Exercises NMSM 2024-2025

Nunziato Damino
matr. 2097564

January 18, 2025

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.

We now show the result of the simulation for $T^* = 0.9$ and $T^* = 2$ in figures 1.1 and 1.2 respectively, in comparison with the supplied data.

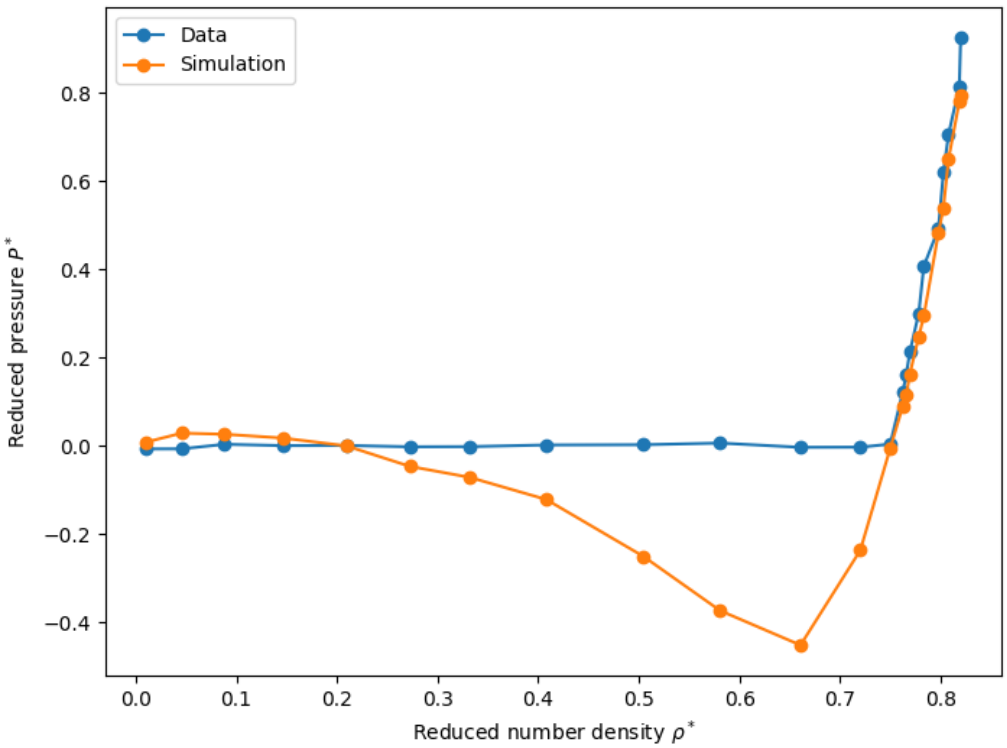

Figure 1.1: Comparison between the supplied data for the pressure-number density plot at $T^* = 0.9$

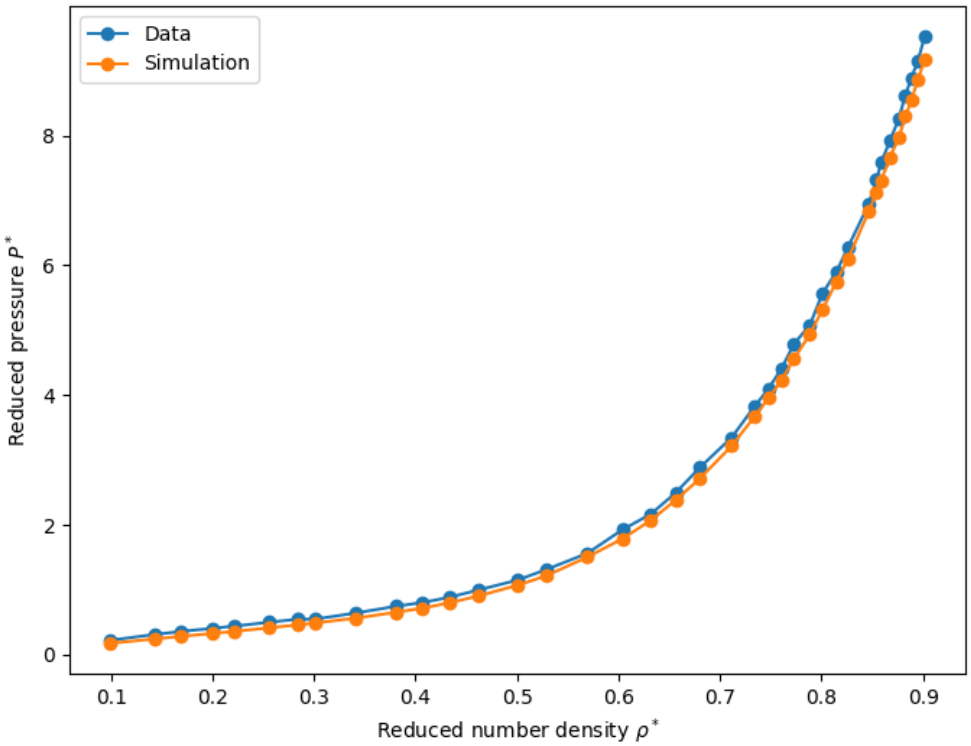

Figure 1.2: Comparison between the supplied data for the pressure-number density plot at $T^* = 2$

Is clear the good agreement for the simulation with the data for $T^* = 2$, above the critical temperature for a Lennard-Jones fluid, which is $T^* = 1.316$ [1], while it seems not good for $T^* = 0.9$.
This can be easily explained if we observe that in figure 1.1 the horizontal line is the saturated vapor pressure, and our simulation points indicate the densities of the coexisting vapor and liquid phases. Over a broad density range, the simulated system is observed to be metastable and even exhibit negative pressure. This phenomenon arises because, in finite systems, the formation of a liquid-vapor interface incurs a significant free-energy cost. For sufficiently small systems, this cost can be so substantial that phase separation becomes unfavorable [2]. Consequently, these issues are most pronounced in small systems and in scenarios where the interfacial free energy is particularly large. For this reason, standard NVT-simulations are not recommended for determining the vapor-liquid coexistence curve or for studying any strong first-order phase transitions in small systems.

Exercise 9: Integration schemes

The idea is to implement the velocity Verlet algorithm and the Gear predictor-correct algorithm of the 5th order specifically for the harmonic oscillator.
One can find said algorithms in the Algorithm appendix.
Before starting the quantitative analysis over these integration schemes, we start with a qualitative inspection against the analytical solution in figure 1.3.
Note that the integration timestep is $\Delta t = 0.001$ and $\omega = 0.1$.

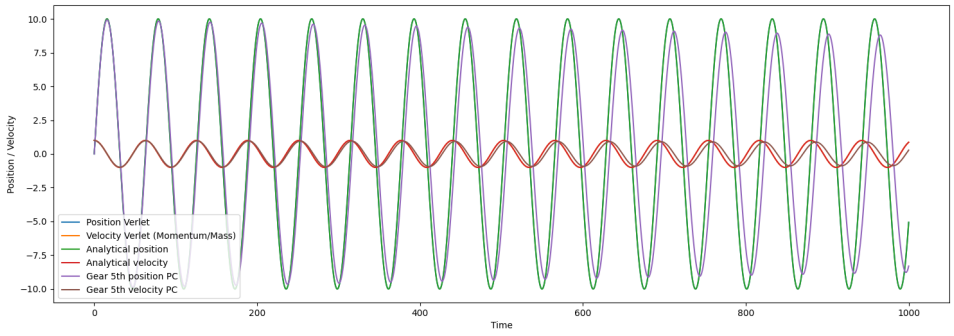

Figure 1.3: Comparison between the analytical solution for position and velocity in an harmonic oscillator with the velocit Verlet and the Gear 5th order predictor-corrector integration scheme.

Is clear that the Gear predictor-correct algorithm of the 5th order presents for long integration time an effect of amplitude reduction and delay, while the velocity Verlet algorithm do not presents these problems.
Now we study the energy conservation of the 2 algorithms. Again we plot the total energy of the system over time for inspection in figure 1.4 and for each algorithm we plot $\frac{E_{algo}(t)-E_0}{E_0}$ respectively in figure 1.5 for the velocity Verlet algorithm and the Gear predictor-correct algorithm of the 5th order.

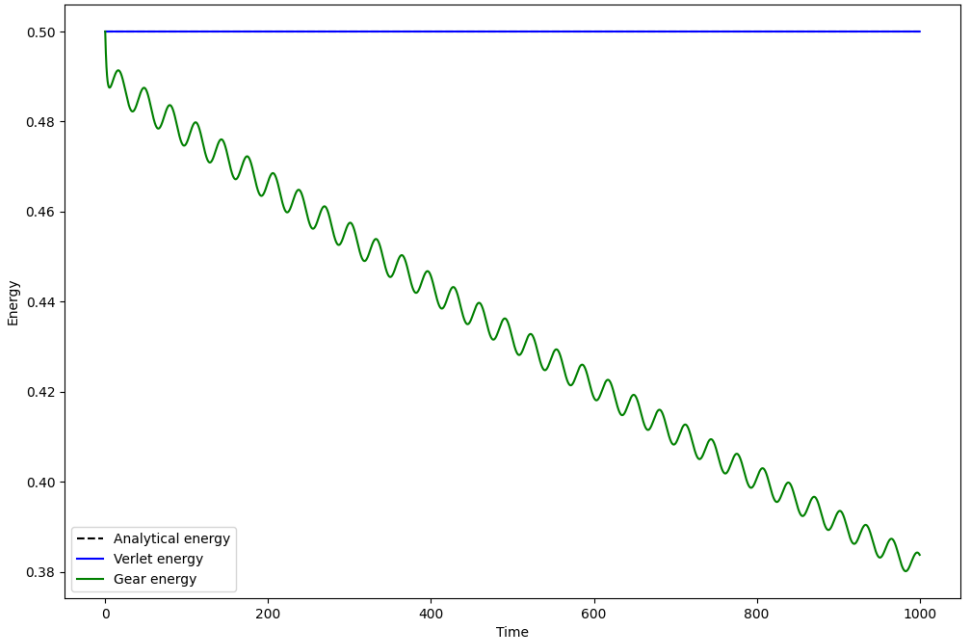

Figure 1.4: Comparison between the total energy in an harmonic oscillator and the energy evaluated with the velocity Verlet and the Gear 5th order predictor-corrector integration scheme.

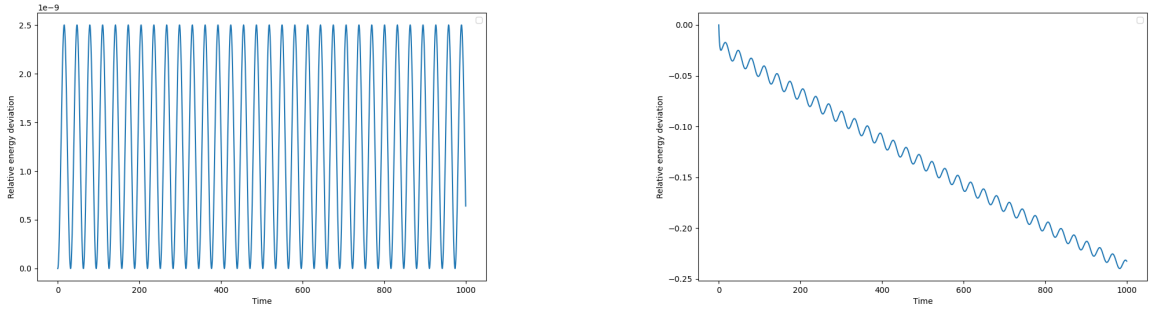

Figure 1.5: (Left) Relative energy deviation from the analytical value for the velocity Verlet integration scheme. (Right) Relative energy deviation from the analytical value for the Gear 5th order predictor-corrector integration scheme.

From this analysis we conclude, as we expected, that the velocity Verlet algorithm is symplectic while the Gear predictor-corrector is not.
Lastly we focus on the velocity Verlet to evaluate its stability for different values of ω. We choose for each iteration a timestep $\Delta t = 0.01\omega^{-1}$ and obtain figures 1.9.

We observe that the deviation is smaller for small ω.

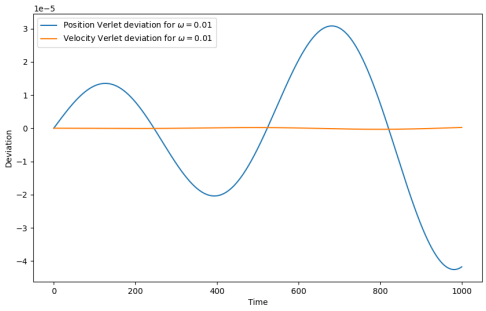

Figure 1.6: Position and velocity deviation for the velocity Verlet integration scheme for $\omega = 0.01$.

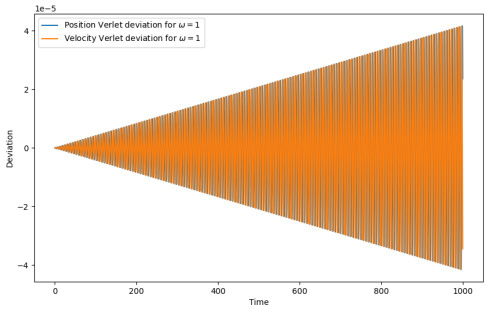

Figure 1.7: Position and velocity deviation for the velocity Verlet integration scheme for $\omega = 1$.

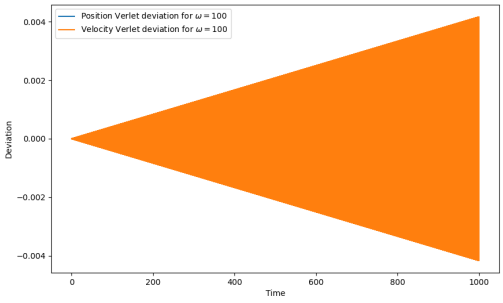

Figure 1.8: Position and velocity deviation for the velocity Verlet integration scheme for $\omega = 100$.

Figure 1.9: Comparison of position and velocity deviations for the velocity Verlet integration scheme.

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

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

Bibliography

[1] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins. The lennard-jones equation of state revisited. *Molecular Physics*, 78(3):591–618, 1993.

[2] Z. W. Salsburg and W. W. Wood. Equation of state of classical hard spheres at high density. *Journal of Chemical Physics*, 37(4):798–804, 1962.