Practice 5

Classical Monte Carlo simulation of a liquid-solid transition

The objective of this exercise is to simulate the liquid-solid transition of a two-dimensional system using a Lennard-Jones interaction potential.

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{5.1}$$

where r is the distance between two interacting particles, σ is known as the "radius" of the particle and ε the typical energy of the potential. The total energy of a particular configuration is given by

$$\frac{E}{N} = \frac{2}{2}k_B T + \frac{1}{N}\left\langle\sum_{i=1}^{N}\sum_{j>1}^{N} U(r_{ij})\right\rangle$$

The first term comes from the fact that every degree of freedom contributes $\frac{1}{2}k_B T$ to the energy of a particle, and we are in 2D. If we define the dimensionless units $r^* = r/\sigma$ and energy $U_{LJ}^* = U_{LJ}/\varepsilon$, we can simplify Equation 5.1 to

$$U_{LJ}^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right] \tag{5.2}$$

and the total energy becomes

$$\frac{E^*}{N} = T^* + \frac{1}{N}\left\langle\sum_{i=1}^{N}\sum_{i<j} U_{LJ}^*(r_{ij}^*)\right\rangle \tag{5.3}$$

Methodology

We will follow a basic simulated annealing scheme to find the optimal crystal configuration, and from there we will start several Monte Carlo simulations for different temperatures. The steps to follow are:

1. Develop a classical Monte Carlo code for a (N, V, T) ensemble for a Lennard-Jones system (eq.5.2) in two dimensions. We will use $N = 242$ atoms.

2. Run an annealing simulation for argon at density $\rho^* = 0.96$ in a square box of size $L \times L$. We expect to obtain the particle configuration having minimal energy, i.e., the perfect crystal lattice.

3. Run a MC simulation for argon at $T^* = 0.5$ and $\rho^* = 0.96$. The displacement should be chosen such that the acceptance probability $p_{\text{acc}} \approx 50\%$.

4. Compute the energy per particle E^*/N (eq.5.3), its standard deviation σ_E, and the radial distribution function $g(r^*)$:

$$g(r) = \frac{1}{\rho} \frac{n(r)}{2\pi r \mathrm{d}r} = \frac{n(r)}{n_{\text{id}(r)}} \tag{5.4}$$

5. Repeat the simulation for the following temperatures: $T^* = \{1.0, 1.5, 2.0, 2.5, 3.0\}$.

6. List the technical parameters (the number of iterations, the displacement amplitude Δt and the acceptance rate) of all the simulations.

7. Plot the radial distribution functions $g(r)$ obtained for the different temperatures.

5.1 First Part: Annealing method to find crystal lattice

In this first part, we will use the simulated annealing scheme to find the optimal ground state configuration starting from a random ensemble of particles.
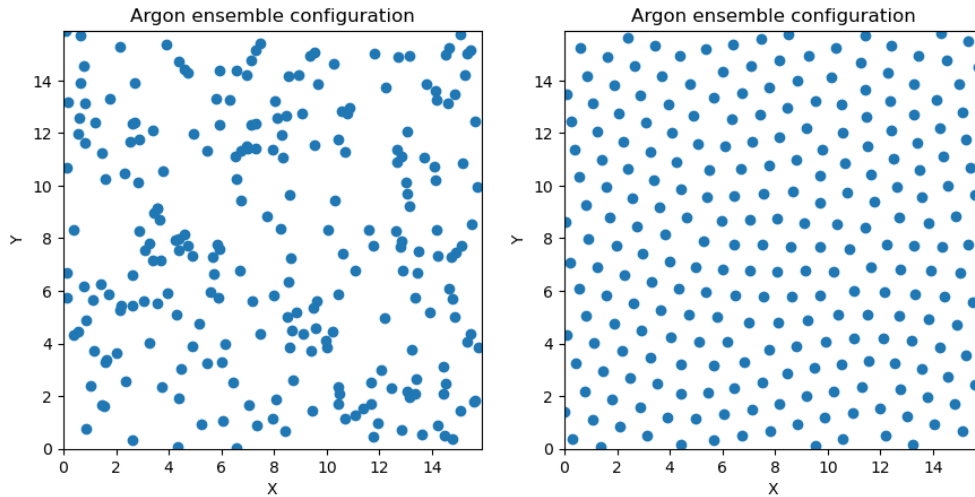
(a) Gas phase for $N = 242$ particles.   (b) Crystal phase for $N = 242$ particles.

Figure 5.1: Simulated annealing method with $T_0^* = 10.0$, $\Delta t = 4 \times 10^{-3}$, $N_{\text{iter}} = 3 \times 10^5$.

The initial configuration corresponds to an ideal gas, since the particle coordinates are generated randomly according to a uniform distribution inside the $L \times L$ box. The volume of the ensemble is calculated from the number of particles and the particle density of the system. Using the fact that the unit cell corresponds to a square box of size $L \times L$, the volume is precisely L^2 and thus, the length of this box is

determined by the density of particles:

$$\rho^* = \frac{N}{V} = \frac{N}{L^2} \longrightarrow L = \sqrt{\frac{N}{\rho^*}}$$

Then, to further check that this is indeed the ground state corresponding to a crystalline lattice, we can plot the radial distribution function of the final state:
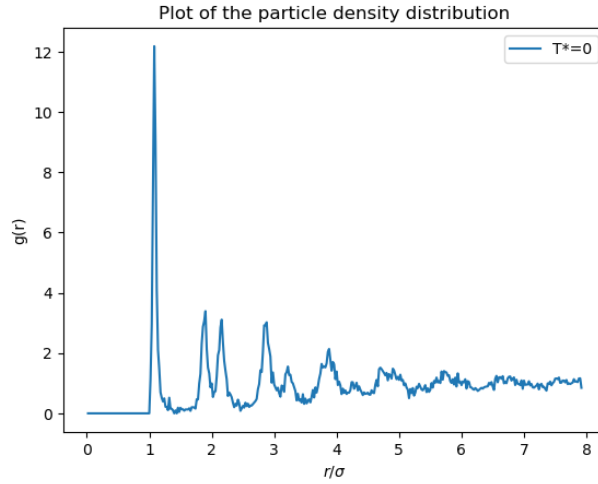

Figure 5.2: Radial distribution function for the crystalline configuration $N = 242$.

In figure 5.2, we can immediately see the many shells of the ground state configuration, represented by the peaks in the RDF plot.

5.2 Second Part: Raising the temperature for MC

Starting from the previous crystalline structure, we will now raise the temperature to $T^* = 0.5$ and run a MC simulation with that fixed temperature.
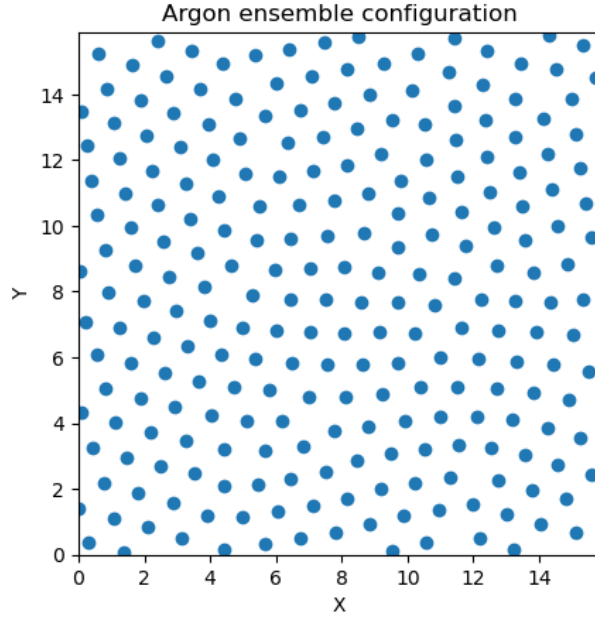
Figure 5.3: Monte Carlo simulation for $T^* = 0.5$, with $N_{\text{iter}} = 100$, $\Delta t = 0.2$, $p_{\text{acc}} = 0.7$.

From Figure 5.3, we cannot really tell if the configuration has changed that much. One thing that we can do, is to plot the radial distribution function and compare it with the previous case
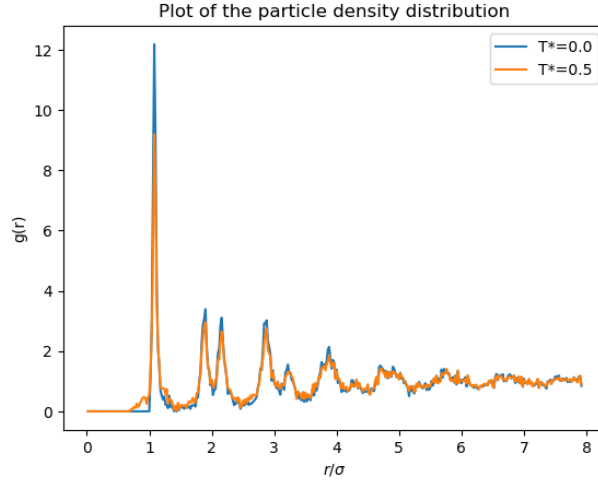

Figure 5.4: Radial distribution function for $T^* = 0.5$ vs $T^* = 0.0$.

In Figure 5.4, we notice that by increasing the temperature to $T^* = 0.5$, the particles forming the shells start to move around their position, effectively decreasing the intensity of the peaks in the RDF plot, and increasing the width of said peaks.

We can also calculate the standard deviation of the energy by saving the value of the energy for many samples (in this case, the number of iterations). The resulting value is $\sigma_E = 0.32229$.

5.3 Third Part: Solid-Liquid Transition

In the final part, we will repeat the procedure that we did previously, but for many different temperatures. For each of them, we first show the final configuration for each temperature, and then plot the comparison of the RDF.
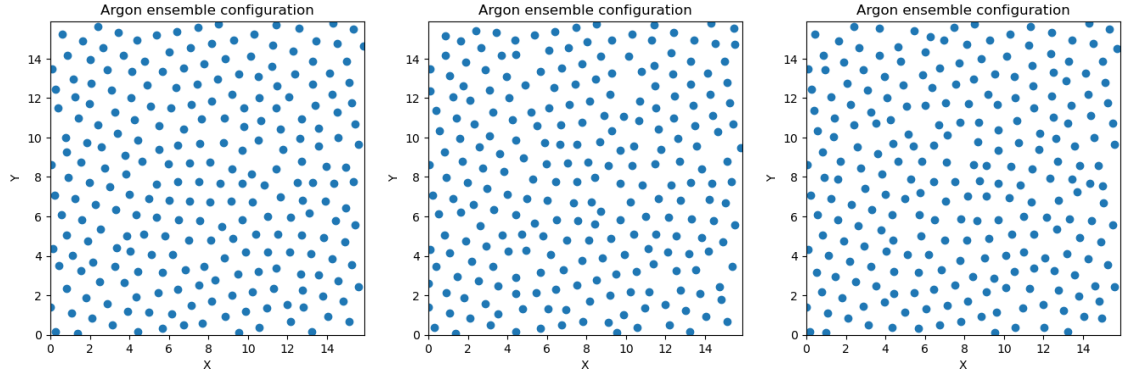
(a) Final configuration for $T^* = 1.0$. (b) Final configuration for $T^* = 1.5$. (c) Final configuration for $T^* = 2.0$.
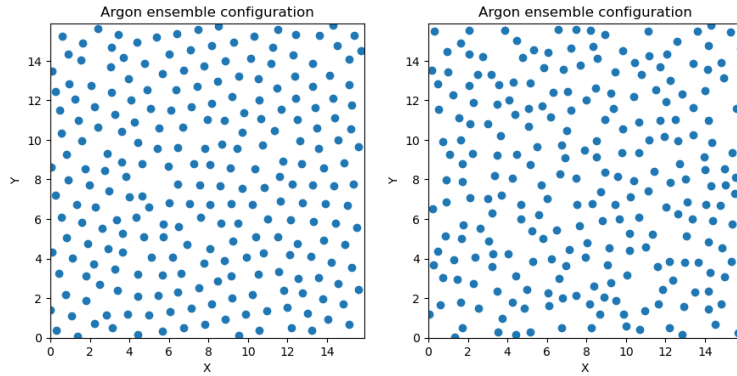
(d) Final configuration for $T^* = 2.5$. (e) Final configuration for $T^* = 3.0$.

Figure 5.5: Monte Carlo simulations for the different temperatures.

Then, in a table, we will show the parameters used in each simulation as well as the standard deviation of the energies.

(a) RDF for $T^* = 1.0$. (b) RDF for $T^* = 1.5$. (c) RDF for $T^* = 2.0$.

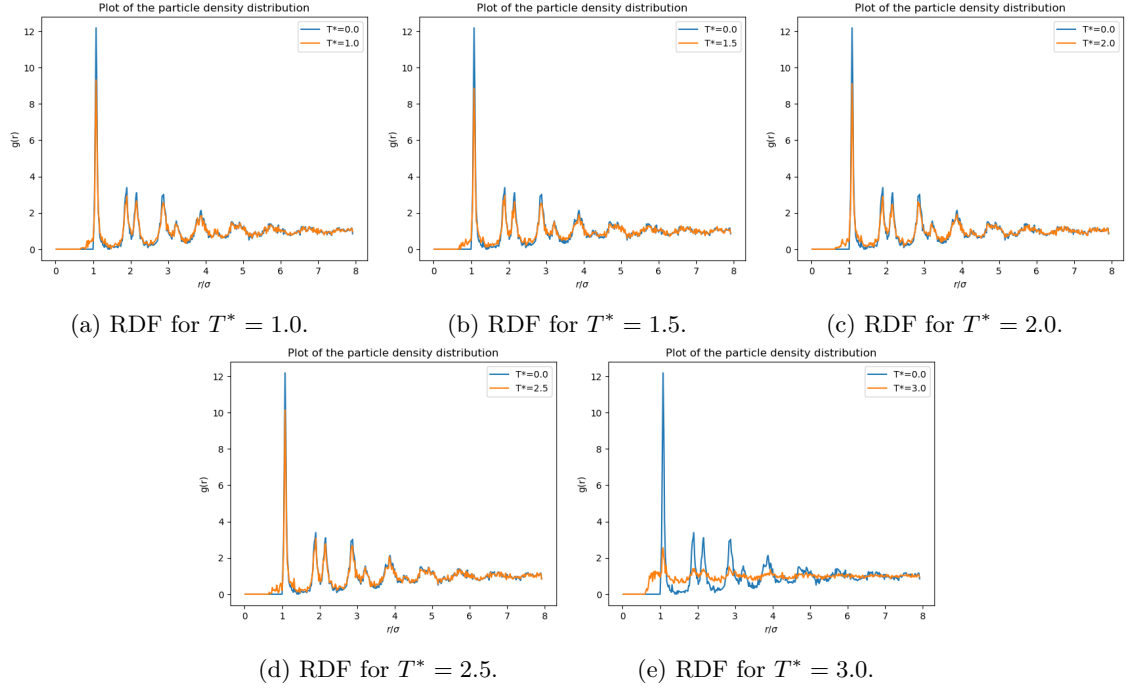(d) RDF for $T^* = 2.5$. (e) RDF for $T^* = 3.0$.

Figure 5.6: Radial distribution functions for the different temperatures vs $T^* = 0.0$.

Looking at Figure 5.6, we can see that the RDF does not vary noticeably for the different values of the temperature. However, between $T^* = 2.5$ and $T^* = 3.0$, there is a big change in the RDF that indicates a phase transition in our ensemble of particles. Specifically, we can see in fig.5.6e that the peaks indicating the different shells in the configuration have disappeared completely; they have been melted, meaning that the ensemble is now in a "liquid" or "gaseous" state, in which the distribution of the particles is more uniform.

	N_{iter}	Δt	p_{acc}	$\mathrm{d}r$	E_{initial}	E_{min}/N	σ_E
T^*:							
0.0	$3 \cdot 10^5$	$4 \cdot 10^{-3}$	0.198	0.02	$1.09 \cdot 10^{24}$	-2.72	
0.5	10^2	0.20	0.70	0.02	-2.22	6.604	0.322
1.0	10^2	0.20	0.71	0.02	-1.47	8.627	0.974
1.5	10^2	0.20	0.80	0.02	-0.72	16.583	3.508
2.0	10^2	0.25	0.77	0.02	0.03	29.099	6.978
2.5	10^2	0.30	0.59	0.02	0.78	20.539	4.102
3.0	10^2	0.30	0.55	0.02	1.53	111.930	34.009

Table 5.1: Minimal energies, standard deviation and parameters used in each simulation.

From the table, we can also see the phase transition take place between $T^* = 2.5$ and $T^* = 3.0$, as

both the final energy and its standard deviation increase enormously. This may indicate that in the energy landscape, by increasing the temperature up to $T^* = 3.0$, we have managed to "jump" over the minimum well that was the crystalline configuration.