Computational Physics Project 1:
Molecular Dynamics Simulation of Argon Atoms

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Abstract

This project was done as a part of the Computational Physics course at Leiden University during the spring semester of the academic year 2024/2025. The goal of the project was to develop a molecular dynamics simulation for a system of argon atoms and study its physical properties for different temperatures and densities. The simulation consisted of a small number of argon atoms (108-864) in a face-centered cubic lattice within a box with periodic boundary conditions and the minimum image convention. Interactions between argon atoms were modeled using Newtonian mechanics and the Lennard-Jones potential. Numerical integration was done with the velocity Verlet algorithm and all equations were transformed into dimensionless units to minimize computational errors and enhance efficiency. Pressure and the pair-correlation function of the system were analyzed in each state, and the results showed that the simulation successfully captured the physical properties of argon atoms across gaseous, liquid, and solid states.

1 Introduction

Molecular dynamics simulations enable to solve the equations of motion of systems that consist of a large number of particles, which would be impossible to solve analytically. The field of molecular dynamics started to emerge in the 1950s, with the works done by B.J. Alder and T.E. Wainwright [1, 2], and was developed further during the 1960s by A. Rahman [7] and L. Verlet [8]. Today, molecular dynamics is one of the most flexible and popular tools available for investigating molecular structure, thermodynamic properties and dynamics [4]. Simulating these kinds of systems is important in many areas, not only physics, but also biology, engineering and other fields.

Well-studied systems in molecular dynamics simulations are ensembles of argon atoms [7, 6, 3]. In such a system, the motion of each particle is governed by Newton's second law:

$$m\frac{\mathrm{d}^2\mathbf{x}}{\mathrm{d}t^2} = \mathbf{F}(\mathbf{x}) = -\nabla U(\mathbf{x}). \tag{1}$$

If the potential depends on the interaction between pairs of atoms, the force term on an atom α is calculated as

$$\mathbf{F}_\alpha = \mathbf{F}(\mathbf{x}_\alpha) = -\sum_{\beta\neq\alpha} \nabla U(\mathbf{x}_\alpha - \mathbf{x}_\beta), \tag{2}$$

where the sum runs over all the other atoms in the system. The most popular way to describe interactions in molecular dynamics is using the Lennard-Jones potential, which consists of an attractive part and a repulsive part [5]. The attractive part comes from Van der Waals interactions and the repulsive part comes from the Pauli repulsion principle. This potential has the following form:

$$U(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{3}$$

where for argon atoms, the values of the parameters are $\epsilon/k_B = 119.8$ K and $\sigma = 3.405$ Å. The force acting between particles is determined by the gradient of the potential, which is

$$\nabla U(\mathbf{x}) = 24\left(\left(\frac{\sigma}{r}\right)^{7} - 2\left(\frac{\sigma}{r}\right)^{13}\right), \quad \text{where} \quad r = |\mathbf{x}|\,. \tag{4}$$

2 Methods

In molecular dynamics simulations, argon atoms are simulated as points that interact due to the Lennard-Jones potential, and the equations of motion are numerically integrated. A powerful method for numerical integration of dynamical systems is the velocity Verlet algorithm [8], where position is given as

$$\mathbf{x}(t+h) = \mathbf{x}(t) + h\mathbf{v}(t) + \frac{h^2}{2m}\mathbf{F}(\mathbf{x}(t)) + \mathcal{O}(h^3), \tag{5}$$

and velocity is

$$\mathbf{v}(t+h) = \mathbf{v}(t) + \frac{h}{2m}\left(\mathbf{F}(\mathbf{x}(t+h)) + \mathbf{F}(\mathbf{x}(t))\right) + \mathcal{O}(h^3), \tag{6}$$

with the h being the time step, which should be sufficiently small. This makes the discretized equations of motion manifestly time-symmetric and, therefore, when forces depend only on the positions of particles, the velocity Verlet algorithm preserves the discretized version of the system's energy.

Our molecular dynamics simulation encompassed a system of a small number (108-864) argon atoms in a cubic box with periodic boundary conditions and the minimum image convention. The atoms were originally placed on a face-centered cubic lattice and their initial velocities were drawn from the Maxwell distribution. The equations of motion were derived from Newtonian mechanics and the Lennard-Jones potential, and we used the velocity Verlet algorithm to perform numerical integration. All equations were transformed into dimensionless units as discussed in 2.1. The simulation code was written in Python, using `NumPy` and `SciPy` libraries for calculations and `Matplotlib` for plotting.

The simulation code took as input the density and temperature of the system (specifying its macrostate), calculated the corresponding size of the simulation box and initial positions and velocities of the atoms, and then found the equilibrium configuration (see 2.3). After reaching equilibrium, the evolution of the system was performed through numerical integration over 1000 timesteps (in SI units, the length of the timestep is $h = 2.15 \cdot 10^{-14}$ s). In one complete simulation, the evolution of the system was run once while measuring the system's energy and particle trajectories. After that, the evolution was run 30 times to collect measurements that needed to be averaged. These were the pair-correlation function and pressure. The process of taking the measurements is described in 2.2.

As the main part of the simulation project, we simulated 108 argon atoms in the following macrostates, corresponding to the three phases of matter:

- **gas:** $\rho = 500$ kg/m^3, $T = 360$ K;
- **liquid:** $\rho = 1350$ kg/m^3, $T = 120$ K;
- **solid:** $\rho = 2000$ kg/m^3, $T = 60$ K.

Results for the three different phases can be found in 3.

We also did one additional simulation where the main goal was to reproduce results for the pair-correlation function found in [7]. The scale of this simulation was different, as we wanted to reproduce the settings of this article. Specifically, the number of particles was now 864, which meant that each evolution was significantly more computationally expensive. Because of this, we ran it only 10 times for just 500 timesteps. The results are presented in 3.4.

2.1 Dimensionless units

It is practical to use dimensionless units in molecular dynamics simulations, because SI units can lead to numbers of very different magnitudes, which can cause rounding errors. Two natural units arise directly from the Lennard-Jones potential: σ for position and ε for energy. Dimensionless distance is thus $\tilde{\mathbf{x}} = \mathbf{x}/\sigma$. The characteristic mass scale is provided by the mass of argon m_{Ar}, which allows us to define the characteristic time $\tau = \sigma\sqrt{m_{Ar}/\varepsilon}$. Dimensionless time can then be defined as $\tilde{t} = t/\tau$, which gives the dimensionless velocity $\tilde{v} = v/\sqrt{\varepsilon/m}$.

Newton's equation in dimensionless units takes the form

$$\frac{\mathrm{d}^2\tilde{\mathbf{x}}}{d\tilde{t}^2} = -\tilde{\nabla}\tilde{U}(\tilde{r}), \tag{7}$$

where the dimensionless potential is given as

$$\tilde{\nabla}\tilde{U}(\tilde{r}) = 24\left(\tilde{r}^{-7} - 2\tilde{r}^{-13}\right). \tag{8}$$

When using these dimensionless units, we can say that we measure length in units of σ, energy in units of ε and time in units of τ.

2.2 Measured quantities

Different phases of matter can be distinguished by analyzing their pair-correlation functions. The pair-correlation function, often denoted by $g(r)$, shows the probability of finding another particle at a distance r with respect to some reference particle. It is given as

$$g(r) = \frac{2V}{N(N-1)}\frac{\langle n(r)\rangle}{4\pi r^2 \Delta r}, \tag{9}$$

where $n(r)$ is the histogram of all particles within a distance $[r, r+\Delta r]$, $\langle n(r)\rangle$ denotes the average over many configurations, V is the volume of the box in which our simulation takes place, and N is the number of particles.

In the article by L. Verlet [8], in addition to the numerical integration algorithm, a formula was also given for the pressure in the system:

$$\frac{P}{k_B T\rho} = 1 - \frac{1}{6Nk_BT}\left\langle \sum_{\alpha}\sum_{\beta>\alpha} |\mathbf{x}_\beta - \mathbf{x}_\alpha| \frac{\partial U}{\partial r}\right\rangle. \tag{10}$$

Within each run of the system's evolution, we collected the time-averaged pressures P_i, and calculated the pressure of the system as the average of the time-averaged pressures: $\bar{P} = \frac{1}{n}\sum_{i=1}^{n} P_i$. The error of the pressure was calculated by collecting variations σ_i^2 within each run $i \in \{1, ..., n\}$, where n is the number of runs. We then took the average $\sigma_{\text{time}}^2 = \frac{1}{n}\sum_{i=1}^{n}\sigma_i^2$. We also determined the variation of the time-averaged pressures, σ_{runs}^2, and calculated the total variation as $\sigma^2 = \sigma_{\text{runs}}^2 + \sigma_{\text{time}}^2$. From this we calculated the standard error of the mean as $\text{SEM} = \sqrt{\frac{\sigma^2}{n}}$. We thus found the final result for the pressure as $P = \bar{P} \pm \text{SEM}$.

Averages $\langle\cdots\rangle$ appearing in formulas (9), (10) would be ensemble averages in statistical physics. To estimate these, we are using time averages as is normally done, and in addition, we are averaging over multiple runs. This is supported by the ergodic hypothesis, which says that for common physical systems, ensemble averages can be estimated by the time averages (for sufficiently long times).

2.3 Finding equilibrium

To study the system at equilibrium, we implemented an algorithm that helped the system get closer to equilibrium before running the actual simulation. Kinetic energy of our system at equilibrium is, from the equipartition theorem,

$$E_{\text{kin}}^{\text{target}} = (N-1)\frac{3}{2}k_BT,$$

where k_B is the Boltzmann constant. We compared this to the current total kinetic energy

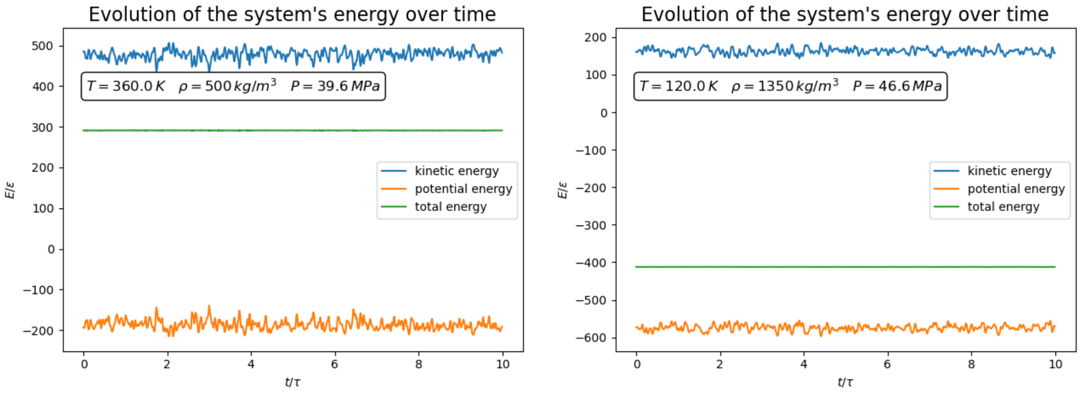
$$E_{\text{kin}}^{\text{current}} = \frac{1}{2}m_{Ar}\sum_{\alpha} v_\alpha^2,$$

and set the allowed difference $|E_{\text{kin}}^{\text{target}} - E_{\text{kin}}^{\text{current}}|/E_{\text{kin}}^{\text{target}}$ to 0.01. The simulation was run for 20 timesteps, then it was checked if the values of the actual and target kinetic energies were close enough. If not, all velocities were scaled with the following parameter:

$$\lambda = \sqrt{\frac{E_{\text{kin}}^{\text{target}}}{E_{\text{kin}}^{\text{current}}}}$$

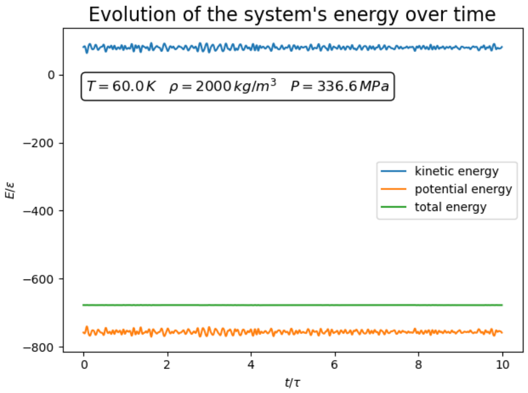
and the cycles were repeated until the system was at equilibrium. After reaching equilibrium, the simulation was run for the aforementioned number of timesteps.

Figures 1a, 1b and 1c show the kinetic, potential and total energy of the system in the gaseous, liquid and solid states (in dimensionless units). Although there are small fluctuations, we can see that the ratio of kinetic and potential energies stays approximately constant, which means that the system is indeed at equilibrium. We can also see that the velocity Verlet algorithm is very efficient at preserving the total energy of the system.



(a) Kinetic, potential and total energy of the system in the gaseous state.

(b) Kinetic, potential and total energy of the system in the liquid state.



(c) Kinetic, potential and total energy of the system in the solid state.

Figure 1: Evolution of the system's energy over time, in three different states.

3 Results and discussion

3.1 Gaseous state

The mean pressure in the simulated system of argon gas was $P_{\text{gas}} = 39.8 \pm 0.1$ MPa. Figure 2 shows the pair-correlation function of argon atoms in the gaseous state. We see that there is the first peak, which is discussed in 3.5. The rest of the plot is relatively flat at a value around $g(r) \approx 1$, since in a gas, the atoms have no preferred positions with respect to each other, and due to the rapid movement we are likely to find particles everywhere within some reasonable distance with very high probability.

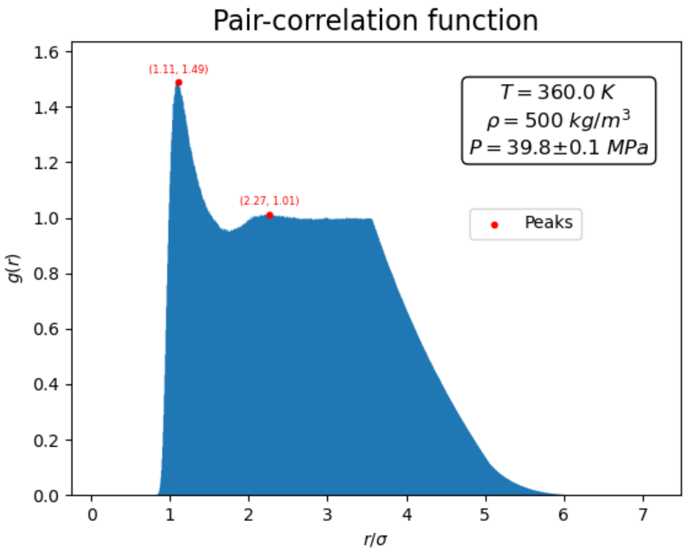


Figure 2: Pair correlation function of argon atoms in the gaseous state.

3.2 Liquid state

The mean pressure in the simulated system of liquid argon was $P_{\text{liquid}} = 46.3 \pm 0.5$ MPa. Figure 3 shows the pair-correlation function of liquid argon. The distribution is less uniform compared to the gaseous phase, which is as expected because there is more structure in the molecular composition of a liquid. One can compare this to the plot 5, where we use 864 atoms instead of just 108 atoms. In that case additional peaks appear, corresponding to neighbors of higher order which are expected for a larger number of atoms.

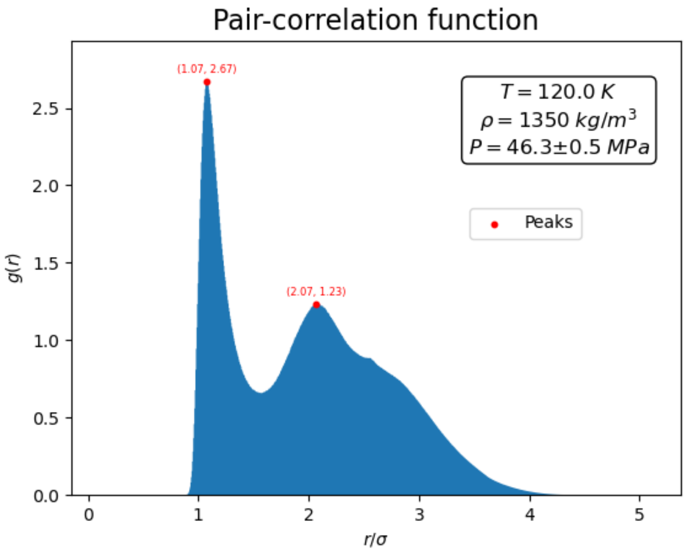


Figure 3: Pair correlation function of argon atoms in the liquid state.

3.3 Solid state

The mean pressure in the simulated system of solid argon was $P = 338.6 \pm 0.5$ MPa. As expected, pressure is much larger in the solid phase compared to gaseous and liquid phases. Figure 4 shows the pair-correlation function of solid argon, which also looks very different compared to gaseous and liquid phases. We can clearly see the impact of the face-centered crystal lattice: there are sharp peaks in the plot, which indicate that the atoms are at certain fixed distances with respect to each other.

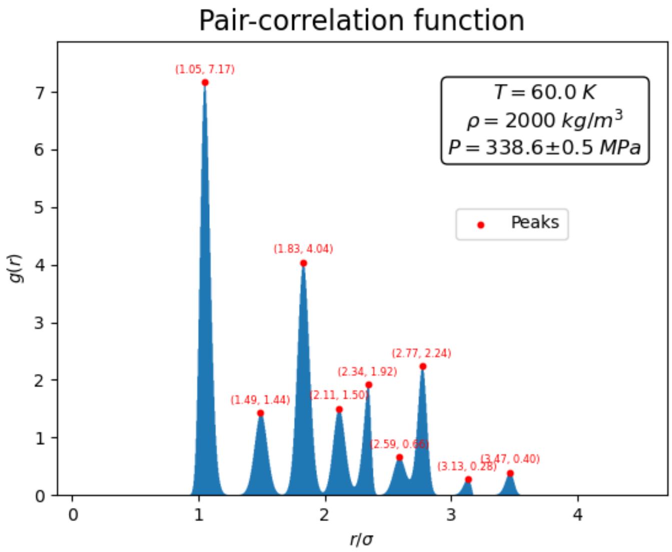


Figure 4: Pair correlation function of argon atoms in the solid state.

3.4 Reproducing results from the literature

Figure 5 shows the pair-correlation function for the same number of particles and the same temperature and density as in [7]. Other details of the setup are discussed in 2. This should correspond to argon in the liquid phase and one can indeed see that it matches the rough shape found in 3.2.

Using these conditions, we found peaks at $1.08\sigma \approx 3.7\text{Å}$, $2.08\sigma \approx 7.1\text{Å}$ and $2.99\sigma \approx 10.2\text{Å}$, which can be compared to [7], where the peaks are at 3.7Å, 7.0Å and 10.4Å, respectively. Our simulation produced results that are very close to the data presented in [7].

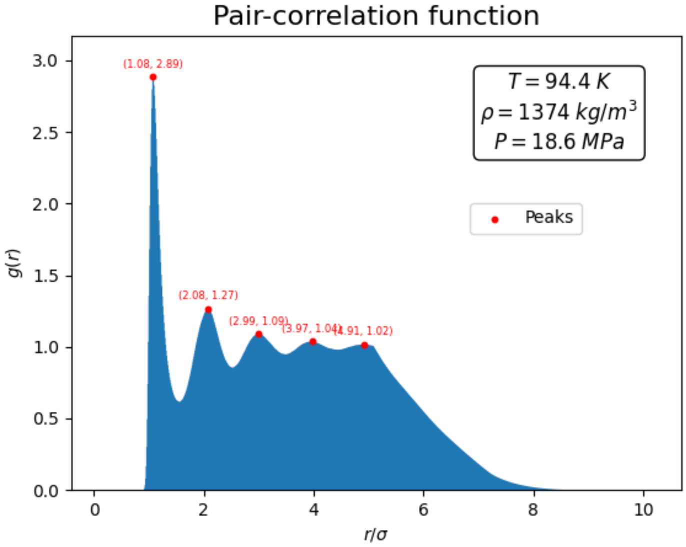


Figure 5: Pair correlation function of argon atoms in the setup of [7] (liquid phase).

3.5 Discussion

In comparing our results with known results of thermodynamics, one should be careful, because the thermodynamic limit - an infinite number of particles - is often used in thermodynamics. Our simulation is very limited in this sense, since we considered a small number of particles. For example, usually it is only in the thermodynamical limit that phase transitions can be defined (there can be no discontinuities for a finite number of particles). Because of this, we cannot assume that the phases can be always easily distinguished. Nevertheless, the features that are indicative of the different phases were also present in our simulation. This was in part possible because we did not consider macrostates near to phase transitions, but well within the corresponding phases.

Because of the minimal image convention, each of the relative particle distances must satisfy $|r_i| < L/2$, where L is the length of each side of the simulation box. Thus, for distance, it must hold that

$$r = \sqrt{r_1^2 + r_2^2 + r_3^2} < \sqrt{3\left(\frac{L}{2}\right)^2} = \frac{\sqrt{3}}{2}L.$$

Because all the plots of the pair-correlation function are from 0 to L, we can clearly see that they match this requirement.

What one can also see on all of the plots is the first peak occurring at approximately 1.1σ. This agrees with the location of the minimum of the Lennard-Jones potential, which is at $2^{1/6}\sigma = 1.12\sigma$. This is because, at smaller distances, the potential is repulsive.

4 Conclusion

The molecular dynamics simulations performed in this project successfully captured the physical properties of argon atoms across gaseous, liquid, and solid states. As shown in section 3.4, our simulation code accurately reproduced the pair-correlation function of liquid argon as presented in the classical work by A. Rahman [7]. The main weakness of our simulation was the small number of particles. In reality, we would be normally dealing with at least an Avogadro number of atoms, and because of this, our simulation can only be considered a crude - although useful - approximation of reality. The obvious next step of improving our simulation would be to implement a more efficient algorithm for calculating the interactions between atoms, which would enable to use more particles in the simulation. For example, finding the interactions on each atom by only considering other atoms up to a cut-off radius.

References

[1] BJ Alder and TE Wainwright. "Phase Transition for a Hard Sphere System". In: *J. Chem. Phys* 27 (1957), p. 1208.

[2] BJ Alder and TE Wainwright. "Studies in molecular dynamics. I. General method". In: *The Journal of Chemical Physics* 31.2 (1959), pp. 459–466.

[3] CL Briant and JJ Burton. "Molecular dynamics study of the structure and thermodynamic properties of argon microclusters". In: *The Journal of Chemical Physics* 63.5 (1975), pp. 2045–2058.

[4] Ben Leimkuhler and Charles Matthews. "Molecular dynamics". In: *Interdisciplinary applied mathematics* 39.1 (2015).

[5] Johannes Lenhard, Simon Stephan, and Hans Hasse. "On the History of the Lennard-Jones Potential". In: *Annalen der Physik* 536.6 (2024), p. 2400115.

[6] David J McGinty. "Molecular dynamics studies of the properties of small clusters of argon atoms". In: *The Journal of Chemical Physics* 58.11 (1973), pp. 4733–4742.

[7] Aneesur Rahman. "Correlations in the motion of atoms in liquid argon". In: *Physical review* 136.2A (1964), A405.

[8] Loup Verlet. "Computer" experiments" on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules". In: *Physical review* 159.1 (1967), p. 98.