

Observing the simulation

We now have a fully working code to simulate a system of Argon atoms in a box for a given input temperature and density. We can now complete the project and study the system at different initial conditions to observe and analyse the different phases of matter.

They can be neatly distinguished by the pair correlation function. This is a statistical tool used in many fields to understand patterns in distributions of data. Given a reference particle, it gives the probability to find another particle at distance r .

In the simulation, you can compute the pair correlation by making a histogram of particles $n(r)$ of all pairs within a distance $[r, r + \Delta r]$ with bin size Δr . We do this for a certain configuration (i.e. a given time in a simulation). This can then be averaged over many different times and different (random) initial conditions with the same ρ and T . We denote this average over many configurations by $\langle n(r) \rangle$. (Note: This averaging is done for each independent bin $[r, r + \Delta r]$.)

The pair correlation function is then given by:

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r}, \quad (1)$$

where V is the volume of the simulation, and N the number of particles. Note that the various factors surrounding $\langle n(r) \rangle$ are chosen in such a way that $g(r) = 1$ if the particles would be homogeneously distributed (e.g. in an ideal gas). *Question for you: Check this is true by using the simulation code!* The pair correlation function has very specific forms in the different states of matter, reflecting the different degrees of order in those states.

Furthermore calculate the pressure for the different states of the system. The pressure P can be obtained from the following formula¹:

$$\frac{P}{k_B T \rho} = 1 - \frac{1}{3N k_B T} \left\langle \frac{1}{2} \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r_{ij})}{\partial r} \right\rangle \quad (2)$$

where r_{ij} denotes the distance between particle i and j , i.e. $r_{ij} = |\mathbf{x}_j - \mathbf{x}_i|$ and U is the Lennard-Jones potential. Once more, the $\langle .. \rangle$ represent an average over many configurations. The first term on the right hand side corresponds to the ideal gas whereas the second provides corrections due to the interaction

¹Interestingly, from the same (Verlet 1961) paper as the time integration algorithm!

between particles that can increase or decrease the pressure. This exact formula, based on the so-called virial theorem, is given here without derivation.

Final milestone:

Simulate Argon in three different states of matter, gas, liquid and solid for our base setup of $N = 108$ atoms. Measure the pressure of the system and plot the corresponding pair correlation function.

Determine the pressure values together with an estimate of the error of the mean by performing several (e.g. 10) independent simulation.

Hints:

(1) You can choose the following (dimensionless) parameters for the different states:

- Gas: $\rho = 0.3$ and $T = 3.0$,
- Liquid: $\rho = 0.8$ and $T = 1.0$,
- Solid: $\rho = 1.2$ and $T = 0.5$.

Question for you: what are the corresponding densities and temperatures in the more conventional SI units? Does that correspond to the correct phases of Argon?

(2) When plotting the correlation function plot only up to distances $r = L/2$.
Question for you: why?

Extensions

There are many ways the project can be extended. This can either be by including more physics, running a larger system, or by extending the analysis.

One possibility is to try to identify the triple point of the system. That requires simulating the system at many different point and figuring out where the phase transition curves join each others. Describe in the report the strategy you would employ to find the location of the triple point. Is the triple point in our model at the correct location when comparing to experimental values?

A second option is to add an electric charge to the atoms/particles. Then add an external electric field (say in the z direction). This will add a force acting on the particles. Try this and describe in the reports what happens in the different phases when the magnitude of the field is increased. Is the behaviour you recover physical?

A third option is to work on the numerical method. One bottleneck towards running very large simulations is the double loop over the particles to compute all the interactions. One way around this is to lay a grid (of what cell size?) on the domain. It can then be used to identify more efficiently what are the particles that have non-negligible contributions to the particle of interest. This reduces the problem complexity from $\mathcal{O}(N^2)$ to $\mathcal{O}(N)$. Describe the algorithm you implemented in the report and demonstrate you can run with > 1000 particles in a reasonable amount of time.