

FYS-MEK1110 Molecular Dynamics Project

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Preface

All scripts referred to in this project paper can be found in my GitHub Repo: <https://github.com/Bergfjord/FYS-MEK1110-Prosjekt/blob/main/python/>. The scripts are named (in Norwegian) after the tasks they correspond to. I have also included all resources used in this paper in the same repository. GIFs of the simulations and figures can also be found there.

I have chosen to exclude "kjørseksempler" from my code as these would be quite enormous and repetitive in the way i have structured my python code. I hope this choice will not cause any inconvenience for the reader.

I had a lot of fun programming for this project. I would definitely recommend condensing steps 1-3 to give the student extra time to mess around after part 4. Having a finished MD simulation tool, the student can now investigate for example sound wave propagation, compressing the "walls" of the box, or letting the gas "fall" into another box etc. I definitely enjoyed being able to experiment with my results from task 4, and I'm certain that future participants would love to have more time to do such things as well, at the cost of less time spent on sections 1-3 perhaps.

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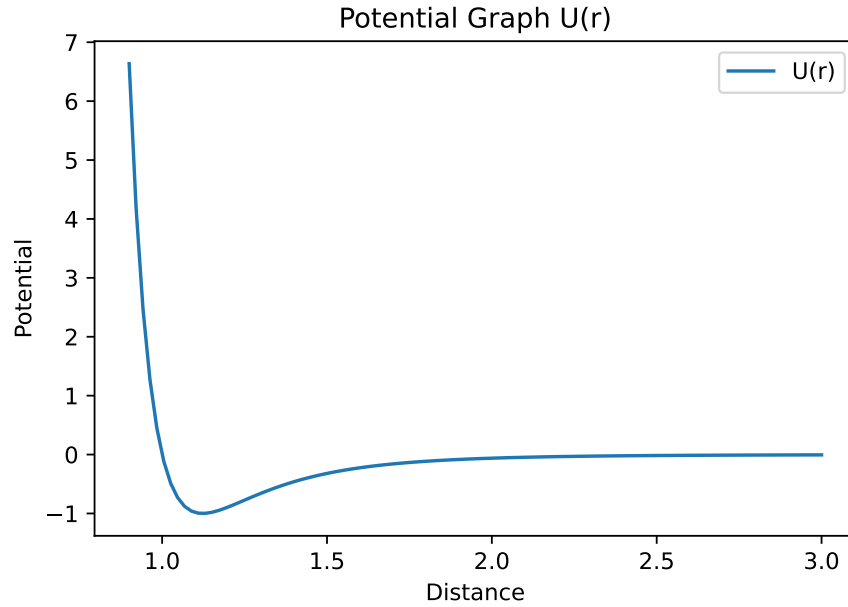
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1 Introduction

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

1a) Understanding the Potential

i



ii

When $r > \sigma$ the first term, $(\frac{\sigma}{r})^{12}$ will clearly dominate, as it will rapidly outgrow the second term. However, in the case when $r < \sigma$ the first term will approach 0 faster than the second term. Thus, in the latter case, the second term will dominate. The dominating term determines the sign of the potential, i.e. the direction of the potential. So the effect is essentially which way the atoms would accelerate if affected by the potential alone.

iii

We need to differentiate equation 1 w.r.t. r and set it to zero. This yields the following

$$\frac{dU}{dr} = 4\epsilon \left(-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right) \quad (2)$$

$$\frac{dU}{dr} = 0 \iff 4\epsilon \left(-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right) = 0 \quad (3)$$

Since ϵ is a non-zero constant, the above equation can only be satisfied if

$$-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} = 0$$

An immediately obvious solution to this equation is to let r tend towards infinity, i.e. $r \rightarrow \infty \Rightarrow \frac{dU}{dr} \rightarrow 0$. This means that a equilibrium point for the potential exists at an infinite distance between the atoms.

Another, more interesting, equilibrium can be found by the algebraic manipulation of equation 3:

$$\frac{12\sigma^{12}}{r^{13}} = \frac{6\sigma^6}{r^7} \Rightarrow r = \sqrt[6]{2} \cdot \sigma \quad \square$$

So the second equilibrium point can be found at $r = \sqrt[6]{2} \cdot \sigma$

iv

As long as the sum of potential and kinetic energy is negative it will oscillate between the equilibrium points. This is clearly the case in $U(r = 1.5\sigma)$. However, the potential is positive for $U(r = 0.95\sigma)$ and the repulsive forces will accelerate the atoms away from each other with energy above the possible potential for attraction. Thus they would continue on their trajectories away from each other indefinitely, ad infinitum.

v

Around the equilibrium point the atoms will oscillate back and forth. This is reminiscent of Hooke's law, were a mass is attached to a spring, and made to oscillate back and forth between a equilibrium point.

1b) Forces and equations of motion

i

We can define the force acted on a atom to be the difference in potential w.r.t distance. The intuition behind this is that a large change in potential corresponds to a large acceleration of the atom, which is proportional to the force applied on the atom (Newtons second law of motion.) Also, the relation is negatively proportional. The higher the force on the atom, the bigger the drop, or reduction, in the atoms potential. thus we can find the force on the atom using the differentiated potential (Equation 2):

$$\begin{aligned}
F &= -\frac{dU}{dr} = -4\epsilon \left(-\frac{12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right) \\
F &= 24\epsilon \left(2\frac{\sigma^{12}}{r^{13}} - \frac{\sigma^6}{r^7} \right)
\end{aligned} \tag{4}$$

Equation 4 yields the force between two atoms determined by their mutual distance. We know from Newton's third Law that both atoms experience the equal and opposite force, so equation 4 describes the force on any given atom in relation to another. This force is a scalar, since r is only a distance scalar, and not a vector in space. However, to model this in the specific case of atom j interaction on atom i , we need to decompose the distance-scalar, r into its respective components of atom positions $r = |\vec{r}_i - \vec{r}_j|$. Placing this into equation 4 yields:

$$F_i = 24\epsilon \left(2\frac{\sigma^{12}}{|\vec{r}_i - \vec{r}_j|^{13}} - \frac{\sigma^6}{|\vec{r}_i - \vec{r}_j|^7} \right) \tag{5}$$

Equation 5 now yields the scalar force on atom i as a function of its spatial coordinates \vec{r}_i and of the corresponding atom j , \vec{r}_j .

The final part of the puzzle is to give the scalar force a direction, as force is supposed to be a vector, and not a scalar. We know that the force will point in the parallel direction of the line spanned between the atoms, so if we multiply the scalar force in equation 5 with the normalized directional vector $\frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|}$ it will yield

$$\vec{F}_i = 24\epsilon \left(2\frac{\sigma^{12}}{|\vec{r}_i - \vec{r}_j|^{13}} - \frac{\sigma^6}{|\vec{r}_i - \vec{r}_j|^7} \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|} \tag{6}$$

Equation 6 is now the complete function of force on the atom i . We can pull out a common factor $|\vec{r}_i - \vec{r}_j|$ to clean up the exponents.

$$\begin{aligned}
\vec{F}_i &= 24\epsilon \left(2\frac{\sigma^{12}}{|\vec{r}_i - \vec{r}_j|^{13}} - \frac{\sigma^6}{|\vec{r}_i - \vec{r}_j|^7} \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|} \\
\vec{F}_i &= \frac{24\epsilon}{|\vec{r}_i - \vec{r}_j|} \left(2 \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|} \\
\vec{F}_i &= 24\epsilon \left(2 \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2} \quad \square
\end{aligned} \tag{7}$$

ii

We know from Newton's second law that acceleration is equal to the sum of forces acted on it, divided by its mass. The total acceleration of the atom is then given by the sum of all other atoms forces, i.e.

$$\vec{a}_i = \frac{d^2\vec{r}_i}{dt^2} = \frac{1}{m_i} \sum_{j \neq i} \vec{F}_i = \frac{1}{m_i} \sum_{j \neq i} 24\epsilon \left(2 \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2}$$

$$\frac{d^2 \vec{r}_i}{dt^2} = \frac{24\epsilon}{m_i} \sum_{j \neq i} \left(2 \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2} \quad \square \quad (8)$$

We iterate over all atoms (except i it self), and sum up the directional forces. Equation 8 gives the i th atom's acceleration as a function of its mass, position, and the position of all other atoms in the system.

This yields the same equation as in the provided task description.

1c) Units

i

We will scale equation 8 using the identities $\vec{r}'_i = \frac{\vec{r}_i}{\sigma}$ and $t' = \frac{t}{\tau}$. We will first investigate the consequences on the left hand side of equation 8:

$$\begin{aligned} d\vec{r}_i &= d(\sigma \cdot \vec{r}'_i) = \sigma \cdot d\vec{r}'_i \\ d(d\vec{r}_i) &= d^2 \vec{r}_i = d(\sigma \cdot d\vec{r}'_i) = \sigma \cdot d^2 \vec{r}'_i. \\ t = \tau \cdot t' &\iff dt = \tau \cdot dt' \iff (dt)^2 = (\tau \cdot dt')^2 = \tau^2 \cdot dt'^2 \end{aligned}$$

From the left hand side transformation the following relation appears:

$$\frac{d^2 \vec{r}_i}{dt^2} = \frac{\sigma \cdot d^2 \vec{r}'_i}{\tau^2 dt'^2}. \quad (9)$$

Now looking at the right hand side of equation 8:

First we see that

$$|\vec{r}_i - \vec{r}_j| = |\sigma \vec{r}'_i - \sigma \vec{r}'_j| = |\sigma(\vec{r}'_i - \vec{r}'_j)| = |\sigma| |\vec{r}'_i - \vec{r}'_j| = \sigma |\vec{r}'_i - \vec{r}'_j|$$

It follows from this that

$$\begin{aligned} &\frac{24\epsilon}{m_i} \sum_{j \neq i} \left(2 \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^{12} - \left(\frac{\sigma}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2} \\ &= \frac{24\epsilon}{m_i} \sum_{j \neq i} \left(2 (|\vec{r}'_i - \vec{r}'_j|)^{-12} - (|\vec{r}'_i - \vec{r}'_j|)^{-6} \right) \frac{\vec{r}'_i - \vec{r}'_j}{\sigma |\vec{r}'_i - \vec{r}'_j|^2} \\ &= \frac{24\epsilon}{\sigma m_i} \sum_{j \neq i} \left(2 (|\vec{r}'_i - \vec{r}'_j|)^{-12} - (|\vec{r}'_i - \vec{r}'_j|)^{-6} \right) \frac{\vec{r}'_i - \vec{r}'_j}{|\vec{r}'_i - \vec{r}'_j|^2} \end{aligned} \quad (10)$$

Equating the new left hand side and right hand side, equations 9 and 10 yields the following relation:

$$\frac{\sigma \cdot d^2 \vec{r}'_i}{\tau^2 dt'^2} = \frac{24\epsilon}{\sigma m_i} \sum_{j \neq i} \left(2(|\vec{r}_i - \vec{r}_j|)^{-12} - (|\vec{r}_i - \vec{r}_j|)^{-6} \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2}$$

$$\frac{d^2 \vec{r}'_i}{dt'^2} = \tau^2 \frac{24\epsilon}{\sigma^2 m_i} \sum_{j \neq i} \left(2(|\vec{r}_i - \vec{r}_j|)^{-12} - (|\vec{r}_i - \vec{r}_j|)^{-6} \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2}$$

It follows from this that the proper choice of τ should be $\tau = \sqrt{\frac{\sigma^2 m_i}{\epsilon}}$ and thus, our final equation is

$$\frac{d^2 \vec{r}'_i}{dt'^2} = 24 \sum_{j \neq i} \left(2(|\vec{r}_i - \vec{r}_j|)^{-12} - (|\vec{r}_i - \vec{r}_j|)^{-6} \right) \frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|^2} \quad (11)$$

which is the correct equation provided in the task description.

One interesting test of our choice of τ is to verify that it is indeed measured in seconds:

$$\begin{aligned} \epsilon &= Nm = kg \frac{m}{s^2} = \frac{[kg][m]^2}{s^2}, \sigma = m, m_i = [kg] \\ \tau &= \sqrt{\frac{\sigma^2 m_i}{\epsilon}} = \sqrt{\frac{m^2 [kg]}{\left(\frac{[kg][m]^2}{s^2}\right)}} = \sqrt{s^2} = s \quad \square \end{aligned}$$

The unit of τ is in seconds.

ii

The characteristic time of a process is used to get a sense for the amount of time a process will use. It is especially useful when processing or computing the dynamics of physical processes as these can apply constants and units which vary vastly in size. Computing with large and tiny numbers often lead to larger errors due to rounding and other limits with bit-representation of numbers. In our case here we will be analyzing the interaction between our atoms with our characteristic time as the designated unit of time.

In order to calculate the characteristic time τ for argon, we first need to calculate the figures in common SI units

$$\sigma = 3.405 \text{ \AA} = 3.405 \cdot 10^{-10} m$$

$$m = 39.95 u = 39.95 \cdot 1.66 \cdot 10^{-27} kg = 6.6317 \cdot 10^{-26} kg$$

$$\epsilon = 1.0318 \cdot 10^{-2} eV = 1.0318 \cdot 10^{-2} \cdot 1.602 \cdot 10^{-19} J = 1.6529 \cdot 10^{-21} Nm.$$

We enter these figures into our choice of τ to get the characteristic time scale

$$\tau = \sqrt{\frac{\sigma^2 m_i}{\epsilon}} = \sqrt{\frac{(3.405 \cdot 10^{-10} m)^2 \cdot 6.6317 \cdot 10^{-26} kg}{1.6529 \cdot 10^{-21} Nm.}} = 2.1567 \cdot 10^{-12} s \quad (12)$$

So the characteristic time for our argon gas molecule interaction is in about 2.16 picoseconds.

2 Two-atom simulations

I wrote a class included all three methods of integration. I used this class throughout

2a) Implementation

i

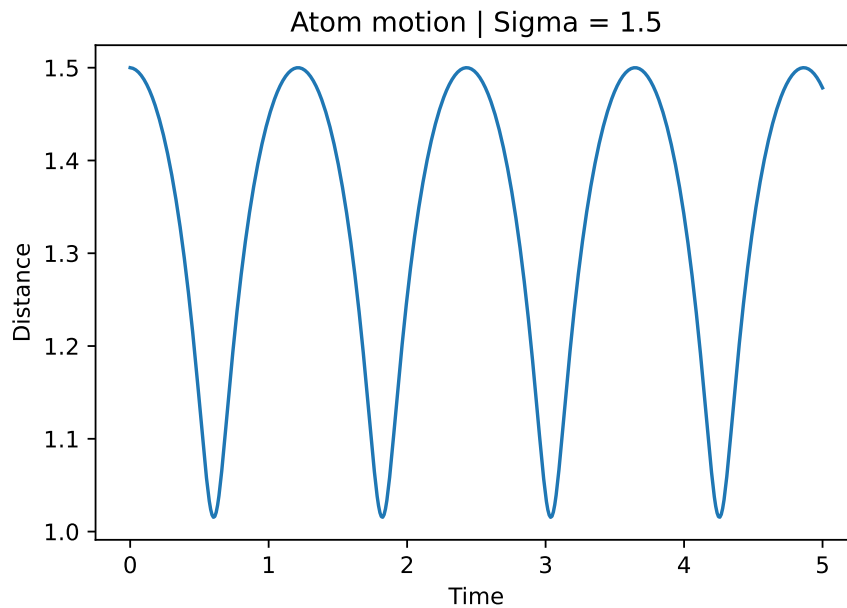
Please see [Oppgave2.py here](#).

2b) Motion

i, ii & iii

The simulation can again be found [here](#).

Sew below for figure of oscillating distances between the atoms.

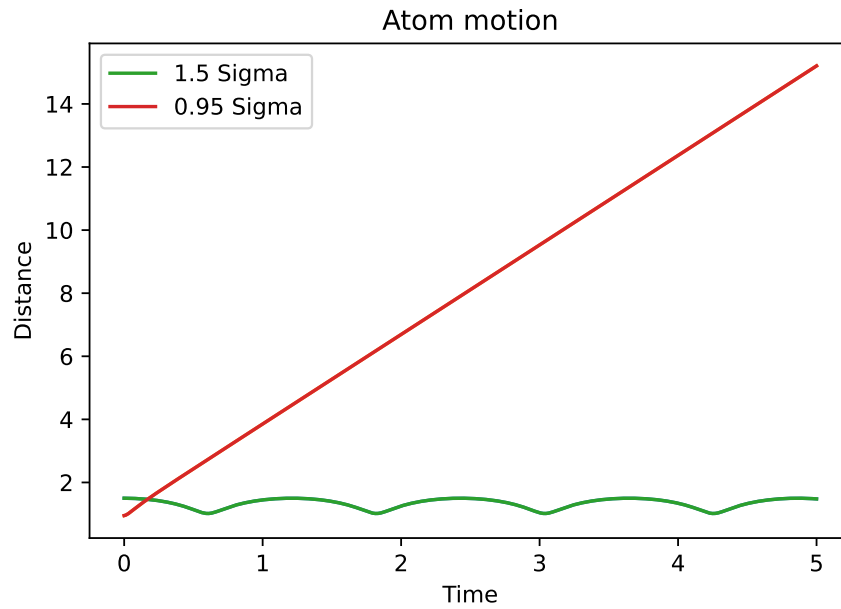


The oscillation fits the expectation described in section on 1A. Since the potential is initially negative, there will be an oscillation back and forth between the equilibrium point.

iv

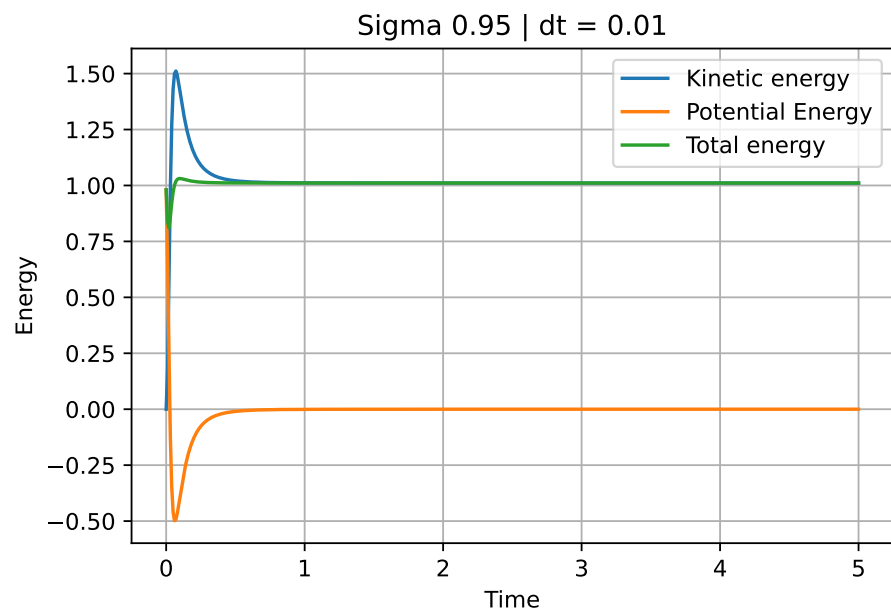
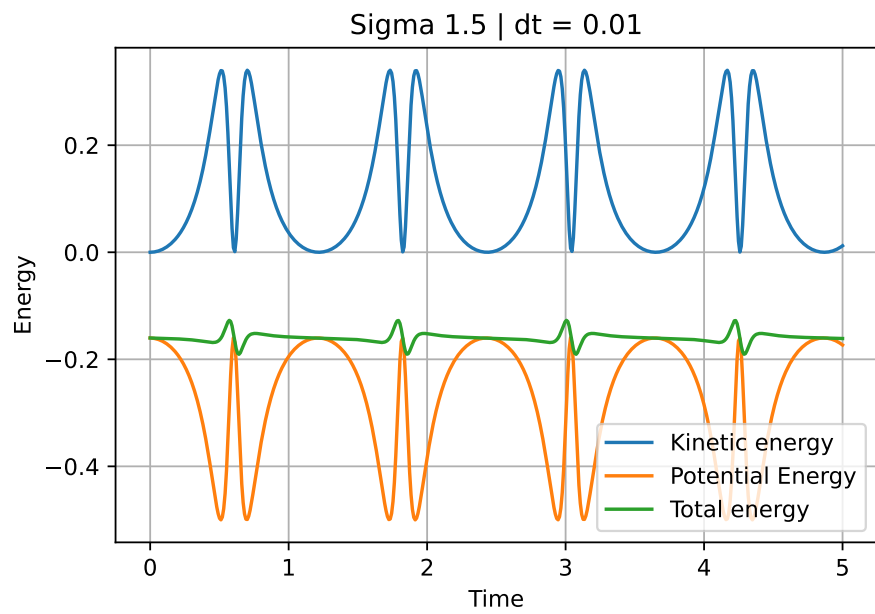
We can see from the following figure that the expected outcome did indeed happen in simulation. As the potential is positive with the distance of 0.95σ ,

the atoms will accelerate away from each other with a speed greater than the force of attraction. Thus we see the atoms move away almost linearly as the forces involved quickly become negligible at greater distances. I have included the oscillating behaviour of 1.5σ for reference.



2c) Energy

i



ii

Yes, the total energy of any system, isolated from external forces, should remain constant. This can be deduced from Newtons laws, using the derived third kinetic equation:

$$2\bar{a}\Delta s = v^2 - v_0^2 \quad (13)$$

where \bar{a} is the average acceleration, Δs is the distance covered, v and v_0 is the objects final speed and initial speed, respectively. We can extract an equation for change in energy by some small manipulations.

$$m\bar{a} = \frac{\frac{1}{2}mv^2 - \frac{1}{2}mv_0^2}{\Delta s} \quad (14)$$

On the RHS of equation 14 we see the change in kinetic energy. i.e. since $\Delta E_k = \frac{1}{2}mv^2 - \frac{1}{2}mv_0^2$

Since $m\bar{a} = \bar{F} = -\frac{\Delta E_p}{\Delta s}$, we see that the LHS of equation 14 is the change in potential over a distance Δs . Thus, combining these arguments with equation 14, we can rewrite it as:

$$-\frac{\Delta E_p}{\Delta s} = \frac{\Delta E_k}{\Delta s}$$

Rearranging, and taking the limit as $\Delta s \rightarrow 0$

$$\frac{dE_p}{ds} + \frac{dE_k}{ds} = 0 \quad (15)$$

i.e. the change in kinetic energy is equal and opposite to the change in potential energy. Another way of expressing this is

$$E_t = E_p + E_k = \text{constant} \quad (16)$$

In order to explain our system, which contains 2 atoms, we need to apply newtons third law (all forces have an equal and opposite reaction) to equation 15. If we initiate the system with both atoms at rest wrt to each other, then the potential energy will be equal for both articles, and the total energy of the system will be equal to the the potential energy at $t = 0$. The evolution of the systems energy will from that point be determined by equation 15.

The momentum of the atoms will in our model always be fixed at zero, as the relative velocities of the atoms will always point in opposite directions, and mass of each atom are equal.

$$\begin{aligned} m_i \cdot \vec{v}_i &= m_j \cdot (-1)\vec{v}_j \\ m_i \cdot \vec{v}_i + m_j \cdot \vec{v}_j &= 0 \end{aligned} \quad (17)$$

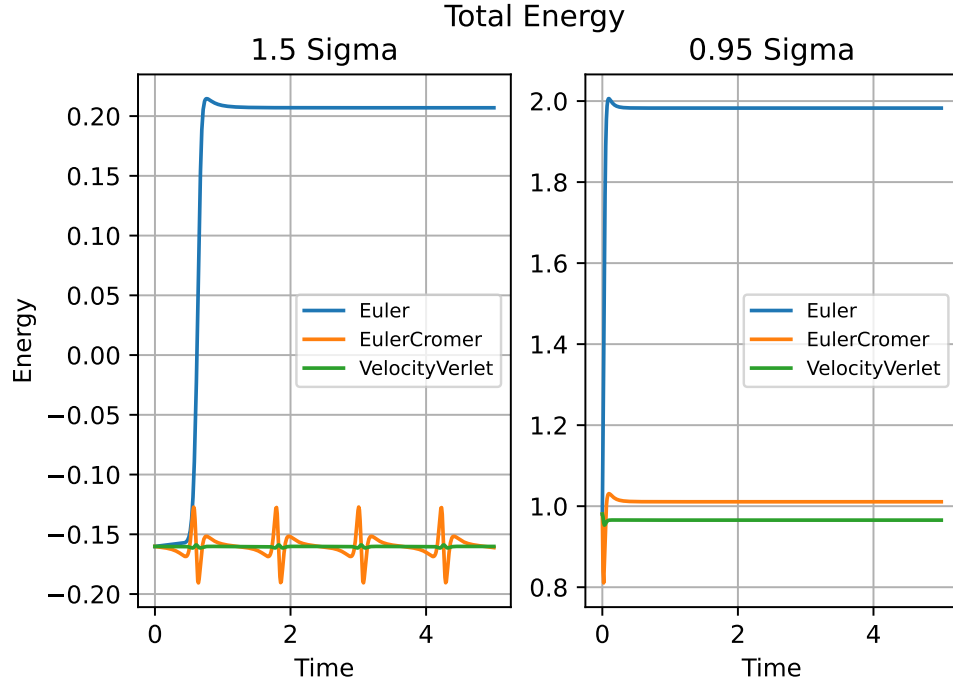
P.S.: this section might have been a bit overkill, but I did enjoy the deduction of the conservation of energy from Newtons laws, so hope the reader won't mind too much.

iii

The figures above show that the total energy of the system actually fluctuates. When the changes in kinetic and potential energy is great, there is a deviation in the total energy. However, the total energy corrects itself, and remains at the initial level over time. This suggests that we should increase the granularity of the analysis, i.e. more time points, as a too discrete time jump might lead to these momentary fluctuations.

iv

The figure below shows the total energy calculated for each method for $\sigma \in 1.5, 0.95$ and with a time step of 0.01.



Immediately we can see that Euler-Cromer and Velocity Verlet are both stable around the initial energy of the system. There are some periodic fluctuations in the 1.5σ case, but this is not too significant.

However, the Euler method is not stable at all for either case of σ . This is likely due to the size of time step and the nature of the error in the Euler method. One key aspect of the Euler method is that the errors are cumulative. This means that the error in the next step will be a function of the time step and the previous error. A resolution of 0.01 with the Euler method gives the atoms too great speed, and the atoms "escape" from each other, i.e. the speed and

position combination that the Euler method erroneously provides is enough to overcome the attractive forces of the Lennard-Jones potential, and they never come together again. That's why both distance-parameters provided yield a sudden increase in total energy, after which it remains constant as both atoms really don't interact beyond "separation".

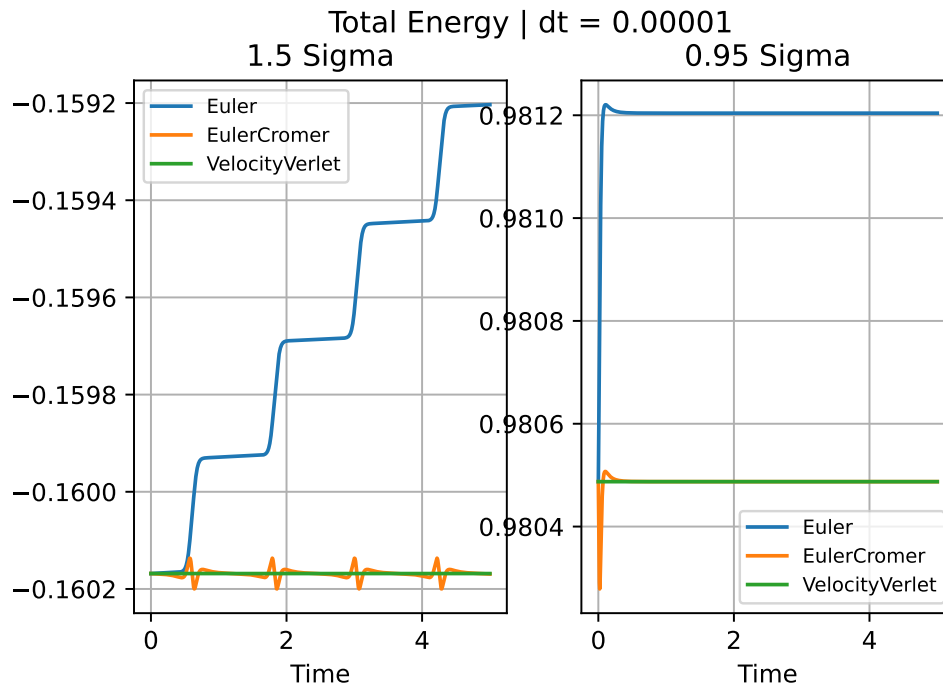
It is likely that the Euler method would benefit from an smaller time step, while both Euler-Cromer and Velocity Verlet could benefit performance wise from a larger time step. This will be the subject of discussion in the next subsection

v

I quickly see a pattern when I iterate through different time step sizes.

First, for Euler-Cromer and Velocity Verlet, the bigger time step of 0.1 gave an permanent error in the total energy. all reductions in the time step size in Euler-Cromer and Velocity Verlet yielded the same fluctuations, only scaled down. Thus I conclude that for these models, the already established time step of 0.01 provides the superior ratio of computational efficiency and precision.

For the Euler method, however, things are not so straight forward. As mentioned earlier the error is cumulative, so we can see that no matter how many time points we apply, there will still be an increase in the error. This is because the error of the Euler method adds a bit more distance at the turning points for the atoms. This increases the potential of the atoms for every oscillation. This error can be reduced by increasing the amount of time steps, but since the error is systematic, and cumulative, the system will have a periodic increase in potential. Consequently, there is no optimal time step size for the Euler method. To illustrate, please see the below figure, where I applied an exaggerated $dt = 0.00001$



As you can see, the energy increases in the Euler method increases.

vi

The Euler method is very fast as the calculations involved are simpler than other methods. However, as discussed in the previous subsection, it suffers from cumulative errors, and this is an issue if the solution we try to approximate has varying curvature.

The Euler-Cromer method fixes the issue we've been discussing in the Euler method by combining the current position and the next velocity to get the next position. The benefit with this method is that it is relatively simple to calculate, and it doesn't have systematically cumulative errors. However, the total energy does fluctuate, which means that some error is being made and corrected (similar error, opposite direction) periodically. This behaviour can be seen visually in the figure in the last section.

The Velocity Verlet includes the acceleration term, so it is accurate in the second order as well. It also conserves the total energy. However, the addition of the extra term means that it won't process as fast as the other two methods.

3 Large Systems

3a) Implementation

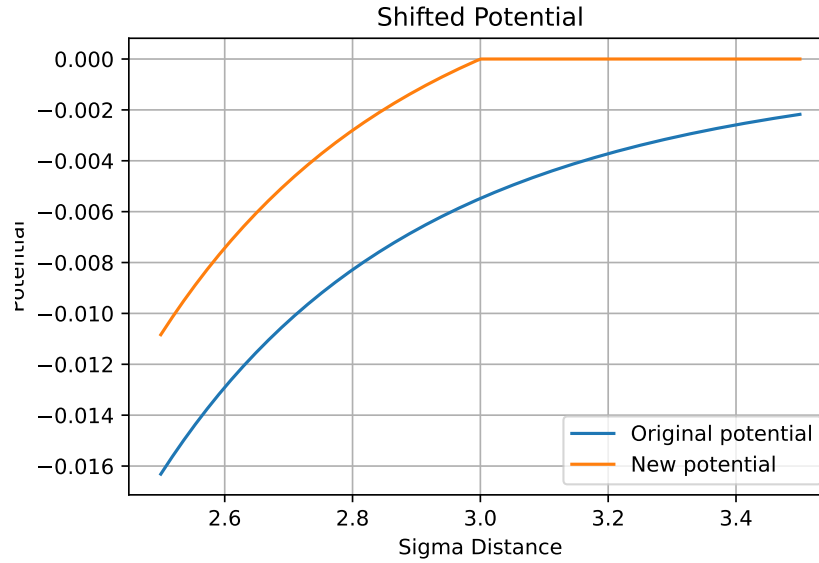
i, ii & iii

I have incorporated the task criteria in the class which I have named VVSolver. Please see [here](#) for the python code. A large effort was spent on vectorization in this section. The result is that a 256 simulation for 5 seconds at 0.01 step size takes about 15 seconds to finish, which is a massive increase in efficiency from previously applied methods.

iv

I have included the potential being set to 0 at distances above 3σ . The shift constant is given by $U(3\sigma)$:

$$U^*(3) = 4 \left((3)^{-12} - (3)^{-6} \right) \approx -0.0055$$



v

The shift in the the potential does not impact the force calculations at all, since this a constant w.r.t. distance, and thus is zero when the force equation is derived from the potential equation by differentiation. (However, the force calculations are affected by setting distances over 3 to 0 potential.)

3b) Verification

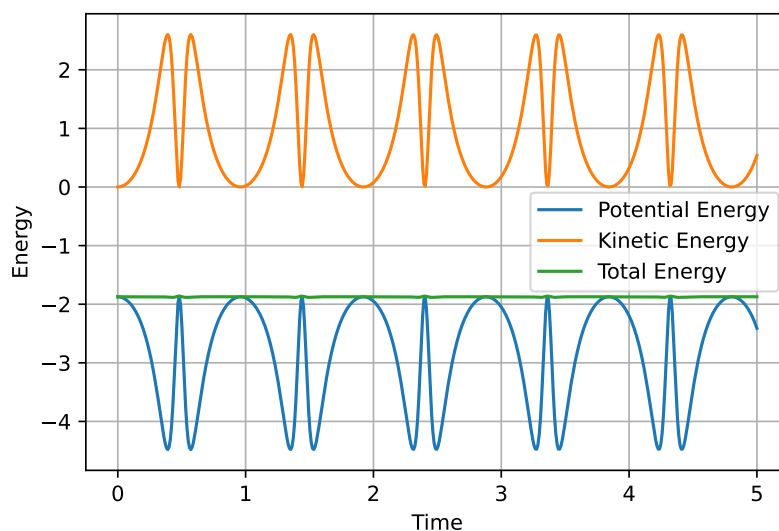
Please see [here](#) for the python program for this entire subs-task.

i, ii & iii

The code runs and works on the two atom and four atom scenario. Plotting the four-atom case in Ovito yields something that looks like a four-leaf clover, oscillating in and out from a common center. It looks like if we copied the two atom case and pasted it in on a different axis (which is in some sense essentially what we've done here).

iv

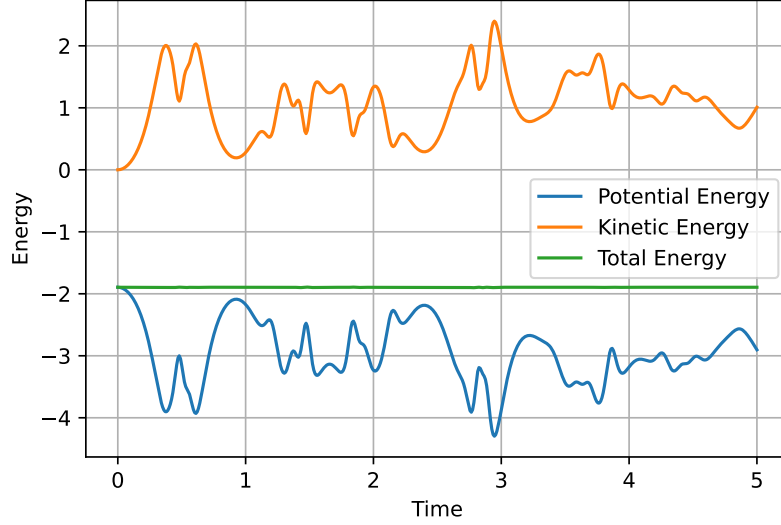
We see the stable oscillating behaviour of the system in the plot below.



v

Here we see more chaotic behaviour from the system. Since the symmetry mentioned earlier is gone, the atoms will adopt a more erratic pattern of collisions. The simulation in Ovito is clearly different from the previous case, and the motion of the system seems more random.

The figure of the energy of the system illustrates this well.



3c) Initialisation

i & ii

Please see [here](#) for the function (*lattice()*, 1.135) and verification of the face-lattice function.

iii

If we divide the mass of four atoms in as cell with the density provided we get the volume of the cell. The mass of four atoms is

$$4m = 4 \cdot 39.95 \cdot 1.66 \cdot 10^{-27} kg = 4 \cdot 39.95 \cdot 1.66 \cdot 10^{-24} g = 2.65268 \cdot 10^{-22} g$$

$$\frac{2.65268 \cdot 10^{-22} g}{1.374 g/cm^3} = 1.9306 \cdot 10^{-22} cm^3$$

The cube root of this will be length of the walls of the cell:

$$d = \sqrt[3]{1.9306 \cdot 10^{-22} cm^3} \approx 5.78 \cdot 10^{-8} cm$$

Knowing $\sigma = 3.405 \cdot 10^{-8}$:

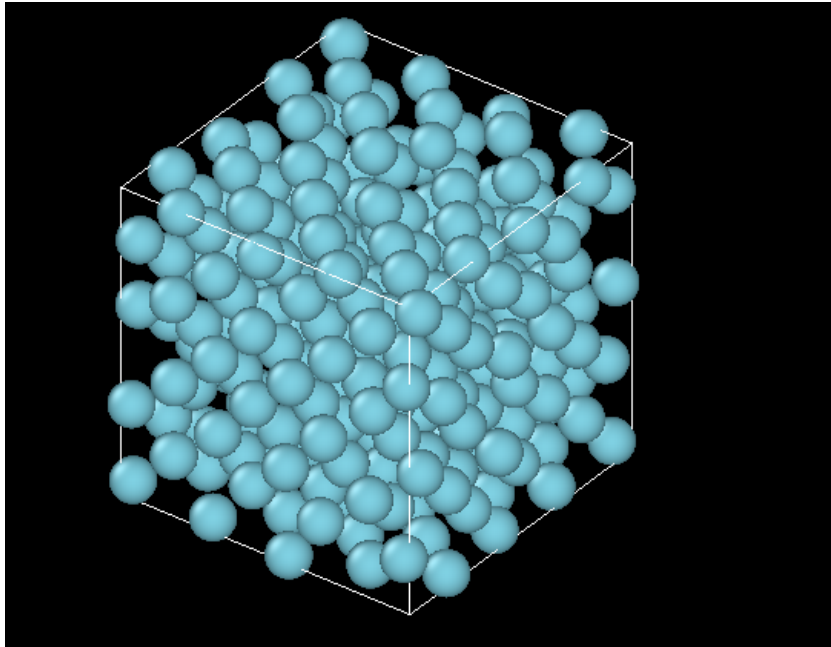
$$\frac{d}{\sigma} = \frac{5.78 \cdot 10^{-8} cm}{3.405 \cdot 10^{-8}} \approx 1.7$$

Thus, a density of $1.374 g/cm^3$ corresponds to a cell distance of $d = 1.7\sigma$

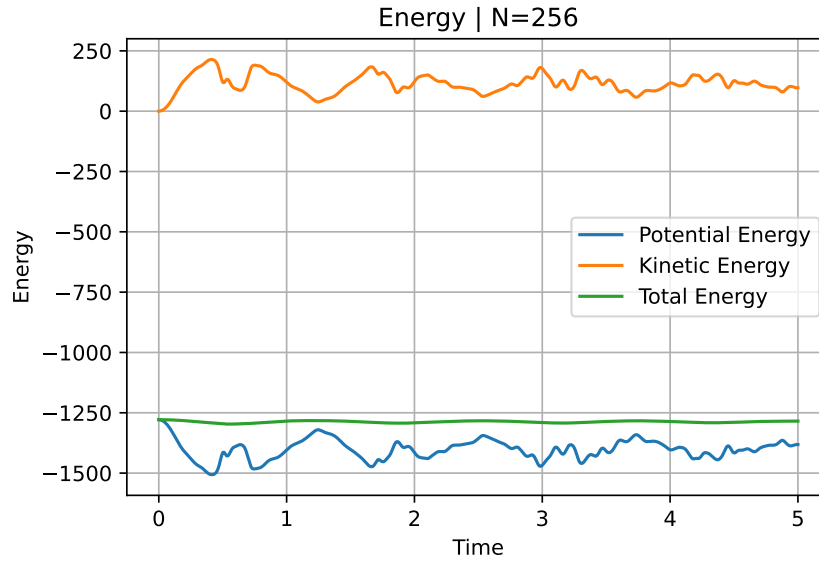
3d) Many atoms, open boundary

i

Please *Oppgave3.py*, function `task_3di()` [here](#) for code.



ii



I can see that the face lattice does pulse in and out towards a common center, but there is a lot of "noise" as each atom also vibrates due to the vibrations of the neighbouring atoms. We can see this pulsing behaviour with the added noise of each atom in the figure. Also, the noise seem to increase and the pulsing behaviour seem to become less distinct over time.

3e) Boundary Condition

i & ii

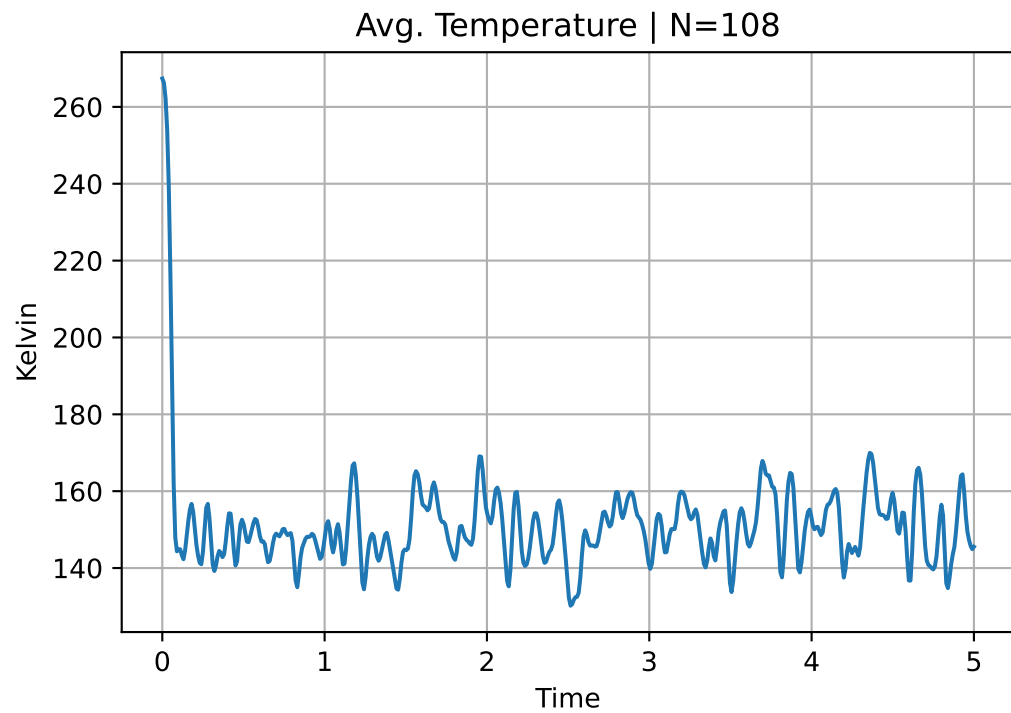
I have decided to incorporate the periodic, and not the reflective boundary conditions. I have commented the changes in the code, which can be seen in [here](#).

4 Science

4a) Temperature

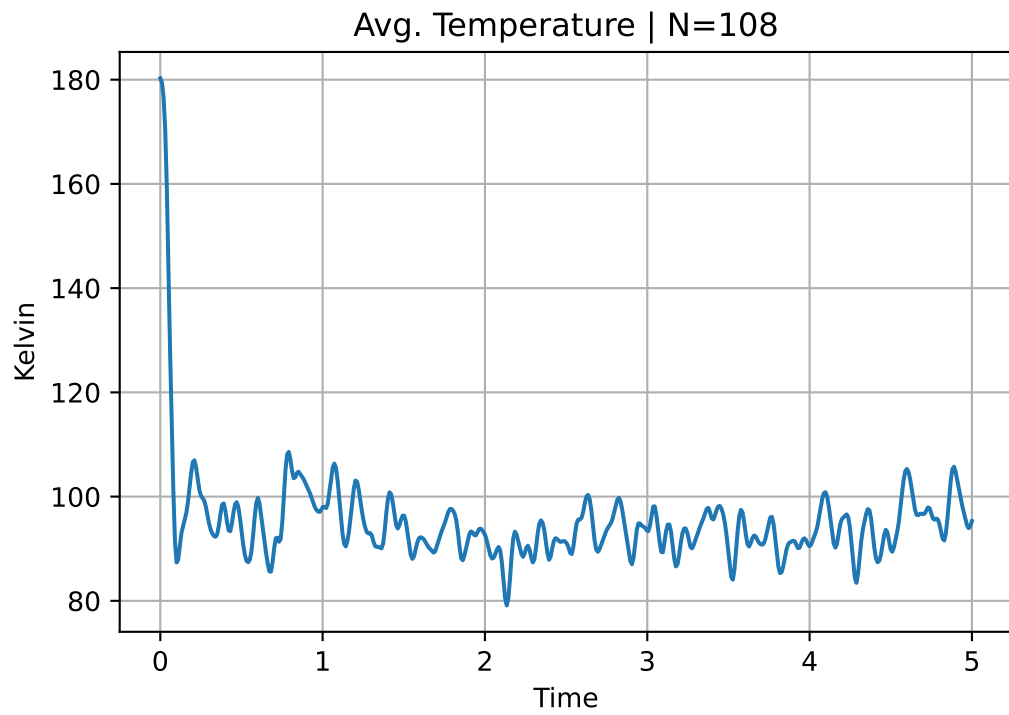
i

See figure below



ii

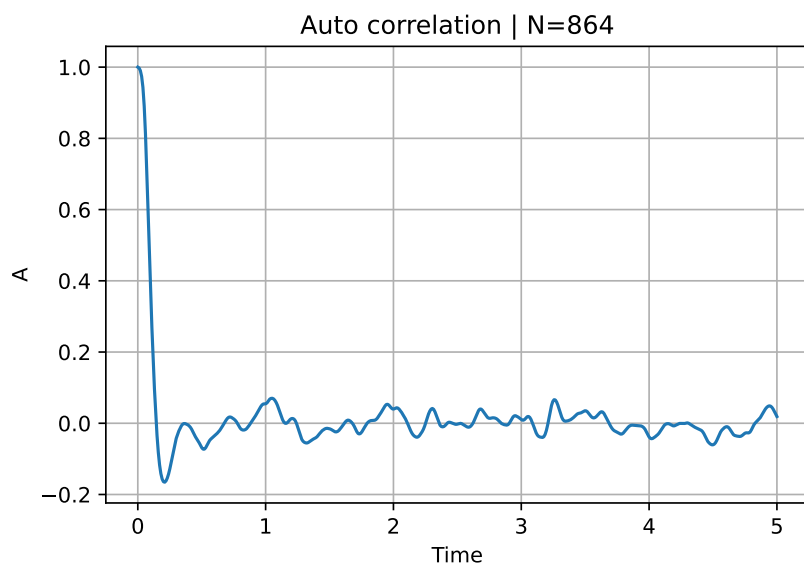
By trial and error I found that the starting temperature of 180 K yields approximately 94.4 K in equilibrium temperature.



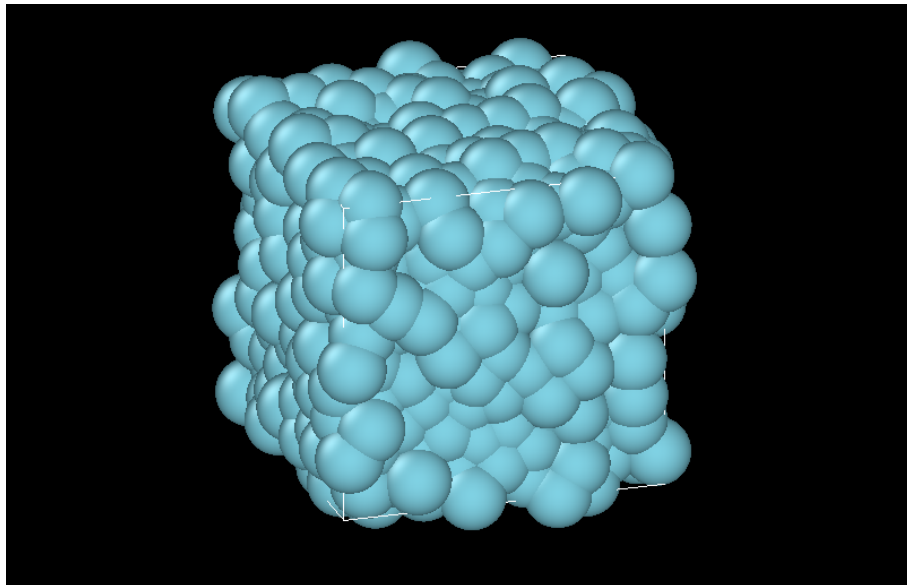
4b) Velocity auto-correlation and diffusion coefficient

i & ii

I ran the simulation with 864 atoms. See figure below for results.



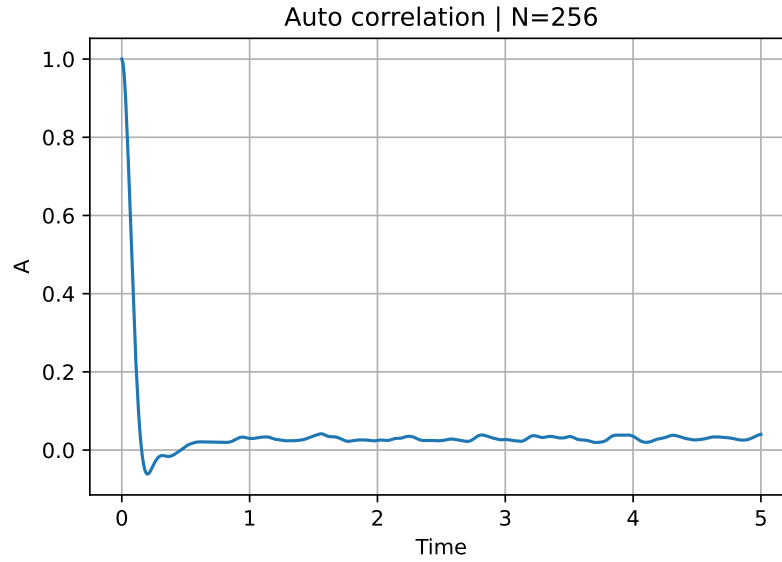
This looks quite similar to the figure in the paper, but it does not look to be converging on 0.



iii & iv

I averaged out the auto correlation from 100 runs of 256 atoms. The initial position and velocity of each run is the last velocity and position of the former

run. Please see figure for the averaged auto correlation below

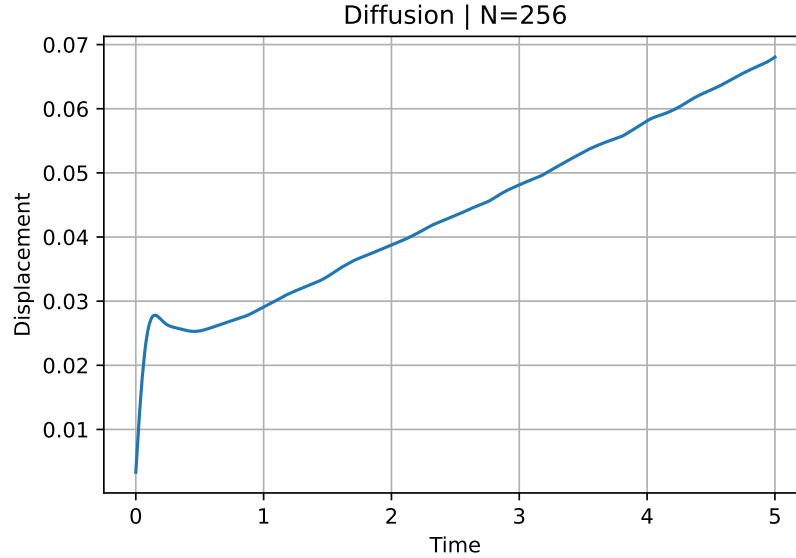


v

I am convinced that something has gone wrong with this calculation. My calculated auto correlation does not have a zero mean as time progresses. This means that when i calculate the diffusion, the result is not converging to a specific value. Instead the integral below diverges.

$$D = \frac{1}{3} \int_0^{\infty} A(t) dt$$

Please see in the figure below the plotted integrated auto correlation as a function of time.



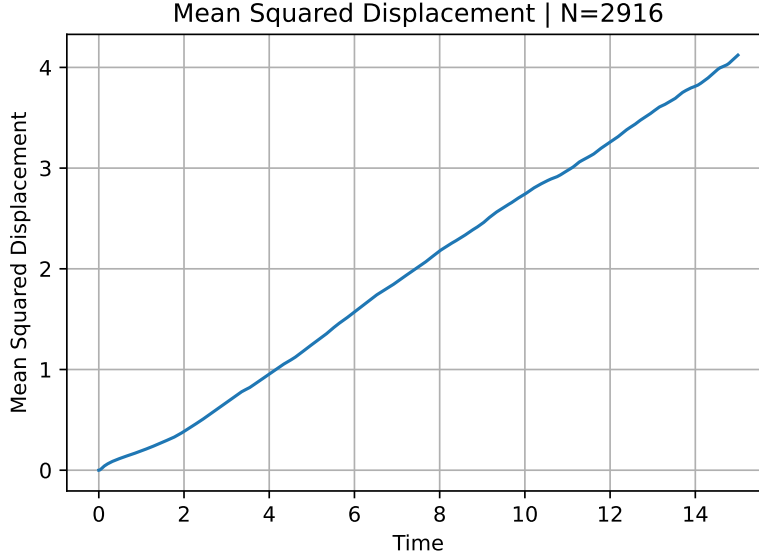
Clearly this does not converge but instead is (almost linearly) increasing with time. I have scanned my code for errors which might be responsible for this deviation from the paper, but my efforts have been less than fruit full.

In a attempt to rectify this failure, I will estimate the diffusion coefficient in the next task. Fortunately i had better luck with the chosen approach there.

4c) Mean squared displacement and diffusion coefficient

i & ii

I ran a pretty big simulation for this part, with 2916 atoms running over 15 seconds (computational time was well over 2.5 hours). I have plotted the figure for the mean squared displacement below



I have estimated the slope of this curve to be about $\frac{4.1\sigma^2}{15\tau}$, which is equal to $6D$, i.e. 6 times the diffusion constant. We can enter the characteristic distance- and time to get units we can compare with the research paper.

$$\tau = 2.1567 \cdot 10^{-12} s, \sigma = 3.405 \cdot 10^{-8} cm$$

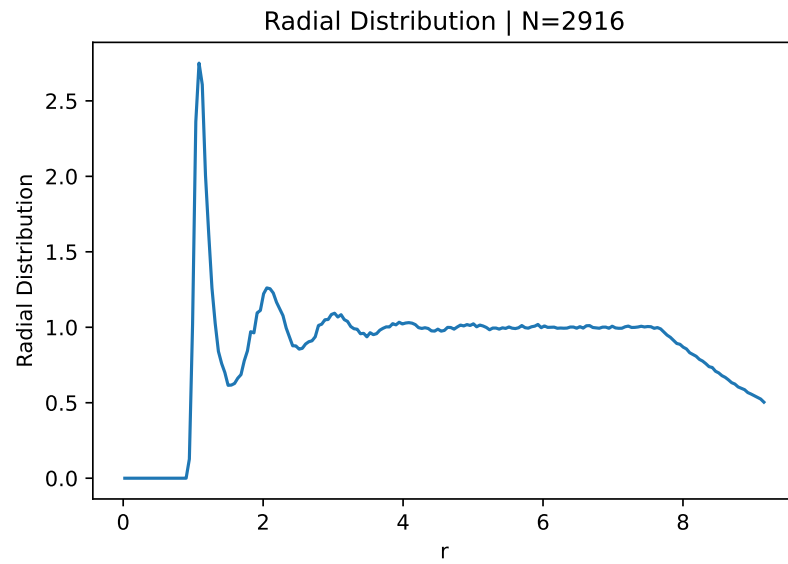
$$\begin{aligned} \Rightarrow 6D &= \frac{4.1 (3.405 \cdot 10^{-8} cm)^2}{15 \cdot 2.1567 \cdot 10^{-12} s} = 1.469 \cdot 10^{-4} cm^2 s^{-1} \\ \Leftrightarrow D &= \frac{1.469 \cdot 10^{-4}}{6} cm^2 s^{-1} \approx 2.45 \cdot 10^{-5} cm^2 s^{-1} \end{aligned}$$

This result is very similar to the result of the paper ($2.43 \cdot 10^{-5} cm^2 s^{-1}$), by a margin of under one percent(!)

4d) Radial distribution function

i

The radial distribution function is approaching 1 nicely. Please see the figure below.



When the radius under investigation begins to go outside the length of the box, the result will start to converge towards 0.