Homework 2 (CSM2)

Due: May 11, 2020.

The purpose of this exercise is that of performing a simple Monte Carlo simulation for the pair potential

$$V(r) = \epsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right) - \frac{\epsilon}{4} e^{-r/\sigma}$$

We work in the canonical ensemble. Temperature and number density are specified by $k_B T/\epsilon = 0.3$ and $\rho\sigma^3 = 0.5$.

Model: Consider a system of N monoatomic molecules in a cubic box of linear size L; in the simulation use the truncated and shifted potential

$$V_{sh}(r) = V(r) - V(r_c) \qquad \text{for } r < r_c$$
$$V_{sh}(r) = 0 \qquad \text{for } r \geq r_c$$

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. All simulations should start from a random configuration of the molecules.

- **a) Role of Δ**. Perform simulations of 10000 iterations using $\Delta = \sigma/8, \sigma/4, \sigma/2, \sigma, 2\sigma$. Take $N = 60$ and $r_c = L/2$. After each iteration save the potential energy, the virial and the number of accepted moves in the iteration.

  For each run, estimate: a) how many iterations should be discarded to be in equilibrium, b) the average acceptance, c) the autocorrelation time in equilibrium for the potential energy and the virial, d) the average potential energy per molecule with its statistical error, e) the pressure with its statistical error. Apply the tail correction to the computations in d) and e) and use adimensional units, computing U/ϵ and $p\sigma^3/\epsilon$.

  Look at the errors on the results obtained as a function of Δ and identify an "optimal Δ", the one that gives the smallest errors. Use the optimal Δ in the simulations below.

- **b) Role of the cut-off**. For $N = 60$, perform simulations of 10000 iterations using an optimal value of Δ, taking now different cutoff values: $r_c = L/8$, $r_c = L/4$, $r_c = 3L/8$. For each simulation measure the average potential energy per molecule and the pressure. Report results with and without tail correction, including the results obtained for $r_c = L/2$ at point a).

- **c) Size effects**. Consider the system with $N = 100$ and $N = 200$ molecules. Perform simulations of 5000 iterations using the optimal value of Δ and $r_c = L/2$.

  For each simulation measure the average potential energy per molecule, the pressure (use the tail correction in both cases) and the pair distribution function $g(r)$. Report $g(r)$ for the two values of N in the same plot versus r/σ.

- **d) Physical units**. Assume that $\epsilon/k_B = 200$ K, $\sigma = 5$ 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.

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

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

The "virial" is the quantity in the average value.

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

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

Meet meeting for explanations and questions at `https://meet.google.com/fgx-evds-mgc`: Th 04/30, 6:00 pm; Tue 05/05, 6:00 pm; Fri 05/08, 6:00 pm.