1.11 Interaction potentials & thermostats

Exercise Show that the fluctuations of the temperature of the system, as defined in class, in the canonical ensemble are

$$\frac{\sigma^2_{T_K}}{\langle T_K \rangle^2} = \frac{\langle T_K^2 \rangle - \langle T_K \rangle^2}{\langle T_K \rangle^2} = \frac{2}{3N} \tag{1.42}$$

Exercise Lennard-Jones fluid in the microcanonical ensemble. Simulate N particles of mass $m = 1$ that are confined to move within a cubic box of length L (with periodic boundary conditions). The particles interact with each other through a Lennard-Jones (LJ) potential

$$V_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right) \tag{1.43}$$

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. (This exercise can be carried on with LAMMPS).

- Generate a suitable, well equilibrated 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.
- 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.

Optional Do not enforce the initial momentum. Pick two extreme cases $r_c = 2^{1/6}\sigma$ and $r_c = 4\sigma$ and discuss what happens.

Pick one between the following two exercises:

Exercise Lennard-Jones fluid with thermostats. Simulate again the same LJ system as in the previous exercise, this time with thermostatting. Among the different choices

- Velocity rescaling
- Berendsen thermostat
- Andersen thermostat
- Nose-Hoover thermostat (Note: this can be done in LAMMPS)

pick two, a non-canonical and a canonical thermostat. 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.

Optional From the same simulations, compute the pressure and compare the results with the first correction of the virial expansion $P = \rho k_B T + k_B T b_2 \rho^2$ with $b_2 \simeq -0.772$ for $T^* = 2$.

Exercise Ideal gas of dumbbells: Consider a system made of N =100 non-interacting dumbbells, each one made of two particles, held together by an harmonic spring with rest distance $r_0 = 1$ (r_0 sets the unit of length). Set, for simplicity, a box $L = 10$ units with periodic boundary conditions. Set the dumbbells initially at random positions in the box; each dumbbell should be at its rest length. Set the initial velocities as in the first exercise (Remember! Each dumbbell is in practice a different system!). Integrate the equations of motion with the Velocity Verlet algorithm. Among the different choices

- Velocity rescaling
- Berendsen thermostat
- Andersen thermostat
- Nose-Hoover thermostat (Note: this can be done in LAMMPS)

pick two, a non-canonical and a canonical thermostat. Fix the reference temperature of the heath bath $T^* = 2$.

- Compute the kinetic energy and verify that the average is consistent with the equipartition theorem $\langle E_K \rangle = 3/2\, N k_B T$.
- Check that the fluctuations of the temperature are consistent/not consistent with the canonical ensemble.
- Check the dyamics of the system in the two cases, by computing the Mean Square Displacement of the dumbbells. Discuss what happens.

optional Do not fix the initial momentum to zero. Discuss what happens.