Exercise 2

Monte Carlo in the NVT ensemble

In this exercise, we will study a 3D Lennard-Jones system in the NVT ensemble. A cubic boxvolume V contains N particles at a given temperature T in any configuration allowed by the potential energy U. The potential is a truncated Lennard-Jones potential:

$$U(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] & r \leq r_c \\ 0 & r > r_c \end{cases}$$

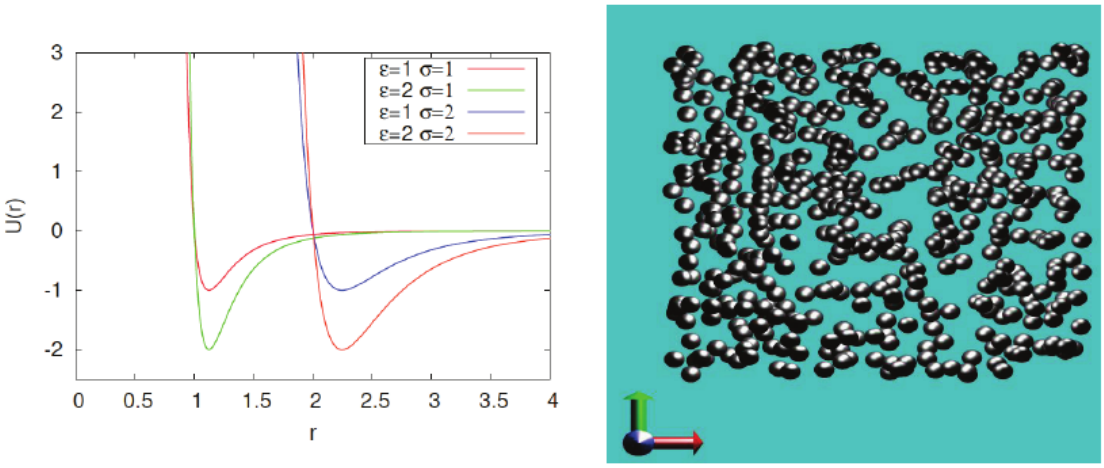

Figure 1: The Lennard-Jones potential and a Snapshot from a NVT MC simulation

We can account for long range contributions to the potential beyond the cutoff radious rc with the usual tail corrections:

$$\frac{u^{tail}}{N} = \frac{8}{3} \cdot \pi \cdot \rho \cdot \varepsilon \cdot \sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c}\right)^9 - \left(\frac{\sigma}{r_c}\right)^3 \right]$$

$$p^{tail} = \frac{16}{3} \cdot \pi \cdot \rho^2 \cdot \varepsilon \cdot \sigma^3 \left[\frac{2}{3} \left(\frac{\sigma}{r_c}\right)^9 - \left(\frac{\sigma}{r_c}\right)^3 \right]$$

$$\mu^{tail} = \frac{16}{3\beta} \cdot \pi \cdot \rho \cdot \varepsilon \cdot \sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c}\right)^9 - \left(\frac{\sigma}{r_c}\right)^3 \right]$$

From a starting particle configuration, a randomly selected particle is randomly translated to generate a new particle configuration. If this MC move takes the particle outside the cube, we need to apply periodic boundary conditions to keep the particle inside the cube. The new configuration is accepted or rejected depending on the Boltzmann factor, which can be calculated knowing the energies of the new and the old configuration. We generate a random number, and if the random number is smaller than the Boltzmann factor:

$$RandomNumber < \exp(-\beta(U^{new} - U^{old}))$$

the move is accepted and otherwise rejected. We sample the phase space with a succession of such MC moves (Markov chain), and the average physical properties of the system can be calculated by arithmetic averages over their sampled values.

Questions:

1. Complete the Monte Carlo program and implement periodic boundary conditions, both for pair interactions (minimum image convention) and for particle displacements. Calculate the average energy of the system at different densities and temperatures. At what conditions is it easier to equilibrate the system?
   Hint: plot the energy as a function of the MC cycle.
2. In the present code, the pressure of the system is not calculated. Modify the code in such a way that the average pressure is calculated. Perform simulations at different densities at $T^* = 2.0$. Up to which density does the ideal gas law hold?
   Hint: The ideal gas contribution to the pressure is already calculated in *sample.f*. It is only necessary to implement the virial contribution in one routine, the rest of the implementation is already in the code.
3. a) Change the potential implemented in the present code (truncated Lennard-Jones) by a truncated and shifted Lennard-Jones potential. Calculate the pressure of the system at $T^* = 1$ and $\rho^* = 0.4$. How does the result compare to the simple truncated Lennard-Jones simulations?

   b) Add the tail correction contributions to the pressure and the original truncated potential. Calculate the pressure of the system at $T^* = 1$ and $\rho^* = 0.4$. How does the result compare to the simple truncated Lennard-Jones potential without tail corrections?