

# Project: Computer simulations of molecular liquids

The aim of this project assignment is to implement the methods of molecular simulation studied in the lectures. You will study the properties of a 2D system of particles interacting via a model interaction potential. You will use Molecular Dynamics (MD) and Metropolis Monte Carlo (MC) algorithms to run the simulations. In the submitted report, summarise the methods, and clearly present and discuss the results.

## The system

Consider  $N$  particles of diameter  $\sigma$  in two dimensions interacting via a pair additive interaction potential. The molecular interactions in systems from atomic gases, molecular liquids, to macromolecular, colloidal and biological systems, usually share common qualitative features: there is a strong repulsion when particles are so close to each other that they start to overlap, and there is typically an attractive interaction between particles at separations of one or more diameters. The usual choice in molecular simulations is the so-called Lennard–Jones (LJ) potential, which was developed to describe atomistic interactions between rare gas atoms:  $u_{LJ}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$ , where  $r_{ij}$  is the distance and  $U_{ij}$  the pair interaction potential between a given pair of particles in the system.  $\sigma$  is the particles' diameter, and  $\epsilon$  is the interaction strength, *i.e.*, the depth of the attractive well (minimum of the potential). It is easy to confirm that the LJ potential has the desired universal properties described above. However, it is a "long-range" potential, which presents a problem in computational implementation. In order to be able to study sufficiently large systems, in computer simulation we usually need the interactions to be of a finite range. Therefore, for practical implementations a cut-off  $r_c$  is introduced and the following potential is usually implemented:

$$u_{ij}^{LJ} = \begin{cases} u_{LJ}(r_{ij}) & \text{if } r_{ij} \leq r_c \\ 0 & \text{if } r_{ij} > r_c \end{cases} \quad (1)$$

The introduction of the cut-off also introduces problems:

- i) the results of the simulations generally depend on the choice of  $r_c$ , and
- ii) the cut-off introduces a discontinuous jump in the potential and therefore a diverging force at  $r = r_c$ , which makes this potential not suitable for use in MD simulations.

To avoid the latter, versions with continuous rather than abrupt cut-off, and truncated and shifted LJ potentials have been implemented. However, all these implementation options make it really difficult to compare the results of different simulations. Furthermore, at least in colloidal or macromolecular domain, there is no real physical justification to use the potential of the LJ functional form, hence we might choose a better model interaction potential, which still satisfy our qualitative requirements, but does not suffer from the above issues. Such potential function should satisfy the following requirements;

1. The potential  $\phi(r)$  should be repulsive at short distances ( $r < \sigma$ ) and attractive up to a cut-off distance  $r_c$  that should not be much larger than  $\sigma$ . As we explain below, we opt for  $r_c = 2\sigma$  for atomic systems, but for colloidal systems, a smaller value  $r_c = 1.2\sigma$  is preferable.
2. The location of the minimum of the potential should be around  $r_{min} \approx \sigma$ .
3. The potential should have the same depth of the attractive well as the LJ:  $\phi(r = r_{min}) = \epsilon$ .
4. At the cut-off, the potential should vanish at least quadratically, such that the pair force vanishes continuously at  $r_c$ .
5. Evaluating the potential should require only few arithmetic operations, and those should be cheap.

There are, of course, many possible choices, but without a detailed requirement originating from microscopic physics, it is always best to choose the least complicated one. Consider the following interaction potential:

$$\phi(r) = \epsilon \alpha \left( \left[ \frac{\sigma}{r} \right]^2 - 1 \right) \left( \left[ \frac{r_c}{r} \right]^2 - 1 \right)^2 \quad (2)$$

We quickly see that it satisfies all of the above criteria. Same as the LJ, if we measure the distances in units of  $\sigma$  and energies in units of  $\epsilon$ , the potential is described by a single parameter, which is the cut-off distance  $r_c$ . Note that the other parameter in the expression,  $\alpha$  is uniquely determined as soon as we fix  $r_c$ , by satisfying the requirement  $\phi(r = r_{min}) = \epsilon$ . It is clear that – unlike the LJ potential – the potential vanishes at  $r = r_c$  by design and that the force vanishes continuously at this point, which is a huge advantage over the LJ. It is also simpler and requires less computational resources to evaluate.

**TASK 1:** Plot the potential  $\phi(r)$  as a function of  $r$ . You must first determine the value of the prefactor  $\alpha$ . To do this, determine the location of the minimum  $r_{min}$  by finding the local extremum of  $\phi(r)$  (do this analytically), and ensure that  $\phi(r_{min}) = \epsilon$ . Do this at two values of the cut-off,  $r_c = 2.0$  and  $r_c = 1.2$ . Compare the functions  $\phi(r; r_c = 2.0)$ ,  $\phi(r; r_c = 1.2)$  and the LJ potential  $u^{LJ}(r; r_c = 2.5)$  and comment on the differences. In the following, you will use these two values for  $r_c$ , whereby  $r_c = 2$  is a good model for atomic systems (matches the original LJ interaction pretty well), while the value  $r_c = 1.2$  is a better choice to model macromolecular and colloidal systems. Fill in the table below:

Potential	Lennard Jones $U^{LJ}(r)$	ATOMIC $\phi^A(r)$	COLLOIDAL $\phi^C(r)$
Minimum $r_c$			
Cut-off $r_c$	2.5	2.0	1.2
Prefactor $\alpha$	N.A.		

## 1 Simulation model

### 1.1 Model setup

Consider a two dimensional system of particles at a fixed volume, number of particles and temperature ( $NVT$  ensemble). In order to simulate the system, define the simulation box of size  $L \times L$  and place  $N$  particles in it. The control parameter is the number density  $\rho = N/L^2$ , i.e., the number of particles divided by the total volume (area in 2D) of the system. The corresponding packing fraction is the area occupied by  $N$  particles divided by the total area:  $\eta \equiv \rho\pi\sigma^2/4$ . In the simulation, you will work with dimensionless quantities (numbers), therefore all distances will be measured in units of particle diameter  $\sigma$ .

### 1.2 Initial conditions

In MC simulations, you will work with particles' positions, which uniquely define the interaction energy of the system. At each simulation step, you will displace a random particle to a new position and accept or reject the move according to the Metropolis rules. In MD, you generally need to keep track of both, positions and velocities of the particles. Therefore, the initial configuration means the  $N$  particle positions for MC and  $N$  positions and  $N$  velocities for MD. In MD, in order to simulate the  $NVT$  ensemble, you need to implement a thermostat. Choose the Andersen thermostat.

Initial conditions can in principle be arbitrary, since you have to equilibrate the system before starting to measure the averages, but you need to avoid particle overlaps. Try with a periodic crystal lattice (e.g. square, hexagonal...), and also with random initial configuration. In the random case, start with an empty simulation box and keep adding particles – rejecting the insertions with particle overlaps. Creating a random configuration at large densities and in large systems can be pretty challenging!

### 1.3 Boundary conditions

The next detail you need to worry about are the system boundaries. If you intend to simulate the actual finite system with a few hundreds or thousands of particles, then you can implement **hard boundaries** meaning that the particles cannot exit the box. Trial moves outside the box are rejected (or particles are reflected from the walls in MD). You will note that in such case the properties of the system depend

strongly on tics size. Usually we want to predict properties of macroscopic systems that are many orders of magnitude larger than what we can simulate on a computer. To do this, we must perform **finite size scaling**: evaluate the properties at increasing system sizes and try to extrapolate the behaviour at  $N \rightarrow \infty$ . This procedure is improved if we consider **periodic boundary conditions** instead of the hard boundaries. In this approach, we think of the system as lying on a (topological) torus and particles escaping at one side simply enter at the other side. Periodic boundaries are implemented so that we copy the system to all four directions (in 2D; in 3D it is 6) and calculate the interaction energies for each particle by summing up the pair interactions with all the neighbours within the chosen cut-off distance – including the particles in the replica systems.

## 2 Equilibration

**TASK 2:** Fix the temperature  $T$  and density (consider two sets:  $T_1=0.728$ ,  $\rho_1 = 0.8442$ , and  $T_2 = 1.0$ ,  $\rho_2 = 0.1$ ). Choose two types of initial conditions: random positions and ordered lattice. In the case of MD, randomly assign velocities to the particles by drawing from a Maxwell distribution. Start the simulations (MC and MD) from the initial conditions and plot the instantaneous total energy at the simulation step ('simulation time')  $t$ :  $U(t) = \sum_{i<j} \phi_{ij}(t)$  as a function of the simulation steps. Evaluate the average energy  $\langle U(T) \rangle = \frac{1}{T} \sum_{t=1}^T U(t)$  and plot that on the same plot as  $U(t)$ .

- Compare the runs from the two initial conditions using MC and MD. What would you use as a good criterium that the system is equilibrated?
- Bring the system into thermodynamic equilibrium (**run simulations long enough!!!**)
- Once in equilibrium, start evaluating the average  $\langle U \rangle$  again and compare the results from various initial conditions and choice of simulation method. What do you observe?
- Besides the average, analyse the fluctuations of the energy and evaluate  $\delta U^2 = \langle U^2 \rangle - \langle U \rangle^2$ .
- Comparing MD and MC, as well as random and ordered initial condition, should be done in these preparatory steps. The subsequent computations should be done only with one of the methods. **From now on, run only MC simulations. Of course, you can also run MD and compare but this is not requested.**

## 3 Finite size scaling

**TASK 3:** After reaching equilibrium, evaluate the average total energy  $\langle U \rangle$  and the mean square deviation  $\delta U^2$  for different system sizes  $N$  (**again, the longer the run, the better the accuracy!!**).

- Plot the diagrams of  $U$  and  $\delta U^2$  vs.  $1/N$ .
- Discuss the magnitude of the fluctuations and what you can say about the limiting value  $U(N \rightarrow \infty)$  (**hint: it is useful to plot on a logarithmic plot**).
- What can you conclude about finite size scaling with periodic boundary conditions and with hard boundaries?

## 4 Radial distribution function

**TASK 4:** Calculate the radial distribution function  $g(r)$  from simulations with periodic boundary conditions at the two sets of parameters  $T, \rho$  from above. Additionally, try for  $T_3 = 0.9$ ,  $\rho_3 = 1.1$ .

- Plot  $g(r)$  vs.  $r$  and discuss the shape of the curves
- Estimate the average total energy from  $g(r)$  using Eq. (4.5.1) from the book. Check the consistency of these results by comparing to the simulation averages  $\langle U \rangle$  obtained above.

## 5 Equation of state

**TASK 5:** Evaluate the pressure (use the virial expression Eqs. (3.4.1), (3.4.2) from the book). Don't forget to correctly implement the tail/impulse corrections (see pages 37-39 and 52 in the book). Plot the equation of state  $p(\rho)$  at two temperatures:  $T_3 = 0.9$  and  $T_4 = 2.0$ . Discuss the results.

## 6 Free energy

**TASK 6** (not compulsory): Sketch the phase diagrams of the fluid for the two values of the parameter  $r_c$ . Compare to the LJ phase diagram (see the book or any other literature). Discuss the following questions:

- What would be the best method to study the gas-liquid coexistence?
- Estimate at what parameters would the system undergo a phase transition from liquid to solid state.
- Describe how would you calculate the free energy of the system in the **i)** liquid state and **ii)** solid state in order to precisely determine the phase stability. This question is advanced and requires appreciable computation time to carry out properly. It will be a bonus if you attempt it but it is definitely not essential that you deliver good numerical results...