

FYS3150 Computational Physics – Project 5

Molecular Dynamics

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December 9, 2016

Abstract

This project used molecular dynamics to simulate a system of argon atoms. Initial velocities were set by the Maxwell-Boltzmann distribution, intermolecular forces were calculated from the Lennard-Jones potential and the Verlet integrator was used to calculate the positions and velocities of the atoms over time. The melting temperature was found to be in the range between 300 K and 350 K when studying the total energy and temperature evolution for different initial temperatures. The diffusion constant for different temperatures at equilibrium was used to find a melting temperature of slightly below 350 K.

GitHub repository with code can be found at: github.com/harmoh/FYS3150_Project_5

1 Introduction

In this project we will use molecular dynamics (MD) to simulate dynamics of argon atoms and explore the phase space. We will use the Maxwell-Boltzmann distribution to set the initial velocities of the atoms in the system, use Lennard-Jones potential to find the potential and calculate the forces between the atoms, and use the Verlet integrator to calculate the positions and velocities from the mass and force. We will also use a front-centered cubic lattice and periodic boundary conditions in order to find the melting temperature of the system and finally calculate the diffusion constant. The system will be modelled by running and plotting a program using C++ and Python. Three dimensional visualisations of the position of each atom through time will be simulated using the software Ovito.

After this introduction there will be a section presenting important theory and units used, then the method section will present relevant algorithms derived. The implementation section explains how the modelling program is set up, relation between the classes and the flow of the functions. The results are presented in the next section, then a short discussion is made before some concluding remarks.

2 Theory

2.1 Maxwell-Boltzmann velocity distribution

The initial velocity of the atoms is given by the Maxwell-Boltzmann distribution such that

$$P(v_i)dv_i = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv_i^2}{2k_B T}\right) dv_i, \quad (1)$$

where m is the mass of the atom, k_B is Boltzmann's constant and T is the temperature. This is the normal distribution with zero mean and the standard deviation given by $\sigma = \sqrt{k_B T/m}$. We also known this as the Boltzmann distribution given by $P(E) \propto \exp(-\beta E)$, where $E = 0.5mv^2$ [1]. The initial velocity of particles in real physical systems are given at random from a certain distribution and are dependent on the initial temperature. Some speeds are more naturally correct than others. The Maxwell-Boltzmann distribution will then give the correct probability for certain speeds and shows a distribution that has a good agreement with that of the real physical system.

2.2 Lennard-Jones potential

In this project, we use the Lennard-Jones potential to calculate the energy between two atoms i and j as

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6 \right], \quad (2)$$

where $r_{ji} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between atom i and atom j , ϵ is the depth of the potential well and σ is the distance where the potential is zero. The optimal parameters for argon are

$$\frac{\epsilon}{k_B} = 119.8 \text{ K} \quad (3)$$

and

$$\sigma = 3.405 \text{ Angstrom}. \quad (4)$$

The potential energy V is given by summing the energy of all pairs of atoms

$$V = \sum_{i < j} U(r_{ij}). \quad (5)$$

The force is calculated by the negative of the gradient of the potential energy

$$\mathbf{F}(r_{ij}) = -\nabla U(r_{ij}), \quad (6)$$

which can be rewritten for one dimension as

$$F_x(r_{ij}) = -\frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_{ij}}. \quad (7)$$

The force in the y and z dimension can be calculated in the same way. We have that

$$\frac{\partial U}{\partial r_{ij}} = \frac{24\epsilon}{r_{ij}^2} \left[2 \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6 \right]. \quad (8)$$

The force between each pair of atoms are added together as all the particles are iterated through. By using minimum image convention, the periodic boundary conditions are met and the computation time can be reduced. By doing this, the Lennard-Jones potential can be truncated by a cutoff distance $r_c = 2.5\sigma$ [2]. The potential then becomes

$$U(r_c) = U(2.5\sigma) = 4\epsilon \left[\left(\frac{\sigma}{2.5\sigma} \right)^{12} - \left(\frac{\sigma}{2.5\sigma} \right)^6 \right]. \quad (9)$$

We set the truncation above the cutoff distance to zero and adjust the potential such that our new combined Lennard-Jones potential becomes

$$U(r_{ij}) = \begin{cases} U(r_{ij}) - U(2.5\sigma) & \text{if } r_{ij} \geq r_c \\ 0 & \text{if } r_{ij} < r_c \end{cases} \quad (10)$$

This way, the Lennard-Jones potential only have to be calculated when the distance between the two atoms in question are greater or equal to the cutoff distance [1, 2].

As mentioned, the depth of the potential well is defined by ϵ and the distance where the potential is zero is given by σ . When the potential is independent of both ϵ and σ , it is equal to them being set to one. Figure 1 shows the Lennard-Jones potential with respect to distance between the atoms when the potential is independent of ϵ and σ .

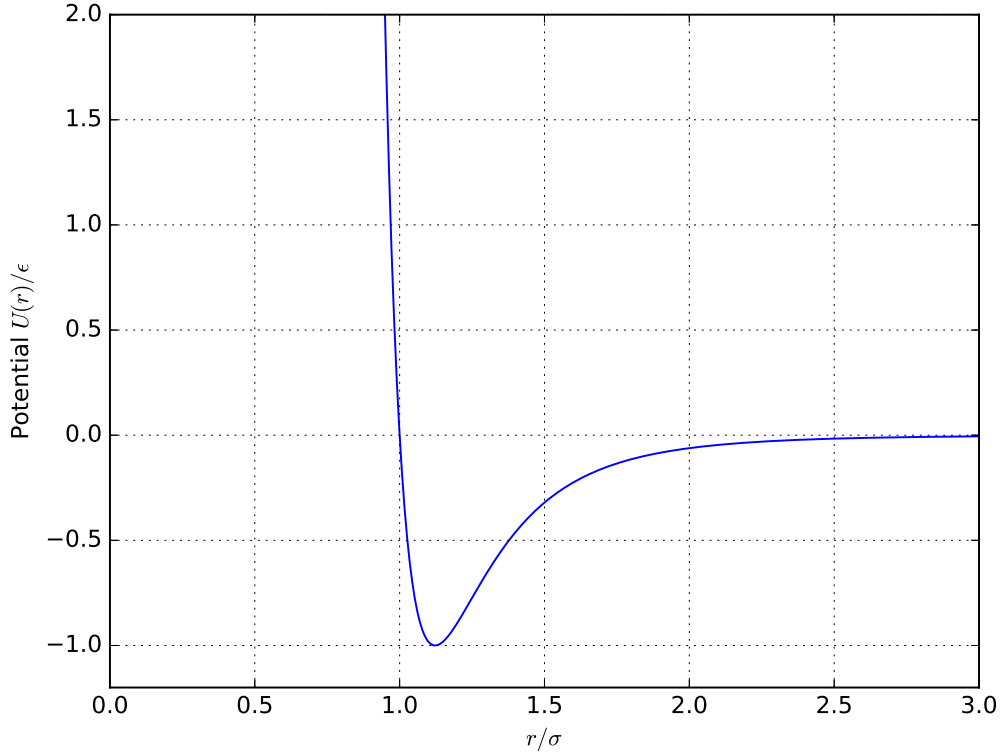


Figure 1: Lennard-Jones potential

2.3 Diffusion constant

The diffusion constant can be calculated in order to find the melting temperature of the system. We use the mean square displacement to the diffusion constant, which is written as

$$\langle r^2(t) \rangle = 6Dt, \quad (11)$$

where D is the diffusion constant and t is time. The mean square displacement for atom i is given by

$$r_i^2(t) = |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2, \quad (12)$$

where $\mathbf{r}_i(t)$ is the position of atom i at time t and $\mathbf{r}_i(0)$ is the initial position of atom i [1]. The diffusion constant then becomes

$$D = \frac{r_i^2(t)}{6t}. \quad (13)$$

2.4 Units

In this project, a lot of very small units are used for relevant values. In order to simplify the calculations, different units are chosen such that the Boltzmann's constant equals 1. Among the chosen units are:

$$1 \text{ unit of length} = 1 \text{ Angstrom} = 10^{-10} \text{ m} \quad (14)$$

$$1 \text{ unit of mass} = 1 \text{ a.m.u.} = 1.661 \times 10^{-27} \text{ kg} \quad (15)$$

$$1 \text{ unit of energy} = 1.651 \times 10^{-21} \text{ J} \quad (16)$$

$$1 \text{ unit of temperature} = 119.735 \text{ K} \quad (17)$$

$$1 \text{ unit of time} = 1.00224 \times 10^{-13} \text{ s} \quad (18)$$

The notation a.m.u. is an abbreviation for atomic mass unit. The class `UnitConverter` convert between these (and other) units and SI or other units.

3 Method

3.1 Periodic boundary conditions

In order to simulate the system within a confined space, periodic boundary conditions is applied. Without these conditions, the atoms would start within a cube and then spread out through space. Periodic boundary conditions let us simulate an infinitely large system by using a model of system with a limited size. The periodic boundary conditions were implemented as shown in listing 1.

```
1   for(int i = 0; i < m_particles.size(); i++) {
2       Particle *particle = m_particles[i];
3       for(int dim = 0; dim < 3; dim++) // In 3 dimensions {
4           if(particle->position[dim] < 0) {
5               particle->position[dim] += m_systemSize[dim];
6           }
7           if(particle->position[dim] >= m_systemSize[dim]) {
8               particle->position[dim] -= m_systemSize[dim];
9           }
10      }
```

```

10     }
11 }

```

Listing 1: Periodic boundary conditions

First, a loop iterates through all particles. Then the main loop goes through three dimensions and check the position of the particles. If the position is outside of the chosen boundaries (system size), the system size in that dimension is either added or subtracted to the position of the particle depending of which side of the boundary it is.

3.2 Front-centered cubic (FCC) lattice

Crystal structure of argon. The FCC lattice used in this project consists of unit cells with groups of atoms such that these can be repeated in order to create larger systems. A unit cell size is denoted as b and set to a constant $b = 5.26$ Angstrom. Four initial atoms are set up with the following coordinate vectors:

$$\mathbf{r}_1 = 0\hat{\mathbf{i}} + 0\hat{\mathbf{j}} + 0\hat{\mathbf{k}} \quad (19)$$

$$\mathbf{r}_2 = \frac{b}{2}\hat{\mathbf{i}} + \frac{b}{2}\hat{\mathbf{j}} + 0\hat{\mathbf{k}} \quad (20)$$

$$\mathbf{r}_3 = 0\hat{\mathbf{i}} + \frac{b}{2}\hat{\mathbf{j}} + \frac{b}{2}\hat{\mathbf{k}} \quad (21)$$

$$\mathbf{r}_4 = \frac{b}{2}\hat{\mathbf{i}} + 0\hat{\mathbf{j}} + \frac{b}{2}\hat{\mathbf{k}} \quad (22)$$

There are in total N such unit cells such that the total system size becomes

$$L = N \times b, \quad (23)$$

where L is the total lattice size in each dimension.

3.3 Verlet algorithm

In this project, the Verlet algorithm in order to calculate the velocity and position for the current time step. The algorithm for one dimension goes as follows:

$$x_{i+1} = x_i + \Delta t v_i + \frac{\Delta t^2}{2} a_i \quad (24)$$

$$v_{i+1} = v_i + \frac{\Delta t}{2} (a_{i+1} + a_i) \quad (25)$$

The acceleration is given as

$$a = \frac{F}{m}, \quad (26)$$

where the force is given by the Lennard-Jones potential. The step length Δt is defined as the given time step per integration. In this project, we use a step length of

$$\Delta t = 1 \times 10^{-15} \text{ s} = 9.97765 \times 10^{-3}. \quad (27)$$

When including the third dimension, two more sets of coupled equations have to be added. The implementation of the Verlet method is done by calculating the system forces before iterating through the bodies and calculating positions and velocities. Forces are updated after periodic boundary conditions are applied and before finding the velocities in order to get the force for the next step.

4 Implementation

This project is mainly developed in C++ for modelling the system and writing results to files. Python was used for reading those files and used in order to make plots of the results. Ovito was used for a three dimensional simulation of the system [3]. The main program in C++ was built up by a set of classes:

- System
- Particle
- StatisticsSampler
- IO
- Verlet
- LennardJones
- vec3
- UnitConverter

Each class has both a `.cpp` file and a `.h` file. The program was run from `main.cpp`, where the classes were instantiated from. The main tasks of each class and the relation between the classes

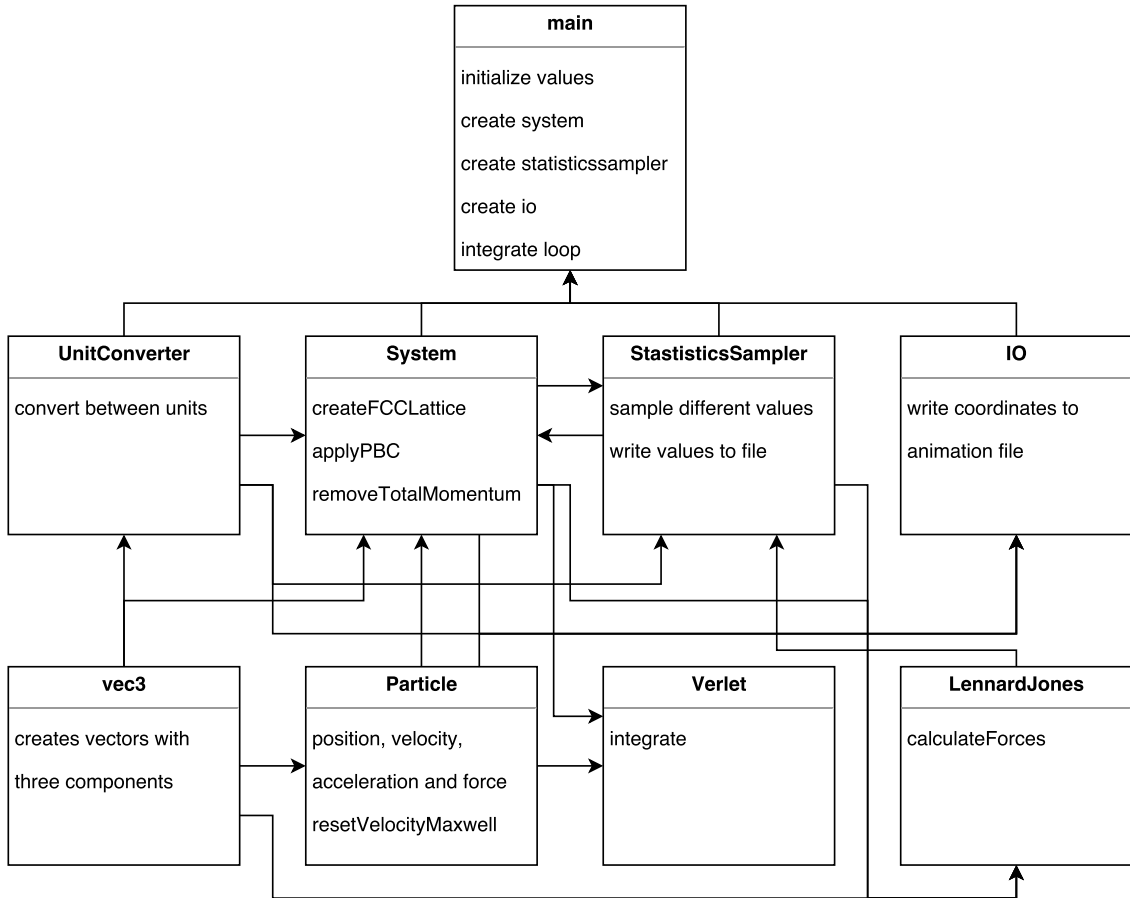


Figure 2: Class diagram of the C++ program

are shown in fig. 2. The program also uses a class called `random.h`, which is used to set the initial velocity to random using Gaussian distribution. The flow of the program developed in C++ is presented by a flowchart in fig. 3.

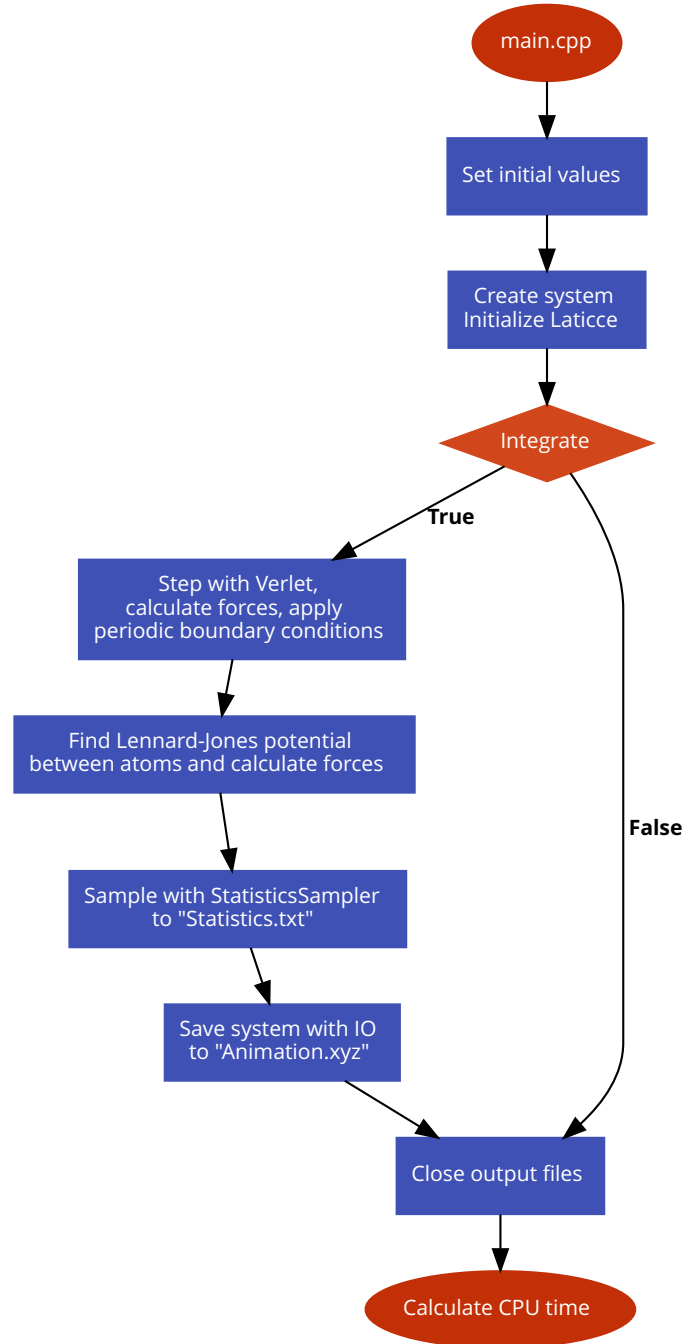


Figure 3: Flowchart of the C++ program

Different Python scripts were used for running and plotting the main program:

- `plotPBC.py` plots the coordinates of one atom in two dimensions in order to see that the function for periodic boundary conditions is working
- `plotLJ.py` makes a plot of the Lennard-Jones potential (this does not run `main.cpp`)
- `plotTotalEnergy.py` makes a plot of the total energy ($E_{total} = E_k + E_p$) over different final temperatures, where the final temperature used is set to $T = 0.5T_i$
- `plotTemp.py` plots of the temperature over time for several different initial temperatures
- `plotTempRatio.py` makes a plot of the temperature ratio T/T_i over time for several different initial temperatures
- `plotDiffusion.py` makes a plot of the diffusion constant over different final temperatures, where the final temperature used is set to $T = 0.5T_i$

5 Result

5.1 Periodic boundary conditions

As described in section 3.1, periodic boundary conditions are applied in order to simulate an infinitely large system with a lattice of limited size. The function was tested for one particle and studied in two dimensions and is shown in fig. 4. As seen in fig. 4a, the particle continues in a

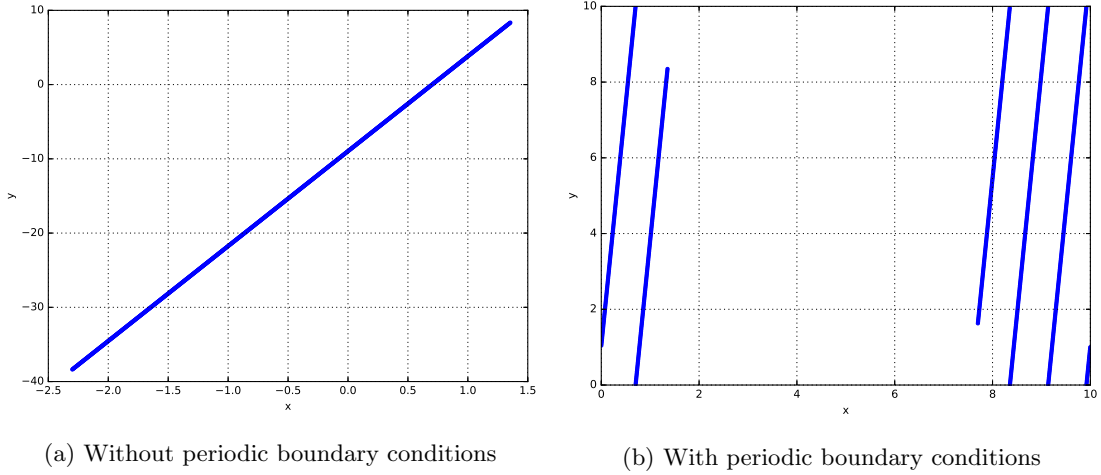


Figure 4: Position of a single atom in two dimensions with and without periodic boundary conditions

straight line out of the system with a lattice size of $L = 10$. This goes as expected and is not a correct representation of the real physical system. Figure 4b shows that the function for applying the periodic boundary conditions work, which was also seen in three dimensions in the simulation software Ovito [3].

5.2 Crystalline structure of argon

The next step in this project was to arrange the atoms in the correct structure for the element argon. This meant arranging them in a crystalline structure by using the initial position defined in section 3.2. Figure 5 shows the FCC lattice with the crystalline structure of the initial position of the atoms presented with Ovito [3].

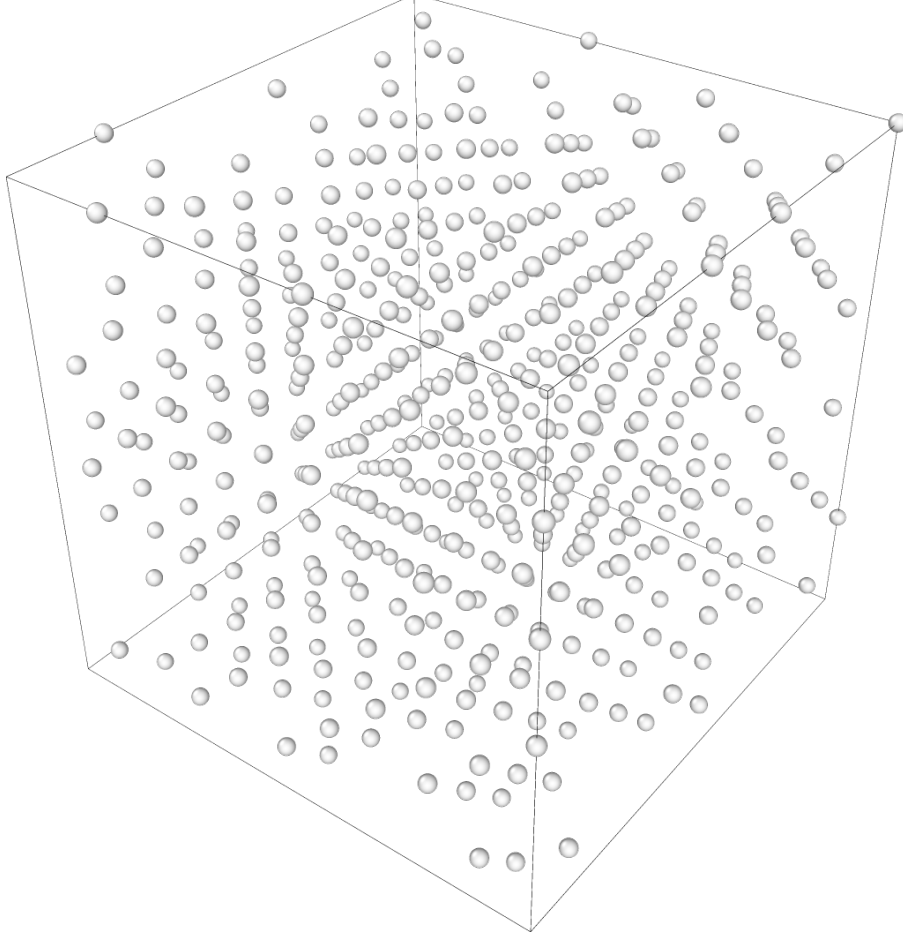


Figure 5: Crystalline structure of argon

The density of the structure is calculated in the `StatisticsSampler` class and printed to file with the rest of the values. The mass of one argon atom is $M = 39.948$ a.m.u., the lattice size is $L = N \times b$, where N is the number of unit cells with four atoms in each and b is the lattice constant set to $b = 5.26$ Angstrom. The density can then be calculated to be (for $N = 1$)

$$\rho = \frac{4M}{(N \times b)^3} = \frac{159.972 \text{ a.m.u.}}{5.26^3 \text{ Angstrom}^3} = 1.099 \frac{\text{a.m.u.}}{\text{Angstrom}^3}. \quad (28)$$

When the density is read from the program, the result becomes

$$\rho = 1.098 \frac{\text{a.m.u.}}{\text{Angstrom}^3}, \quad (29)$$

which is approximately the same.

5.3 Melting temperature

In order to better understand the system, the melting temperature needs to be studied. First, the total energy is investigated. The potential energy is calculated from the Lennard-Jones potential and the kinetic energy is calculated from the sum of the velocity and mass of all atoms in the system. The total energy shown in fig. 6. The total energy is plotted with respect to final temperature $T = 0.5T_i$. We can observe that the total energy linearly increase and passes zero when the final temperature is approximately 318 K. This may indicate a melting temperature for the system. It can be noted that the total energy for each initial temperature was conserved throughout the period that the system was run for, which can be seen in the "Statistics" files in the folder "Results" (available in the GitHub repository). Since the energy is conserved for this system, the drop in kinetic energy will result in an equal addition to the potential energy. This can also be observed in the "Statistics" files.

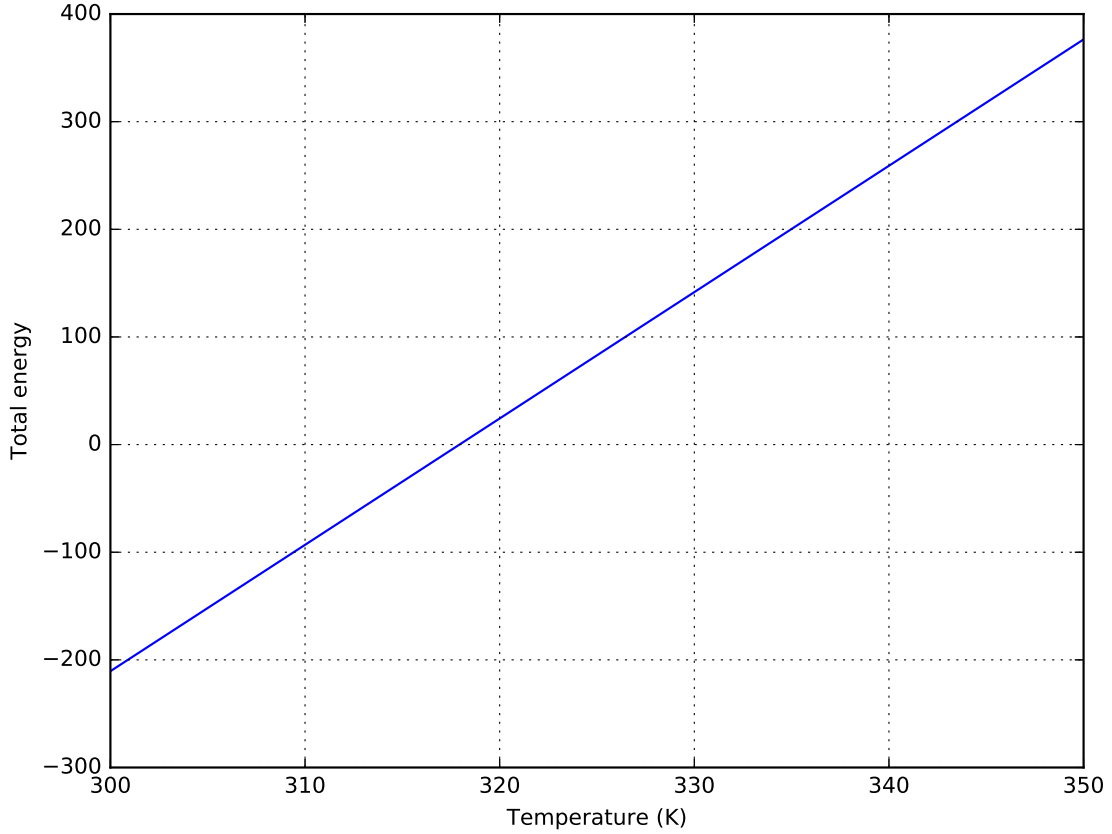


Figure 6: Total energy over temperature after 1000 time steps

Different initial temperatures were selected and the temperatures were plotted over time to study how the temperature changed over time. Figure 7 shows the temperature over 1000 time steps for initial temperatures between 50 K and 1000 K. The temperature for all test shows a large initial drop during the first 100 steps and then a pretty stable evolution as the equilibrium is reached. It can be observed that the higher the initial temperature, the more unstable the final temperature becomes. The temperatures start to be unstable for initial temperatures of around 600 K and above, where the final temperature is around 300 K. This may indicate that the system has a melting temperature somewhere above 300 K, which corresponds with the total energy.

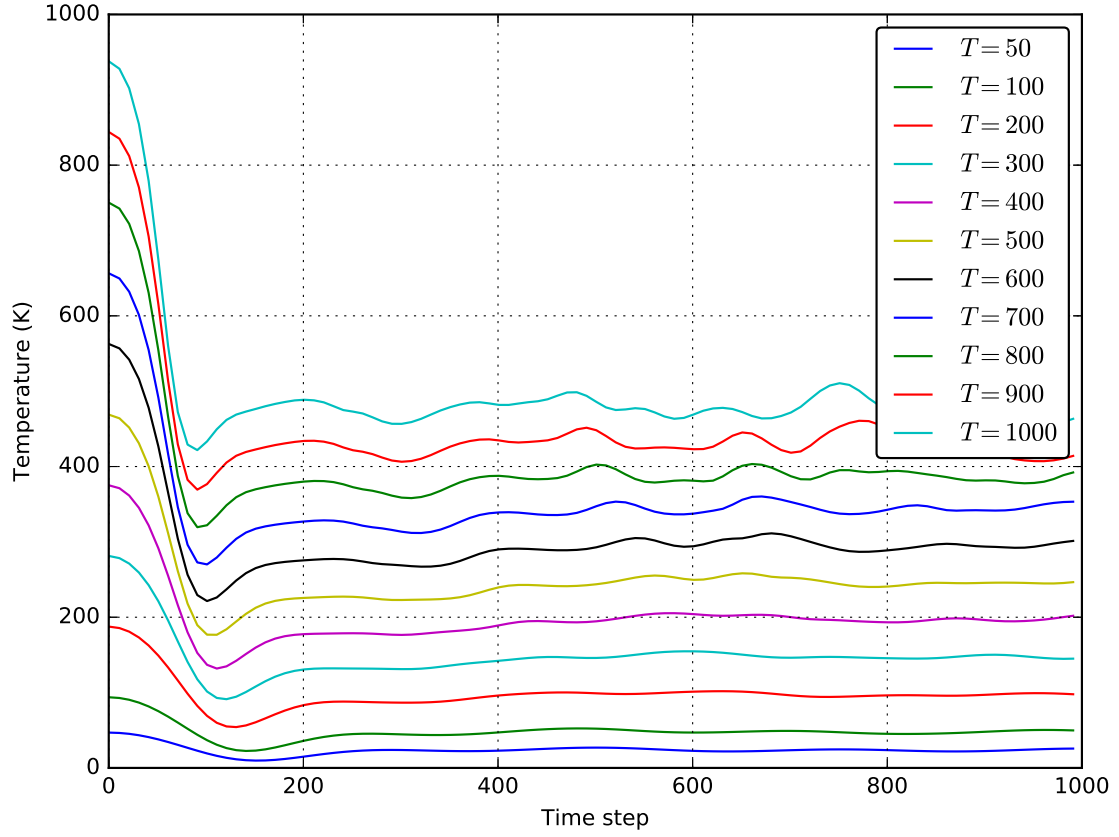


Figure 7: Temperature over time

The ratio between the temperature at equilibrium and the initial temperature was also studied and is shown in fig. 8 over 2000 time steps with initial temperatures ranging from 50 K to 800 K. The initial pattern is very similar between the different initial temperatures, where the lower initial temperatures shows a higher drop. All the different initial temperatures seem to more or less reach their equilibrium at around 500 time steps, where the temperature stabilizes at approximately half of the initial temperature such that

$$T \approx 0.5T_i. \quad (30)$$

We know that the temperature is proportional with the kinetic energy as it is given by

$$T = \frac{2}{3} \frac{E_k}{N_{atoms}k_B}, \quad (31)$$

where E_k is the kinetic energy, N_{atoms} is the number of atoms and k_B is Boltzmann's constant (here equal to one) [1]. The high initial drop in temperature also implies a high drop in kinetic energy. Since the mass is constant for the atoms, the kinetic energy (and temperature) is really only dependent on the velocity of the atoms. The initial velocity is given in a random direction by the Maxwell-Boltzmann distribution explained in section 2 and is dependent on the initial temperature. As soon as the atoms start to move, they get closer to other atoms and will have repulsive forces (given by the Lennard-Jones potential). This will often result in a sudden decrease in velocity. Hence, the large initial drop in kinetic energy and temperature.

The three dimensional simulation software Ovito was used frequently in this project to get a visualization of the model produced [3]. This was a good opportunity to study the movement of

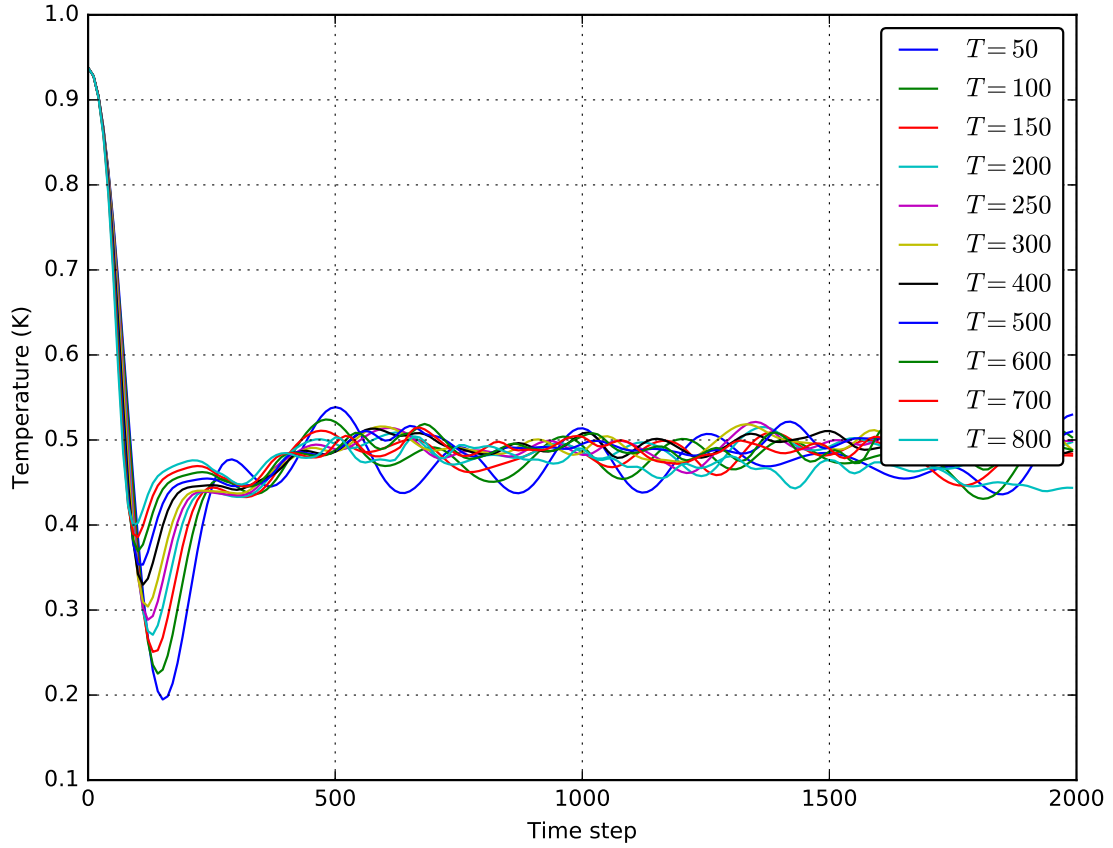


Figure 8: Temperature ratio over time

the atoms in the system in order to observe the melting temperature. The *.xyz files produced was used in Ovito and several videos of the simulation were made for initial temperatures between 50 K and 800 K (the videos are available under the folder "Animation" in the GitHub repository). At low temperatures, it is easy to observe that the atoms move a little bit around, but mainly stay in the same spot. At higher temperatures, the movement becomes larger, but the atoms still move around in their "area". Only when the initial temperatures are above 600 K, it is possible to see that some atoms start to move away from their initial position, then their final position becomes more or less random. This shows an indication that the system has reached its melting temperature.

5.4 Diffusion

As seen in section 2.3, the diffusion constant can be found by calculating the distance between the initial position and the final position for each atom. In other words, since we know that the atoms move away from their initial position when system is above the melting temperature, the diffusion constant should increase significantly when the temperature is above the melting temperature. For temperatures below the melting temperature, the diffusion constant should be close to zero considering that the atoms stay very close to their initial position. It is also important to use periodic boundary condition for both current position and the initial position such that the actual distance traveled by each atom is considered. If periodic boundary conditions is applied for the

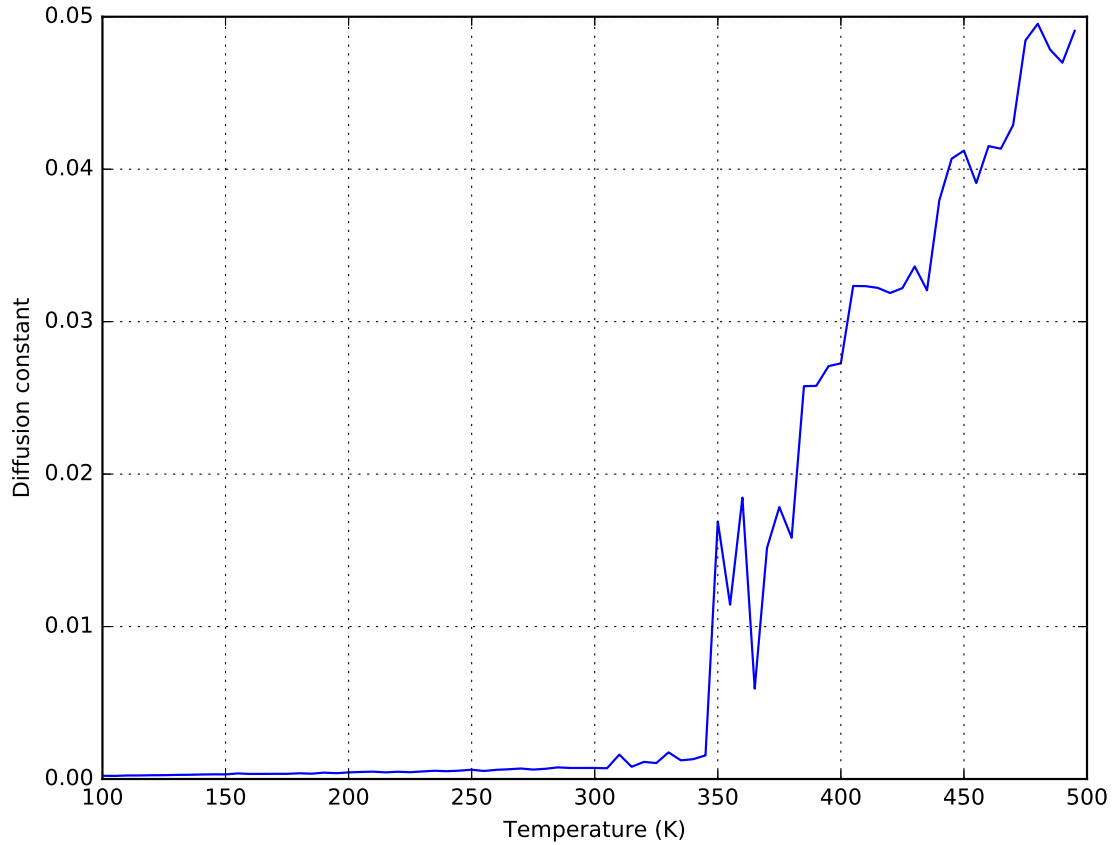


Figure 9: Diffusion constant over temperature after 10^4 time steps

initial position of an atom each time the current position is out of bounds, then it will give the same result as if the periodic boundary conditions were not applied for either positions in the first place. Figure 9 shows the diffusion constant plotted over different final temperatures after 10^4 time steps. The final temperature used is $T = 0,5T_i$ and the plot ranges from an initial temperature of 200 K to an initial temperature of 990 K with 10 K between each point. The diffusion constant stays close to zero until the temperature reach almost 350 K, where the initial temperature was 700 K. The increase is significant, as expected, and keeps increasing with increasing temperatures. This suggests that the melting temperature of the system is just below 350 K, which shows a good agreement with the total energy, temperature evolution and visual observation using Ovito. Another way to study the diffusion constant would be to make a plot over time for temperatures around the melting temperature. This way, it would be easy to see if the system had melted at a given temperature.

6 Discussion

A quick Internet search reveals the the melting temperature of argon is given to be approximately 84 K. However, in this project, the melting temperature has been found to be slightly larger than 300 K. This might be explained by different densities and pressures. It was found earlier that the density of this system is just above one atomic mass unit per cubic Angstrom. We have not investigated the pressure for this system. Since we use a front-facing cubic lattice, the volume of

the system stays the same and the pressure is free to change. Usually, experiments are performed under constant pressure with variable volume. This will constitute a great difference and may be the main reason for the large difference in melting temperature.

7 Conclusion

In this project we have used molecular dynamics to simulate a system consisting of argon atoms and studied the melting temperature and found the diffusion constant for several different initial temperatures. Initial velocities were set by using the Maxwell-Boltzmann distribution, energy and forces were calculated from the Lennard-Jones potential and the Verlet integrator was used to calculate positions and velocities of the atoms over time. These methods were used to achieve a correct representation of the real physical system. By using periodic boundary conditions, a system with limited lattice size could be used to simulate a real physical system of infinite size.

The melting temperature could first be approximated by studying the temperature and temperature evolution for different initial temperatures, finding the total energies for different temperatures at equilibrium and by observing the system in a three dimensional simulation of the positions of the atoms in the system. All these methods showed a good agreement and the melting temperature could be approximated to be somewhere between 300 K and 350 K. A range of 50 K for a melting temperature is not very precise, this is where calculation of the diffusion constant comes in. This is dependent on the average distance each atom has traveled from the initial position. Therefore, when the system is in a solid state, the atoms stays more or less in the same position, but when the system is in a liquid state, the atoms travel around at random. The melting temperature from the diffusion constant of different temperatures at equilibrium was found to be slightly below 350 K, which again shows a good correlation with previous results.

References

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