A simulation of argon gas

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Abstract

In this report the approach to make a temperature dependent simulation of argon gas is given. With this simulation the effect of the temperature on the lattice structure can be seen. In the simulation the argon gas particles are assumed to be point particles, thus their only interaction is given by the Lennart-Jones potential. The system is given in reduced units, in order to be able to use more manageable numbers. For the time evolution the Verlet method is used, because this is more stable than the Euler method. In order to approach an infinite space the minimal image convention is implemented. To verify whether the code is working correctly two observables are calculated, namely the specific heat and the pair correlation function, together with their error. The value found for the specific heat is $Cv = 1.5 \pm 0.5$ which corresponds with the value of $Cv = 1.19$ found in the literature [1]. The pair correlation function has been calculated for different temperatures and has been compared to literature. The pair correlation clearly shows a change of the movement of the particles for different temperatures.

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1 Introduction

In the world around us we see solids, liquids and can sometimes see gases. This state changes as a result of change in temperature. It is material specific for which temperature something is a gas, liquid or solid. In order to understand why the phase transitions happen, one has to study materials at an atomic scale. One option is to make a simulation such as Verlet has demonstrated [2].

In this report the results of a simulation of argon gas will be given. Since argon is a noble gas it has a very small interaction with other particles, which means it can be simulated using point particles. The main interaction is therefore the attractive and repulsive force. Since the model is temperature dependent the movement of the particles can be seen for different temperatures, thus also for different phases.

In chapter two the methods used in the simulation are given. This includes the physical background of the program as well as the computational background. In chapter three the results of the observables, which are calculated are given and compared with literature. Also the performance of the program is given and discussed. In chapter four the conclusion is given. In the appendix A the task division per week can be found together with a general work organization.

2 Methods

2.1 Interaction

Argon is a noble gas so interaction with other atoms is negligible. Even though argon is not reactive it should still interact with other atoms. It is known that argon atoms have a neutral charge so for this project the coulomb interaction is omitted. Excluding these possible interactions we are left with the Lennard Jones potential. The potential is given as

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]. \tag{1}$$

The parameters σ and ϵ are argon gas specific constants, r is the distance between the observed atom and a secondary atom.
The force between the particles is based on this potential and can be derived as can be seen below.

$$\begin{aligned} \vec{F}(r) &= -\nabla U(r(x,y,z)) \\ &= 4\frac{\epsilon}{\sigma} \left[12 \left(\frac{\sigma}{r}\right)^{13} - 6 \left(\frac{\sigma}{r}\right)^{7} \right] \frac{\vec{r}}{r} \end{aligned} \tag{2}$$

In equation 2 $\vec{r}$ represents the position vector of a secondary particle.

2.2 Scaling

Reduced units were introduced to simplify the simulation. By reducing the units the values of the system change into manageable orders. To obtain the new units the constants have been divided by their typical values, yielding constants such as: the mass of an argon atom, k_B, σ and ϵ of value 1. By doing this the results are given in terms of the constants.

2.3 Minimal image

Because of programming limits the system has to be a finite box, for which boundary conditions have to be simulated. Assumed is that if a particle leaves the box at one side it will reappear at the other side. Essentially the particle is copied over space by a period D which corresponds to the dimension of the system in x,y and z direction.
To make sure that the 'teleportation' of particles does not induce a discontinuity in the interaction between the particles the nearest image convention is being used. The nearest image convention essentially makes sure that the interaction between particle one and particle two only depends on particle two in the box and its periodic version at +1 and -1 times the period. Only the particle whichever is closest to particle one will have an interaction. An example in two dimensions is shown in figure 1:

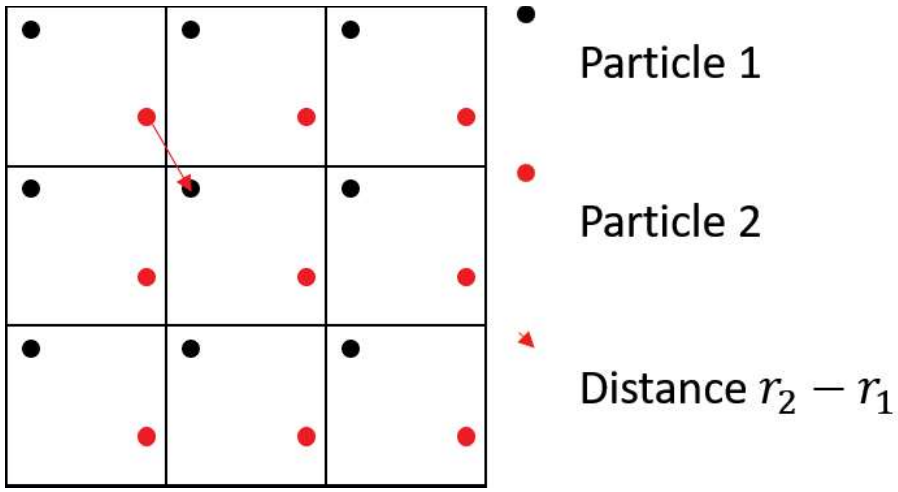


Figure 1: The nearest image convention in two dimensions. The only interaction is between particle 1 and 2 which are closest together. The box in the centre is the simulated area and the eight boxes around illustrate the periodic occurrence of the particles.

Due to this only a relatively small box has to be programmed, but interaction from outside the box is still taken into account. As a result it approaches being infinitely large. For a good representation of the gas one would still need a lot of particles before it would represent the assumed nature of the gas.

2.4 Time evaluation

To further increase the stability of the system and avoid discontinuities a good time evaluation is needed. An example of a more commonly known method is Euler evaluation. This method approximates the physical interaction by discrete steps. For instance the position can be calculated using:

$$x(t + \Delta t) = x(t) + \Delta t v(t)$$

By using the velocity v at time t the traveled distance is calculated and added to the position at time t.
The Euler evaluation works but there is a better alternative that expands the evaluation and approximates a continuous interaction more closely. The method uses the Verlet algorithm [2]. The time evaluation of the position and velocity are computed using,

$$\begin{aligned} \vec{x}(t + \Delta t) &= \vec{x}(t) + \Delta t \vec{v}(t) + \frac{\Delta t^2}{2} \vec{F}(\vec{x}(t)) \\ \vec{v}(t + \Delta t) &= \vec{v}(t) + \frac{\Delta t}{2} \left(\vec{F}(\vec{x}(t + \Delta t) + \vec{F}(\vec{x}(t) \right) \end{aligned} \tag{3}$$

2.5 Initial velocity and scaling

Assuming that the system contains an ideal gas we need to give the particles a velocity when the simulation gets initialised. The velocity of all particles should agree with the Maxwell-Boltzmann distribution:

$$f(v) = e^{-m*v^2/(2k_bT)}$$

When the system gets initialised it will not be stable at the start. To be able to extract any information from the simulation it should first stabilize. This is done by scaling the kinetic energy of the system. This is achieved by multiplying the velocity of the particles with the scaling value λ:

$$\lambda = \sqrt{\frac{(N-1)3k_bT}{\sum_i mv_i^2}} \tag{4}$$

After re-scaling of the velocity at different time steps the system is expected to converge to a stable total energy. At this point it is possible to extract the data in form of observables.

2.6 Observables

The particles are simulated in a three dimensional box with a face centered cubic (FCC) lattice structure. To see whether the system is properly simulating the movement of argon gas at a certain temperature, so called observables are calculated. In this report the specific heat and the pair correlation function are calculated together with their error. To calculate observables, averages over the simulation time after the system has reached equilibrium are used.

$$\langle A \rangle = \frac{1}{n-n_0} \sum_{i>n_0}^{n} A_i$$

Here A represents the observable, n is the total number of time steps and n_0 gives the time step at which equilibrium is reached.

2.6.1 The specific heat

The specific heat was calculated using the following equation [1].

$$Cv = -\frac{3N}{2} \frac{1}{\frac{3N*(\langle E_k^2 \rangle - \langle E_k \rangle^2)}{2\langle E_k \rangle^2} - 1} \tag{5}$$

In this equation Cv is the specific heat, N the number of particles and E_k the kinetic energy.
The specific heat was calculated using five successive values of the kinetic energy. This was repeated ten times and the average of this gives the value of the specific heat. Then those ten values were the input of the autocorrelation function in order to calculate the error.

2.6.2 Pair correlation

For the calculation of the pair correlation the following equation has been used.

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \tag{6}$$

In this equation $g(r)$ represents the pair correlation, V is the volume of the box, r is the distance between the particles, $n(r)$ is a histogram of the number of particles within the distance $r + \Delta r$ where Δr is the binsize.

2.7 Error calculation

To calculate the error of the observables the autocorrelation function, $\chi(t)$ has been used.

$$\chi_A(t) = \frac{1}{n_0 - t} \sum_{n=1}^{n_0 - t} A_n A_{n+t} - \frac{1}{n_0 - t} \sum_{n=1}^{n_0 - t} A_n * \frac{1}{n_0 - t} \sum_{n=1}^{n_0 - t} A_{n+t} \tag{7}$$

In this equation t gives the corresponding time step, n_0 is the total simulation time. Once $\chi_A(t)$ is known it can be fitted to $e^{\frac{-t}{\tau}}$ in order to get τ. Then τ can be used to calculate the error using the following equation.

$$\sigma_A = \sqrt{\frac{2 * \tau}{n_0} \langle A^2 \rangle - \langle A \rangle^2} \tag{8}$$

3 Results

The simulation is performed for different values of the temperature. The idea is to observe the different phases of argon. The observables are used to investigate if the system actually works as expected. The values of the observables can be compared with the literature.
To see if the system stabilizes one can look at the total energy of the system. An example of the energy of the system over time is given in figure 2. The system runs from time t = 0 to t = 20 in steps of Δt = 0.004 for every simulation described in this section..

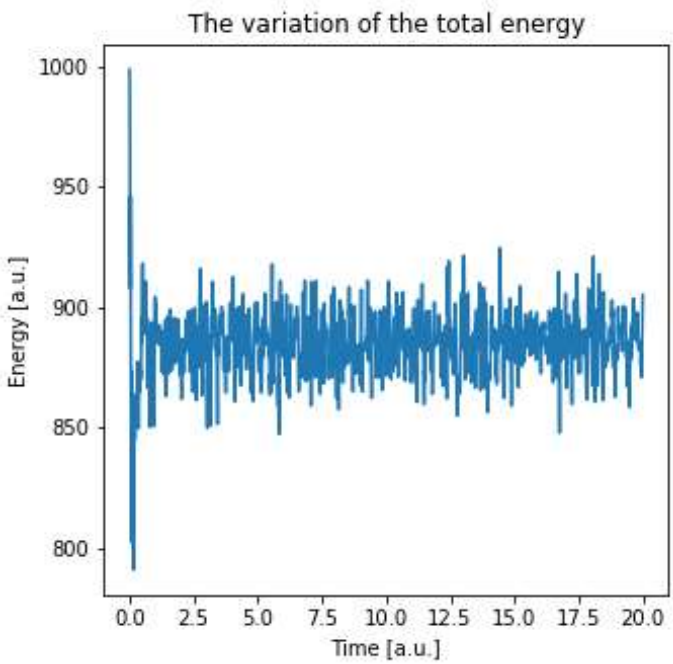
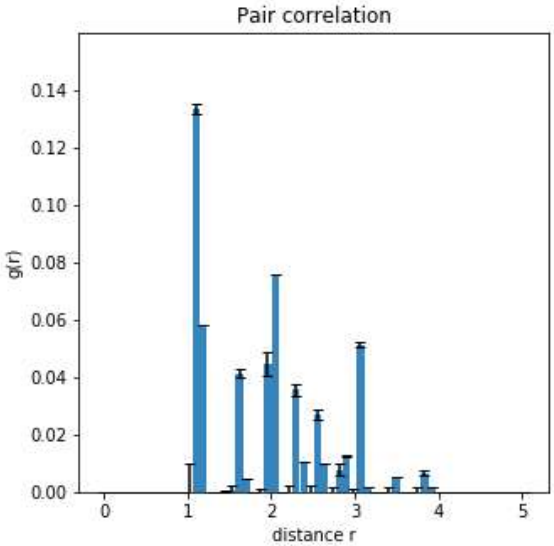


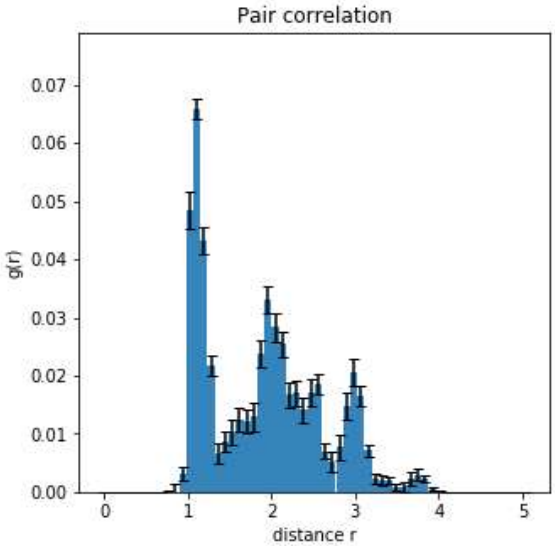
Figure 2: The total energy of the system when the temperature is set at 0.827 and a density of 1.06 calculated for a box containing 108 particles. After some time the energy stabilises and oscillates around the system energy.

3.1 Pair correlation

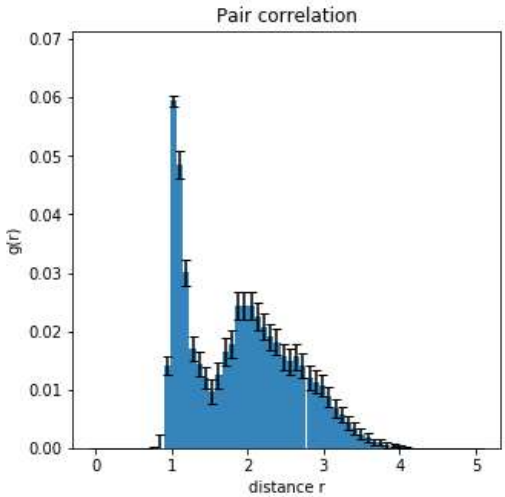
The pair correlation can clearly indicate the phase of argon. This is because it shows how the spacing between the atoms is divided. The pair correlation for different temperatures is shown below in figure 3:



(a)



(b)



(c)

Figure 3: The pair correlation for three different temperatures: T = 0.01 (a), 0.5 (b) and 0.8 (c). The density was set at $\rho = 0.88$ and the box lengths were set at 5.

It can clearly be seen in figure 3 that for different temperatures the spacing between argon atom is different. The values found show that for low temperature the lattice is rigid and that for high temperatures the particles move around more freely. The error is calculated over the last twenty values of the pair correlation. For the temperature of T = 0.5 and 0.8 the uncertainty is bigger. This indicates that the values vary more over time compared to

the pair correlation for T = 0.01. From the plots it can be concluded that the argon is in different phases.

3.1.1 Comparison to literature

The pair correlation functions shown in figure 3 show that the phase of argon changes in the simulation, but does not show if the behaviour is as would be expected. To make sure that the results are representative a simulation was run with similar constants as shown in the literature [3]. The temperature was set at T = 0.827 and the density at $\rho = 1.06$.

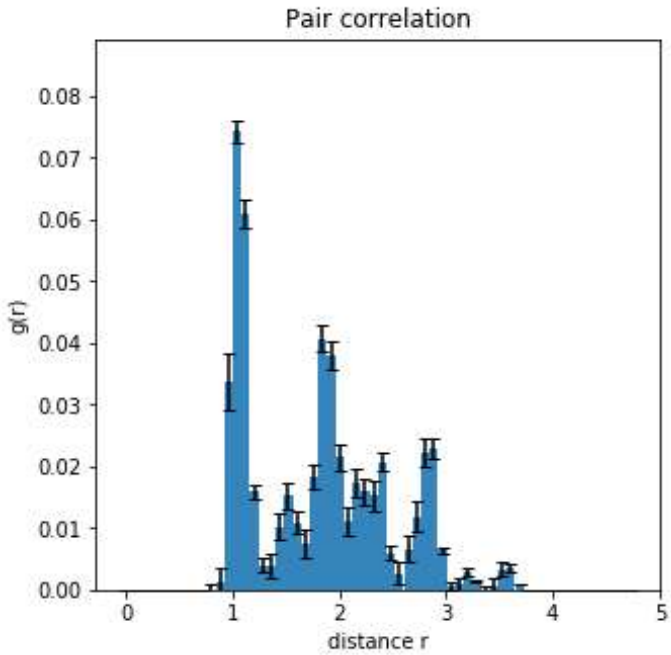


Figure 4: The pair correlation for temperature T = 0.827 and density $\rho = 1.06$.

The main difference observed between the literature and the simulation is the value of the function at higher distances. A possible explanation could be that in the literature the simulation box is larger and thus there will be bigger distances between the particles.

3.2 Specific heat

The specific heat is calculated using as the density, $\rho = 0.85$ and for the temperature $T = 0.88$. The calculated specific heat of the system is calculated to be $Cv = 162 \pm 53$. Since there are 108 particles in the system, the specific heat per particle is $Cv = 1.5 \pm 0.5$.

In the literature it can be found that using the same values for T, ρ the specific heat per particle is $Cv = 1.19$ [1]. This means that value found for the specific heat corresponds with the literature.

3.3 Performance of the simulation

The simulation underwent some drastic changes along the project with the reason being improving performance. When running a simulation of a large system it is of course very important that the calculations are as effective as possible. For this project this meant that usage of for loops was avoided as much as possible.
At first instance when the simulation contained everything what was needed the computation time took around 15 minutes. The performance test was done by using the profiler function in Spyder. The results indicated that for example calculating the pair correlation for every time step took a lot of time. To speed up the computation the calculation was set to be performed only in the last section of the simulation. Other small modifications have been made to further increase the computation speed which is now around 3 minutes on the same device. This does not mean that the simulation could be optimised even more but the biggest factors that delay the computation have been altered.
The performance of the code was only tested for N = 108 particles and 5000 time-steps per simulation.

4 Conclusion

The pair correlation graphs clearly show a different lattice structure for different temperatures, which corresponds with what was expected. Comparing the pair correlation to the literature shows similarity but is very different at high distances which indicates a different simulation size [3]. The found specific heat per particle is $Cv = 1.5 \pm 0.5$ which corresponds with the literature value of $Cv = 1.19$ at $T = 0.88$ [1].
Using this simulation, the temperature effects on a lattice can be seen. The effects can be seen best when looking at the pair correlation, the specific heat is mainly used to verify the code with the literature. In order to verify the code even more, other observables such as the pressure or the diffusion rate could be calculated.

References

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[3] Jos Thijssen. *Computational physics*. Cambridge university press, 2007.