Atomic modeling of argon

Project 5 — FYS3150

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Abstract

In this project we explore the world of molecular dynamics. We are first presented with the skeleton of a working MD-program, and we are asked to implement the functionality we need as we go along. We look at the time evolution of a system of argon, with an initial face-centered cubic lattice configuration. The atoms are under the influence of the Lennard-Jones potential. We use the Velocity-Verlet as our time integrator of choice, and we compare this to the Euler-Cromer method in terms of energy conservation properties. We also compute the melting temperature of argon, by means of the Einstein relation and diffusion constant. All visualizations of the system has been performed using the program `VMD`. As always, relevant code can be found on my GitHub page:

github.com/qTipTip

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1 Introduction

Molecular dynamics (referred to as MD), deals with the time evolution of a system of particles, typically atoms or molecules. Being first explored in the late 1950's, it has had a wide range of applications, in fields as materials science, biochemistry and biophysics. Some of the more pioneering works in molecular dynamics are often found in the study of chemical physics and more specifically proteins. In 1975, Levitt and Warshel [3] simulated protein folding and in 1976 Cooper [1] presented results on thermodynamic fluctuations in protein folding with methods comparable to todays standards. More related to our project are the results of A. Rahman in 1964 [5] where he simulates liquid argon and find his simulations to more or less agree with experiments.

In order to verify the molecular dynamics model one can for instance compare with physical experiments. For molecular systems one particular method is of special interest, namely nuclear magnetic resonance spectroscopy. Molecular Dynamics can take on many forms. Notable in the addition to what we examine in this project, is the Monte-Carlo and Brownian dynamics variants of MD.

Molecular dynamics is based on the simple idea of considering a finite number of molecules and letting them interact for a fixed amount of time, which gives us an idea of how the system evolves. In this project we examine what goes into creating a working MD-program that can compute various physical quantities and then proceed by considering some specific systems where we look at, amongst other, the kinetic energy, the initial temperature required in order to reach a desired final temperature, and finding the diffusion constant for the system in order to compute the melting temperature.

The construction of the program will be covered in section 2, where some of the motivation behind each addition to the program will be discussed. In section 3 we employ our newly implemented program and look at some specific systems.

2 Building a working MD-program

Initially, we are presented with the skeleton of a MD-program, and we are tasked with filling in the blanks. In this section, we walk through each of the steps that went into the implementation of the program, from skeleton to working program. The process can be summarized as following:

1) Introduce periodic boundary conditions.

2) Implement a function for setting the net-momentum for the system to zero.

3) Make the atoms conform to a face-centered cubic lattice configuration.

4) Introduce the force model to the system, given by the Lennard-Jones potential.

5) Implement the Velocity-Verlet algorithm in order to get a better conservation of energy.

6) Write functions for sampling and storing physical quantities.

7) Miscellaneous changes.

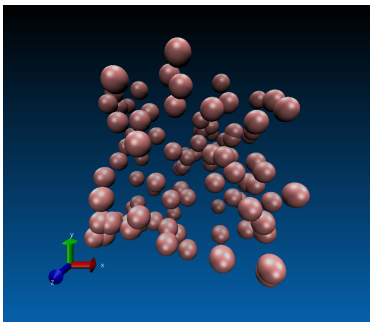


Figure 1: First iteration of the program — no boundary conditions and no force acting on the atoms. The atoms move with a constant speed in the direction of their initial velocity and the initial positions are uniformly distributed.

Running the program in its initial state yields a random configuration of the atoms. Since there is no force acting on the molecules they move in straight lines determined by their initial velocity vector. Their motion is unbounded, due to the periodic boundary condition not being implemented yet. This can be seen in figure 1.

2.1 Periodic boundary conditions

We want our system to conform to periodic boundary conditions. The reasons for doing this is that a finite system with periodic boundary condition more closely resembles that of an infinite size. It is important that the bounding box which determines the boundary of the system is of sufficient size, so we do not get artifacts that arise from the fact that an atom can interact with itself.

There are two approaches to the implementation of periodic boundary condition. The most basic, and the one we will employ here is to have an atom exit through one face of the bounding box, and reappear through the opposite face.

Another approach is to not restrict the coordinates of the atom using the bounding box, and instead use the *periodic image* of the atom when calculating interactions with "nearby" particles.

We implement the function `applyPeriodicBoundaryConditions` in the `System`-class. Our method is simply iterating over each atom, and in the cases where we find an atom outside the bounding box, we add/subtract the size of the box. If we let the vector $\mathbf{r}_i$, with components r_q for $q = x, y, z$, denote the position of atom i at any given time, we simply let the position be governed by the following relation:

$$r_q = \begin{cases} r_q + L_q, & r_q < 0; \\ r_q - L_q, & r_q > L_q; \\ r_q, & \text{else.} \end{cases}$$

Here L_q is assumed to be the dimensions of the system in direction $q = x, y, z$.

During simulations we need to be a bit cautious about what we define as the *distance between* two atoms i and j. Typically, we see this as the distance through the system, but due to our periodic boundary conditions there might be a shorter path through one of the borders of the system. This is formally

stated as the *minimum image criterion*[4].

2.2 Zero out momentum

The Maxwell-Boltzmann distribution is good for velocities because it fairly accurately represents the way velocities are distributed in an ideal gas. The distribution was defined initially by Maxwell, for the specific purpose of describing particle speeds inside a stationary container with no interaction. The distribution is directly dependent on the temperature of the system as well as the mass of each particle. We want to initialize each atom with a random velocity given by the Maxwell-Boltzmann distribution. Mathematically, the distribution function reads

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

As shown in figure 2, increasing the temperature yields a more even velocity distribution. The problem that arises when using the Maxwell-Boltzmann distribution is that in its initial state the system has a non-zero net momentum. This causes the system to drift. This is why we want to implement the function `removeMomentum` in the `System`-class. Its purpose is to compute the total momentum of the system, and then remove a small portion of momentum from each atom in order to have a net momentum of zero.

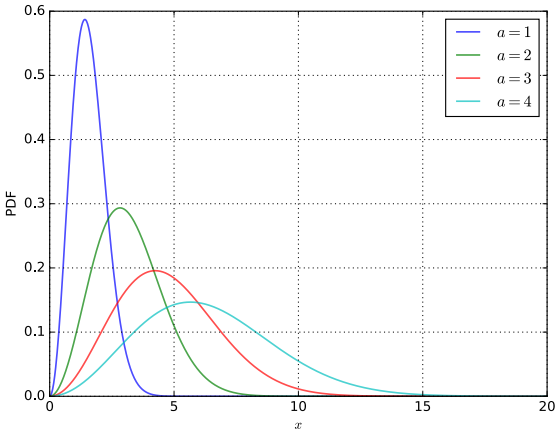


Figure 2: The Maxwell-Boltzmann distribution for a varying scale parameter $a = k_B T/m$. As we can see, increasing the temperature increases the likelihood of an atom being assigned an arbitrary velocity, where as for low temperatures the distribution is biased towards one specific velocity.

We compute the velocity of the center of mass of the system, and then subtract this velocity from each atom. Let m_i and v_i denote the mass and velocity of atom i respectively and let M and V denote the total mass of the

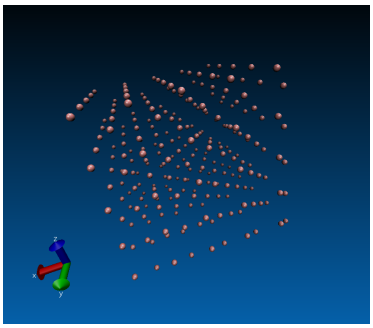


Figure 3: Initial configuration of a FFC-based lattice. We have here used a lattice constant $b = 5.26$Å and the number of unit cells in each dimension is $N = 5$. This specific system has a density of $\rho = M/V = 4N^3m/b^3N^3$ where m is the mass of each atom, b and N given as above. This evaluates to approximately $0.1445\,\text{a.m.u/Å}^3$.

system and the velocity of the center of mass. Then

$$V = \sum_{i=1}^{n} m_i v_i, \quad M = \sum_{i=1}^{n} m_i$$

where n is the total number of atoms in the system. We then need to subtract the value $V_{\text{sub}} = V/M$ from each v_i.

2.3 Face-centered cubic lattice

We now, instead of having random initial positions, want the atoms to form a crystal structure. In a face-centered cubic lattice (FCC), each unit cell has, in addition to the eight corner lattice points, one lattice point for each face.

A *unit cell* is a group of atoms which can be stacked on top and next to each other to form a grid structure. The *lattice constant* defines the size of the unit cell, and is denoted b. In this project we are assuming cubic grids, so we let N denote the number of unit cells in each dimension.

We now define a local coordinate system for each unit cell as

$$\mathbf{r}_1 = 0\hat{\mathbf{i}} + 0\hat{\mathbf{j}} + 0\hat{\mathbf{k}}, \qquad \mathbf{r}_2 = \frac{b}{2}\hat{\mathbf{i}} + \frac{b}{2}\hat{\mathbf{j}} + 0\hat{\mathbf{k}},$$
$$\mathbf{r}_3 = 0\hat{\mathbf{i}} + \frac{b}{2}\hat{\mathbf{j}} + \frac{b}{2}\hat{\mathbf{k}}, \qquad \mathbf{r}_4 = \frac{b}{2}\hat{\mathbf{i}} + 0\hat{\mathbf{j}} + \frac{b}{2}\hat{\mathbf{k}}.$$

The origin for an arbitrary unit cell is then given (globally) as

$$\mathbf{R}_{i,j,k} = i\hat{\mathbf{u}}_1 + j\hat{\mathbf{u}}_2 + k\hat{\mathbf{u}}_3$$

We implement the function `createFFCLattice` in the `System`-class which takes N and b as arguments. The initial configuration for an example system is displayed in figure 3.

2.4 Lennard-Jones potential

The Lennard-Jones potential approximates the interaction between a pair of atoms. In its most common form it reads

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

where r_{ij} is the distance between atom i and atom j and ε is the depth of the potential well. The quantity σ is the distance for which the potential is zero. With an expression for the potential we can sum over all distinct pairs of atoms and acquire an expression for the total potential energy V:

$$V = \sum_{i>j} U(r_{ij}).$$

The force exerted on atom i by atom j is then given as the negative gradient of the potential between the two:

$$\mathbf{F}(r_{ij}) = -\nabla U(r_{ij}).$$

The three force-components are given by:

$$F_q(r_{ij}) = -\frac{\partial U}{\partial r_{ij}} \frac{\partial r_i j}{\partial q_{ij}} \quad (q = x, y, z)$$

Analytically, this evaluates to

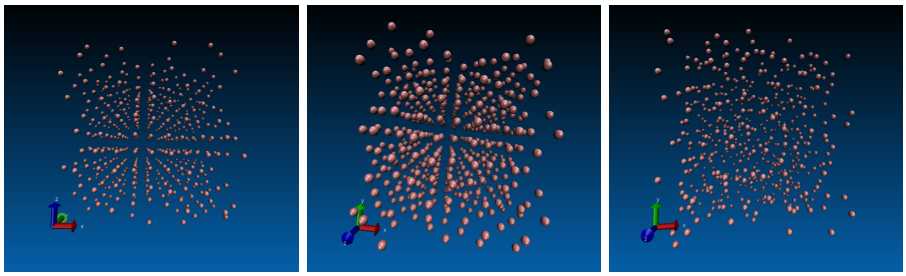
$$F_q(r_{i,j}) = 24\varepsilon \left[\left(\frac{2\sigma^{12}}{r_{ij}^{13}} \right) - \left(\frac{\sigma^6}{r_{ij}^7} \right) \right] \quad (q = x, y, z).$$

The brute force way of computing this is summing over each distinct pair of atoms, and computing the mutual force between them. This however, constitutes a fairly heavy computational load that quickly scales with the size of the system. For a total of n atoms in the system, we have a time complexity of $\mathcal{O}(n^2)$. Luckily more efficient methods are available, most notably is the Cell list method.

2.4.1 Cell lists

The main idea behind cell lists is that at some fixed distance, the force induced by the potential between two atoms is negligible and there is therefore no need for computing it. If we for each atom i keep track of all atoms within this fixed distance, which we will call r_{cut}, at any given time step, we can greatly reduce the number of computations needed.

We divide the domain of our system into *cells*, each with an edge length of at least the cut-of radius of the potential. This ensures that if we only compute the mutual forces between atoms in the same or adjacent cells, then the atoms are never a distance farther than r_{cut} apart. For each integration step we check the validity of the list of neighbors for each atom by iterating through each atom in the system, and checking whether it has moved a distance larger than r_{cut}



(a) $T = 400$K (b) $T = 700$K (c) $T = 900$K

Figure 4: Snapshots taken of the system at frame 500/999 for temperatures of 400, 700 and 900 kelvin. It is a bit difficult to conclude from the pictures, one really needs to see the system in motion, but the system do behave more or less like a solid, a liquid and a gas for respective temperatures. It is possible to see a certain change in the entropy of the system across the three images. These made use of the Velocity-Verlet integration method.

since the last time the list of neighbors was built. It is interesting to note that we have to rebuild the neighbor lists more often for higher temperature due to the velocities being proportional to the temperature.

We additionally need to rescale our potential so that it takes into consideration the cut-off radius. We define the scaled potential $U' = U(r_{ij}) - U(r_{\text{cut}})$ when $r_{ij} < r_{\text{cut}}$ and 0 otherwise.

There is a quite subtle consideration which is often overlooked, and that is the fact that in order to make use of cell-lists, we need a sufficient number of unit cells in each dimensions. Otherwise, there is not enough room for our cells. In the program, if the number of unit cells is less than or equal to 5, we employ our old potential. If it is larger, we use the new scaled potential with cell lists.

By implementing cell-lists we reduce the computation of the forces from $\mathcal{O}(N^2)$ to $\mathcal{O}(N)$.

2.4.2 Choice of parameters

We need to chose the parameters σ and ε so that they are suited for simulation of argon. It turns out that $\sigma = 3.405$Å and $\varepsilon = 119.8k_B$K with $k_B = 1$ in MD-units are appropriate values for argon.

Argon has a melting point of ≈ 84K and a boiling point of ≈ 87K. If we run the simulations, once for a temperature of 80K, once for 170K and finally once for $240K$ we should see indications of three different phases (see section 3.2 for the choices of these temperatures). The results shows that the model does not manage to capture these phase transitions. This is probably attributed to the Lennard-Jones potential. If we run the simulations for initial temperatures of $400K, 700K$ and $900K$ we should see indications of phase change. We will get back to this in section 3.3. Snapshots taken at the same point in time for all three cases are presented in figure 4.

2.5 Velocity Verlet, a symplectic integrator

In order to improve upon the fairly poor energy conservation of the Euler-Cromer method, we chose to implement the Velocity Verlet integrator. The algorithm is dependent on us having computed the forces for the first step and consists of three steps per time-step:

$$\begin{aligned}\mathbf{v}(t+\Delta t/2) &= \mathbf{v}(t) + \frac{\mathbf{F}(t)}{m}\frac{\Delta t}{2},\\ \mathbf{r}(t+\Delta t) &= \mathbf{r}(t) + \mathbf{v}(t+\Delta t/2)\Delta t,\\ \mathbf{v}(t+\Delta t) &= \mathbf{v}(t+\Delta t/2) + \frac{\mathbf{F}(t+\Delta t)}{m}\frac{\Delta t}{2}.\end{aligned}$$

We implement this algorithm in the `integrate` method in the `VelocityVerlet`-class. The method takes a system of atoms and a time step Δt as arguments. We also introduce the private auxiliary variable `m_first_step`, which helps us take care of the initial calculation of the forces.

Of interest now is how our new method of integration compares with the old one. One way of looking at this is by examining the fluctuations in the total energy as functions of the time step Δt. This will be examined in section 3.1.

2.6 Sampling quantities

We now have pretty much a working program, however we still need to sample the physical properties of the system at each time step. For this we turn to the `StatisticsSampler`-class where we will implement the methods for sampling the density, kinetic and potential energy and temperature of the system. The methods are named accordingly.

We first start by considering the kinetic and potential energy of the system. We already have computed the potential energy, in the `LennardJones`-class, so we are now interested in computing the kinetic energy. The kinetic energy of an arbitrary atom i is defined as $E_k^i = m_i v_i^2/2$, and so the total kinetic energy E_k of the system is simply

$$E_k = \sum_{i=1}^{n} E_k^i = \sum_{i=1}^{n} \frac{1}{2} m_i v_i^2,$$

where m_i and v_i is the mass and velocity atom i and n is again the total number of atoms in the system.

We are also interested in the instantaneous temperature of the system, and the equipartition theorem [2] can help us with this. The theorem relates the average energy of a system to its temperature and gives us the relation $\langle E_k \rangle = (3/2)k_B T$ which can be solved for temperature:

$$T = \frac{2}{3}\frac{E_k}{nk_B}.$$

Notice the removal of the brackets — we are only interested in the *instantaneous* temperature at any point in time. We also recall that since our units are scaled, Boltzmann's constant is equal to one.

2.7 Miscellaneous changes

In order to ease the implementation of the python framework used to run the simulations, we need to make some auxiliary changes to the `main`-method of the program. First of all, we are interested in comparing the two integration methods the program currently supports, so we add a fourth possible command line argument for setting the integration method. The program defaults to Velocity-Verlet.

We also need a way of changing the time step Δt used in the simulations. This is also implemented as a command line argument, and we use a default time step of $\Delta t = 1.0 \times 10^{-15}$ seconds.

In order to compute the *mean square displacement* in section 3.3 we need to keep track of the initial position of each atom. We therefore introduce a variable `m_initialPosition` in the `Atom-class` which is set during initialization. When computing the diffusion constant D, we need to make sure that $r_i^2(t)$ is the true displacement, and not the displacement relative to the nearest periodic image. This will be implemented in the `applyBoundaryConditions`-method and is as simple as in addition to moving the position of the atom, also move the initial position of the atom by the same amount, because then the relative distance between instantaneous position and initial position is equal to the true displacement.

2.8 Program Flow

A flow-chart describing the execution of the program can be seen in figure 5. I only a few of the more vital processes are described in detail.

3 Simulations

In this section we consider various systems and simulate them using the program devised in the previous section.

3.1 Energy conservation of integration method

We initially decided to use the Velocity-Verlet integration method instead of Euler-Cromer because of its good energy conservation. It is therefore of interest to examine exactly what kind of impact this change of integration method has for our simulations. We now simulate a set of similar systems and look at how the fluctuations in total energy scales with the time step ΔT. In order to do this we can consider the standard-deviation of the total energy.

We are going to run the simulations for a starting temperature of 300 kelvin, and vary the time step from 1.0×10^{-15} to 1.0×10^{-14} seconds with 40 intermediate values. The results, as shown in figure 6, tells us exactly how much better Velocity Verlet is when it comes to energy conservation.

3.2 Initial to final temperature

We are now interested in determining what initial temperature T_i is needed in order to have a final temperature of T. One way of examining this is by looking at the ratio T/T_i. As we can see in figure 7 the ratio stabilizes around

$T/T_i = 0.5$. Solving this for T_i tells us that if we are interested in a final temperature of T, then we should chose our initial temperature to be

$$T_i = 2T.$$

As we see from the plot, the temperature drastically drops just after the initial state. This is because $T \propto E_k$, i.e., the temperature is proportional to the kinetic energy, and since the potential has not yet kicked in, the kinetic energy is at its maximum. While what we have just observed is an empirical result, we can alternatively look at the virial theorem [6], which relates the time average of the kinetic energy to the time average of the potential energy. This gives us a description of this stabilization independent of the temperature.

3.3 Melting temperature of system

In order to measure the melting temperature of the system, we can use the Einstein relation which states the following:

$$\langle r^2(t) \rangle = 6Dt.$$

D is here the diffusion constant, t is time and the *mean square displacement* is calculated as

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

for atom i. Solving this for D gives yields

$$D = \frac{\langle r^2(t) \rangle}{6t}.$$

We can now make set of simulations for varying initial temperature T_i and store the final value for the diffusion constant for each final temperature T. The results are shown in figure 8 and tells us that the system melts around a temperature of $T = 0.5T_i$, which here amounts to a temperature of about $304K$.

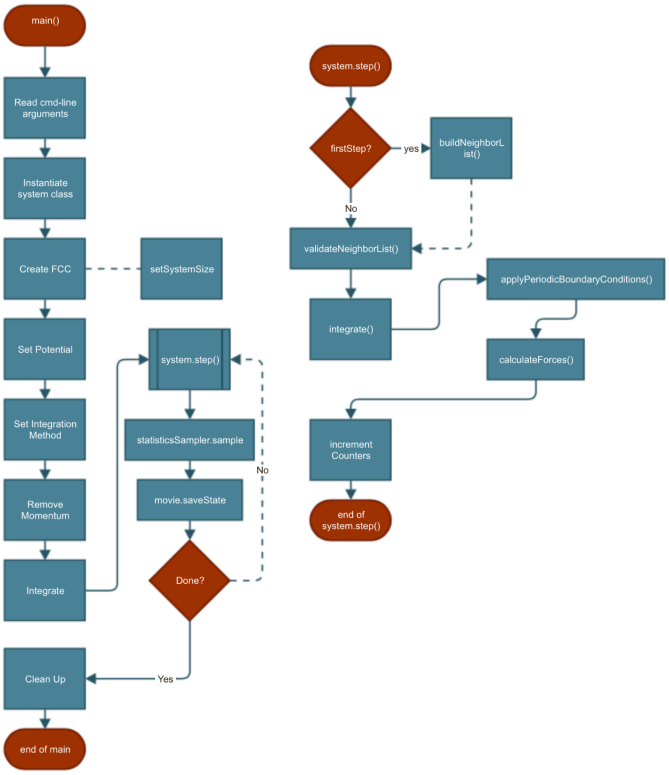


Figure 5: A flow-chart of the program execution. The method `system.step` is described in more detail because it is what constitutes most of the program and is therefore included as a separate subprocess. The chart quite crude, and is meant to give an overarching idea of how the program executes.

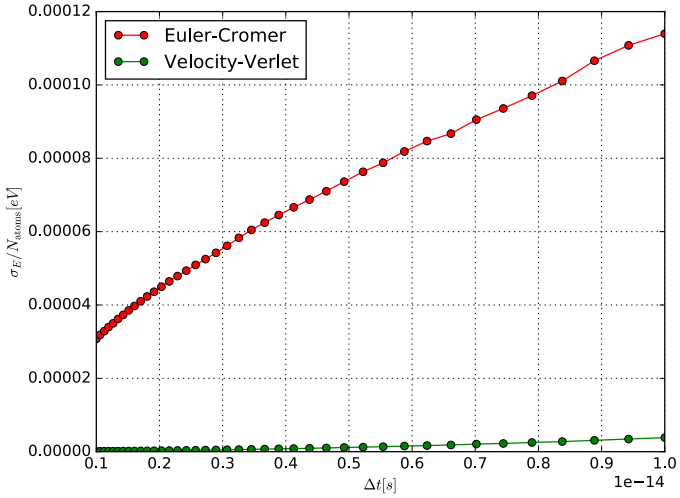


Figure 6: The standard deviation of the total energy as a function of the time-step Δt with the energy being per atom. This clearly shows the benefits of using Velocity-Verlet over Euler-Cromer. While Euler-Cromer gives rise to fluctuations that scale somewhat linearly in the time step Δt, the fluctuations attributed to Velocity-Verlet is negligible in comparison.

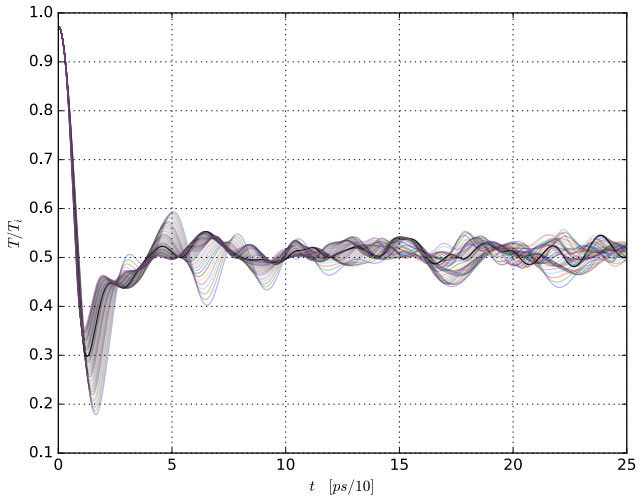


Figure 7: Plotting the ratio between initial and instantaneous temperature for varying T_i. Each individual graph corresponds to one value of T_i and the ratio is plotted against time given in units of tenths of a picosecond. Here the initial temperatures ranges from 20 to 500 kelvin, with 48 intermediate steps. As we can see the ratio stabilizes around 1/2. The graph of an arbitrary temperature has been highlighted in black.

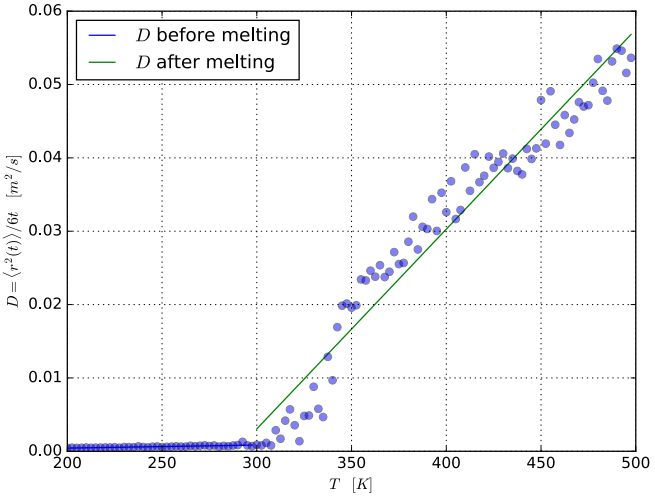


Figure 8: The diffusion constant as a function of temperature. We here see that D abruptly increases at the temperature of $T = 304K$ which indicates that the crystal is melting. The two lines are the linear graphs best fitted to the noisy data. The diffusion constant is given in units of area per second.

4 Conclusion

In this project we have mainly been concerned with the properties of argon. We have most notably looked at how a molecular dynamics simulation of argon using the Lennard-Jones potential behaves. The results tells us that the experimental values for argon are not properly reflected in the simulations, however the system does more or less behave as it should, albeit for a larger temperature. When considering the force model we made some optimizations to the potential, and only looked at the interactions between atoms sufficiently close to each other. This lead to a significant increase in simulation speed, from a time complexity of $\mathcal{O}(N^2)$ to one of $\mathcal{O}(N)$.

We also chose to implement the Velocity Verlet algorithm as our time integrator, in preference over the more basic Euler-Cromer method. This lead to a more stable energy conservation over varying time steps. The improvement was from approximately linear to a constant.

We also considered the melting temperature of argon, and measured it to be somewhere close to $300K$, which does not really coincide with the experimentally observed melting temperature of approximately $84K$. Despite this disparity the system at least behaves consistently.

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