

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 $\rho^* = 0.95, 0.92, 0.88, 0.85, 0.80, 0.70, 0.60$, 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-Tobochnik, 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.