Due: May 14, 2018.

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

\[ V(r) = A \left( \frac{\sigma}{r} \right)^{12} - B \left( \frac{\sigma}{r} \right)^{6} \]

for \( r < r_c \)

and \( V(r) = 0 \) for \( r > r_c \). Take \( B/A = 1 \). Fix the temperature so that \( A/(k_B T) = 0.5 \). 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 \( N = 60 \) molecules and fix the box size \( L/\sigma \) so that \( \rho \sigma^3 = 0.5 \). Perform simulations of 5000 iterations using an optimal value of \( \Delta \) according to the analysis done above. Use \( r_c = 3L/8, r_e = L/4 \). 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 \( L/\sigma \) so that \( \rho \sigma^3 = 0.5 \). Perform simulations of 5000 iterations using an optimal value of \( \Delta \) according to the analysis done above. Set \( r_e = L/2 \) 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 \( g^{(2)}(r) \).

- **Physical units.** Assume that \( A/k_B = 150 \) K, \( \sigma = 0.30 \) nm. Compute the molar density in mole/cm\(^3\), the energy per particle in eV and the pressure in Pascal.

**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

\[ d = \left[ d_x^2 + d_y^2 + d_z^2 \right]^{1/2} \]

where \( d_x \) is defined by

\[ d_x = x_1 - x_2; \quad d_L = d_x - L \cdot \text{ANINT}(d_x/L); \]

ANINT is the function that returns the closest integer (\( \text{ANINT}(2.1) = 2., \text{ANINT}(2.6) = 3., \text{ANINT}(-1.6) = -2. \)). The function ANINT is built in FORTRAN, while it can be easily defined in C, using \( \text{floor()} \).

Tail corrections for energy and pressure:

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