Simulation of a System of Argon Atoms
Written report

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Molecular Dynamics (MD) is of major interest for different fields of research, such as structural biology and material science. In this report we introduce some of the fundamental concepts of the simulation of particles interacting with each other through some potential. We discuss the discretization of the Newtonian Equation of Motion (EOM) and the simulation step to model the evolution of the system. Further, we investigate different physical properties, such as the pair correlation and the pressure, and compare these quantities to our theoretical expectation and some already verified values.

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Introduction

Molecular dynamics, i.e. the simulation of the movement of molecules or atoms interacting with each other can be used in a very broad range of fields. For example in biophysics and structural biology such methods are used for modeling the interaction between different molecules or even the formation of new molecules. In this report we want to give some insights on a quite fundamental simulation of a system of atoms with interaction modeled via Lennard-Jonnes potential. In the following we present the simulated system, the methods used for the simulation and the respective results. We conclude with the discussion whether the physical properties of the simulated system match our expectation and what could be the reasons for possible discrepancies. The code can be found online repository.

1 Simulated System

The physical system which we are trying to simulate with this model is a system of neutral Argon atoms in different phases. In this chapter we will provide the physical description of the simulated system and a list of its physical properties, which we will later use to evaluate our simulation.

1.1 Physical system

The considered system is an infinite volume of Argon atoms with a specified (number)density and temperature. As known from Statistical Mechanics, the atoms velocity distribution is given by a Maxwell-Boltzmann distribution. Denoting the velocity of a particle with $\mathbf{v}$, the probability density is given by

$$p(\mathbf{v}) = 4\pi \left(\frac{m}{2\pi k_\mathrm{B} T}\right) v^2 \exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right) . \tag{1.1}$$

The Argon atoms are electrically neutral and interact with each other according to the Lennard - Jones (L-J) potential, modelling soft attractive and repulsive forces. The L-J potential for two particles i and j with respective positions $\mathbf{r}_i$ and $\mathbf{r}_j$ ($\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$) reads

$$V_{\text{L-J}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] , \tag{1.2}$$

where ε denotes the depth of the potential well (referred to as *dispersion energy*) and σ the zero-crossing of $V_{\text{L-J}}$ and the *size of the particle*.
The corresponding force on a particle i through another particle j is then given by

$$\mathbf{F}_{ij}(r) = -\frac{\mathrm{d}V}{\mathrm{d}\mathbf{r}} = \mathbf{e}_\mathbf{r} \cdot \left(-\frac{\mathrm{d}V}{\mathrm{d}r}\right) = \mathbf{e}_\mathbf{r} \cdot 4\frac{\varepsilon}{\sigma}\left[12\left(\frac{\sigma}{r}\right)^{13} - 6\left(\frac{\sigma}{r}\right)^{7}\right] . \tag{1.3}$$

The interaction yields the Newtonian EOM's

$$m\ddot{\mathbf{r}}_i = \sum_{j\neq i} \mathbf{F}_{ij} . \tag{1.4}$$

For Argon specifically the values of m, σ, and ϵ are given as

$$\begin{aligned}
&m_{Ar} = 6.6 \times 10^{-26}\text{kg},\\
&\epsilon = 119.8 \times k_B = 119.8 \times 1.380649 \times 10^{-23}\text{J} = 165.4 \times 10^{-23}\text{J},\\
&\sigma = 3.405\text{Å} = 3.405 \times 10^{-10}\text{m}.
\end{aligned}$$

These constants will be later used in chapter 2 to introduce scale-less units for our simulation.

We are aiming to solve this system for an infinite volume (or in reality for some very large volume with a large amount of particles) with a given number of atoms per volume (i.e. number density) and temperature. In the following section we present the physical properties of the system which will later be used for the evaluation of the investigated physical properties. We will also describe how these properties are expected to behave for different parameters and why.

1.2 Physical properties

The aim of our simulation is to observe Argon atoms interacting via Lennard-Jones potential in different phases. In terms of doing that we will try to observe how the system behaves in gaseous, liquid and solid phase. The first thing we want to observe is the movement of particles depending on the density and temperature.

In terms of trajectories, gaseous phase should obviously be characterized by chaotic movement of atoms in the spatial domain. On the other hand, the solid phase is characterized by its crystal structure, the molecules vibrate around their fixed position in the crystal lattice. Argon especially has the so called Face Center Cubic (FCC) crystal structure. For the liquid phase the movement is a bit more difficult to describe via this intuition. We expect some kind of intermediate state between the static solid phase and the completely chaotic gaseous phase.

1.2.1 Pair correlation

One of the ways to study the movement of molecules is to study their level of organization. For that we will be using so called *pair correlation function*, it basically tells us which relative distances of particles have the greatest occurrence. It is properly defined in the following way

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r}, \tag{1.5}$$

where V is the volume and N is the number of particles. $\langle n(r) \rangle$ is defined as the average number of occurrence of the relative distance of particles in the interval $[r, r + \Delta r]$. The prefactors arise from the fact that the considered volume $[r, r + \Delta r] \Leftrightarrow V = 4\pi r^2 \Delta r$ is increasing for r. Since we want to study a property, which would be constant for a homogeneous system, we normalize by the considered volume. For example for gaseous phase we will then expect $g(r)$ to be close to constant homogeneous distribution $g(r) = 1$.

The other extreme, the solid phase, would be defined (at $T = 0\,\text{K}$ without any thermal vibration) with peaks at the distance of the nearest neighbors of different order. The first peak, corresponding to the nearest neighbors would have a high magnitude in comparison to the second peak, corresponding to the second closest atoms. This originates in the structure of the FCC lattice, where the amount of neighbors varies in an oscillating way. This can be seen in figure 1.1.

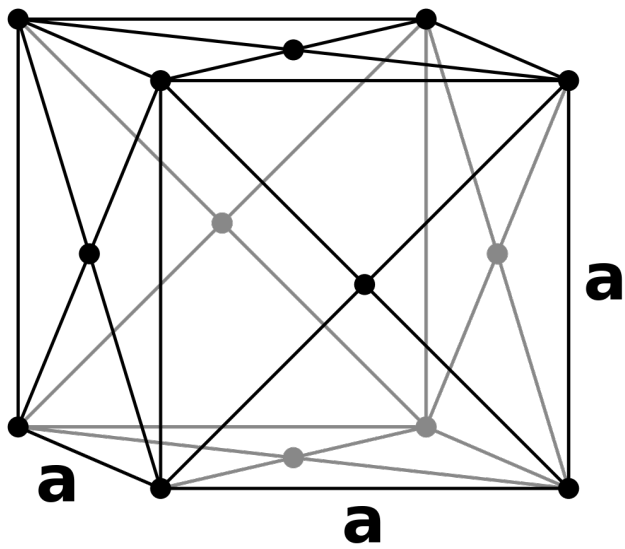


Figure 1.1: *Unit cell of a FCC lattice structure. [1]*

By considering multiple of those unit cells, one can deduct that the number of neighbors of different order are given by:

Order	Number of Neighbors	Distance
0	12	$\sqrt{2}\frac{a}{2}$
1	6	a
2	8	$\sqrt{\frac{3}{2}}a$
3	4	$\sqrt{10}\frac{a}{2}$
$\vdots$	$\vdots$	$\vdots$

Table 1.1: *Distribution of neighbors in the FCC lattice.*

Therefore we expect for the solid phase (for $T \neq 0\,\mathrm{K}$ smeared) peaks at the positions of the neighbors of different order with different magnitudes. Again, for the liquid phase we expect some kind of intermediate state between the constant, homogeneous distribution and the single peaks for specific distances.

1.2.2 Pressure

Another important variable is the internal pressure P. From the Virial theorem it can be shown that the state equation is given by

$$P = k_B T \rho - \frac{\rho}{3N} \left\langle \frac{1}{2} \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r_{ij})}{\partial r} \right\rangle , \tag{1.6}$$

where U is the potential, T is the temperature, r_{ij} is the distance of particles i and j, ρ is the number density and N is the number of particles. For L-J specifically we then get the expression for the pressure P as

$$P = k_B T \rho - \frac{\rho}{3N} \left\langle \frac{1}{2} \sum_i \sum_{j>i} 4\epsilon \left(\frac{6}{r_{ij}^6} - \frac{12}{r_{ij}^{12}} \right) \right\rangle . \tag{1.7}$$

This expression also gives us means to investigate the phase diagram (so called P-T diagram) for Argon molecules. In the literature [2] we find the phase diagram of Argon given by figure 1.2 and the critical point is at $T = 150.72\,\mathrm{K}$ and $P = 4.862\,586\,8\,\mathrm{MPa}$.

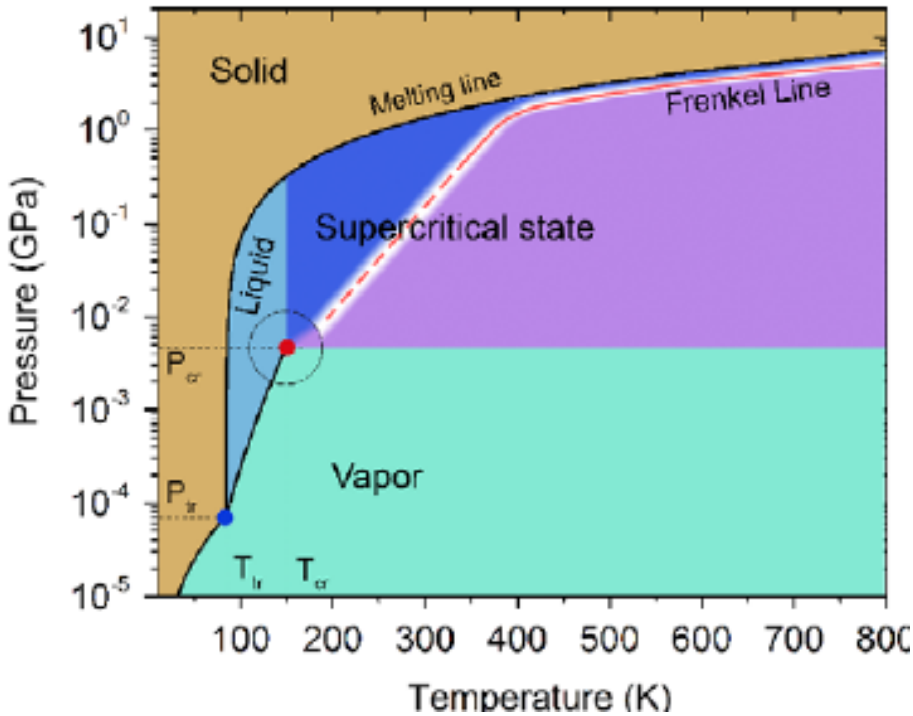


Figure 1.2: *P-T phase diagram for Argon. [2]*

We will run our simulation for three distinct phases: gas (number density 0.3, temperature 359.4 K), liquid (number density 0.8, temperature 119.8 K) and solid (number density 1.2, temperature 59.9 K)[1]. With our results of the measurements and the phase diagram above, we will verify the phases as such.

[1] *Number densities are in our simulation units which will be introduced in chapter 2.*

2 Simulation Methods

In this chapter we will introduce the methods and units used in the simulation. First we will discuss the simulation units, after that we will look at the possibilities of discretizing the EOMs. Next we will discuss the problem of boundary condition and simulating of seemingly infinite system as well as the problem of converging to equilibrium. The following part describes how we measure the target properties of our simulated system. As the very last we will introduce adding charge to the particles and an external constant electric field acting on the system.

2.1 Units

Before we discuss the numerics and the workarounds of simulating an infinite volume, we come up with a system of independent scale-less units. They are introduced to help with solving the issues connected to rounding numbers and setting reasonable *small* time steps for our simulations. The main reason for doing this is that, as we have seen in the chapter 1, the scales of different variables for the molecules themselves are very small. If we were to simulate in SI units, the simulation will be prone to quite significant rounding errors. By rescaling the units we are trying to avoid this and to simplify the use of constants in our code. We will see later that by using these units most of our equation will become almost constant-free. Here is an overview of our computational units for different variables[1]

$$
\begin{aligned}
\text{Length:} \quad & \tilde{x} = x/\sigma, \\
\text{Velocity:} \quad & \tilde{\mathbf{v}} = \frac{d\tilde{\mathbf{v}}}{d\tilde{t}} = \mathbf{v}/\sqrt{\frac{\epsilon}{m}}, \\
\text{Time:} \quad & \tilde{t} = t/\sqrt{\frac{m\sigma^2}{\epsilon}}, \\
\text{Energies:} \quad & \tilde{E} = E/\epsilon, \\
\text{Forces:} \quad & \tilde{\mathbf{F}} = \mathbf{F}/\left(\frac{\epsilon}{\sigma}\right), \\
\text{Density:} \quad & \tilde{\rho} = N/\tilde{L}^3 = \rho/\left(\frac{m}{\sigma^3}\right), \\
\text{Pressure:} \quad & \tilde{P} = \tilde{T}\tilde{\rho} - \frac{\tilde{\rho}}{3N}\left\langle \frac{1}{2}\sum_i \sum_{j>i} \tilde{r}_{ij} \frac{\partial \tilde{U}(\tilde{r}_{ij})}{\partial \tilde{r}} \right\rangle = P/\left(\frac{\epsilon}{\sigma^3}\right), \\
\text{Temperture} \quad & \tilde{T} = T/\left(\frac{\epsilon}{k_B}\right).
\end{aligned}
$$

Plus as we have already mentioned earlier, for Argon specifically we have

$$
\begin{aligned}
& m_{Ar} = 6.6 \times 10^{-26}\text{kg}\,, \\
& \epsilon = 119.8 \times k_B = 119.8 \times 1.380649 \times 10^{-23}\text{J} = 165.4 \times 10^{-23}\text{J}\,, \\
& \sigma = 3.405\text{Å} = 3.405 \times 10^{-10}\text{m}\,.
\end{aligned}
$$

Thereby we are simulating in time units of $\sqrt{\frac{m\sigma^2}{\epsilon}} = 2.15 \times 10^{-12}$s. If we use the equipartition theorem for one particle, the velocity of one Argon molecule is given as

$$
v = \sqrt{\frac{3k_BT}{m}} \rightarrow \tilde{v} = \sqrt{\frac{3k_BT}{\epsilon}} = \sqrt{\frac{3T}{119.8}}\,. \tag{2.1}
$$

[1] *The density ρ is normal density, but the density in the equation for pressure is a number density, that is the reason for the missing mass m in the conversion.*

For temperatures around 100 K we get typical velocities of order one. This means that in our units we get reasonable simulation time step of order $10^{-2} - 10^{-3}$.

2.2 Discretization of EOM

The easiest kind of discretization method for the NEWTONIAN equations of motion is the EULER method which gives the following prescription for updating position and velocities

$$\mathbf{x}(t+h) = \mathbf{x}(t) + \mathbf{v}(t)h, \tag{2.2}$$

$$\mathbf{v}(t+h) = \mathbf{v}(t) + \frac{1}{m}\mathbf{F}(\mathbf{x}(t))h, \tag{2.3}$$

where h is our simulation time step. In our units the m in the second equation disappears.

This approach however does not conserve the energy of the system, mainly because it is not time-symmetric. Because of that we will be using a different way of discretizing our equations. There are several ways of doing that, we will be using the so-called *velocity Verlet algorithm.* The prescription for calculating the positions and velocities is then given as

$$\mathbf{x}(t+h) = \mathbf{x}(t-1) + \mathbf{v}(t)h + \frac{h^2}{m}\mathbf{F}(\mathbf{x}(t)), \tag{2.4}$$

$$\mathbf{v}(t+h) = \mathbf{v}(t) + \frac{h}{2m}(\mathbf{F}(\mathbf{x}(t+h)) + \mathbf{F}(\mathbf{x}(t))). \tag{2.5}$$

These equations do not conserve energy for each time step, but in the long run the total energy of the system just fluctuates around some fixed value. Furthermore they are also to the second order of precision. In our units the m also disappears from the equations making it scale-less again.

Note: Our simulation also has the option to switch into the Euler and normal Verlet method, see documentation.

2.3 Minimum Image Convention

The next important question are the boundary conditions of our simulation box. Since we are aiming to investigate much bigger system then we are actually simulating (an infinite volume system), we choose to use *periodic boundary conditions.* This specifically means that whenever some particle leaves the box, it will come out as a new particle with the same velocity on the other side of the box. We can imagine that we are simulating the infinite volume by piecing together an infinite amount of copies of our simulation box right next to each other.

This however brings out one important problem, and that is which particles should the particle interact with. One would say, that because of simulating an infinite system, the particle should interact even with particles outside of our simulation box. That would however mean interacting with all of the infinite amount of copies (and actually even with it's own copies). This is obviously not realizable, so we need to cut down the number of interactions which we want to actually take into account. This is where the *minimum image convention* procedure comes in.

Minimum image convention basically means we will take into account only the closest copies of all the other particles. Since the potential decays with the growing distance of particles, we will neglect all the other interaction as they are negligible. This means that for each particle we will find the closest copy of all the other particles in our simulation box. Finding the distances

to the closest copies might seem at first sight an expensive operation, but the procedure can be shortened by the following formula:

$$\text{distance}(\mathbf{r}_i, \mathbf{r}_j) = \left(\mathbf{r}_i - \mathbf{r}_j + \frac{l}{2}\right) \%l - \frac{l}{2}\,, \tag{2.6}$$

where l corresponds to the length of the simulated box and the % operation would be similar to the modulo operator in real space or the division with rest.

2.4 Driving System to Equilibrium

The last important part to discuss is the question of initial conditions. Our goal is to choose some reasonable initial conditions for our simulation, so that it simulates the system in the state we want to observe it in. For us this means we are looking for an equilibrium state. Naturally, no matter what initial conditions we choose, the system will arrive at the equilibrium state eventually, but it can take quite a long time for it to do so. So we will introduce initial conditions and a procedure to reach this state in much shorter time.

As we have mentioned in the chapter 1, we are looking for such an initial temperature that gives us Gaussian distribution of velocities. So we will begin with drawing random initial velocities from Gaussian probability distribution

$$p(v_i) \sim \exp\left(-\frac{mv_i^2}{2k_\mathrm{B}T}\right) = \exp\left(-\frac{\tilde{v}_i^2\epsilon}{2k_\mathrm{B}T}\right) = \exp\left(-\frac{\tilde{v}_i^2}{2\tilde{T}}\right). \tag{2.7}$$

This will however not yet give us the system in the equilibrium, because we are drawing the velocities randomly. To get closer to the equilibrium, we will let the system evolve for some short amount of time and then check if it already has the right total kinetic energy. If not, we will rescale the current velocities and continue the simulation for another short amount of time. We will continue repeating the scaling of velocities until the total kinetic energy of the system is close to the correct one.

The correct kinetic energy of the system with a given temperature is given by the equipartition theorem as

$$E_{kin}^{tot} = (N-1)\frac{3}{2}k_BT, \tag{2.8}$$

because we are working with 3 dimensional system with $(N-1)$ degrees of freedom (one is fixed because of the conservation of total momentum of the system).

This means that we will be scaling the velocities in the following fashion

$$\mathbf{v}_i \to \lambda\mathbf{v}_i, \tag{2.9}$$

where the scaling factor λ is given as

$$\lambda = \sqrt{\frac{(N-1)3k_BT}{\sum_i mv_i}} = \sqrt{\frac{(N-1)3k_BT}{(\sum_i m\tilde{v}_i)\epsilon}} = \sqrt{\frac{(N-1)3\tilde{T}}{\sum_i \tilde{v}_i}}. \tag{2.10}$$

This seals the question of initial velocities, but now we need to set initial positions as well. Since we want regular distribution of atoms in the solid phase (crystal lattice), we are choosing to arrange them in a FCC lattice (see chapter 1 on physical properties).

Note: After drawing the random velocities we found out that the random picking does not result in zero total momentum of the system. The system will probably has some small non-zero total momentum which will not be affected by the scaling. It is necessary to correct this, otherwise for example in the solid case we will get a traveling crystal structure in the direction of this total momentum.

2.5 Addition: External electric field

Our model also has a option of adding an external constant electric field into our simulation. The initialization is done exactly the same, i.e. without the electric field, since we want to have the system in the equilibrium first. After relaxing to the equilibrium the external electric field $\mathbf{E}$ is switched on at the beginning of the simulation. All particles are assigned the same (positive) charge q in the units of an electric charge of a proton $e = 1.602 \times 10^{-19}$ C (i. e. the Argon atom is now an Argon ion Ar^+). The electric force acting on one Argon ion is then

$$\mathbf{F}_E = q\mathbf{E}. \tag{2.11}$$

Since for the electric potential ϕ holds that

$$\mathbf{F}_E = -\nabla\phi, \tag{2.12}$$

we can choose the potential energy in the form (assuming $\mathbf{E}$ constant and setting some integration constant to zero)

$$U_E(\mathbf{x}) = q\phi = -q\mathbf{E}\mathbf{x}, \tag{2.13}$$

where $\mathbf{x}$ is the current position of the particle.

As we have mentioned before the scale-less simulation units in this case are the following

$$\begin{aligned} \text{Charge:} \quad & \tilde{q} = q/e, \\ \text{Electric field:} \quad & \tilde{\mathbf{E}} = \mathbf{E}/\left(\frac{\epsilon}{\sigma e}\right). \end{aligned}$$

We naturally expect that this kind of electric field will make the particles drift in the direction of the electric field. For solid case this should be clearly visible even for weaker electric fields, since the overall movement of atoms is normally within much smaller range then for liquid and gas. Also for gas we would expect that it is necessary to apply much stronger electric field to visibly disturb the natural chaotic movement of the particles. For liquid we would again expect something in between.

3 Evaluation

In order to get a feeling on the interaction of particles and the trajectories of only a few of them, we first consider the collision of two particles who are heading almost head to head in figure 3.1.

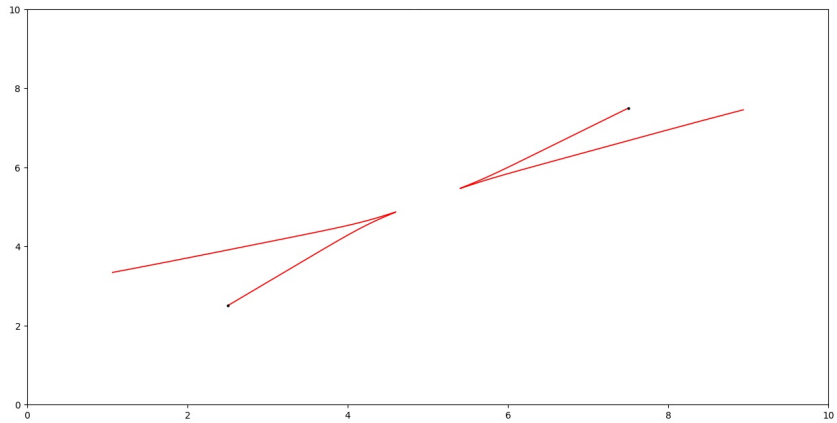
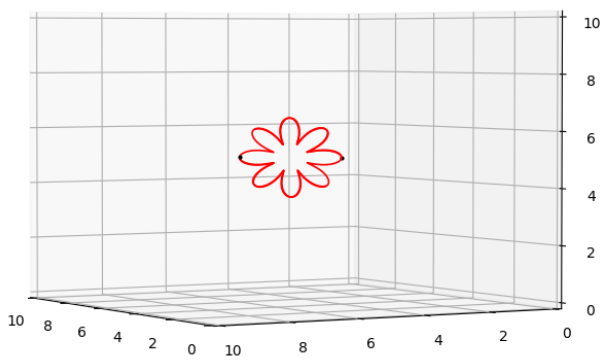


Figure 3.1: *Two particle close to head-to-head collision.*

We see that the for small distances ($\tilde{r} < 1$) the strong repulsive force makes their occurrence unlikely. Since the Lennard-Jones potential if scaling with r^{-6}, the interaction of distant particles is negligible and they proceed in a linear motion. Only when the particles come close to each other one can see non linearities.
Note: For special initial conditions we also found orbits of the Lennard-Jones potential (see following flower picture).



Let us know consider the three phases.

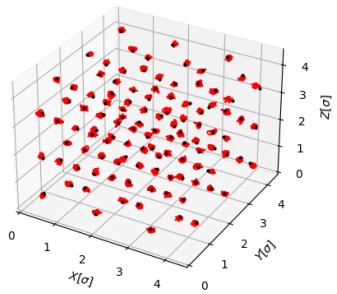


Figure 3.2: *Trajectories of 108 particles in the solid phase simulated for* $5\tilde{t}$.

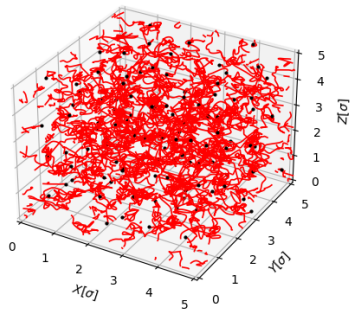


Figure 3.3: *Trajectories of 108 particles in the liquid phase simulated for* $5\tilde{t}$.

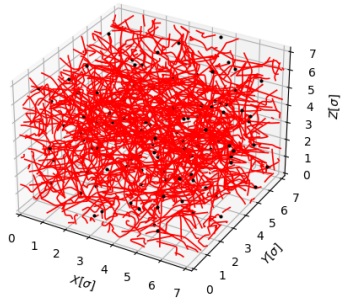


Figure 3.4: *Trajectories of 108 particles in the gaseous phase simulated for* $5\tilde{t}$.

It can be easily seen that the particles in the solid phase (figure 3.2) remain in the FCC structure and only perform some thermal vibration around their position of rest due to the non vanishing temperature. This matches our expectation.
Additionally, one can see that the gaseous phase (figure 3.4) shows completely chaotic behavior, where the particles move all around the box, not limited by their initial positions. The bigger total kinetic energy can be seen in the fact, that the trajectories of the particles cover almost the whole box, in comparison to the liquid phase (figure 3.3).
Here we also see chaotic movement, still with larger areas without any particle passing over time.

3.1 Position Distribution Histograms

As we described in section 1.2.1, the particle correlation can be seen as a measure of how particles order in the box. Figures 3.5-3.7 show the measured correlations. We have simulated each phase 5 times for the time $\tilde{t} = 5$[1] with total number of particles in all simulations being 108. During each simulation we have measured 5 times, which gave us 25 measurements for each phase in total. These measurements than have been averaged (or rather their histograms). It is also worth mentioning that due to the minimal image convention and effect of the fact, that we are simulating a cube rather that a sphere, only the distances with relevant data are shown in the histograms, specifically only the distances up to half of the simulation box.

[1] *In SI units this corresponds to* 10.75×10^{-12} *s.*

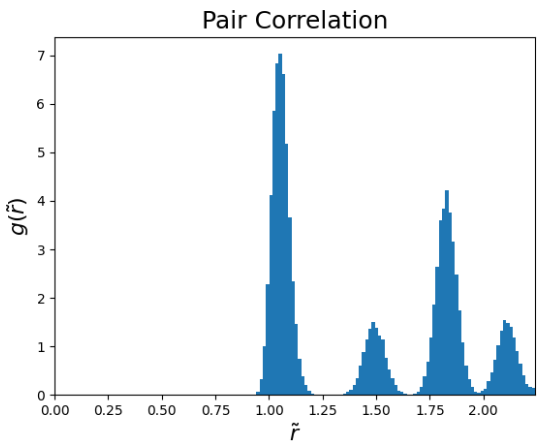


Figure 3.5: *Particle pair correlation for the solid phase.*

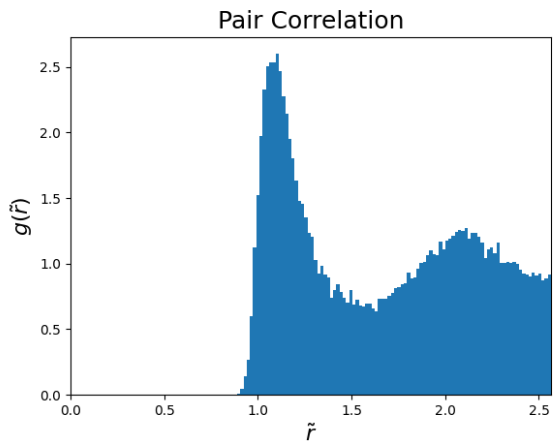


Figure 3.6: *Particle pair correlation for the liquid phase.*

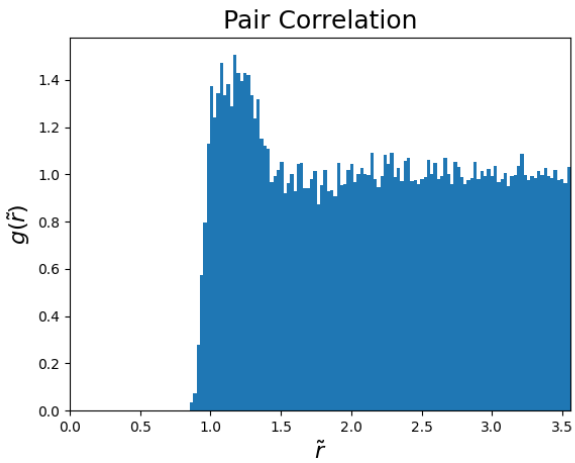


Figure 3.7: *Particle pair correlation for the gas phase.*

Figure 3.5 verifies the previously mentioned theoretical expectations. We see sharp peaks around the positions of the neighbors of different order. The length of a unit cell for the specified parameter[2] of $\tilde{\rho} = 1.2$ and $\tilde{T} = 0.5$ is given by $a \approx 1.5$. Therefore the distance to the nearest neighbor would be $\frac{\sqrt{2}}{2}a \approx 1.06$ which coincides with the mean of the first peak in the plot. All the other peaks match also the theoretical expectation of the distances in an FCC lattice. Moreover, the magnitude of the peaks also differ in the way we predicted. The smearing of the peaks originates in the non vanishing thermal energy of the system. We also see that the movement of the particles around their position of rest have no prioritized direction, which leads to the symmetry of the peaks around their mean.
Furthermore, figure 3.7 matches our expectations in the most parts. Considering the regime $\tilde{r} > 1$ we see a mostly homogeneous, constant distribution $g(\tilde{r}) = 1$. For $\tilde{r} < 1$ the distribution is also constant, but zero. This is caused by the strong repulsive force of the Lennard-Jones potential for small distances. An occurrence of such a distance between two particles is very unlikely. More intriguing is the overpopulation of distances close to $\tilde{r} = 1$. This overpopulation might result from the pushed back particles of $\tilde{r} < 1$. If there would be no interaction between the particles, we would expect $g(r) = 1, \forall r$, but by slowly increasing the magnitude of the

[2] *Initial parameters of all simulations in SI units can be found in the next section which discusses pressure of the system.*

repulsive force, one pushes back the particles at $\tilde{r} < 1$ and produces thereby overpopulated regime close to the lowest possible distance between particles.
The liquid phase (figure 3.6) on its own is difficult to interpret, but it takes that exact intermediate state between the solid phase, with sharp peaks, and the gaseous one, with a nearly homogeneous distribution. The peaks of the FCC structure are visible[3], still the whole distribution got spread over all $\tilde{r} > 1$ and therefore also the magnitude of the peaks decreased.

3.2 Pressure

Simultaneously with the pair correlation we also measured the pressure of the system in all of the simulations. The resulting histograms for all three phases can be seen in figures 3.8-3.10. together with calculated mean value and variance.

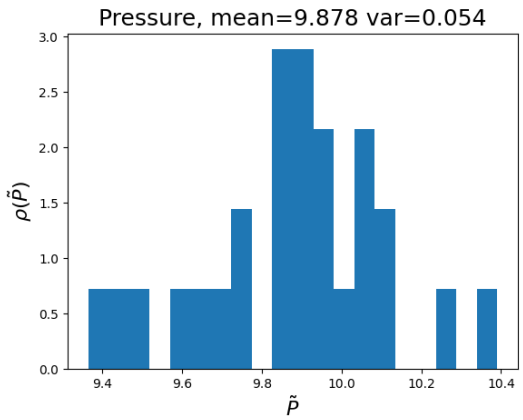


Figure 3.8: *Histogram of measurement of pressure for solid phase.*

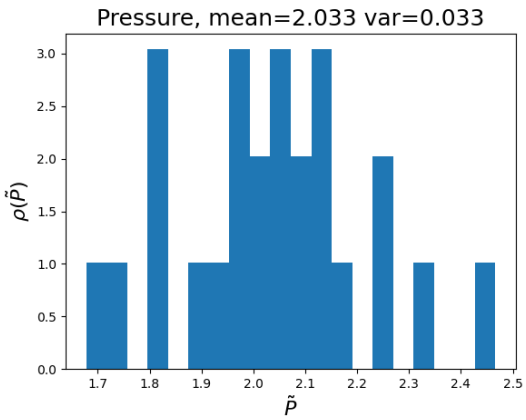


Figure 3.9: *Histogram of measurement of pressure for liquid phase.*

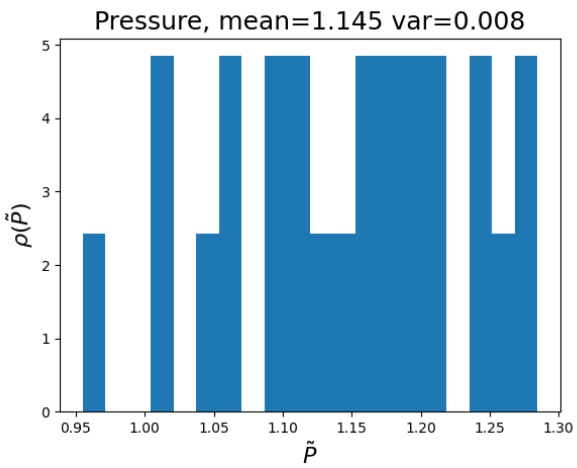


Figure 3.10: *Histogram of measurement of pressure for gas phase.*

In this case it is probably useful to leave our simulation units and actually put our results into SI units. The following table sums up all the parameters and results in both sets of units.

[3] *These peaks are at different positions because of the different phase parameters $\tilde{\rho} = 0.8$ and $\tilde{T} = 1.0$. Still the positions of the peaks are in accordance to the theoretical expectation of the FCC lattice*

Parameters and pressure results in simulation and SI units						
	$\tilde{T}$	T [K]	$\tilde{\rho}$	ρ [kg/m^3]	$\tilde{P}$	P [MPa]
Solid phase	0.5	59.9	1.2	2016.3	9.878(54)	413.9(23)
Liquid phase	1.0	119.8	0.8	1344.2	2.033(33)	85.2(14)
Gaseous phase	3.0	359.4	0.3	504.1	1.1446(78)	47.97(34)

Table 3.1: *Pressure results and initial parameters of all simulations in simulation and SI units.*

Qualitatively, the measurements of the pressure confirm the naming of the phases as solid, liquid and gaseous (compare phase diagram 1.2). We tried to find some values of pressure for our set of parameters in the literature to compare our results. Overall it was unfortunately not a very successful search, but for the gas and liquid phase we found results for similar parameters each. In case of the gas phase in [3] for the parameters T = 400 K and ρ = 510.2 kg/m^3 the resulting pressure was 50 MPa. For the liquid phase we compared with [4] where for the T = 120 K and ρ = 1417.7 kg/m^3 their resulting pressure is P = 81.06 MPa. From this at least we can assume that our results are in the valid ranges, since the values are similar to ours.

3.3 Addition: External electric field

We have run several simulations of different phases to observe how the constant external electric field and its strength affects the trajectories of particles in the gas, liquid and solid state. We have let the system to evolve for a time interval $\tilde{t} = 2$ each time, the electric field has been oriented along the x axis and had the strengths 0.2, 2.5 and 5.0 in our simulation units[4]. We observe exactly what we expected and that is that particles are accelerated in the direction of the field and hence obtain a shift in this direction.

[4] *This means that in the SI units we are dealing with 6.06, 75.80 and 181.93 MV/m.*

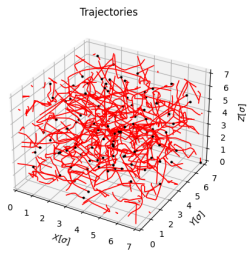


Figure 3.11: *Trajectories of 108 particles in the gaseous phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (0.2,0,0)^\top$.

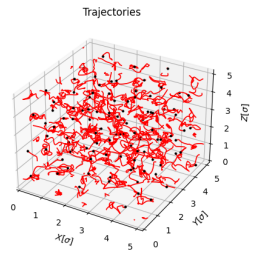


Figure 3.12: *Trajectories of 108 particles in the liquid phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (0.2,0,0)^\top$.

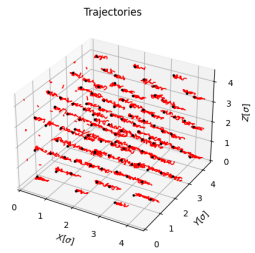


Figure 3.13: *Trajectories of 108 particles in the solid phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (0.2,0,0)^\top$.

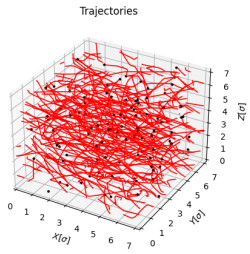


Figure 3.14: *Trajectories of 108 particles in the gaseous phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (2.5,0,0)^\top$.

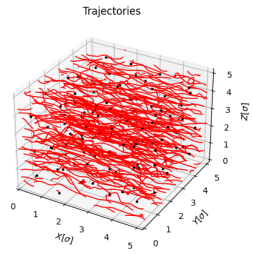


Figure 3.15: *Trajectories of 108 particles in the liquid phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (2.5,0,0)^\top$.

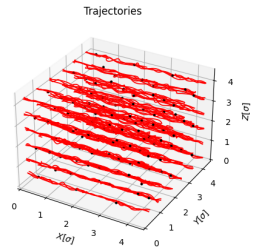


Figure 3.16: *Trajectories of 108 particles in the solid phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (2.5,0,0)^\top$.

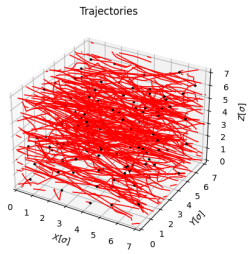


Figure 3.17: *Trajectories of 108 particles in the gaseous phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (5.0,0,0)^\top$.

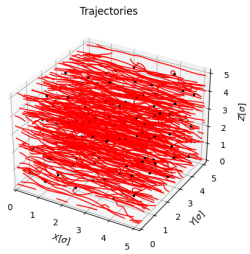


Figure 3.18: *Trajectories of 108 particles in the liquid phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (5.0,0,0)^\top$.

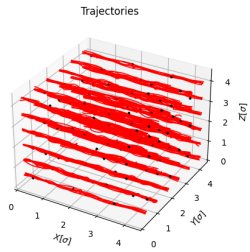


Figure 3.19: *Trajectories of 108 particles in the solid phase simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (5.0,0,0)^\top$.

In figures 3.11 - 3.19 we can see how different strengths of field affect the movement of the particles. Even quite small electric field makes particles in solid phase shift in the direction of the field, but to disturb the chaotic movement of liquid and gas particles is not that easy. For the strength 5.0 in all cases we see that the movement along the x axis dominates. Still, for the solid phase, we see the ordered structure of the atoms in the $y - z$ plane. Again, the movement of the liquid and gaseous phase looks more chaotic. Since we increased the electric field strength, even for the chaotic movement with the overall faster particles, the movement in the x direction dominates.

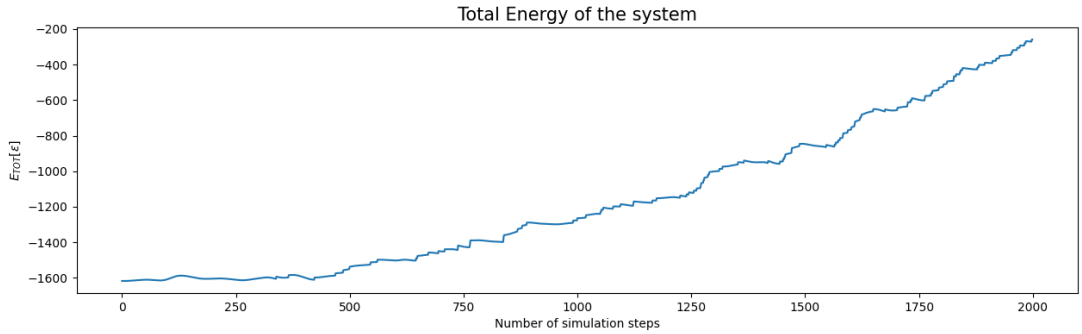


Figure 3.20: *Growing total energy of the liquid system simulated for* $2\tilde{t}$ *with an external electric field* $\tilde{\mathbf{E}} = (2.5,0,0)^\top$

It is also worth mentioning that in this case the system is no longer in equilibrium so because of the acceleration of particles we also expect (and observe) uphill tendency in total energy of the system, example for liquid system can be seen on figure 3.20.

Conclusion

Starting with the two-body problem, the interaction was visualized with a nearly heads on collision of two Argon atoms. The strong repulsive force for distances $r < \sigma$ was visualized by the non linearities of the movement as well as the not far-reaching nature of the L-J potential ($r \propto r^{-6}$ for big r) through the linear movement of distant particles.
Also in the many body problem the theoretical expectations were fulfilled. The solid phase is characterized by some small thermal vibration around their position of rest, which were given by the FCC lattice structure. With growing thermal energy and smaller density, the particles moved faster and in a chaotic manner.
The first quantitative output investigated were the position distribution histograms. The sharp peaks of the solid phase were in accordance to the expected ones through the FCC lattice. Going to the chaotic behavior of the liquid and gaseous phase, one saw the smearing of the distribution all the way to the constant homogeneous distribution. Additionally, the histograms gave also insights on the rare occurrence of distances $r < \sigma$ again, due to the strong repulsive force.
We did not find many values which would be suitable for us to compare our results with. For the solid phase we unfortunately found none, but for gaseous and liquid phase we managed to find similar values in the literature which agree with our results. The measured pressures also confirm the phases to be solid, liquid and gaseous, respectively.
The introduction of an external constant electric field led to the constant shift and acceleration of the particles in direction of the field. In the simulation it can be seen that the total energy of the system increases with the time.
It might be interesting to introduce time dependent electrical fields and the Coulomb interaction between the particles. Also one might work on the speed of the implementation.

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Acronyms

EOM Equation of Motion

L-J Lennard - Jones

MD Molecular Dynamics

FCC Face Center Cubic

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