

Project 5 - FYS 4150

Melting point of argon using molecular dynamics simulations

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Abstract

The FCC structure of argon is studied using the Lennard-Jones potential and the Velocity Verlet algorithm. The potential parameters are $\sigma = 3.405 \text{ \AA}$ and $\epsilon = 119.8 k_B$. The lattice constant used is $a = 5.26 \text{ \AA}$. The temperature ratio $T_{\text{equilibrium}}/T_{\text{initial}}$ is studied and shows a discontinuity at $T \approx 320 \text{ K}$. The diffusion constant is found to show a similar discontinuity at the same temperature. These discontinuities give the temperature for the melting point of argon at $T \approx 320 \text{ K}$ and $p \approx 1214 \text{ bar}$. The discontinuous behavior indicates the solid \rightarrow liquid transition is of 1st order.

All programs used can be found on the GIT page: <https://github.com/mathisre/Project-5-FYS4150>.

1 Introduction

Knowing the behavior of molecules is something that is useful in many different branches of science. It can be useful in biology to study the flow of blood and the delivery of oxygen to parts of our body. It is useful in chemistry to track how the molecules move around and interact. It is useful in many areas of physics. For example using molecular dynamics one can study phase transitions and better understand the structure and temperature behavior of solids, liquids and gases.

Argon has a stable solid FCC composition at low temperatures. As the temperature increases the atoms gain more kinetic energy. Eventually the kinetic energy is strong enough to break the solid structure. This is a phase transition from solid to liquid form. The temperature at which this happens is called the melting point.

Molecular dynamics simulations is limited by the size of the simulation. A liquid or a solid of a few grams might have $\sim 10^{23}$ atoms in it. That amount of particles cannot be simulated. Periodic boundary conditions can be applied to study bulk properties of an infinitely large structure using a smaller one. Even with periodic boundaries using larger amounts of atoms will give better results.

This project will look at the FCC structure of argon using lattice parameter $a = 5.26 \text{ \AA}$. We will use 5 unit cells in each direction, totaling 125 unit cells corresponding to 500 atoms. The aim is to find the temperature (melting point) for the solid \rightarrow liquid phase transition.

2 Theory

2.1 Lennard-Jones potential

Argon is a noble liquid, and as such the electrostatic attraction between two atoms can be neglected. The interaction between neutral atoms can be described using the Lennard Jones potential [1]. It is

$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

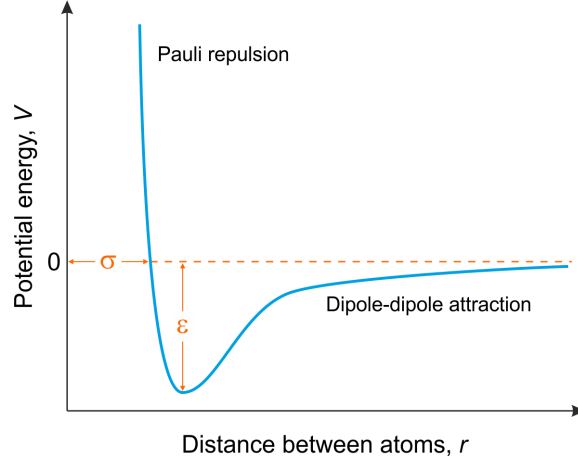


Figure 1: Potential energy between two atoms given by the Lennard-Jones potential. The potential features a stable minimum. Image taken from [2].

where σ is a constant that determines the strength of the interaction. $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the separation distance between a pair of atoms. The potential consists of one attractive term and one repulsive term. The $(\sigma/r_{ij})^6$ term is attractive, and $(\sigma/r_{ij})^{12}$ is repulsive. The attractive term represents the Van der Waals forces and takes effect at medium ranges. The repulsive term represents the Pauli repulsion that occurs when electron orbitals overlap. The repulsive term only takes effect at short ranges.

The strong repulsive term at short ranges and the medium range attractive term ensure that the potential has a minimum. It can be seen in Fig. 1. The minimum means that the Lennard-Jones potential can display stable systems. The position of the minimum of the potential is the position at which the atoms will place themselves in an ordered fashion. This will only happen at low temperatures, the mean energy is too high for atoms to sit still at high temperatures.

The total potential energy is the sum of Eq. 1 for all pairs of atoms,

$$V = \sum_{i>j} U(r_{ij}). \quad (2)$$

Note that each pair is only counted once. The force exerted by one atom onto another is

$$\mathbf{F}(r_{ij}) = -\nabla U(r_{ij}). \quad (3)$$

Using the cartesian xyz coordinates, the force in the xyz directions is

$$F_x(r_{ij}) = -\frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial x_{ij}}. \quad (4)$$

The force between two atoms can be calculated analytically, starting with the potential derivative:

$$\frac{\partial U}{\partial r_{ij}} = \frac{24\epsilon}{r_{ij}} \left[2 \left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]. \quad (5)$$

The position derivative is

$$\frac{\partial r_{ij}}{\partial x_{ij}} = \frac{\partial}{\partial x_{ij}} \left(\sqrt{x_{ij}^2 + y_{ij}^2 + z_{ij}^2} \right) = \frac{x_{ij}}{\sqrt{x_{ij}^2 + y_{ij}^2 + z_{ij}^2}} = \frac{x_{ij}}{r_{ij}}. \quad (6)$$

Putting it all back into Eq. 3, the force in the x-direction is

$$F_x(r_{ij}) = 4\epsilon \left[12 \frac{\sigma^{12}}{r_{ij}^{13}} - 6 \frac{\sigma^6}{r_{ij}^7} \right] \frac{x_{ij}}{r_{ij}}. \quad (7)$$

Generalizing to three dimensions gives the force vector

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

Note that the force is in the same direction as \mathbf{r}_{ij} . This makes sense as the force acts only radially between the atoms.

2.2 Ideal liquid law and the Maxwell-Boltzmann distribution

Argon is neutral and as such its liquid phase can be treated as an ideal liquid. The ideal liquid law is

$$p = nk_B T, \quad (9)$$

where p is the pressure, n is the particle density, k_B is Boltzmann's constant and T is the temperature. The ideal liquid approximation is also used to find the temperature of the argon system. Each atom has $0.5k_B T$ kinetic energy for each degree of freedom. The result is

$$K = \frac{3}{2} N k_B T. \quad (10)$$

Solving the equation for the temperature yields

$$T = \frac{2K}{3Nk_B}. \quad (11)$$

The velocities of particles in a liquid are typically distributed according to the Maxwell-Boltzmann distribution given by

$$P(v_i)dv_i = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp \left(-\frac{mv_i^2}{2k_B T} \right) dv_i. \quad (12)$$

v_i is the velocity of particle i . The distribution is temperature dependent and ensures that the total kinetic energy of the system will return approximately the same temperature from Eq. 11 as the temperature that was put into the distribution. It is only approximately because in this case we only use 500 atoms. As the number of atoms increases, the temperatures become more and more equal.

The RNG used for the Maxwell-Boltzmann distribution is the Mersenne twister [3]. The Mersenne twister has a period of $2^{19937} - 1$ numbers. The random numbers in this project are only used to compute initial velocities of atoms. With 500 atoms that is only 1500 random numbers per lattice.

2.3 FCC-lattice

As a solid Argon, has a stable crystal FCC structure with lattice parameter $a = 5.26 \text{ \AA}$. The FCC structure contains four atoms per unit cell. The positions of the atoms in a unit cell placed at $(0, 0, 0)$ are:

$$\mathbf{r}_1 = 0\mathbf{i} + 0\mathbf{j} + 0\mathbf{k}$$

$$\mathbf{r}_2 = \frac{a}{2}\mathbf{i} + \frac{a}{2}\mathbf{j} + 0\mathbf{k}$$

$$\mathbf{r}_3 = 0\mathbf{i} + \frac{a}{2}\mathbf{j} + \frac{a}{2}\mathbf{k}$$

$$\mathbf{r}_4 = \frac{a}{2}\mathbf{i} + 0\mathbf{j} + \frac{a}{2}\mathbf{k}$$

Using 4 atoms per unit cell and that the volume of a unit cell is a^3 , the density is

$$\rho = \frac{m}{V} = \frac{4m_{Ar}}{a^3} = \frac{4 * 39.95 \text{ u}}{(5.26 \text{ \AA})^3} = 1823.25 \text{ kg m}^{-3}, \quad (13)$$

where u is the unified atomic mass unit $1u = 1.66 * 10^{-27} \text{ kg}$ and $1\text{\AA} = 10^{-10} \text{ m}$. The number density is

$$n = \rho/m_{Ar} = 2.75 * 10^{28} \text{ m}^{-3}. \quad (14)$$

This project will deal with periodic boundary conditions such that the densities are constant.

2.4 Brownian motion and the diffusion constant

The Brownian motion of atoms and molecules can be classified using the diffusion constant. Diffusion is the movement of atoms from a high density region to a low density region. The diffusion constant gives information about how much the atoms move. The diffusion constant should be low for a solid, because the atoms cannot move around much in a solid. The diffusion constant should be non-zero for a liquid or a liquid, because now the atoms should be able to move. Therefore the diffusion constant can be used to identify a solid \rightarrow liquid/liquid phase transition.

The Einstein relation [4] relates the diffusion constant to the mean of the atomic displacement. It is

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = 6Dt, \quad (15)$$

where D is the diffusion constant and $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ is the mean particle displacement squared at after a time t.

3 Methods

3.1 Velocity Verlet algorithm

The Velocity Verlet algorithm is used to evaluate new time steps. Using time step h, the algorithm is

$$\mathbf{r}_{i+1} = \mathbf{r}_i + \mathbf{v}_i h + \mathbf{a}_i h^2, \quad \mathbf{a}_{i+1} = \frac{\mathbf{F}(\mathbf{r}_{i+1})}{m}, \quad \mathbf{v}_{i+1} = \mathbf{v}_i + \frac{h}{2}(\mathbf{a}_i + \mathbf{a}_{i+1}).$$

The error in the position is of the order $\mathcal{O}(h^4)$. The velocity error follows $\mathcal{O}(h^2)$. The small error in specifically the position is important for molecular dynamics studies.

3.2 Code structure

The code used to simulate the FCC argon lattice uses object orientation. It is very useful specifically for molecular dynamics because of how we can structure the code and run it in different ways. The rough structure of the program is described in Fig. 2. There are two versions of the code. `short.cpp` !!!! runs simulations for one temperature and produces an .xyz file with data from every time step. `other.cpp` !! runs simulations for a range of temperatures and saves time, temperature and the diffusion constant. It also produces a .xyz file for each temperature, but with steps fewer data points to save space. The basic structure of the programs is the same. The programs initialize the system parameters such as temperature, σ , ϵ . Then the FCC lattice is created in the system class and the velocity-verlet timesteps are performed to generate data.

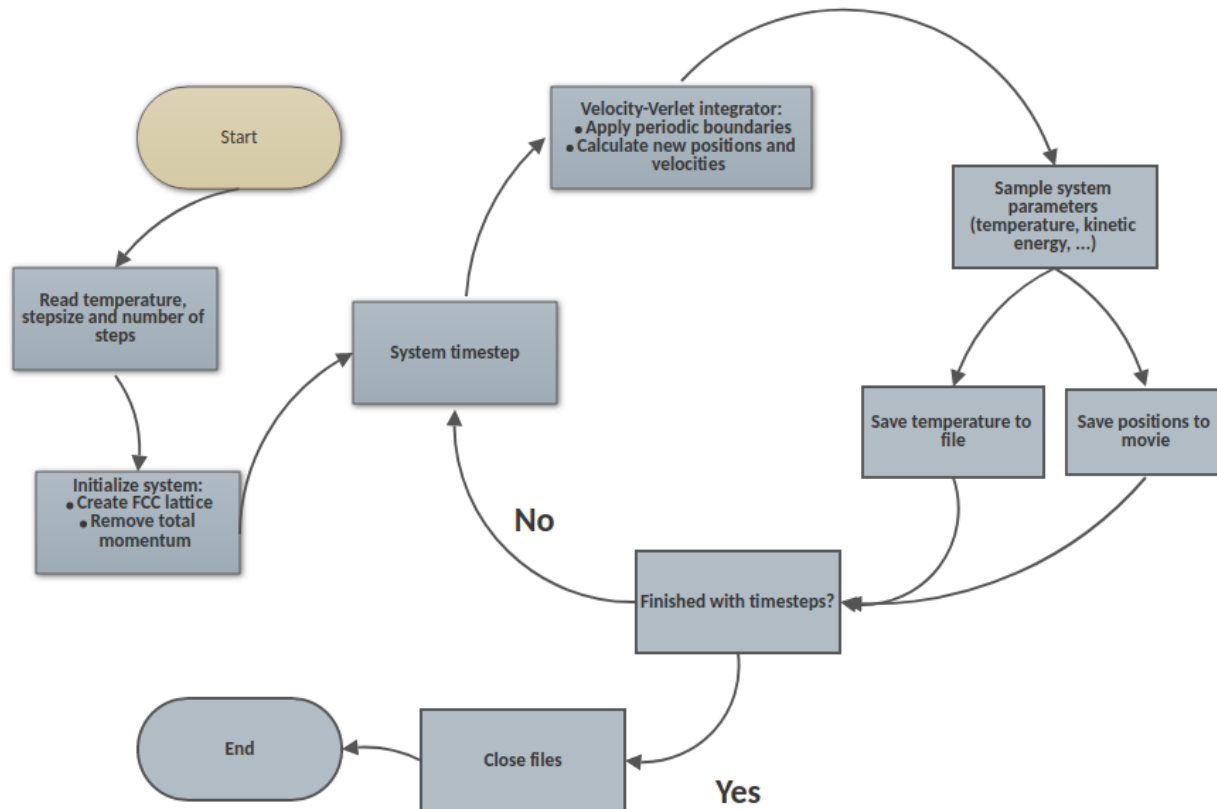


Figure 2: Flowchart detailing how the code operates.

3.3 Periodic boundary conditions

Periodic boundary conditions (PBC) are used to simulate properties of larger solids and liquids using a smaller number of atoms. It is applied by shifting atoms by the lattice size if the atom is detected outside the lattice.

```

void System::applyPeriodicBoundaryConditions(){
    for (Atom *atom : m_atoms) {
        if (atom->position[0] > m_systemSize[0]) atom->position[0] -= m_systemSize[0];

        if (atom->position[1] > m_systemSize[1]) atom->position[1] -= m_systemSize[1];

        if (atom->position[2] > m_systemSize[2]) atom->position[2] -= m_systemSize[2];

        if (atom->position[0] < 0) atom->position[0] += m_systemSize[0];

        if (atom->position[1] < 0) atom->position[1] += m_systemSize[1];

        if (atom->position[2] < 0) atom->position[2] += m_systemSize[2];
    }
}

```

3.4 Set net momentum to zero

When the FCC lattice is created the net momentum is not necessarily zero. This occurs because the velocities are drawn randomly from the Maxwell-Boltzmann distribution. To imitate a real lattice we would rather want the net momentum to be zero. Doing so ensures that the lattice is stable.

```
void System::removeTotalMomentum() {
    total_momentum.zeros();
    double numb_atoms = 0;
    for (Atom *atom : m_atoms) {
        total_momentum += atom->velocity * atom->mass();
        numb_atoms++;
    }
    vec3 total_momentum_per_atom = total_momentum / numb_atoms;
    total_momentum.zeros();

    for (Atom *atom : m_atoms) {
        atom->velocity += -1*total_momentum_per_atom / atom->mass();
        total_momentum += atom->velocity * atom->mass();
    }
}
```

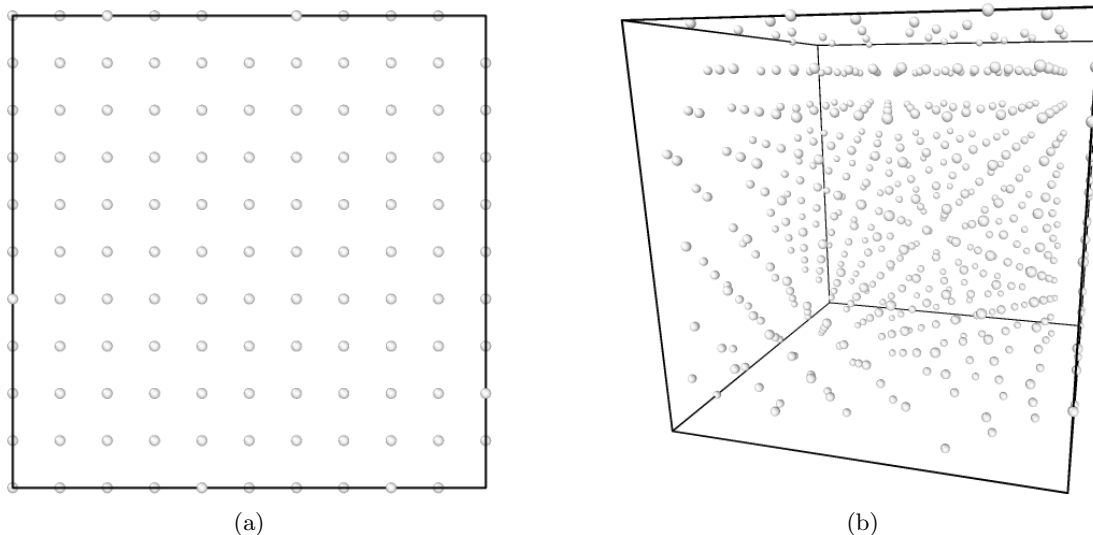


Figure 3: Initial FCC lattice using 5 unit cells in each direction. The lattice contains 500 atoms in total. (a) shows a 2D view from the side. (b) shows the same lattice but from a different perspective.

3.5 Mean displacement

The mean displacement is used in Eq. 15 to find the diffusion constant. When the FCC is created an initial_position vector is created for each atom. The displacement is how far away the current position is from the initial position. The atoms close to the periodic boundary might cross the boundary and end up on the other side of the lattice. The displacement of such an atom would be very large because it has traveled the entire lattice, even though it has only traveled a short distance. To correct this the code checks if the displacement is more than half the lattice size and shifts the displacement such as to follow the particle movement. A consequence of this is that if an atom moves through the entire lattice, across the periodic boundary and back to its initial position, the displacement is zero. However physically the displacement

should be large. The result is that the diffusion constant measured for the liquid state is a bit lower than the true value.

```
double System::meanDisplacement(){
    meanDispSqr = 0;
    vec3 Disp;
    for (Atom *atom : m_atoms) {
        Disp = atom->position - atom->initial_position;
        for (int u = 0; u<3; u++){
            if (Disp[u] > 0.5*Periodicsize) Disp[u] += -Periodicsize;
            if (Disp[u] <= -0.5*Periodicsize) Disp[u] += Periodicsize;
        }
        meanDispSqr += Disp.lengthSquared();
    }
    meanDispSqr /= N;
    return meanDispSqr;
}
```

4 Results and discussions

Fig. 3 shows the FCC argon lattice created by the code and visualized using Ovito. The atoms are structured in an ordered fashion. The temperature of the lattice is 200 K, but any lattice looks identical at the first time step. Fig. 4 shows a 2d view of the argon structure after a moderate amount of time has passed. Fig. 4a shows an ordered argon solid at 100 K. Even though the atoms have moved around from their initial position in Fig. 3a, the basic FCC structure is preserved. and Fig. 4b shows disordered argon at 1000 K.

What this shows is that argon is a solid at 100 K and a liquid at 1000 K. Therefore there is a phase transition from solid to liquid somewhere between 100 K and 1000 K.

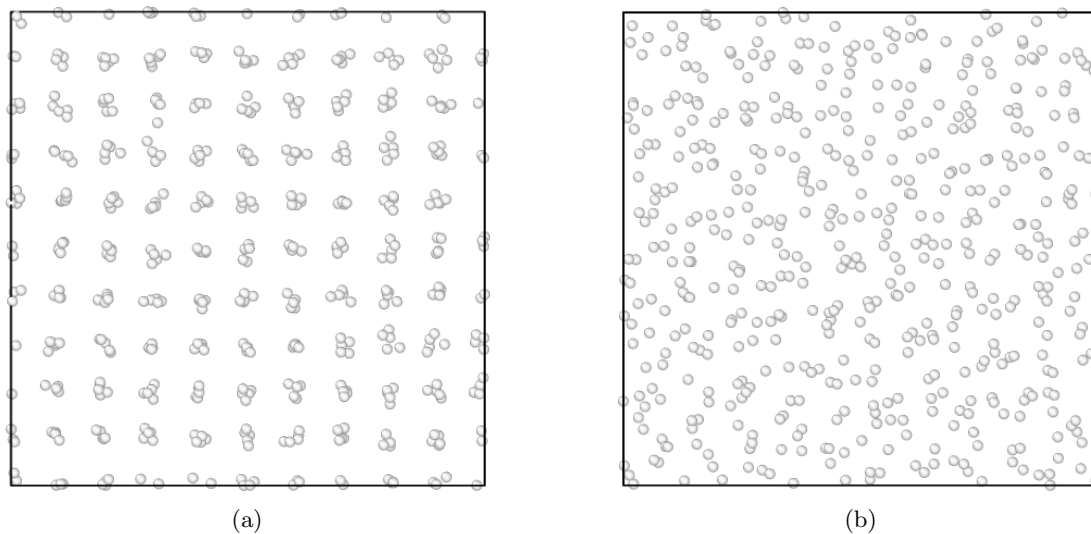


Figure 4: Images of the argon structure after a moderate amount of timesteps. (a) shows the atoms at a temperature $T \approx 150$ K and (b) has $T \approx 1200$ K. In the low temperature case, the atoms are still ordered. In the high temperature case the atoms are disordered.

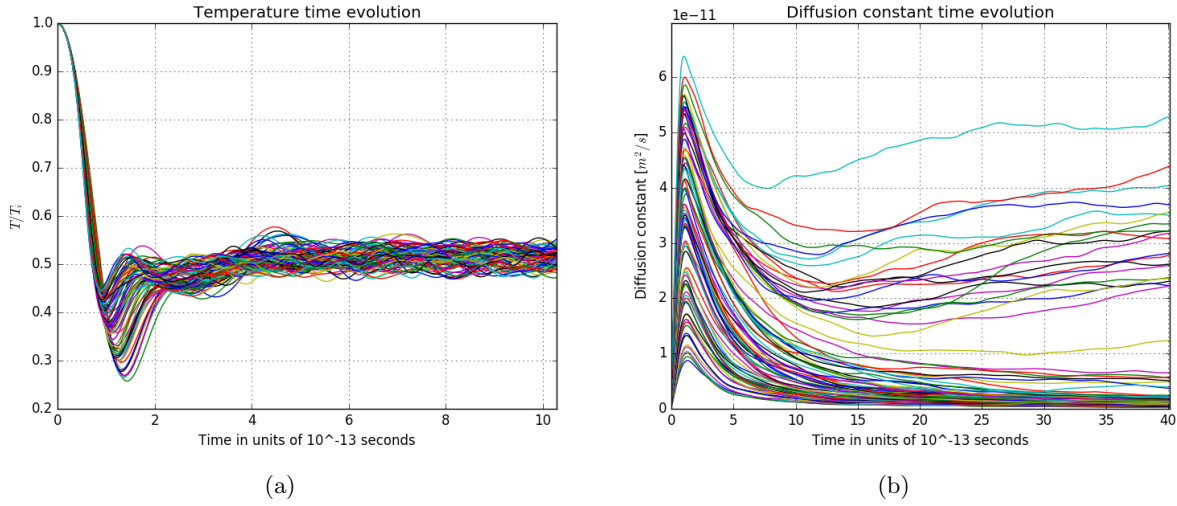


Figure 5: Time variation of temperature (a) and diffusion constant (b) for initial temperatures between 100 K and 900 K in increments of 10 using a step size of 10^{-15} . In (a), the lower initial temperatures reach a lower minimum in the first minimum. In (b), the higher temperatures have a higher diffusion constant.

4.1 Time evolution of temperature and diffusion constant

Fig. 5a shows the time evolution of the relative temperature T/T_i for initial temperatures ranging from 100 K to 900 K in increments of 10 K. The temperature starts off at the initial temperature and then the temperature quickly decreases. The temperature then oscillates around approximately 50% of its initial value. If the initial temperature is small, then the initial temperature dip is larger. For an initial temperature of 50 K the temperature quickly dips to 30%, but for initial temperature 890 K the temperature only dips to 45%. The temperature stabilizes after approximately 10^{-12} s. The temperature then oscillates with a spread of about 5%.

What happens is that the FCC lattice is created with an initial temperature that sets the random velocity using the Maxwell Boltzmann distribution (Eq. 12). The randomly distributed and so there are fluctuations. Some particles with large velocities and some with small. Entropy dictates that the system should move to a more uniform state. Hence system should drive towards an equilibrium where the velocities are more evenly distributed.

Since the kinetic energy is dependent on the square of the velocity, an evenly distributed state will have less kinetic energy than a randomly distributed one. The temperature is proportional to the kinetic energy (Eq. 11) meaning the temperature of the system should decrease. The system should reach some equilibrium where the mean parameters do not change in time. This is observed in Fig. 5a as the temperature flattening out. The temperature does oscillate by about 5% of the initial temperature.

Fig. 5b shows the diffusion constant calculated using Eq. 15. The low temperatures lie at the bottom and the higher temperatures lie above. The temperatures start at 100 K and end at 900 K with increments of 10 K. The diffusion constant has an initial spike for all temperatures. If the temperature is low, the diffusion constant approaches zero afterwards. If the temperature is high, the diffusion constant slowly converges to some value as the system reaches an equilibrium.

The initial spike in the diffusion constant corresponds to the initial minimum in the temperature. The atoms in the lattice are created with a randomly distributed velocity. Initially all the atoms move away from their initial positions. Therefore the mean displacement is initially large, and therefore also the diffusion constant. Once the atoms move a bit from their positions, atoms meet other atoms. Then the atoms get pushed back a bit, the result is that the diffusion constant reduces. For the solid case the atoms shift back to their original position and move around it without leaving. Therefore the diffusion constant should be

low. For the liquid phase, the atoms have enough kinetic energy to move away from their initial positions. The result is a high diffusion constant.

4.2 Melting point of argon

Fig. 6 shows the temperature dependence of the values from Fig. 5. The values are made by taking the mean of Figs. 5a and 5b, from $(90 \text{ to } 100) \times 10^{-13} \text{ s}$. It is important to use a larger sample than at least the oscillations in the temperature ratio Fig. 5a. Those oscillations are of the order $\sim 10^{-13} \text{ s}$. The x-axis is the mean equilibrium temperature of the argon.

Fig. 6a shows the temperature dependence on the temperature ratio T/T_i . The ratio steadily increases from 50 K - 320 K. Then at 320 K, the temperature ratio discontinuously drops from 0.53 to 0.46. At the same time, the equilibrium temperature drops from 320 K to 305 K.

This tells us that a phase transition occurs at this temperature. As the temperature of the body passes 320 K, 7% of the temperature disappears. When the argon reaches the phase transition any added heat will not go to the lattice, but rather to turning the solid structure into a liquideous structure. Increasing the initial temperature gives energy to break the FCC structure, without increasing the actual temperature of the equilibrium body.

Fig. 6b shows the temperature dependence of the equilibrium diffusion constant. The constant is ≈ 0 up until $\sim 320 \text{ K}$ and then the constant starts to increase. The temperature of the body decreases slightly as already explained. The diffusion constant increases by a factor of 6 without changing its temperature. From there the diffusion constant gradually increases up to $\sim 4.5 \times 10^{-11}$.

The value of the diffusion constant at temperatures above 300 K indicates that the particles are free to move. Therefore the FCC argon lattice is broken and is now in a liquideous state. The melting point at which this happens is 320 K. Using the number density n from Eq. 14, the pressure at $T = 320 \text{ K}$ is

$$p = nk_B T = 1214 \text{ bar.} \quad (16)$$

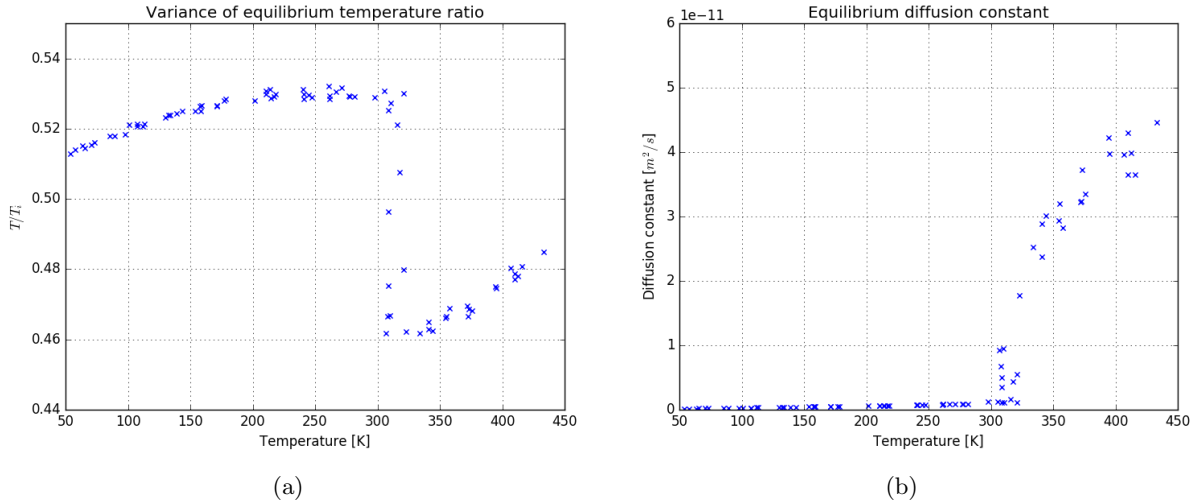


Figure 6: Temperature variance of (a) mean relative temperature and (b) the diffusion constant. The graph is made using an average of the last 1000 values from Fig. 5. The timestep used in the calculations is 10^{-15} s .

4.3 Random seed

The seed for the calculations is random such that every time the program is run, a different set of random numbers is used. The result is that the velocities drawn from the Maxwell-Boltzmann distribution are

different each time. And since the temperature of the body is dependent on the velocity, the temperature is different. It also means that the total energy of the system changes a bit.

Since the temperature variance in % is about the same, the uncertainty is larger for the higher temperatures.

5 Conclusions

Using simulations of the molecular dynamics of argon, we found the FCC argon structure to have a solid→liquid phase transition at $T \approx 320 \pm \text{K}$ and $p \approx 1214 \text{ bar}$. The argon density is 1824.2 kg m^{-3} . The transition is clearly visible in the relative temperature and the diffusion constant. The transition is observed to be 1st order due to the apparant discontinuities in the mentioned parameters.

The values of the diffusion constant should be lower than the real diffusion constant for the reasons discussed in section 3.5. This could be fixed by giving the atom class the positions of the previous time step as a property. Then in the `system.meanDisplacement` function we could use the current position and the previous position to determine whether an atom has passed the periodic barrier. Then the mean displacement could be calculated appropriately to give the displacement the way the atom has traveled. Due to the late realization of this issue, there was no time to run simulations again. The issue should not change the temperature at which the melting of argon occurs, only the value of the diffusion constant.

References

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