Homework 2 (CSM2)

Due: May 9, 2019.

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

Model: Consider a system of N monoatomic molecules in a cubic box of linear size L interacting via a pair potential

$$V(r) = \infty \qquad \text{for } r < d$$
$$V(r) = -\epsilon \left[\frac{d^6}{r^6} - \frac{d^6}{r_c^6} \right] \qquad \text{for } d \leq r < r_c$$

and $V(r) = 0$ for $r > r_c$. In the following always fix the temperature so that $\epsilon/(k_B T) = 0.5$ and L/d so that the density is $\rho d^3 = 0.4$. 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 (sequentially) proposed move on *all* particles.

- **a) Starting configuration with** $N = 60$. Consider a random configuration of the molecules. Some of them will overlap (their distance is less than d) so that the potential energy is infinite. Perform some iterations using $\Delta = d$, $r_c = d$, until all overlaps are absent. Then, stop and save the configuration on disk. Use it as the starting configuration in all simulations mentioned in b) and c).

- **b) Role of** Δ. Starting from the configuration determined in a), perform simulations of 5000 iterations using $\Delta = d/6, d/3, d, 2d, 3d$. For each run, estimate how many iterations should be discarded to be in equilibrium, the average acceptance and potential energy per molecule. For the potential energy compute the autocorrelation time in equilibrium and the correct error. 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 $U/k_B T$.

- **c) Role of the cut-off**. Consider again the the starting configuration with $N = 60$ determined in a). Perform simulations of 5000 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 potential energy per molecule. Compare results with and without tail correction.

- **d) Size effects**. Consider the system with $N = 100$ and $N = 200$ molecules. For each N, determine a starting configuration with finite energy as discussed in point a). Then, perform simulations of 5000 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 potential energy per molecule; the pair distribution function $g(r)$ and, in particular, its value at contact $(r \to d+)$; the average pressure (compute $pd^3/k_B T$). Always use the tail correction. Compare the results for the energy with those obtained for $N = 60$. Report $g(r)$ for the two values of N in the same plot versus r/d.

- **e) Physical units**. Assume that $\epsilon/k_B = 150$ K, $d = 30$ nm. Compute the molar density in mole/cm^3, the temperature in K, the potential energy per particle in eV and the pressure in Pascal for the system analysed here (use the estimates of energy and pressure obtained for $N = 200$)

Technical details.

[**Distances**] . 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.

[**Potential energy**]. Use the expression for $V(r)$ reported at the beginning for the update. In the calculation of the average energy use instead the expression with no subtraction:

$$V_t(r) = \infty \qquad \text{for } r < d$$
$$V_t(r) = -\epsilon \frac{d^6}{r^6} \qquad \text{for } r \geq d$$

[**Pressure**]. It should be computed using

$$p = \rho k_B T + \frac{2\pi}{3}\rho^2 k_B T d^3 g(d+) - \frac{\rho}{3N}\left\langle \sum_{i<j} r_{ij} V'(r_{ij}) \right\rangle.$$

[**Tail corrections for energy and pressure**]:

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