FYS3150
Project 5

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December 20, 2018

Abstract

In this final project, we have used molecular dynamics with the Lennard-Jones potential to model argon. Through calculations of the diffusion constant, we obtain an estimate of the melting point at $T_m = 78$ K, compared to the actual melting point of argon at $T_m = 83.8$ K.

The basic structure of our implementation, including the Velocity Verlet solver, was developed for modelling the solar system in Project 3, demonstrating the usefulness of writing general solver classes.

1 Introduction

Described as "Laplace's vision of Newtonian mechanics" [1], molecular dynamics (MD) is a method of simulating the motion of atoms and molecules by numerical integration of Newton's laws of motion. MD is applied in both physics, chemistry and biology. It's a popular method for modelling large biological molecules like proteins, but can also be used to look at e.g. crack propagation in solid materials. In this project, we will run MD simulations using the well-known Lennard-Jones potential to model the interaction between argon atoms.

A MD simulation is not meant to give us the true trajectories of atoms or molecules, but rather enables us to explore the phase space and sample thermodynamic properties like energy and temperature. In this project, we will sample microstates from the microcanonical ensemble (NVE). Through computation of the diffusion constant at different temperatures, we will try to estimate the melting point of argon.

In Project 3, we developed object-orientated code for modelling the solar system. Most of the basic structure, including the velocity Verlet solver, has been reused in this project.

This project also links with Project 4, where we applied Monte Carlo computations on the two dimensional Ising model. Both involve sampling from a thermodynamic ensemble to investigate phase transitions, but while MD simulations are based on solving differential equations, Monte Carlo simulations depend on probability distribution functions and random numbers.

2 Theory

2.1 Lennard-Jones Potential

We will use the Lennard-Jones potential to model the interactions between the argon atoms. The potential energy between atom i and j is given by

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

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$, ϵ is the depth of the potential well, and σ is the distance at which the potential is zero. The parameters ϵ and σ is adjusted and optimised for the compound that is being modelled.

The force between the atoms are given by

$$
\begin{aligned}
\vec{F}(r_{ij}) &= -\nabla U(r_{ij}) \\
&= -\frac{\partial U}{\partial r_{ij}} \hat{r}_{ij} - \frac{1}{r_{ij} \sin \theta_{ij}} \frac{\partial U}{\partial \phi_{ij}} \hat{\phi}_{ij} - \frac{1}{r_{ij}} \frac{\partial U}{\partial \theta_{ij}} \hat{\theta}_{ij} \\
&= -\frac{\partial U}{\partial r_{ij}} \hat{r}_{ij} \\
&= -4\epsilon \left(-12 \frac{\sigma^{12}}{r_{ij}^{13}} + 6 \frac{\sigma^6}{r_{ij}^7} \right) \hat{r}_{ij} \\
&= \frac{24\epsilon}{r_{ij}} \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \hat{r}_{ij}
\end{aligned}
$$

The x-component of the force is given by

$$
\begin{aligned}
F_x(r_{ij}) &= -\frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_{ij}} \\
&= \frac{24\epsilon}{r_{ij}^2} \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] x_{ij}
\end{aligned}
$$

where $x_{ij} = x_i - x_j$. We get similar expressions for the y- and z-component.

2.2 Thermodynamic Properties

The total potential energy of the system is given by

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

where we sum over every pair of atoms (only once).

The total kinetic energy is given by

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

where N is the number of atoms and m_i and v_i is the mass and speed of atom i.

We can estimate the temperature by using the equipartition theorem. For a monatomic gas like argon, we get that

$$\langle E_k \rangle = \frac{3}{2} NkT$$

where k is the Boltzmann constant. This gives us the following expression for the instantaneous temperature:

$$T = \frac{2}{3} \frac{E_k}{Nk}$$

The diffusion constant can be computed from the Einstein relation:

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

where $r_i^2(t) = |\vec{r}_i(t) - \vec{r}_i(0)|^2$ is the mean square displacement of atom i, D is the diffusion constant and t is time. Solving for D, we get that

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

2.3 Units

In order to work with reduced units, i.e. $\epsilon = 1$, $\sigma = 1$ and $k = 1$, we define the following units:

- 1 unit of length = $\sigma = 3.405 \cdot 10^{-10}$ m

- 1 unit of energy = $\epsilon = 1.651 \cdot 10^{-21}$ J

- 1 unit of temperature = $\frac{\epsilon}{k} = 119.581$ K

For convenience, we also choose the unified atomic mass unit $u = 1.66054 \cdot 10^{-27}$ kg as the unit of mass.

The units of time and diffusivity can be derived from these units. For time, we have that Energy = Mass $\times \frac{\text{Length}^2}{\text{Time}^2}$ ($E = mc^2$), which gives Time = Length $\times \sqrt{\frac{\text{Mass}}{\text{Energy}}}$. For the diffusivity, we have that Diffusivity = $\frac{\text{Length}^2}{\text{Time}}$ = Length $\times \sqrt{\frac{\text{Energy}}{\text{Mass}}}$ (Einstein relation). This gives us the following units:

- 1 unit of time = $\sigma \sqrt{\frac{u}{\epsilon}} = 3.415 \cdot 10^{-13}$ s

- 1 unit of diffusivity = $\sigma \sqrt{\frac{\epsilon}{u}} = 3.395 \cdot 10^{-7}$ m^2/s

2.4 Molecular Dynamics procedure

When exploring the phase space through MD simulations, we assume that the ergodic hypothesis is obeyed. That is, we assume that we reach the microstates of the system according to the probabilities given by the ensemble we sample from.

To avoid boundary effects we need to apply periodic boundary conditions, both when calculating positions and distances. We have used the minimum-image convention in our implementation [3].

Our MD procedure goes as follows:

1. Initialise the system, placing the argon atoms in a FCC (face-centred cubic) lattice with velocities according to the Maxwell-Boltzmann distribution (see below).

2. Calculate the total momentum of the system, and remove momentum from every atom equally so that the net momentum becomes zero.

3. Integrate using the Velocity Verlet method (see Project 3).

4. For each time step, sample thermodynamic properties.

Solid argon forms an FCC lattice. Each unit cell contains four atoms, with the origin of unit cell (i, j, k) given by

$$\vec{R}_{ijk} = ib\hat{\imath} + jb\hat{\jmath} + kb\hat{k}$$

and the local coordinates of the atoms in each unit cell by

$$\vec{r}_1 = 0\hat{\imath} + 0\hat{\jmath} + 0\hat{k}$$

$$\vec{r}_2 = \frac{b}{2}\hat{\imath} + \frac{b}{2}\hat{\jmath} + 0\hat{k}$$

$$\vec{r}_3 = 0\hat{\imath} + \frac{b}{2}\hat{\jmath} + \frac{b}{2}\hat{k}$$

$$\vec{r}_4 = \frac{b}{2}\hat{\imath} + 0\hat{\jmath} + \frac{b}{2}\hat{k}$$

where b is the lattice constant. By changing this parameter, we can decide the density of the system, which again affects the melting point. We choose the lattice parameter so that the density is that of liquid argon at the melting point ($\rho = 1417$ g/L).

When it comes to initialising the velocities, we treat argon as an ideal gas. The probability distribution in terms of velocity for an ideal gas is given by the Maxwell-Boltzmann distribution:

$$P(v_i) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_i^2}{2kT}\right)$$

where v_i is the x-, y- or z-component of the velocity. This is the Boltzmann distribution with $E = \frac{1}{2}mv^2$. We also recognise it as a normal distribution with $\mu = 0$ and $\sigma = \sqrt{\frac{kT}{m}}$.

3   Implementation

The programs used in this project can be found on `https://github.com/egilsk/fys3150x/tree/master/project5`.

To visualise our simulation results, we have used OVITO [2].

4   Results

For some examples of visualisations with OVITO, follow the links below:
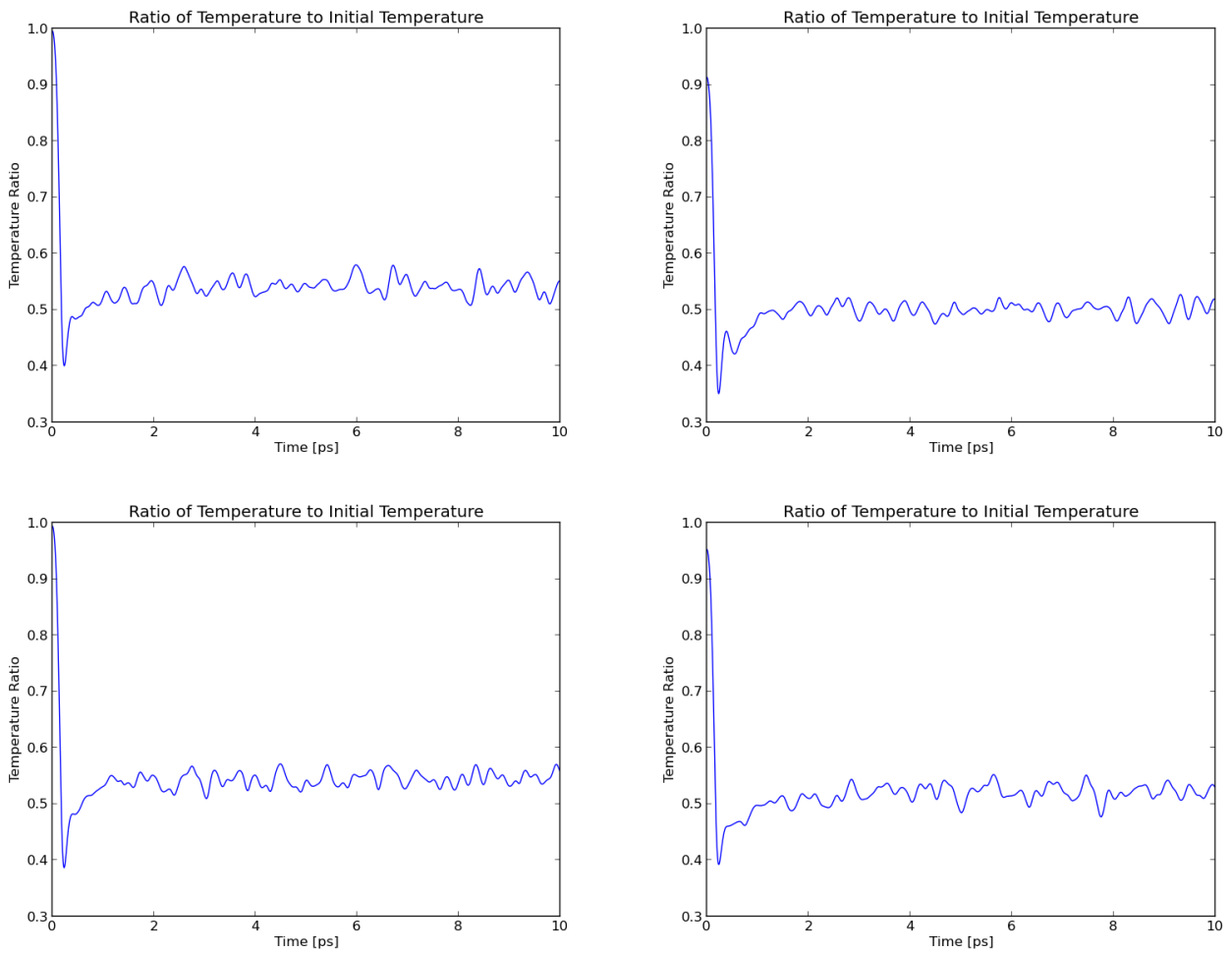
Solid: Youtube

Liquid: Youtube

Figure 1: The ratio of the instantaneous temperature to the initial temperature as a function of time, with four different random seeds ($n_{\text{steps}} = 1000$, $n_{\text{atoms}} = 500$, $T_{\text{initial}} = 100$ K).
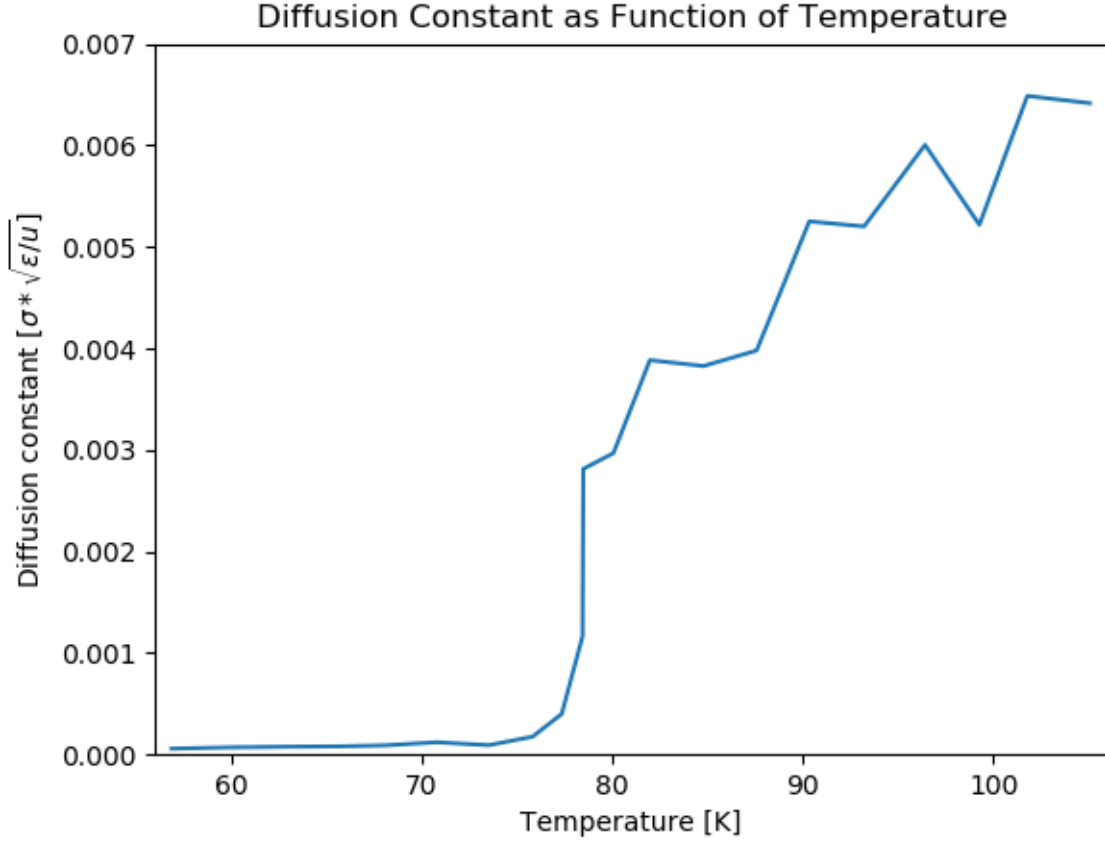
Figure 2: The diffusion constant as a function of temperature ($n_{\text{steps}} = 3000$, $t = 30$ ps, $n_{\text{atoms}} = 500$, $n_{\text{temperature}} = 21$). The system is equilibrated before starting the calculations ($t_{\text{equilibration}} = 0.5$ ps).

5 Discussion

Visualising the results with OVITO, we see that the system goes from a solid to a liquid state at an initial temperature between 100 and 200 K. In the solid state, we see the atoms moving back and forth, but they generally stay in the same lattice positions. In the liquid state, however, the movement increases considerably and we can see atoms swapping positions.

With a lattice parameter $b = 5.26$ Å, which leads to the system having the density of solid argon, the crystal doesn't melt until the initial temperature is around 600 K. Hence, the melting point is heavily dependent on the density of the system.

From Figure 1, we see that the instantaneous temperature quickly (within one picosecond) drops to about one half of the initial temperature, before reaching an equilibrium state. This is due to the fact that we initialise the system with only kinetic energy. As the calculations get going, some of this energy is transformed to potential energy, and since the energy is conserved (our numerical integrator is symplectic) the kinetic energy (and temperature) drops accordingly. At equilibrium, we see that the total energy is partitioned more or less equally between kinetic

and potential energy.

From Figure 2, we see a significant increase in the diffusion constant just below 80 K, at around 78 K. This corresponds to a phase transition from the solid to the liquid phase at $T_m \approx 78$ K. This is somewhat lower than the actual melting point of argon, which is $T_m = 83.8$ K. This might be due to the modest size and duration of our simulation, or a suboptimal choice of parameters (given the heavy dependence on density).

6   Conclusion

We have looked at argon through molecular dynamics simulations using the Lennard-Jones potential to model the interactions between the atoms. We have reused much of the code structure from Project 3, demonstrating the power and convenience of writing general solver classes.

Through the temperature dependence of the diffusion constant, we obtain an estimate of the melting point of argon at $T_m \approx 78$ K. This is a bit (~ 7 %) off the actual melting point of 83.8 K. We have also seen, like in Project 4, that when looking at physical systems it's important to allow for equilibration before getting underway with statistical physical and thermodynamic calculations.

Throughout this course, we have been exposed to a range of important aspects of computational science, including (but not limited to) scaling of equations, evaluating the accuracy and performance of our algorithms, analysing computational errors and developing clean and testable code. In addition, we have been introduced to a wide range of fascinating algorithms for solving a diversity of problems in science, as well as some interesting physics. Thank you!

References

[1] Tamar Schlick. Pursuing Laplace's vision on modern computers. In *Mathematical Approaches to Biomolecular Structure and Dynamics*, pages 219–247. Springer, 1996.

[2] Alexander Stukowski. Visualization and analysis of atomistic simulation data with ovito– the open visualization tool. *Modelling and Simulation in Materials Science and Engineering*, 18(1):015012, 2009.

[3] Wikipedia contributors. Periodic boundary conditions — Wikipedia, the free encyclopedia, 2018. [Online; accessed 18-December-2018].