Homework 2 (CSM2)

Due: May 2, 2016.

The purpose of this exercise is that of performing a simple Monte Carlo simulation.

Model: Consider a system of monoatomic molecules interacting via a pair potential

$$V(r) = \frac{A\sigma e^{-r/\sigma}}{r} \qquad \text{for } r < r_c,$$

$V(r) = 0$ for $r > r_c$. Fix the temperature so that $A/(k_B T) = 1.5$. Consider N molecules in a cubic box of linear size L/σ and always fix L/σ so that the density is $\rho\sigma^3 = 0.6$. The basic move in the Monte Carlo simulation is $x \to x' = x + \Delta(r_1 - 0.5)$, $y \to y' = y + \Delta(r_2 - 0.5)$, and $z \to z' = z + \Delta(r_3 - 0.5)$, where r_1, r_2, and r_3 are random numbers uniformly distributed between 0 and 1. One iteration consists in one proposed move on *all* particles.

- **Role of Δ**. Consider a system with $N = 60$ molecules and fix the box size L/σ so that $\rho\sigma^3 = 0.6$. Perform simulations of 4000 iterations using $\Delta = L/10, L/5, L/4, L/3, L/2, L$, starting each simulation from a random configuration of molecules. For each run, estimate how many iterations should be discarded to be in equilibrium, the average acceptance in equilibrium, the average pressure and potential energy per molecule. For the pressure and energy compute the autocorrelation time in equilibrium and the correct errors. Take $r_c = L/2$ in all cases and apply the tail correction. Which is the range of optimal values of Δ (those for which errors are smaller) ?

  [Use adimensional units: compute $E/k_B T$ and $P\sigma^3/k_B T$].

- **Role of the cut-off**. Consider again the system with $N = 60$ molecules and fix the box size L/σ so that $\rho\sigma^3 = 0.6$. Perform simulations of 4000 iterations using an optimal value of Δ according to the analysis done above. Use $r_c = 3L/8$, $r_c = L/4$. For each simulation measure the average energy per molecule and average pressure in reduced units. Compare results with and without tail correction.

- **Size effects**. Finally, consider the system with $N = 100$ and $N = 200$ molecules and fix L/σ so that $\rho\sigma^3 = 0.6$. Perform simulations of 2000 iterations using an optimal value of Δ according to the analysis done above. Set $r_c = L/2$ in all cases.

  For each simulation measure the average energy per molecule and average pressure in reduced units. Compare results with and without tail correction. In the run with $N = 200$ also compute the pair distribution function $g^{(2)}(r)$.

Warning. Be very careful in computing the distance between two molecules. If the two molecules have coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2), the distance d is given by

$$d = [d_x^2 + d_y^2 + d_z^2]^{1/2}$$

where d_x is defined by

$$d_x = x_1 - x_2; \qquad d_x = d_x - L * \texttt{ANINT}(d_x/L);$$

`ANINT` is the function that returns the closest integer (`ANINT(2.1) = 2., ANINT(2.6) = 3., ANINT(-1.6) = -2.`). The function `ANINT` is built in FORTRAN, while it can be easily defined in C, using `floor()`: `ANINT(x) = floor(x + 0.5)`. d_y and d_z are defined analogously.

Tail corrections for energy and pressure:

$$\Delta E_{\text{tail}} = 2\pi\rho \int_{r_c}^{\infty} dr\, r^2 U(r), \qquad \Delta P_{\text{tail}} = -\frac{2\pi}{3}\rho^2 \int_{r_c}^{\infty} dr\, r^3 U'(r),$$