1.9 Off-lattice simulations: basics

Exercise Reduced units: Tyipical sets of parameters for Argon and Kripton are $\sigma_{Ar} = 3.41\mathring{A}$, $\sigma_{Kr} = 3.38\mathring{A}$ for their typical size and $\epsilon_{Ar}/k_B = 119.8K$ and $\epsilon_{Kr}/k_B = 164.0K$.

- At the reduced temperature $T^* = 2$, what is the temperature of Argon and Kelvin?
- A typical value of the integration time step for MD is $\Delta t = 0.001\tau$. Convert it in SI units for Argon and Kripton.
- Compute the expression for the friction coefficient and the dynamical viscosity in reduced units.

Exercise Off lattice Monte Carlo: write a code to simulate a Monte Carlo off lattice in 3D. A Monte Carlo sweep will consist of N trial moves, where N is the number of particles in your system. For each trial move:

1. Select a particle at random
2. Propose a displacement in each direction. The maximum displacement should be set as a parameter d_{max}.
3. Compute the energy of the system before the displacement.
4. Displace the particle and compute the energy of the system after the displacement
5. Accept or reject according to the Metropolis rule.

Implement periodic boundary conditions. (*Note:* this exercise is just a warm up for the next ones. We suggest to write the code in such a way it can be expanded fairly easily.)

Exercise Off lattice Monte Carlo of Hard Spheres: the Hard Sphere model is a paradigmatic model in Soft Matter (despite the naming would not suggest so). The interaction energy between two hard spheres is zero if the separation distance is larger than the diameter of the particle σ and infinite otherwise. For simplicity set σ =1 as the unit of length.
In practice, in such a case one can simplify the Metropolis acceptance rule as follows:

1. reject every displacement that brings any two particles closer than σ – call it an *overlap*. For convenience, assign a very large energy to the configuration if an overlap is present, so that it can be plotted more easily.
2. accept every displacement that keeps every pair of particles at a distance larger than σ or that removes an overlap.

An acceptable state for a Hard Sphere system has zero energy and is homogeneously distributed in the simulation box. The first condition is easily checked; for the second, one can either look at the density along the different axis or at the radial distribution function.
For a system of N =100 particles:

- Starting from random initial conditions (i.e. generate the initial coordinates at random) test the performance of the code for different values of d_{max} between 0.01 σ and 1 σ (consider at least 5 values) at different values of the number density $\rho = N/V$ = 0.05, 0.3, 0.5, 1. Perform an average over at least 10 realizations. Discuss what happens at the acceptance ratio and at the energy as a function of d_{max} upon varying the density.
- Perform the same test, this time starting from a simple cubic crystal with a primitive cell of fixed length σ.

Exercise Off lattice Monte Carlo of Lennard Jones particles: the Lennard-Jones interaction is another paradigmatic interaction potential, often used to implement "self-avoidance" in MD simulations or as a paradigmatic example of gas-liquid phase separation. It reads

$$V_{\mathrm{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] & \text{for } r < \sigma_{cut} \\ 0 & \text{for } r \geq \sigma_{cut} \end{cases} \tag{1.19}$$

where σ =1, ϵ =1 are the units of length and energy and σ_{cut} is the so-called cut-off length and is set, for this exercise, to half the box size. Beyond this cut-off, we introduce two tail corrections: one for the energy (per particle)

$$u^{tail} = \frac{8}{3}\pi\rho \left[\frac{1}{3} \left(\frac{\sigma}{\sigma_{cut}} \right)^{9} - \left(\frac{\sigma}{\sigma_{cut}} \right)^{3} \right] \tag{1.20}$$

and one for the pressure

$$P^{tail} = \frac{16}{3}\pi\rho^{2} \left[\frac{2}{3} \left(\frac{\sigma}{\sigma_{cut}} \right)^{9} - \left(\frac{\sigma}{\sigma_{cut}} \right)^{3} \right] \tag{1.21}$$

Perform two sets of simulations, one at reduced temperature T^* =2 (above the critical temperature) and one at T^* =0.9 (well below the critical temperature) an compute, for both cases, the equation of state in the pressure-density plane. Compare the results with the equation of state for the two temperature (data shared in Google Drive).