Assignment 3: Liquid Equilibrium

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February 19, 2025

1 Introduction

In this report, we use our Molecular Dynamics (MD) simulation to study the thermodynamic properties of our system. These can include the specific heat capacity c_V or the average temperature $\bar{T}$.

Another set of observables studied here are the ones related to the local structure of our fluid. In our case, what we implement is the so-called Radial Distribution Function $g(r)$.

What both thermodynamics and structural properties have in common is that they are time-independent correlations, i.e. static equilibrium averages, which are useful for the validation of equilibrium, for comparison in experimental data, for predicting macroscopic behaviour, etc.

The Results and Discussion section 3 includes plots and reports of these properties in order to study our system at equilibrium.

2 Theory and Methods

2.1 Understanding Equilibrium

Equilibration refers to the process of allowing the system to reach a stable, thermodynamically consistent state before measurements are taken.

Our system is initially set up with atoms placed in a regular lattice with random velocities. Hence, it is because of the interactions between particles and our initial conditions that system needs time to redistribute energy and settle into a steady-state condition.

The purpose of equilibration is then, to allow the system to reach thermal and mechanical equilibrium. Which involves: relaxing initial artificial configurations, ensuring the kinetic and potential energies fluctuate around stable averages, establishing a well-defined temperature distribution - we do not

mention pressure since we are working in the NVE ensamble - and allowing the radial distribution function $g(r)$ to converge to a stable structure.

2.2   Radial Distribution Function (RDF)

The radial distribution function or pair-correlation function $g(r)$ is the radial number density $\rho(r)$ over the average number density $\bar{\rho} = N/V$ which is a very useful measure of the structure of a fluid at molecular length scales. The use of $g(r)$ provides us with a statistical description of the local packing and particle density of the system, by describing the average distribution of particles around a central reference particle[1]. For a single particle it can be computed as:

$$g(r_i) = \frac{\rho(r_i)}{\bar{\rho}} = \frac{V}{N} \frac{h(r_i)}{4\pi r_i^2 \Delta r} \tag{1}$$

where $4\pi r_i^2 \Delta r$ is the volume of the ith spherical shell of thickness Δr and area $4\pi r_i^2$ at distance r_i, and $h(r_i)$ is the number of particles in that shell. So $h(r_i)$ is a histogram of minimum-image distances from a considered atom to the others.

2.3   Specific Heat Capacity c_V

The heat capacity C_V is an extensive property that tells us how much heat energy is needed to raise the temperature of a system. By making use of a property that only depends on the type and phase of the given substance and that can be applied to systems of arbitrary size we obtain the intensive property known as the Specific Heat Capacity or Specific Heat, c_V[2].

Its units are [J/K/mol] and can be computed as:

$$c_V \approx \left(\frac{2}{3k_B} - \frac{4N\sigma^2(k)}{9k_B^3 \bar{T}^2} \right)^{-1} \tag{2}$$

where $k = K/N$ is the kinetic energy per atom, $\bar{T}$ is the average temperature and the variance in k is computed as:

$$\sigma^2(k) = \frac{1}{n} \sum_{i=1}^{n} (k_i - \bar{k})^2 \tag{3}$$

from a large number n of time steps.

3   Results and Discussion

3.1   Study of the evolution of energies over time

In order to study equilibration we run our MD simulation for a sufficiently long time: $t = 20$ ps and plot $\mathcal{K}, \mathcal{V}$ and $\mathcal{H}$.
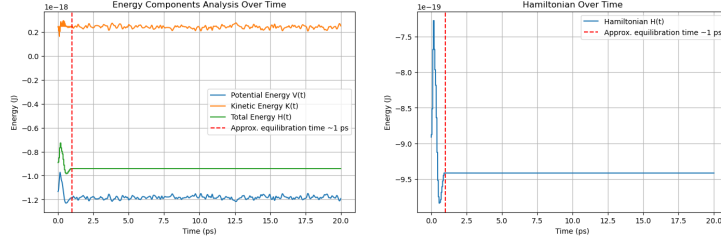

Figure 1: Evolution of $\mathcal{K}, \mathcal{V}$ and $\mathcal{H}$ over time.

From Figure 1 we can see that before equilibrium, around $(0 - 1)$ ps, the kinetic energy shows a rapid increase and fluctuations. This is likely due to velocity rescaling adjusting the particle's velocities to reach the target temperature. The fluctuations are larger in this phase, indicating that the system is still adjusting. The potential energy starts at a relatively high (less negative) value and decreases rapidly. This suggests that particles are initially far from their equilibrium positions and quickly rearrange due to interatomic forces. After the initial drop, it starts fluctuating around a stable mean. And the Hamiltonian fluctuates significantly. This is expected because the kinetic and potential energies are adjusting dynamically. The fluctuations suggest that the system has not yet reached a steady state.

After equilibration (around 1 ps onwards), the kinetic energy fluctuates around a stable mean value, indicating thermal equilibrium. The fluctuations are smaller than in the transitory phase. The potential energy also fluctuates around a stable average. No large shifts, indicating the system has settled into a steady-state. And the Hamiltonian becomes constant. This suggests that energy exchange between kinetic and potential energy has balanced, which is typical in equilibrium.

Since fluctuations before equilibrium are not just due to the natural relaxation of the system but also because of velocity rescaling, we plot the evolution of temperature over time. This is due to the fact that temperature is directly related to kinetic energy via:

$$T = \frac{2K}{3Nk_B} \qquad (4)$$

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if $T(t)$ stabilizes, it means velocity rescaling is no longer making large adjustments.
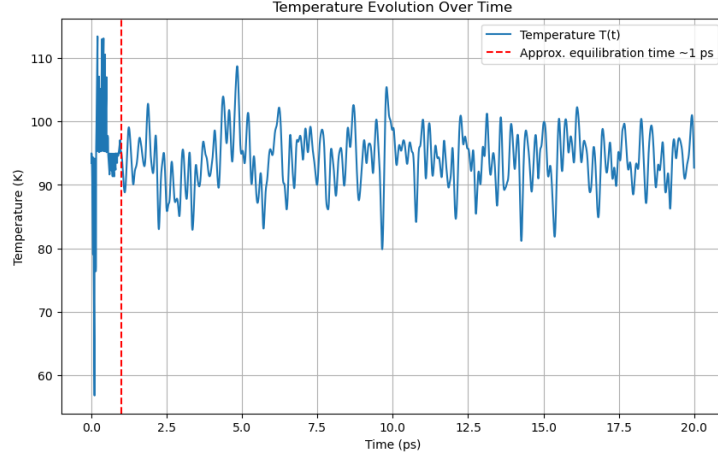

Figure 2: Time evolution of the temperature in MD simulation.

Figure 2 shows how the temperature initially fluctuates significantly, which is likely due to the system adjusting from the initial conditions, but starts to stabilize after around 1 ps. There, temperature oscillates around 90-100 K which is close to our target temperature of 95 K. There are some lower peaks at around 10 and 15 ps and a higher peak at around 5 ps which go between 80 and 110 K.

Overall, we can say temperature stabilizes since its fluctuations around a mean value are due to the fact that we compute T from kinetic energy, which naturally varies over time.

3.2   Radial Distribution Function and Averages

Next in our study, we plot the evolution of $g(r)$ from $t = 0$ ps to equilibrium:
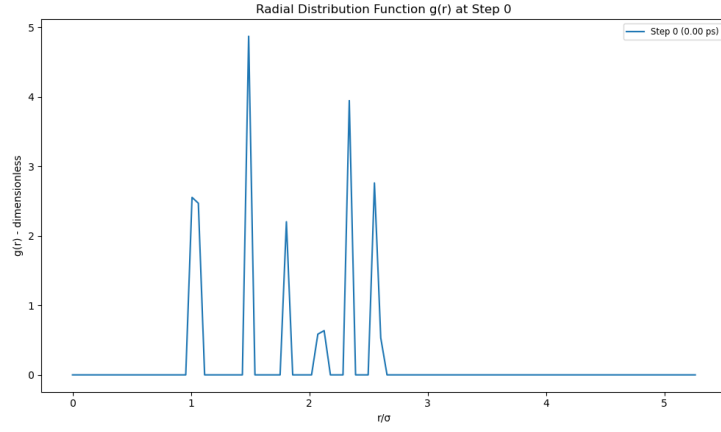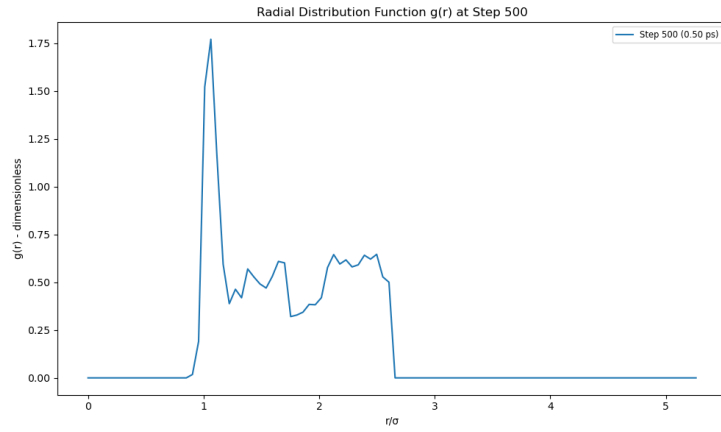

Figure 3: RDF at $t = 0$ ps.
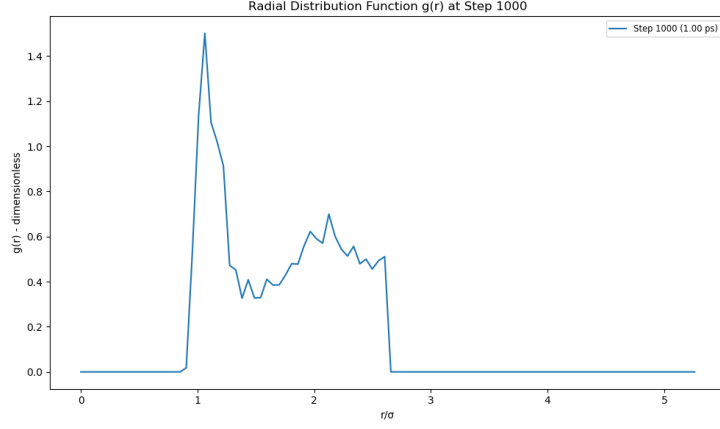

Figure 4: RDF at $t = 0.5$ ps.
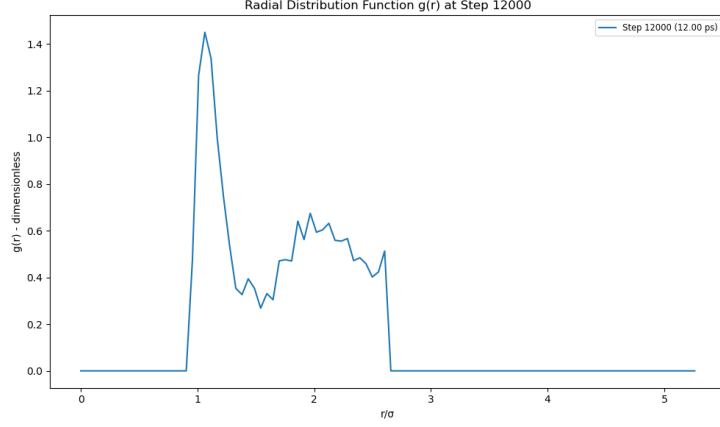
Figure 5: RDF at $t = 1$ ps.

Figure 6: RDF at $t = 12$ ps.

From Figure 3 we see how $g(r)$ is distributed at $t = 0$ ps. This result is consistent because we initialize the atoms on a perfect simple cubic lattice. $g(r)$ is computed by binning pairwise distances into finite-width bins - 100 bins in our simulation. These distances fall into these bins, resulting in finite-width peaks corresponding to the lattice structure. The multiple sharp peaks correspond to well-defined interatomic distances: the first peak represents the nearest-neighbour distance, the second peak correspond to second-nearest neighbours, and so on.

As mentioned above, the peaks from Figure 3 appear because the atoms are initially placed at specific positions, unlike in a liquid where $g(r)$ would be smoother.

We start seeing that liquid-smoother structure of $g(r)$ over time from

Figure 3 to Figure 6. This is because thermal motion causes the sharp peaks to broaden and eventually smooth out as the structure becomes more disordered.

We also note that from reaching equilibrium in $t = 1$ ps - seen in Figure 5 - to a an arbitrary time - $t = 12$ ps - after equilibrium Figure 6, $g(r)$ does not change much only before equilibrium (Figure 5). This is because when reaching equilibration the radial distribution function stabilizes since the distribution of particles and their interactions become steady. This means that the probability of finding a particle at a distance r from a reference particle remains constant.
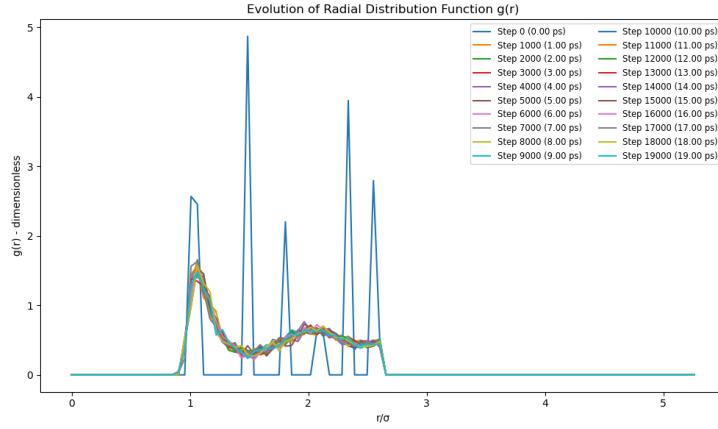

Figure 7: Evolution of $g(r)$ over time.

Finally, we plot the time-averaged $\bar{g}(r)$ and report $\bar{\mathcal{K}}, \bar{\mathcal{V}}, \bar{T}$ and c_V at equilibrium. We have computed these outputs at 2000 steps in our simulation i.e. at $t = 2$ ps.
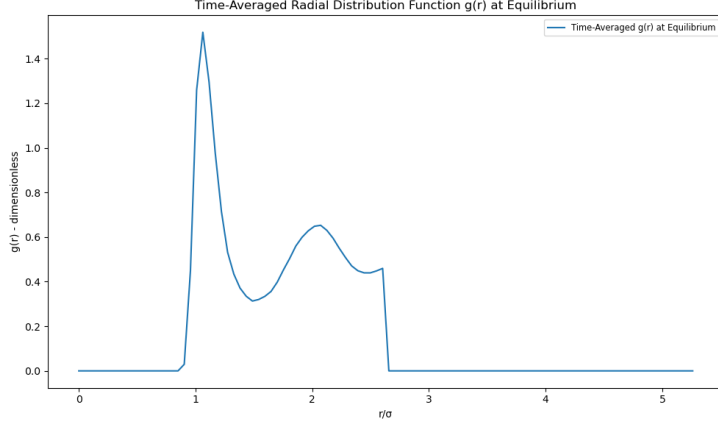

Figure 8: Time-averaged RDF at equilibrium.

From Figure 8 we can see how $\bar{g}(r)$ is distributed at equilibrium. We can observe a first peak (around 1.4 at $r/\sigma \approx 1$) which suggests strong nearest-neighbour correlations, a second peak (around 0.6 at $r/\sigma \approx 2$) which implies some influence of second-nearest neighbours and a vanishing pair-correlation function at $r/\sigma > 3$ which indicates that beyond a certain distance particles behave as if they are uncorrelated, suggesting the system is not crystalline but fluid-like which is our case.

The average potential energy has a value of $\bar{\mathcal{V}} \approx -1.18 \times 10^{-18} J$. The negative output confirms that particles are in a bound state, meaning attractive interactions (from the Lennard-Jones potential) dominate.

The average kinetic energy has a value of $\bar{\mathcal{K}} \approx 2.41 \times 10^{-19} J$ which aligns with the obtained averaged temperature. And the average temperature is $\bar{T} \approx 93.27 K$ which is very close to our target temperature $T = 95 K$.

The specific heat is $c_V \approx 3.58 \times 10^{-23} J/K/mol$ seems quite small. However, specific heat capacity calculations can be sensitive to the averaging process.

References

[1] Libretexts. (2025, February 7)*1.2: Radial Distribution Function. Chemistry.* Chemistry LibreTexts. `https://chem.libretexts.org/Bookshelves/Biological_Chemistry/Concepts_in_Biophysical_Chemistry_(Tokmakoff)/01%3A_Water_and_Aqueous_Solutions/01%3A_Fluids/1.02%3A_Radial_Distribution_Function`

[2] Libretexts. (2020, November 5)*13.2: Specific Heat.* Physics LibreTexts. `https://phys.libretexts.org/Bookshelves/University_Physics/Physics_(Boundless)/13%3A_Heat_and_Heat_Transfer/13.2%3A_Specific_Heat`