Exercises NMSM 2024-2025

Nunziato Damino
matr. 2097564

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Exercise 8: Off-lattice Monte Carlo simulations

Pen & Paper - Reduced units

In order to convert from reduced units to SI units, specifically temperature and time, we simply do the conversion:

$$T^* = \frac{k_B T}{\varepsilon} \iff T = \frac{\varepsilon T^*}{k_B} \qquad t^* = \frac{t}{\tau} \iff t = \tau t^* \quad , \tau = \sqrt{\frac{\bar{m}\sigma^2}{\varepsilon}} = \sigma\sqrt{\frac{\bar{m}}{k_B}\frac{k_B}{\varepsilon}}$$

Where σ, $\bar{m}$, ε are respectively the reference unit for length, mass and energy for the system considered.

If we consider a reduced temperature $T^* = 2$, then for Argon and Krypton :

$$T_{\mathrm{Ar}} = 239.6 \text{ K} \qquad T_{\mathrm{Kr}} = 328.0 \text{ K}$$

Moreover, if we consider a timestep of $\Delta t = 0.001\tau$, we have respectively for Argon and Krypton:

$$\Delta t_{\mathrm{Ar}} = 2.160 \text{ fs} \qquad \Delta t_{\mathrm{Kr}} = 2.650 \text{ fs}$$

Numerical exercise

In this exercise we study a Lennard-Jones fluid using a Monte Carlo approach.
The Monte Carlo simulation we want to implement is simple: we want to perform a Monte Carlo sweep consisting of N local moves, where $N = 500$ is the number of particles in the system, where each local move consist in a uniform displacement of a particle chosen at random.
Once a MC sweep is done, the new configuration is accepted or rejected using a Metropolis filter. A total of $T = 10000$ sweeps are performed and then the pressure is measured, discarding an appropriate amount of sweeps for equilibration.
The displacement in the local move is chosen such that the acceptance rate of said filter is $\sim 50\%$.

We begin by making some general considerations. Having set for our simulation the reference unit for length and energy repsctively $\sigma = 1$ and $\varepsilon = 1$, the reduced units coincides with the SI units.
One here has 2 choices in the code implementation: write a general code where each conversion between reduced and SI units is made, or to write a specific implementation for our system.
Both approaches have their merits : the first makes the code more mantainable and expandible, but slower, the second makes it more efficient, but problem-specific.
We choose for our implementation the second approach.

Of particular interest are some optimization made during the simulation :

- Given that we want to evaluate quantities in function of the number density ρ, we can either change the number of particle N or the simulation box volume V.
  While mathematically equivalent, given that most of the algorithms are dependent on N, is convenient to change V.

- In the implementation of the PBC one has to pay particular attention in not using the standard `round` implementation in Python, which implement the so called banker's round.
  One has instead to use the numpy function `np.round` (or even better `np.rint`) which implement the nearest integer round, the correct one and typical of C/Fortran.

- In the Metropolis filter if we pursue a naive approach, i.e. we evaluate the energy difference of the system between the final and the initial configuration as is, we found ourselves an algorithm of time complexity $\mathcal{O}(N^2)$, where N is the number of particle in the system.
  If we observe instead that in one local move the only quantity that changes is the potential contribution of the displaced particle, we can cut the time complexity to $\mathcal{O}(N)$.
  This also imply that the energy tail contribution in the context of the Metropolis filter is irrelevant.

Exercise 10 : Interaction potentials & thermostats

Pen & Paper - Canonical fluctuactions

We want to prove that, in a canonical ensemble (NVT) :

$$\frac{\sigma_{T_K}^2}{\langle T_K|T_K\rangle^2} = \frac{\langle T_K^2|T_K^2\rangle - \langle T_K|T_K\rangle^2}{\langle T_K|T_K\rangle^2}$$

Proof - From the equipartition theorem, in the NVT ensemble:

$$\langle T_K|T_K\rangle = \frac{2}{3Nk_B}\langle E_K|E_K\rangle \qquad \langle T_K^2|T_K^2\rangle = \left(\frac{2}{3Nk_B}\right)^2 \langle E_K^2|E_K^2\rangle$$

So that the temperature variance can be written as :

$$\sigma_{T_K}^2 = \langle T_K^2|T_K^2\rangle - \langle T_K|T_K\rangle^2 = \left(\frac{2}{3Nk_B}\right)^2 (\langle E_K^2|E_K^2\rangle - \langle E_K|E_K\rangle^2)$$

Moreover we have that the energy variance can be written in the NVT ensemble as:

$$\sigma_{E_K}^2 = \langle E_K^2|E_K^2\rangle - \langle E_K|E_K\rangle^2 = k_B T^2 C_V$$

Also the heat capacity :

$$C_V = \frac{3}{2}k_B T$$

Putting all together:

$$\sigma_{T_K}^2 = \left(\frac{2}{3Nk_B}\right)^2 k_B T^2 \left(\frac{3}{2}k_B T\right) = \frac{2}{3N}T^2$$

Then one can evaluate the initial statement, in a NVT ensemble :

$$\frac{\sigma_{T_K}^2}{\langle T_K|T_K\rangle^2} = \frac{\frac{2}{3N}T^2}{T^2} = \frac{2}{3N}$$

Exercise 11 : Langevin and Brownian dynamics

Pen & Paper - Brownian time and length scales

We begin by considering the Langevin equation in the form:

$$m\ddot{\vec{x}} + m\gamma\dot{\vec{x}} + \sqrt{6m\gamma k_B T}\bar{\xi}(t) = 0$$

In the particular case in which the particle is considered spherical, with a diameter $\sigma = 10^{-8}\ m$, has roughly the same density of water and diffuse in water, we have in the limit of low Reynolds number that $m\gamma = 3\pi\eta\sigma$, where η is the water viscosity.
With the parameters considered we have:

$$m = \frac{4}{3}\pi\rho\frac{\sigma^3}{8} \sim 10^{-22}\ kg \qquad m\gamma = 3\pi\eta\sigma \sim 10^{-10}\ kg \cdot s^{-1}$$

So in this case we can neglect the inertial force and write:

$$m\gamma\dot{\vec{x}} + \sqrt{6m\gamma k_B T}\bar{\xi}(t) = 0$$

Implying that we are in the diffusion regime. We can then simply estimate the time to diffuse in water over a distance equal to the particle diameter by :

$$\sigma^2 = 6Dt = 6\frac{k_B T}{3\pi\eta\sigma}t \qquad \Longleftrightarrow \qquad t \sim 4 \cdot 10^{-7}\ s$$

If we instead start our calculations considering $\tilde{\sigma} = 5\ \mu m$, we have

$$\tilde{\sigma}^2 = 6Dt = \qquad \Longleftrightarrow \qquad t \sim 4 \cdot 10^{-1}\ s$$