with a set of velocities and positions as opposed to only sets of positions?

4. Write a Java program to simulate the (i) Lennard-Jones and (ii) Weeks-Chandler-Anderson fluid, via the velocity Verlet algorithm. Your program should allow the user to choose the density of the system, and which of the two model to simulate. You should use periodic boundary conditions. The program should also be able to show a visualisation of the state of the lattice as it is running. You can simulate either the 2D or 3D system (ideally both, though you may find the 2D system simpler to visualise and hence debug). In 3D, you can measure the density via the particle volume fraction, $N\pi/6\sigma^3/V$ (V is the volume of the simulation box). In 2D, you can measure density through the particle surface fraction, $N\pi/6\sigma^3/A$ (A is the area of the simulation box).

5. Use your code to compute the kinetic and potential energy of the system, plot them versus time and show that their sum remains constant. How does this depend on the choice of (i) density and (ii) δt?

6. The temperature of the system can be defined via the equipartition theorem as
$$T = \frac{1}{k_B d(N-1)} \sum_i m_i |\mathbf{v}_i|^2 \tag{5}$$
where d is the number of spatial dimensions, N is the number of particles and k is Boltzmanns constant. (Note that the factor $N-1$ takes into account that the total momentum of the system is a conserved quantity, which effectively reduces the number of degrees of freedom per particle by the number of spatial dimensions). Show the plot of the temperature as a function of time for a given initial condition, and comment the results.

7. The velocity Verlet algorithm simulates a system in the NVE ensemble (the particle number N, the volume of the simulation box V and the total energy E are all constant in this ensemble). To simulate a system in the NVT ensemble, one needs to use a thermostat. By using the Brownian dynamics thermostat, modify your code so that a system at a fixed temperature is now modelled. Plot the temperature as a function of time for a given initial condition, and show that, indeed, it now is approximately constant.

8. Using this last code, simulate a Weeks-Chandler-Anderson fluid, in 3D. Calculate the mean-square displacement of a particle as a function of time in the equilibrium state, and investigate the manner by which it grows as a function of time (for a volume fraction $\rho_{\text{vf}} = N\pi/6\sigma^3/V$ equal to 0.1, 0.3 and 0.5).