

## Homework 2 (CSM2)

Due: April 27, 2015.

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

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

$$U(r) = \frac{A\sigma^2 e^{-r/\sigma}}{r^2} \quad \text{for } r < r_c,$$

$U(r) = 0$  for  $r > r_c$ . Fix the temperature so that  $A/(k_B T) = 1$ . Consider  $N$  molecules in a cubic box of linear size  $L/\sigma$  and always fix  $L/\sigma$  so that the density is  $\rho\sigma^3 = 0.5$ . The basic move in the Monte Carlo simulation is  $x \rightarrow x' = x + \Delta(r_1 - 0.5)$ ,  $y \rightarrow y' = y + \Delta(r_2 - 0.5)$ , and  $z \rightarrow z' = z + \Delta(r_3 - 0.5)$ , 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  $\Delta$ .** Consider a system with  $N = 50$  molecules and fix the box size  $L/\sigma$  so that  $\rho\sigma^3 = 0.5$ . 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 energy per molecule with errors (be careful about correlations). Take  $r_c = L/2$  in all cases and apply the tail correction. Which is the range of optimal values of  $\Delta$  (those for which errors are smaller) ?

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

- **Role of the cut-off.** Consider again the system with  $N = 50$  molecules and fix the box size  $L/\sigma$  so that  $\rho\sigma^3 = 0.5$ . Perform simulations of 4000 iterations using an optimal value of  $\Delta$  according to the analysis done above. Use  $r_c = 3L/4$ ,  $r_c = 2L$  (in this last case, each particle interacts with some of its images). 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  $N = 75$ ,  $N = 100$ , and  $N = 200$  molecules and fix  $L/\sigma$  so that  $\rho\sigma^3 = 0.5$ . Perform simulations of 2000 iterations using an optimal value of  $\Delta$  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.

**Warning.** Be very careful in computing the distance between two molecules. If the two molecules have coordinates  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$  with  $0 \leq x_i \leq L$ , etc., the distance  $d$  is not given by

$$d = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2}$$

Instead, one should define

$$\begin{aligned} d_x &= |x_1 - x_2| & \text{if } |x_1 - x_2| < L/2 \\ d_x &= L - |x_1 - x_2| & \text{if } |x_1 - x_2| > L/2 \end{aligned}$$

(analogous definitions hold for  $d_y$  and  $d_z$ ) and define

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

A fast implementation is the following. Let ANINT be a function that returns the closest integer (ANINT(2.1) = 2., ANINT(2.6) = 3., ANINT(-1.6) = -2.). We can define  $d_x$  with the following two instructions:

$$d_x = x_1 - x_2$$

$$d_x = d_x - L * \text{ANINT}(d_x/L)$$

This is identical to the previous definition, apart from an (irrelevant) sign. The function ANINT is built in in FORTRAN, while it can be easily defined in C, using floor(): ANINT(x) = floor(x + 0.5).