10 Interaction potentials & thermostats

Canonical fluctuations (pen&paper) Show that the fluctuations of the temperature of the system, as defined in class, in the canonical ensemble are

$$\frac{\sigma_{T_K}^2}{\langle T_K \rangle^2} = \frac{\langle T_K^2 \rangle - \langle T_K \rangle^2}{\langle T_K \rangle^2} = \frac{2}{3N} \tag{1.23}$$

Lennard-Jones fluid in different ensembles
Note: This exercise can be carried out with LAMMPS.
Simulate N particles of mass $m = 1$ in a cubic box of length L (with periodic boundary conditions). The particles interact with each other through a Lennard-Jones (LJ) potential

$$V_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right) \tag{1.24}$$

where σ =1 and ϵ =1. Choose $L = 10\sigma$ and $\rho = N/V = 0.2\sigma^{-3}$. Integrate the equations of motion with the Velocity Verlet algorithm.
Generate a suitable initial condition. Choose one of the two strategies introduced in one of the previous exercise sessions. Draw the initial velocity distribution from the equilibrium (Maxwell-Boltzmann) distribution at $T^* = 1$, enforcing the total momentum to zero.

- NVE ensamble: Simulate the system without a thermostat. Check the effect of the cut-off radius: perform different simulations, increasing the cut-off from $r_c = 2^{1/6}\sigma$ to $r_c = 4\sigma$ with steps $\Delta r_c = 0.2\sigma$ (round the numbers to the first decimal place after the first one). After equilibration (if needed), compute the radial distribution function to compare the different cases.

- NVT ensamble: Introduce now a thermostat, picking one non-canonical (Velocity rescaling or Berendsen) and one canonical (Andersen or Nose-Hoover – Note: the latter can be done in LAMMPS). Simulate again the same LJ system as in the previous exercise. Fix the reference temperature of the heath bath $T^* = 2$. Integrate the equations of motion with the Velocity Verlet algorithm. Compute the kinetic energy and verify that, in both cases, the average is consistent with the equipartition theorem $\langle E_K \rangle = 3/2\, N k_B T$ upon varying the number of particles in the system (keeping the box size fixed); keep $\rho \leq 0.2$. Check that the fluctuations of the temperature are consistent/not consistent with the canonical ensemble upon varying the number of particles in the system as above.