

Molecular Dynamics of Argon Atoms

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Abstract

A system of 108 Argon particles was modelled using a molecular dynamics simulation. This was done for the gas, liquid and solid phase for which the pressure and pair correlation function were determined. Furthermore, the impact of an electric field on the system was studied.

1 Introduction

Molecular dynamics (MD) simulations touch on many aspects of physics and are a valuable resource to compare theoretical models to experimental results. In this report, we present a molecular dynamics simulation of Argon particles for the gas, liquid and solid phase. Additionally, the impact of a constant electric field on the system was studied. We determined the pressure and pair correlation function of the three phases which agree with previous literature.

This report first contains a section on the relevant theory of molecular dynamics. The Lennard-Jones potential, electrostatics and thermodynamics in such a system are discussed. The third section explains the methods used for the simulation, after which our results are presented. Lastly, the report is concluded by a comparison to the literature, a discussion of the flaws of this simulation and a suggestion for improvements.

2 Theory

2.1 Lennard-Jones Potential

At the core of MD simulations are interactions between the individual molecules. These interactions can be separated into two types, bonded and non-bonded. Bonded interactions take place within molecules, between atoms which are connected in some way. Bonded interactions might include terms to change the length of a chemical bond, or change the angle of a bond.

All other interactions between atoms are classed as non-bonded interactions. This simulation consists entirely of Argon atoms, so only non-bonded interac-

tions need to be considered. These can be modelled with the Lennard-Jones (LJ) potential.

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where r is the distance between the two particles, σ is the distance at which the LJ potential between the two particles is zero and ϵ is the depth of the potential well (a measure of how strongly the two particles attract each other). Quantities σ and ϵ are often called the “Van der Waals radius” and the “dispersion energy”.

The LJ potential consists of a short range repulsive term and a (relatively) long range attractive term. The r^{-6} attractive term comes from the London dispersion force, which is (the weakest) part of the Van der Waals forces. Van der Waals forces are weak attractions between atoms which do not cause chemical bonds to be formed. Often called induced-dipole dipole interactions, London dispersion forces are temporary attractive forces between two electrically neutral atoms which have formed temporary electric dipoles.

The short range repulsive term models the Pauli exclusion principle by stopping particles from getting too close. The r^{-12} exponent does not have a rigorous physical justification. It is computationally efficient as it is just the square of the other r^{-6} term.

2.2 Electrostatics

The Lennard-Jones potential models intermolecular attractions between electrically neutral atoms or molecules. Once the constituent atoms of our system have nonzero electric charge, electrostatic interactions must be considered. Two equally charged monopoles in vacuum interact through the Coulomb potential:

$$U_{\text{C}}(r) = \frac{1}{4\pi\epsilon_0} \left[\frac{q^2}{r} \right] \quad (2)$$

where r is the distance between the two particles, q is the particle’s electric charge and ϵ_0 is the permittivity of the vacuum. A material specific relative permittivity ϵ_r , representing the polarizability of the medium, can be added to reduce the effectiveness of this interaction.

This Coulomb interaction is much longer range than the Lennard-Jones potential. The Coulomb interaction is one of the strongest interactions in molecular systems, with the interaction between two charged particles falling off with $1/r$. The long range nature of this interaction can cause problems in simulations with periodic boundary conditions. For example, the commonly used minimum image convention, where each particle only feels the effect of the nearest copy of every other particle, is not valid for this interaction. However in systems consisting of identical atoms with identical charge, the Coulomb interaction leads

the atoms to configure themselves in a “maximally repulsive” state. This phase is not of interest in this project.

An external electric field could also be applied to the system. Applying a constant electric field in an arbitrary direction (z), each particle will change their potential energy by:

$$\Delta U_E(z) = E_z q \Delta z \quad (3)$$

where E_z is the electric field, q is the charge of the particle and Δz is the distance the particle travels in the z -direction. In this simulation it is assumed that the particles are far away from the source of the field compared to the box length L .

2.3 Thermodynamics

It is sufficient to treat the Argon atoms as classical point particles. For this system the quantum effects are negligible and implementing them would only cause longer computational time. However for systems like Helium, which becomes a superfluid at low temperatures, our simulation would not be valid, as this phase transition is a purely quantum effect [3].

The argon atoms in our simulation thus follow the laws of classical statistical physics. Firstly, their velocities follow the Maxwell distribution, where each the magnitude of each i th component is chosen from

$$p(v_i) \sim e^{-mv_i^2/(2k_B T)} \quad (4)$$

with $p(v_i)$ the probability distribution, m the mass of the particles, v_i the velocity component along one of the spatial directions and T the temperature [2].

Once the system has thermalised, the total kinetic energy can be related to the temperature via the equipartition theorem. In thermal equilibrium energy is shared evenly among all independent degrees of freedom [1]. In practice this means

$$E_{\text{kin}} = (N - 1) \frac{3}{2} k_B T \quad (5)$$

as total momentum is conserved, leaving the system with only $(N-1)$ relevant degrees of freedom. Here N are the number of particles and $k_B T$ is the thermal energy.

Other state quantities can be determined as well. An expression for the pressure can be derived from the virial theorem, which relates the time averaged kinetic energies of a set of point particles to the total potential energy of the system [8]. The pressure is calculated to be

$$\frac{P}{k_B T \rho} = 1 - \frac{1}{3Nk_B T} \left\langle \frac{1}{2} \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r_{ij})}{\partial r} \right\rangle \quad (6)$$

where P is the pressure, T is the temperature, N the number of particles, r_{ij} the distance between particles i and j and $U(r_{ij})$ the Lennard-Jones potential between particles i and j .

Another useful quantity is the pair correlation function, which describes the distances between particles (equation 7). This quantity shows characteristic behavior for each of the phases that can occur in a system of Argon atoms - solid, liquid or gas [8]. The phase of the system depends on the density and the temperature. The pair function can thus be used to determine the phase of the Argon atoms for various combinations of density and temperature.

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \quad (7)$$

where $g(r)$ is the pair correlation function, V is the volume, N is the number of particles, $\langle n(r) \rangle$ is the average of the histograms, r is the distance between the particles and Δr is the bin size that was used to compute the histogram.

3 Methods

A set of 108 Argon particles was simulated in python. The particles were initially placed in an FCC lattice which consisted of 9 unit cells in a box with lengths L . The length was calculated from the density and the number of particles via equation 8.

$$L = \left(\frac{N}{\rho} \right)^{1/3} \quad (8)$$

where L is the length of the system, N is the number of particles and ρ is the density. In order to mimic an infinite system, periodic boundary conditions with the minimum image convention were used.

The initial velocities of the particles were chosen such that they resulted in a Maxwell velocity distribution (equation 4). Thus, they were drawn from a Gaussian distribution centered at $v = 0$ with the following width

$$\sigma_v = \sqrt{\frac{k_b T}{m}} \quad (9)$$

where k_b is the Boltzmann constant, T is the temperature and m is the mass of the particles.

The positions and velocities were evaluated using the velocity Verlet algorithm:

$$\mathbf{x}(t+h) = \mathbf{x}(t) + h\mathbf{v}(t) + \frac{h^2}{2m}\mathbf{F}(\mathbf{x}(t)) \quad (10)$$

$$\mathbf{v}(t+h) = \mathbf{v}(t) + \frac{h}{2m} [\mathbf{F}(\mathbf{x}(t+h)) + \mathbf{F}(\mathbf{x}(t))] \quad (11)$$

where $\mathbf{x}(t)$ is the position at time t , $\mathbf{v}(t+h)$ is the velocity at time $t+h$, h is the time step and $\mathbf{F}(\mathbf{x}(t))$ is the force.

For each time step, first the positions of the particles were calculated using the positions of the previous time step and the force between the particles of the previous time step (equation 10). Secondly, the force between the particles was calculated for the new positions using a Lennart-Jones potential (equation 1). Lastly, the new velocities were calculated using the force calculated in this and the previous time step (equation 11).

Before the actual simulation was run to obtain the physical properties of the system, the system was first equilibrated. This was done by running the simulation for a small number of time steps (in this case, 10 time steps), after which the total kinetic energy of the system was calculated. This value was compared to the equilibrium value that can be derived from the equipartition theorem (5). These energy values were used to compute the following scale factor:

$$\lambda = \sqrt{\frac{(N-1)3k_B T}{\sum_i m v_i^2}} \quad (12)$$

where λ is the scale factor, N is the number of particles, T is the temperature, m is the mass of the particles and v_i is the velocity of the particles.

If the scale factor differed from unity by a value larger than a certain threshold value (here, 0.01 was chosen), all the velocities were re-scaled by the scale factor. This process was repeated until the scale factor was sufficiently close to 1 and the system was therefore sufficiently close to equilibrium. After this procedure, the actual simulation was started, which was run for 100 time steps.

During each time step, the positions of the particles, kinetic energy and potential energy and pressure were recorded. The pressure was calculated as described in equation 6. Furthermore, halfway during and at the end of the simulation, a histogram of the distance between the particles was computed. The average of the histograms of 10 simulations was used to calculate the pair correlation (7).

3.1 Charged Particles

Besides the Lennard-Jones potential, an electrical potential can also be added to the simulation. Then, a force will be induced on particles with non-zero electric charge. Here, a constant external electric field was applied in the z -direction. Since each Argon atom has the same charge, a constant force in the same direction is induced on all particles. The electric charge of all atoms was set to zero while the system was equilibrating. In finite electric fields, the constant force that is induced can lead to large particle velocities, which never come close to the equilibrium value derived from the equipartition theorem. Once the system has thermalized the electric charge of each atom is switched on.

3.2 Simulation parameters

For each of the different phases, the size of the time steps was taken to be 0.01 and the simulation was run for 100 time steps. For the Lennard-Jones potential, $\epsilon/k_B = 119.8$ K and $\sigma = 3.405$ Å were used as per the previous literature.

The density and temperature for the three phases are given in table 1.

Phase	Density	Temperature
Gas	0.3	3.0
Liquid	0.8	1.0
Solid	1.2	0.5

Table 1: The used density and pressure (in reduced units) for the gas, liquid and solid phase

4 Results

Figure 1 shows the energy of the system during a simulation of the gas phase. The total energy is conserved throughout the entire simulation, as expected for a closed system. This is an important prerequisite for any valid physical simulation.

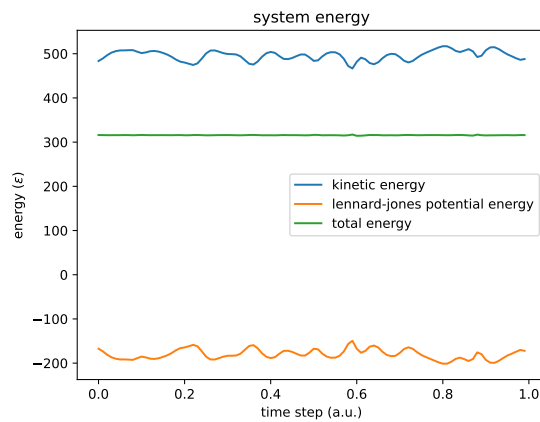


Figure 1: Kinetic, potential and total energy of the system plotted as a function of the time step.

During each simulation the pressure was calculated from the mean pressure in each time step. The average pressure in each of the phases are shown in table 2. This average was taken over 10 simulations. The error was calculated as the standard deviation of the value of the 10 simulations.

Phase	Pressure (reduced units)
Gas	0.96 ± 0.02
Liquid	0.99 ± 0.05
Solid	8.7 ± 0.1

Table 2: The average pressure for the three phases.

The pair correlation functions are shown in figure 2, 3, 4. Figure 2 shows the pair correlation for the gas phase. The graph shows that the pair correlation increases for small distances between the particles, until it reaches its peak at roughly a distance of σ (3.405 Å). After the peak, the correlation function becomes constant at $g(r) = 1$.

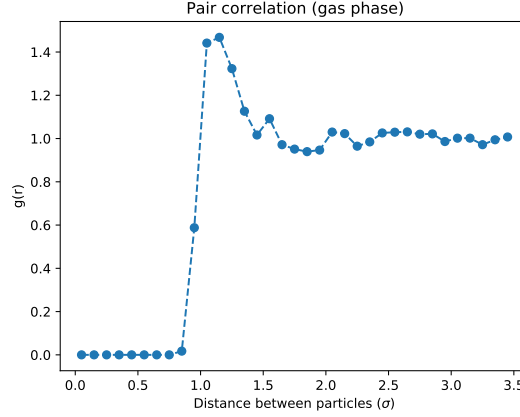


Figure 2: The pair correlation function of the gas phase. The distance between the particles is plotted in units of σ , as defined in the previous section. The pair correlation function ($g(r)$) is plotted in dimensionless units. The function shows a peak at distance σ after which it goes to $g(r) = 1$.

The pair correlation for the liquid phase is given in figure 3. In the figure can be seen that the pair correlation function oscillates around $g(r) = 1$ with peaks at σ and 2σ . The distance between the particles is plotted in units of σ , as defined in the previous section.

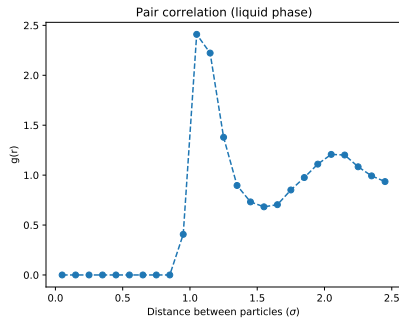


Figure 3: Correlation function of the liquid phase.

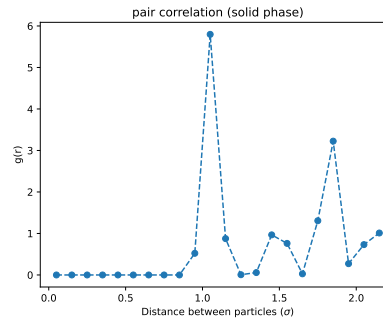


Figure 4: Correlation function of the solid phase.

Figure 4 shows the pair correlation for the solid phase. There are clear peaks visible at 1σ , 1.5σ and 1.8σ . These correspond to the locations of the other atoms in each unit cell. Hence the solid phase exhibits a periodic, crystalline structure.

4.1 Electric field

The properties of the simulation change once the particles have a nonzero electric charge. Applying a constant electric field increases the potential energy of the particles. As the simulation evolves the particles lower their electrical potential energy, increasing their velocities as a result. Depending on the sign of their charge, these particles are being attracted or repelled in the direction of the applied field.

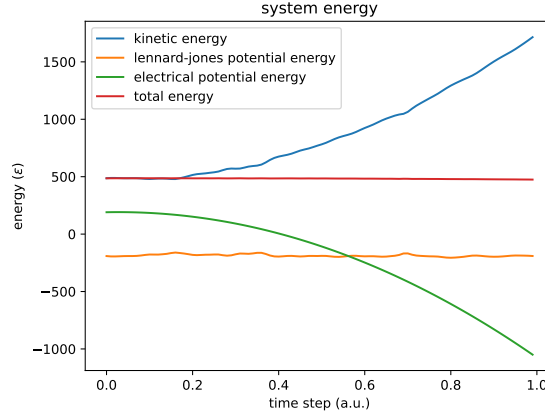


Figure 5: Energy of a charged Lennard-Jones gas under the influence of an external electric field ($E_z = 5.0$, reduced units) is conserved throughout.

Strong applied fields have a detrimental effect on the solid phase. The periodic crystal structure is destroyed as all particles are accelerated in the same direction. In effect, the electric field rips these ions off their lattice sites, creating a phase of matter more akin to a plasma (a gas of ionised particles) than a solid. However this is only visible in our non-moving reference frame (e.g. the movie). From the point of view of the individual atoms nothing has changed because they experience the same electrical force. The correlation function (Fig. 6) of a charged Lennard-Jones solid ($T = 0.5$, $\rho = 1.2$) at strong fields ($E_z = 5.0$) is identical to that of a neutral Lennard-Jones solid. Note that this is not physical; In a real crystal closer atoms would experience a greater electrical force, destroying the periodic lattice structure.

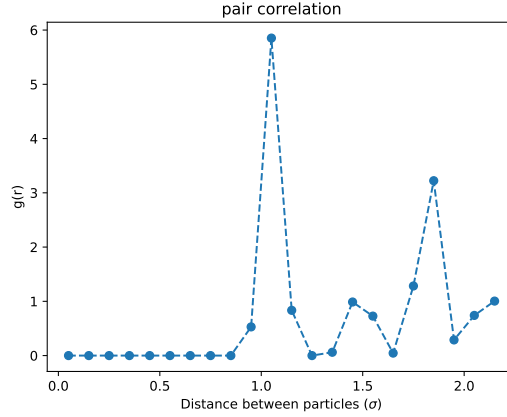


Figure 6: Correlation function of a charged Lennard-Jones solid under an external electric field ($E_z = 5.0$). The structure is identical to Fig. 4.

5 Conclusion and discussion

A molecular dynamics simulation of 108 Argon particles was run in order to determine the pressure and pair correlation function for the gas, liquid and solid phase. The pressure was found to be 0.96 ± 0.02 , 0.99 ± 0.05 and 8.7 ± 0.1 respectively. For the gas phase, the determined pair correlation function showed a peak at a distance of σ , after which it became constant at $g(r) = 1$. The pair correlation function of the liquid phase oscillated with peaks at integer values times σ . The solid phase has a correlation function with peaks at distances of 1σ , 1.5σ and 1.8σ which correspond to the lattice sites in an FCC lattice. These results agree with previous research. [4, 5, 6, 7].

Furthermore, the impact of an electric field on the system was studied. Strong electric fields were found to destroy the periodic lattice structure of the solid phase, effectively turning the solid into a plasma. However the far field approximation (each particle feels the same electrical force) meant that the correlation function of the charged Lennard-Jones solid did not change. This is a factor that could be improved in future simulations.

As mentioned, the Coulomb force between the argon atoms was not taken fully into account in our simulations for simplicity reasons. The simulation could therefore be improved by implementing a Coulomb interaction term between the particles evaluated with the Ewald summation technique [9]. The currently used minimum image convention should be replaced by “lattice sum electrostatics”. This is because the long range nature of the Coulombic interaction means that contributions from many particle copies (not just one) should be considered.

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