

# A molecular dynamics simulation of argon atoms using periodic boundary conditions

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**Abstract**—By means of numerical methods, it is possible to simulate the movement of a finite number of particles in what is called a molecular dynamics (MD) simulation. We report on an MD simulation of 864 argon atoms in a cubic domain of computation. The simulation data is then used to determine values for the energy, temperature, pressure and specific heat contained in the system. By studying the pair correlation function and diffusion we are able to identify the phase of the argon. Obtained results are in agreement with the famous work of Loup Verlet.

## I. INTRODUCTION

FOR systems of many particles, physical quantities can be determined by means of ensemble averages over all particles. Experimentally, this is no easy feat; experiments where a large number of atomic particles are tracked simultaneously are difficult to realise and it is nigh on impossible to evaluate the ensemble average due to the sheer number of particles in real world systems. We can, however, analyse systems containing a large amount of particles using the computational methods of molecular dynamics simulations. For the simulation we report here, we consider argon atoms. Argon, a Van der Waals gas, is a prime candidate for such simulations as the only inter atomic force in this gas is the Lennard Jones potential. Consequently, dipole interactions, hydrogen bonds, magnetic interactions, etc. can all be disregarded, simplifying the calculations. Moreover, as Argon is a noble gas, it is chemically very stable.

The goal is to simulate the movement of argon atoms in a cubic control volume and determine values of several physical quantities. These include the energy, temperature, pressure, heat capacity and state of aggregation.

Firstly, necessary theoretical details for the realisation of the simulation will be explained. Subsequently, the methods to implement the theory and to determine relevant physical quantities will be clarified. Thereafter, the simulation results will be presented and conclusions will be drawn.

## II. THEORY AND METHODS

### A. Interaction model

The first problem at hand is the interaction between individual argon atoms. In our simulation we describe the interactive forces by the Lennard-Jones potential, which is written as follows [1]:

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

Here,  $\epsilon$  represents the minimum value of the potential,  $\sigma$  the distance for which the potential equals zero, and  $r$  stands for

the distance between two particles. The force is obtained by taking the negative gradient of the potential, which results in the following expression for the magnitude of the force:

$$F = 24\epsilon \left[ 2 \left( \frac{\sigma^{12}}{r^{13}} \right) - \left( \frac{\sigma^6}{r^7} \right) \right] \quad (2)$$

The first term in equation 2 manifests itself as a strong, short range, repulsive force. Its physical origin is the Pauli exclusion principle, which states that no two fermions can ever be in the same state [2]. At the same time, atoms are also attracted to each other by the second term that represents the Van der Waals force.

As a result of the forces on the particles, the particles will be subject to acceleration. This relation is simply described by Newton's second law:

$$F = m \cdot a \quad (3)$$

### B. Initial conditions

The next problem is that of the state of the particles at the start of the simulation. Every particle has to have a position and a velocity from the very beginning. Choosing these at random should work in theory, but then it would take many iterations for the system to reach some sort of equilibrium. Instead, we will use the FCC (Face Centred Cubic) crystal structure for the initial positions of the particles and the Maxwell-Boltzmann distribution for the initial speed of the particles.

Concerning the initial position of the particles, the space should be evenly filled, and no two particles can be in the same position at any time. Also, we want the initial positions to be as close to the equilibrium as possible to minimise the time it takes to stabilise. Solid argon has an FCC crystal structure [4], so it makes sense to also use this configuration for the initial condition.

The velocity distribution of particles at a given temperature is described by the Maxwell-Boltzmann distribution. This is a probability density function dependent on the particle mass  $m$ , the temperature  $T$ , Boltzmann's constant  $k$ , and naturally the particle velocity  $v$ ; it is given below [3].

$$f(v) = \sqrt{\left( \frac{m}{2\pi kT} \right)^3} 4\pi v^2 \exp \left( -\frac{mv^2}{2kT} \right) \quad (4)$$

Evidently, the distribution has the shape of weighted Gaussian curve. As the temperature increases, the maximum of the probability density function will shift to higher  $v$ . As a result, higher particle speeds become more likely which agrees with the notion that particles will move more as they are heated.

It should be noted that the Maxwell-Boltzmann distribution only provides us with information on the particle speed, the direction in which they are moving is still completely random.

### C. Boundary condition

For the boundary condition, there is a choice to be made. One option is the 'hard wall' boundary condition. In this case, when a particle passes the boundary, its position and velocity are mirrored with respect to this boundary; it bounces back. This way, we essentially simulate a number of particles trapped in a box. Alternatively, we can simulate a continuous space by having particles that leave the domain enter on the other side again with the same velocity. This way we simulate a small part of a larger system. In this simulation, the latter option, referred to as periodic boundary conditions, will be used.

### D. Energy

The total energy in the simulated system is distributed between the potential and the kinetic energy. The potential energy is of course due to the Lennard-Jones potential, which is given in equation 1. The kinetic energy is written as:

$$K = \frac{1}{2}m \sum_{i=1}^N v_i^2 \quad (5)$$

where  $m$  is the particle mass and  $v$  the particle velocity. As there are no sources of energy in the system the total energy of the system consisting of the potential and kinetic energy has to stay constant. Varying total energy would indicate a problem in the simulation.

### E. Temperature

For the calculation of the temperature, Boltzmann's equipartition theorem is a convenient tool [3]. It reads

$$3(N-1) \times \frac{1}{2}kT = \left\langle \frac{1}{2}m \sum_{i=1}^N v_i^2 \right\rangle \quad (6)$$

with  $N$  the number of particles,  $k$  Boltzmann's constant,  $T$  the temperature,  $m$  the particle mass, and  $v$  the particle velocity. The term on the right-hand side is the kinetic energy. By rewriting equation 6, we can obtain an expression for the instantaneous temperature at any time.

### F. Pressure

The pressure  $P$  is related to known variables by the virial equation below [5], which is named as such because the summation it contains is referred to as the virial.

$$\frac{P}{\rho kT} = 1 - \frac{1}{3NkT} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r_{ij})}{\partial r_{ij}} \right\rangle_{\text{cut-off}} - \frac{2\pi N}{3kTV} \int_{r_{\text{cut-off}}}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r) dr \quad (7)$$

The left hand side of this equation is called the compressibility factor, a dimensionless quantity that will be often used in

this report. Furthermore,  $g(r)$  denotes the pair correlation function, discussed further on, while the cut-off subscript indicates that summation only has to be done for particle pairs separated by less than some cut-off distance. This would reduce the computational load of the program. However we will not implement such a scheme and therefore  $r_{\text{cut-off}}$  would be roughly comparable to the size of the computation domain. As the Lennard-Jones potential falls off very fast with distance the integral will not contribute very much to the compressibility factor and we therefore ignore it. The expression now simplifies to the form in equation 8.

$$\frac{P}{\rho kT} = 1 - \frac{1}{3NkT} \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r_{ij})}{\partial r_{ij}} \quad (8)$$

### G. Specific heat

The number of particles, the volume and the total energy stay constant in the microcanonical ensemble, which is the case in our system. Therefore, the Lebowitz formula [6] can be used to calculate the specific heat at constant volume which reads

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N} - \frac{1}{C_v} \quad (9)$$

where  $K$  is the kinetic energy,  $\delta K$  is the fluctuation in the kinetic energy,  $N$  is the number of particles and  $C_v$  is the specific heat. The equation can be rewritten to obtain an expression for the specific heat that can be used in the simulation. For an ideal monatomic gas, the theoretical specific is determined to be  $\frac{3}{2}k_B$  per particle [5], so we expect our simulation of argon in the gas phase to produce the same result. According to the Dulong-Petit law [7], the specific heat for a harmonic solid is  $3k_B$  per particle. Hence, the simulation of solid argon should also give this value.

### H. Correlation function

The pair correlation function is useful for determining the phase of the simulated system. The pair correlation is given as [5]:

$$g(r) = \frac{2V}{N(N-1)} \left[ \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \right], \quad (10)$$

where  $r$  is the distance between the atoms and  $n(r)$  the number of atoms spaced between  $\Delta r$  at a radius of  $r$ .

If the system is in the solid state, we expect that all atoms are on a FCC grid. In accordance to the Lennard-Jones potential, we expect to see sharp peaks in the pair correlation if  $r$  is a multiple of  $2^{1/6}\sigma$ , which is the minimum of the potential, but also the distance between a face center and a corner of the unit cell. There will also be a peak at  $2^{2/3}\sigma$ , which is the distance between the edges of the unit cell. For a liquid state the atoms are found in spheres whose radii are multiples of  $2^{1/6}\sigma$ . Due to the lack of lattice structure and faster movement of the argon atoms, we expect the peaks to be less sharp than for the solid. For the gas state we expect no correlation.

### I. Diffusion

The diffusion constant of a system can be found by plotting the mean squared displacement as a function of time. If the system shows diffusive behaviour the displacement should follow

$$\langle x^2 \rangle = Dt \quad (11)$$

where  $D$  is the diffusion constant. The system should be become diffusive after a time larger then the typical collision time. For solids the diffusion constant should be zero as the atoms are stuck in a grid, while the diffusion constant for the gas phase should be higher than for the liquid phase as the atoms move faster and are less affected by the other molecules.

## III. IMPLEMENTATION

This section discusses the implementation of the model described above.

### A. Reduced units

First of all, it is important to notice that we work in reduced units, i.e. the mass of an Ar atom, the Boltzmann constant, and the Lennard-Jones parameters  $\epsilon$  and  $\sigma$  are all set to 1. As a result we can ignore some constant factors in the theoretical formulae, but more importantly, there will no longer be extremely small variables. The latter is beneficial because the precision of variables on the computer is limited, making calculations with very small numbers complicated.

The other side of the story is that the simulation results are also in reduced units rather than in the physical units used in experiments. [8]. However, the obtained simulation results can be directly translated into physical units for comparison with experiments. For example, length is now expressed in units of  $\sigma$ , and energy in terms of  $\epsilon$ . Now, the units of other quantities such as the velocity can be obtained using dimensional analysis. For instance, the unit of  $\sqrt{\epsilon/m}$  is  $m/s$ , so the velocity in reduced units is given in terms of  $\sqrt{\epsilon/m}$ . Additionally, the reduced unit for time is  $\sigma(m/\epsilon)^{1/2}$ , but for the purpose of brevity will be referred to as  $\tau$  henceforth.

### B. Initializing particle positions and velocities

We divide the domain of computation into FCC unit cells, and position the four particles per unit cell. In order to avoid problems at the boundary, no particles are to be placed directly on the boundary. As each unit cell contains 4 atoms (one at the vertex, three on the faces), and we want to have  $n^3$ ,  $n \in 1, 2, 3, \dots$  cells to fill the entire domain with FCC cells, we restrict ourselves to particle numbers of  $4 \cdot n^3$ ,  $n \in 1, 2, 3, \dots$  [5].

To generate the initial velocities, random numbers satisfying the Maxwell-Boltzmann distribution are generated first. Subsequently, randomly oriented unit vectors are generated. These unit vectors are then multiplied by the random numbers from the Maxwell distribution to create initial velocity vectors. These random velocity vectors do not add up to zero, resulting in movement of the centre of mass. Hence, to keep the system from drifting, the velocity of the centre of mass is subtracted from all the velocity vectors.

### C. Calculating interatomic forces

The atoms are moved around by integrating the equation of motion of each particle. Since we are doing classical physics, the equation of motion of a single atom is just Newton's second law with the Lennard-Jones force filled in. The total force on atom  $i$  is determined by summing the Lennard-Jones forces that each of the other  $N - 1$  atoms applies to the atom  $i$  under consideration:

$$\vec{F}_i = \sum_{\substack{j=1 \\ j \neq i}}^N 24 (\vec{r}_i - \vec{r}_j) \left[ 2 \left( \frac{1}{|\vec{r}_i - \vec{r}_j|} \right)^{14} - \left( \frac{1}{|\vec{r}_i - \vec{r}_j|} \right)^8 \right] \quad (12)$$

Because of Newton's third law, for each pair of atoms we can add the calculated force vector to the total force vector of one of the atoms and subtract it from the total force vector of the other atom. In this way, the number of force calculations is halved, which decreases the computation time.

In calculating the forces it is important to notice that using periodic boundary conditions implies that each atom does not only interact with all the other atoms in the system cell, but also with the atoms in the copies of that cell. Hence, the summation in equation 12 would consist of infinitely many terms. However, the Lennard-Jones force rapidly decays with distance, so it is sufficient to take into account only the nearest copies of the other atoms. This is called the minimum image convention. It basically comes down to determining for each component  $r_\alpha$  of the position vector whether the difference between two atoms in the system cell is smaller than  $-L/2$ , between  $-L/2$  and  $L/2$  or larger than  $L/2$ , where  $L$  denotes the length of the system cell in each direction, and manipulating that difference in such a way that the new difference is smaller than  $L/2$  in absolute value. Therefore, it is implemented by using a 'round to integer' function 'rint' as follows [5]:

$$(r_{i,\alpha} - r_{j,\alpha}) \rightarrow (r_{i,\alpha} - r_{j,\alpha}) - \text{rint} \left( (r_{i,\alpha} - r_{j,\alpha})/L \right) \cdot L \quad (13)$$

### D. Moving the atoms around

The equations of motion are integrated using the so called velocity-Verlet algorithm. The main advantages of this algorithm are its great stability and the fact that it evaluates both the positions and velocities at the same moment in time, which is nice for calculating kinetic energies, for example. If we let  $h$  denote the time step, the algorithm computes the positions of the atoms and their velocities at a time  $h$  later according to:

$$\begin{aligned} \vec{r}(t+h) &= \vec{r}(t) + h \vec{v}(t) + h^2 \vec{F}(t)/2 \\ \vec{v}(t+h) &= \vec{v}(t) + h \left[ \vec{F}(t+h) + \vec{F}(t) \right] / 2 \end{aligned} \quad (14)$$

The errors in the algorithm are in the order  $h^4$ . However, this algorithm needs two force arrays for calculating the velocities.

We can avoid this by implementing an equivalent form of the algorithm that looks like:

$$\begin{aligned}\vec{v}(t) &= \vec{v}(t) + h\vec{F}(t)/2 \\ \vec{r}(t+h) &= \vec{r}(t) + h\vec{v}(t) \\ \vec{v}(t+h) &= \vec{v}(t) + h\vec{F}(t+h)/2\end{aligned}\quad (15)$$

Here, between the second and third equation the forces at time  $t+h$  are calculated using equation 12 using the positions at time  $t+h$  obtained from the second equation [5]. It should be noted that the atoms could move out of the system cell. As we have chosen periodic boundary conditions the atoms should enter again on the opposite side. This is implemented by using a remainder function that outputs the new position vector components  $r_\alpha$  as the division remainder of the position vector components and the cell length:

$$r_\alpha \rightarrow \text{remainder}(r_\alpha, L) \quad (16)$$

#### E. Rescaling

Before starting the simulation the number of iterations is fixed. This number should be large enough for the system to reach equilibrium. However, in experiments the temperature rather than the total energy is controlled. Hence, in order to be able to compare the simulation results with experimental results, we need to rescale the velocities a number of times such that the system comes to equilibrium at the desired temperature  $T_D$ . This is implemented by:

$$\vec{v}_i \rightarrow \sqrt{\frac{T_D}{T_i}} \vec{v}_i \quad (17)$$

The current temperature  $T_i$  is calculated using equation 6. After a rescaling the temperature will again drift away from  $T_D$ , but this effect decreases as the system approaches equilibrium [5]. If the temperature starts fluctuating around a certain value, equilibrium is reached and the rescaling can be stopped. From this moment on several physical quantities can be determined.

#### F. Determining physical quantities and errors

The physical quantities that are described in the theory section are determined by just implementing the equations 5 till 11. Here we see the advantage of the velocity-Verlet algorithm that outputs both the particle positions and velocities at the same moment in time as both are needed to calculate these quantities. Furthermore, it is important to mention that we incorporate the calculation of the potential energy and the virial, which is necessary for the pressure, in the loop that calculates the interatomic forces, such that we reduce the amount of required calculations. Since we are interested in the values at equilibrium, we only average the outcomes of the iterations after we stop rescaling. In order to calculate the error in this average, the signal has to be split up into equally long sections that have uncorrelated averages, i.e. the sections should be longer than a typical oscillation around the equilibrium value. Then, we calculate the variance in the section averages, divide by the number of sections and calculate the square root. This method, which is called data

blocking, yields the error in the average. The error is calculated for a few section lengths. If the error for some section length significantly differs from the other errors, we know that this section length is too small, which implies that the section averages are not uncorrelated, or too large, which means that not enough sections could be created to calculate the error in a reliable way [5].

### IV. RESULTS

In this section we present and discuss the simulation results. Unless stated otherwise, simulations are performed with 864 particles, a time step of 0.004 and 6000 iterations. Rescaling is done after every 20 iterations, but we stop rescaling after 1000 iterations so we use 5000 iterations to determine the physical quantities.

#### A. Energies and Temperature

The energy and temperature of the system are both essential quantities. On account of the rescaling algorithm, the temperature is expected to be at the set value, but some variation is to be expected. As can be seen in figure 1, which depicts the first 2000 iterations of a 6000 iteration simulation, the temperature does tend to the set value, which is 2 in this case. The simulation yields a temperature of 1.9886. With a block length of 250, the error is 0.0007; with other block lengths the error deviates up to 0.0002 from this value. Based on the found temperature and error, one can conclude that the result conflicts with the set temperature, but the difference is very small. Table I shows some more set temperature and measured temperature pairs. Here, we also see that the set temperature and the measured temperature slightly differ.

Figure 2 shows the energy per particle for the same simulation. The total energy is seen to be piecewise constant, which means energy is conserved except when a rescale occurs. Energy conservation is a first check to see if the simulation functions correctly; this simulation passed. As expected, kinetic energy is seen to be positive; the negative potential is explained by the fact that the Lennard Jones potential is mostly negative. Only when particles are very close together there can be a positive contribution to the potential energy, but the density is too low for this in the simulation. Potential energy per particle is found to be  $-5.433 \pm 0.001 \epsilon$ . Some more simulation results for the average potential energy per particle can be found in table I. They are all in good agreement with values reported by Verlet [1].

#### B. Pressure

We do not explicitly investigate the pressure, but the compressibility factor, which is given by equation 8. Our results can be observed in table I and figure 3.

In general, we observe that for fixed particle density and increasing temperature the compressibility factor, and therefore the pressure, increases. This is correct from a physical point of view: The higher the temperature, the more kinetic energy the atoms have, so the larger the force they exert on a unit surface. Furthermore, we observe that for increasing particle

TABLE I

SIMULATION RESULTS WITH ERRORS IN BRACKETS. THE PARTICLE DENSITY  $\rho$  AND THE DESIRED TEMPERATURE  $T_D$  ARE FIXED BEFOREHAND.  $T_M$  IS THE MEASURED TEMPERATURE OF THE SYSTEM, WHICH IS A MEASURE FOR THE AVERAGE KINETIC ENERGY PER PARTICLE. THE AVERAGE POTENTIAL ENERGY PER PARTICLE  $U_i$ , THE COMPRESSIBILITY FACTOR, AND THE SPECIFIC HEAT AT CONSTANT VOLUME ARE SHOWN AS WELL.

$\rho(1/\sigma^3)$	$T_D(\epsilon/k_B)$	$T_M(\epsilon/k_B)$	$U_i(\epsilon)$	$\beta p/\rho(-)$	$c_v(k_B/m)$
0.001	2.0	2.0011 (0.0002)	-0.0055 (0.0003)	0.9993 (0.0002)	1.50093 (0.00008)
0.3	3	2.973 (0.0013)	-1.747 (0.002)	1.107 (0.003)	1.635 (0.008)
0.35	1.6	1.623 (0.002)	-2.339 (0.003)	0.584 (0.008)	1.80 (0.02)
0.4	1.45	1.463 (0.002)	-2.695 (0.003)	0.442 (0.006)	1.81 (0.02)
0.45	1.1	1.123 (0.003)	-3.226 (0.004)	-0.095 (0.008)	2.23 (0.04)
0.45	1.55	1.548 (0.002)	-2.989 (0.003)	0.558 (0.007)	1.84 (0.02)
0.45	1.75	1.761 (0.002)	-2.902 (0.003)	0.767 (0.007)	1.81 (0.02)
0.45	2.95	2.942 (0.002)	-2.593 (0.003)	1.390 (0.004)	1.73 (0.01)
0.5	1.35	1.335 (0.003)	-3.388 (0.004)	0.326 (0.008)	2.06 (0.03)
0.55	2.65	2.689 (0.002)	-3.204 (0.003)	1.656 (0.007)	1.81 (0.02)
0.65	0.9	0.910 (0.001)	-4.587 (0.004)	-0.69 (0.02)	2.13 (0.06)
0.65	1.6	1.610 (0.001)	-4.201 (0.001)	1.34 (0.01)	1.94 (0.05)
0.75	0.85	0.849 (0.001)	-5.313 (0.001)	-0.28 (0.02)	2.2 (0.1)
0.75	1.1	1.087 (0.001)	-5.129 (0.001)	0.98 (0.01)	2.2 (0.1)
0.75	1.3	1.304 (0.001)	-4.970 (0.002)	1.67 (0.01)	2.19 (0.07)
0.75	2.85	2.870 (0.002)	-4.006 (0.002)	3.142 (0.002)	2.03 (0.04)
0.8	1	1.013 (0.0007)	-5.491 (0.001)	1.398 (0.009)	2.361 (0.008)
0.85	0.65	0.629 (0.002)	-6.201 (0.002)	-0.64 (0.03)	3.4 (0.1)
0.85	0.75	0.745 (0.001)	-6.055 (0.001)	0.75 (0.01)	2.5 (0.1)
0.85	0.9	0.899 (0.001)	-5.890 (0.001)	1.85 (0.01)	2.5 (0.2)
0.85	1.2	1.207 (0.001)	-5.576 (0.002)	3.08 (0.01)	2.5 (0.1)
0.85	2.2	2.239 (0.002)	-4.698 (0.003)	4.23 (0.01)	2.34 (0.08)
0.88	0.95	0.938 (0.001)	-6.000 (0.001)	2.86 (0.01)	2.6 (0.1)
0.88	1.1	1.127 (0.001)	-5.790 (0.002)	3.58 (0.01)	2.59 (0.07)
1.2	0.5	0.493 (0.001)	-7.448 (0.002)	26.03 (0.01)	3.0 (0.1)

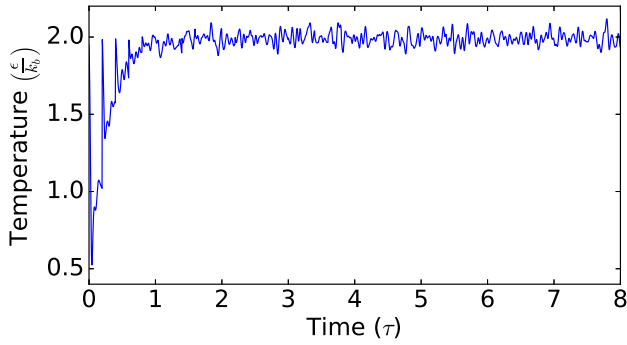


Fig. 1. Temperature as a function of time for 2000 iterations; rescaling occurs every 50 iterations up to iteration 1000. The temperature settles just below the set value ( $T_D = 2$ ) at  $1.9886 \pm 0.0007$ .

density at constant temperature, the compressibility factor and pressure increase as well. This is caused by the fact that a higher particle density results in more particles interacting with a unit surface, so in an increased pressure.

Hence, the simulation seems correct in a qualitative way, but we also want to know if it is good in a quantitative way by checking whether our values correspond well to other simulations and experiments described in literature. To this end we use Verlet's original paper [1]. It turns out that our results are generally in good agreement with Verlet's simulation results and the experimental results from others that he included in his paper. However, in the cases that  $\rho = 0.45$  and the desired temperature  $T_D = 1.55$  and that  $\rho = 0.5$  and  $T_D = 1.35$  Verlet's tabulated results significantly differ from ours. At the same time, our values seem to correspond with the experimental data in Verlet's paper, so there is no real issue

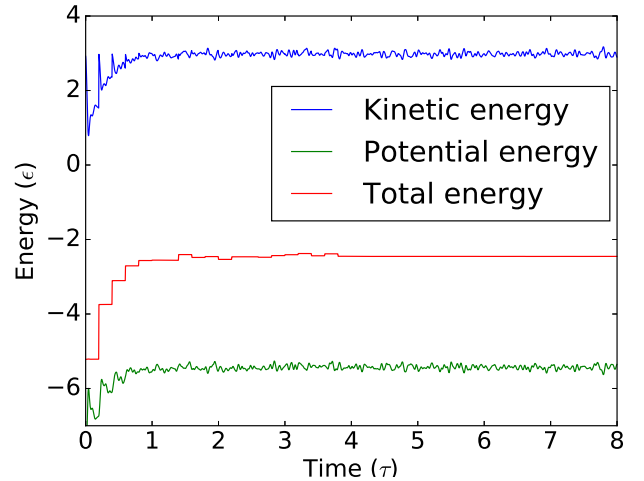


Fig. 2. The sum of the potential and kinetic energy per particle for  $\rho=1.2$  and  $T_D=2$ . Total energy remains conserved in between and after rescale operations, which are done up to  $\tau=4$ .

here.

Furthermore, there is a very remarkable result; under some circumstances the compressibility factor and pressure are negative, which is contrary to physical intuition. Still, this is a common occurrence in MD simulations. According to [9] and [10], this issue is caused by the fact that at the given temperature the density is too low for the system to be stable in the liquid or solid phase. The fact that the compressibility factor for  $\beta \approx 1.2$  is much higher for  $\rho = 0.85$  than for  $\rho = 0.75$  and becomes positive again supports this.

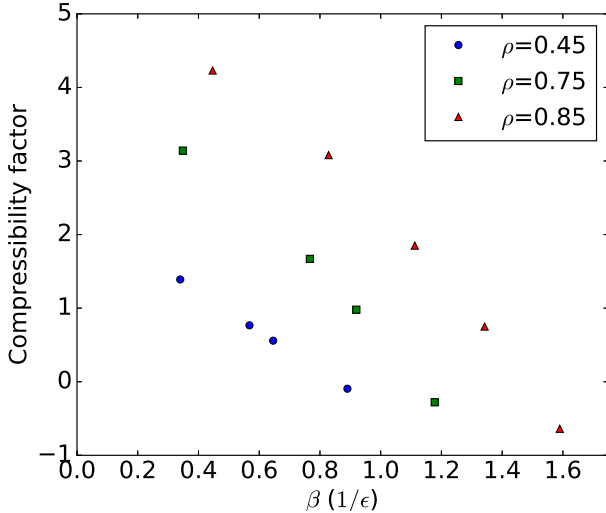


Fig. 3. Compressibility factor as a function of  $\beta$  for different particle densities. Errors can be found in table I, because they are too small to plot them as errorbars here.

### C. Phases of argon

It should be possible to see in which phase argon resides at certain simulation values. As stated in the theory the pair correlation and the displacement look different for each phase. According to Thijssen[5], argon should be in the liquid phase for  $T = 1$  and  $\rho = 0.8$ . For  $T = 0.5$  and  $\rho = 1.2$  argon should be solid and for  $T = 3$  and  $\rho = 0.3$  it should be in the gas phase.

The results of the simulation done with these values can be found in figure 4. We first look at the pair correlations shown in the top row of the figure, we see that they differ significantly. For the solid phase we can clearly see the fcc grid back as there are peaks visible at multiples of  $2^{1/6}\sigma$  and at  $2^{2/3}\sigma$ . The peaks are a bit widened as the atoms still move a little around their equilibrium positions. For the liquid phase we only see peaks around multiples of  $2^{1/6}\sigma$ , which is as expected. Because the atoms move faster in a liquid, the peaks are much broader compared to the solid. For the gas we only see a small peak at  $2^{1/6}\sigma$ , but the correlation is flat until we reach the end of the domain. It is clear that in a gas there is almost no correlation between the pairs, with the only exception the peak at the minimum of the Lennard-Jones potential.

Next we look at the mean squared displacement of the particles. The solid phase stand out from the other two phases. There is no change after an initial jump just after we start measuring, indicating that the particles do not diffuse as one would expect of atoms in a grid. For the liquid phase we also see an initial fast increase, but then the mean squared displacement starts following the expected linear behaviour. The linear behaviour of the gas phase begins almost immediately, but the graph shows that the squared displacement converges after a while. This is because we simulate a domain which has a finite length and so there is a maximum displacement. In the gas phase the atoms move so fast that this maximum is reached very fast.

### D. Specific heat

The specific heat determined in the simulations can be compared with theoretical values explained in the theory section. Due to our choice of reduced units, our expected result for the ideal gas limit is  $C_v = \frac{3}{2}k_b = \frac{3}{2}$ . An ideal gas is composed of particles that only interact through elastic collisions, which means the density needs to be chosen small. Running the simulation with  $T = 2$  and  $\rho = 0.001$  results in a specific heat of  $C_v = 1.50093 \pm 0.00008$ , which is close to the ideal gas approximation. The theoretical specific heat of  $C_v = 1.5$  does not fall within the error margin as the particles do still interact. However, the particles interact much less at lower densities, which causes the kinetic energy per particle and the specific heat to stay relatively constant, explaining the low error value. Lower densities result in specific heat values that are even closer to the ideal gas limit.

Solid Argon is expected to have a specific heat of  $C_v = 3k_b = 3$  in reduced units. By running the simulation with the parameter  $T = 0.5$  and  $\rho = 1.2$ , which have previously been confirmed to result in the simulation of a solid, we obtain the result  $C_v = 3.0 \pm 0.1$ , which is indeed the expected result.

In between the two limits, the specific heat takes on intermediate values. Setting the parameters to  $T = 3$  and  $\rho = 0.3$ , which was confirmed to result in a simulation of Argon in the gas phase, gives a specific heat of  $C_v = 1.635 \pm 0.008$ , indicating that the ideal gas approximation does not hold anymore. With the parameters given for the liquid phase,  $T = 1$  and  $\rho = 0.8$ , the specific heat is found to be  $C_v = 2.36 \pm 0.08$ , which is close to the exact center of  $C_v = 2.25$  between the two limits. Other values for  $C_v$  obtained from various simulations can be found in table I.

## V. CONCLUSION

We have successfully created an MD simulation of argon atoms in a cubic domain of computation using periodic boundary conditions. This is proved by the fact that energy is conserved during the simulation and that the physical quantities that we determined, like the average potential energy per particle and the compressibility factor, are in agreement with values found in literature. Values found for the specific heat at constant volume satisfy the theoretical limits that are known for ideal gasses and solids. The pair correlation function turned out to be an excellent tool for determining the phase of the system. The gas, liquid and solid phases have all been observed. Furthermore, calculations of the mean squared displacement also yielded characteristic information about each of the phases.

In the future, we can try to build a simulation program for the canonical or  $NVT$ -ensemble which better resembles experimental conditions, because in experiments often the temperature rather than the total energy is controlled. This requires the implementation of a thermostat, which would be a nice challenge for the future. We can even go one step further and simulate in the isothermal-isobaric or  $NpT$ -ensemble, in which the pressure is also kept constant. This is often the case in experiments as well and, amongst other things, it requires incorporating the volume as a dynamical variable in

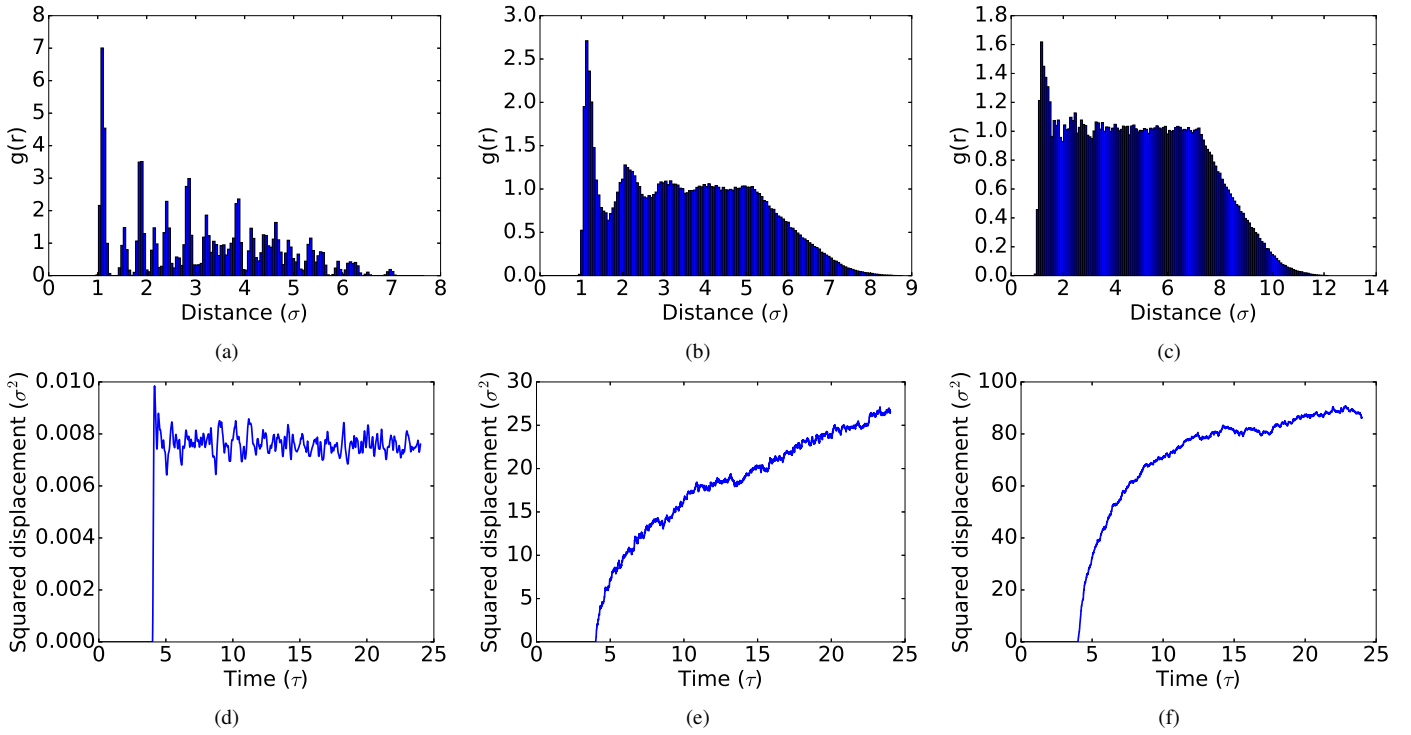


Fig. 4. Sub-figures (a), (b), and (c) depict the pair correlation for the solid, liquid and gas phase of argon, respectively. Their respective displacements can be found in sub-figures (d), (e), and (f).

the equations of motion. Another possibility for future research is simulating polyatomic molecules. Then, we also have to consider intramolecular forces. Lastly, we can try a completely different technique, the Monte Carlo method, and compare the results with molecular dynamics results [5].

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