Exercises Lecture XI
Classical fluids:
simulation with Metropolis Monte Carlo
(and with Molecular Dynamics)

1. **Monte Carlo Simulation of hard disks**

   Write a code for a Monte Carlo simulation of hard disks in 2D. One example is `hd-MC.f90`, which makes use of the *periodic boundary conditions* and the *minimum image convention* to calculate the minimum distance (function `separation`).
   If σ is the *diameter of the disks*, the highest possible density is $\rho_{max}=2/(\sqrt{3}\sigma^2)$. It is convenient to use σ as unit length and measure all lengths in terms of σ and use the *reduced density*, defined in general as $\rho^* = \rho\sigma^d$, where d is the dimensionality of the system. The highest possible *reduced density* is $\rho^*_{max} = \rho_{max}\sigma^2 = 1.1547$, corresponding to the maximum *packing fraction* $f = area_{occupied}/area_{available} = \pi/(2\sqrt{3}) = 0.9069$.

   (a) Start simulating the fluid with a density close to the maximum one. To this purpose, it is convenient to set the initial positions of the particles on a hexagonal (or triangular) lattice that ensures the maximum *packing fraction*. Choose for instance $N = 16$ and a rectangular box with dimension $L_x = 4.41\sigma$ and $L_y = 0.5\sqrt{3}L_x$. Calculate ρ^* and compare it with ρ^*_{max}. A reasonable first choice for the maximum random displacement in a Monte Carlo simulation is $dxmax = dymax = 0.1\sigma$. Calculate the corresponding *acceptance ratio*. Allow at least 500 MC steps for equilibration and average over $nmcs \geq 500$. Calculate $g(r)$. A reasonable choice for the bin width `dr` for the calculation of $g(r)$ is `dr`=0.1.

   (b) Reduce progressively ρ^*, saving the configuration of a run and using it as the input for the new run at lower ρ^*. Keeping the ratio L_x/L_y fixed, it is sufficient to rescale homogeneously all the positions. It may be convenient to vary progressively also $dxmax$ and $dymax$ in order to keep an *acceptance ratio* of the order of 50%. Calculate $g(r)$ for ρ^* =0.95, 0.92, 0.88, 0.85, 0.80, 0.70, 0.60, and 0.30; plot and compare the profiles (how many peaks? where? ...)

   (c) Take "snapshots" of the disks at intervals of about 10 to 20 MC steps per particle. Do you see any evidence of the solid becoming a fluid at lower densities?

2. **Monte Carlo simulation of a Lennard-Jones system**

Consider particles interacting with the Lennard-Jones potential:

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

It is convenient to use the adimensional quantities $E^* = E/\epsilon$, $T^* = k_B T/\epsilon$, $\rho^* = \rho\sigma^2$ for energy, temperature and density respectively. For numerical simulations use Periodic Boundary Conditions and the *minimum image convention*, with a *cutoff radius* for the potential consistent with the size of the simulation box. *(No draft code is given)*

(a) Start with $T^* = 0$ and calculate the energy E_0^* of the ground state of the system. Choose $N = 16$, $L_x = 4.5\sigma$, $L_y = (6\sqrt{3}/2)\sigma$, and the particles on a triangular lattice: the system is therefore close to the equilibrium, and a few MC steps are already enough to have a good estimate of E_0^*. Does the energy per particle change if you consider bigger systems at the same density?

(b) Increase the temperature $T^* = 3.5$ and calculate E^* and $g(r)$.

(c) Describe qualitatively $g(r)$ and compare it with the hard disks case.

(d) Repeat the calculations for a smaller density, expanding by a factor of 1.5 the dimensions of L_x and L_y. Compare with the previous results and with the hard disks case with the same density.

3. **Molecular dynamics of a Lennard-Jones system** *(Optional)*

The program `LJ-MD.f90`, from Gould-Tobochnick, considers a bidimensional Lennard-Jones system, and makes use of the *velocity-Verlet* algorithm for the numerical integration of the Newton equations of motion to perform a *molecular dynamics* simulation. In 1D (with obvious extension in higher dimensions) the algorithm is:

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} a_n (\Delta t)^2$$

$$v_{n+1} = v_n + \frac{1}{2}(a_{n+1} + a_n)\Delta t$$

The new position x_{n+1} is used to find the new acceleration a_{n+1}, which is used together with a_n to obtain the new velocity v_{n+1}.

(a) Consider a system with $N = 16$ particles in a square box with $L = 6$. Choose $\Delta t = 0.01$ and test the program: follow the trajectories of the 16 particles making a plot, and check that the total energy is approximately conserved.

(b) Calculate the pair correlation function $g(r)$ for some of the cases with density and temperature proposed in the exercise with Monte Carlo simulation. Compare the results obtained with the two methods.