

Molecular Simulation of Argon

Computational Physics Assignment 1

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Abstract

Background: Because atoms can hardly be observed directly, computer simulations can predict how atoms behave on the micro and nano scale.

Methods: A volume of size L^3 filled with 108 Argon atoms is simulated. The boundaries are periodic to imitate an infinite space of particles. Newton's second law is used to calculate the motions of the particles. The Euler method and the Verlet method are used and compared.

Results: The Verlet method calculates stable values for the total energy. The structure the atoms assume aligns with the expectations. The calculated pressures are close to theoretical values, except when ρ and T get close to the critical value. The Euler method yields unphysical results for E_{tot} ; it goes up spontaneously.

Conclusion: The Verlet method calculates more accurate results than the Euler method, as the Verlet method conserves the total energy of the system.

1 Introduction

Laboratorial limitations will not always allow to observe physical phenomena at the micro and nano scale, leaving a gap in our understanding. This gap can be explored by simulating the behaviour of particles from underlying physics principles, facilitating studies of dynamic evolution of systems. Therefore, molecular dynamics is a great way to understand the behaviour of certain substances at the atomic level. However, systems consisting of multiple moving objects are generally very difficult to solve. As an example, even though we are able to accurately predict the motions of a two-body system, a general three-body system will have no analytical solution¹. In these cases, we can turn to numerical simulations where the motions of particles are calculated in discrete time steps. With the invention of computers, these types of calculations became much faster and allowed simulations of systems with hundreds of particles. In 1964, Rahman[4] used a "digital computer" to simulate 864 argon atoms at a fixed temperature and density, and studied its behaviour. Rahman used classical dynamics with a two-body central-force interaction to calculate the

¹Stable solutions to the three-body problem do exist, see https://en.wikipedia.org/wiki/Three-body_problem#/media/File:5_4_800_36_downscaled.gif.

behaviour of the atoms. We will expand on this by studying the phases of argon at different temperatures and densities, though for fewer atoms.

1.1 Kinematic theory

Argon is relatively easy to simulate since it's a noble gas. Interactions between individual atoms are simplified as a Lennard-Jones potential (with r denoting the distance):

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

This potential is attractive over large distances, but strongly repulsive at distances smaller than the characteristic distance σ (see Figure1). It has a minimum at $2^{1/6}\sigma \approx 1.12\sigma$.

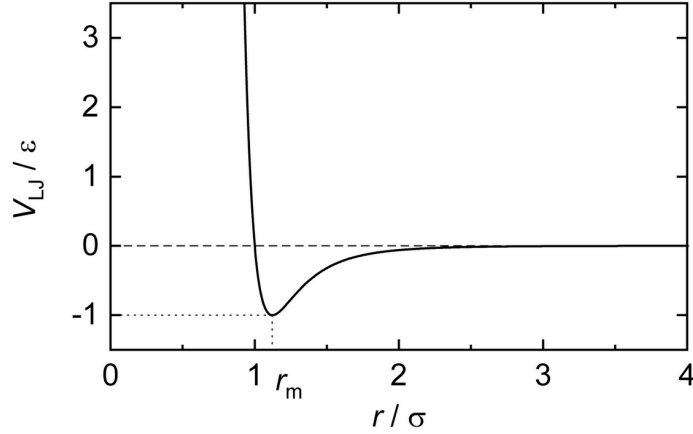


Figure 1: Lennard-Jones potential[5]

Lighter noble gases have much lower phase transition temperatures. At atmospheric pressure, Helium boils at 4.2K and remains liquid down to absolute zero. Neon boils at a slightly higher temperature of 27.1K. Still, this results in very high velocities and small forces between atoms which means the simulations need to run for a long time and the time step has to be very small. Argon, with a mass of 39.96u and a boiling point at 87.3 K leads to simpler simulations. Table 1 gives the Lennard-Jones parameters and mass of the Argon atom.

	Argon	
Mass:	39.96	[g/mol]
ϵ/k_B :	119.8	[K]
σ :	3.405	[Å]

Table 1: Lennard-Jones parameters and mass of the Argon atom

To predict the motion of the particles, Newton's second law is used:

$$m \frac{d^2 \mathbf{x}}{dt^2} = \mathbf{F}(\mathbf{x}) = -\nabla U(\mathbf{x}) \quad (1)$$

Therefore, the force on a particle at \mathbf{x}_i as a result of another particle at \mathbf{x}_j is

$$\begin{aligned} F(\mathbf{x}_i) &= -\nabla U(\mathbf{x}_i - \mathbf{x}_j) \\ &= -\frac{dU(r_{ij})}{dr_{ij}} \frac{\mathbf{x}_i - \mathbf{x}_j}{r_{ij}} \end{aligned}$$

Where $r_{ij} = |\mathbf{x}_i - \mathbf{x}_j| = \sqrt{x^2 + y^2 + z^2}$. The total force on a particle is obtained by summing over all other particles:

$$\begin{aligned} F_{tot}(\mathbf{x}_i) &= \sum_{i \neq j} \left[-\frac{dU}{dr_{ij}} \frac{\mathbf{x}_i - \mathbf{x}_j}{r_{ij}} \right] \\ &= \sum_{i \neq j} \left[\left(12 \left(\frac{\sigma}{r_{ij}} \right)^{13} - 6 \left(\frac{\sigma}{r_{ij}} \right)^7 \right) \frac{\mathbf{x}_i - \mathbf{x}_j}{r_{ij}} \right] \end{aligned}$$

1.2 Natural units

Interactions between atoms happen at a scale of nanometers, and the mass of the atoms is around 10^{-27} . Working with such small numbers is prone to rounding errors. This can be solved by using natural units which result in quantities on the order of 1. The Lennard-Jones potential interacts at distances of σ , so a new unitless variable for distance can be constructed: $\tilde{r} = \frac{r}{\sigma}$. To have a dimensionless potential, \tilde{U} is defined as: $\tilde{U}(\tilde{r}) = U(r)/\epsilon = 4(\tilde{r}^{12} - \tilde{r}^6)$. A dimensionless time unit is derived:

$$\frac{d^2 \tilde{\mathbf{x}}}{d\tilde{t}^2} = \sigma^{-1} \frac{d^2 \mathbf{x}}{dt^2} = -\sigma^{-1} \frac{1}{m} \nabla U(r) = -\frac{\epsilon}{m\sigma} \nabla \tilde{U}(\tilde{r}) = -\frac{\epsilon}{m\sigma^2} \tilde{\nabla} \tilde{U}(\tilde{r})$$

To reduce this equation to the simplest form of

$$\frac{d^2 \tilde{\mathbf{x}}}{d\tilde{t}^2} = -\tilde{\nabla} \tilde{U}(\tilde{r})$$

the dimensionless time unit needs to be $\tilde{t} = t / \sqrt{\frac{m\sigma^2}{\epsilon}}$.

The velocity becomes: $\tilde{v} = \frac{\tilde{\mathbf{x}}}{\tilde{t}} = v \sqrt{\frac{m}{\epsilon}} \rightarrow \tilde{v} / \sqrt{\frac{m}{\epsilon}}$.

Inserting these units into the equation for kinetic energy ($\frac{1}{2} m v^2$) gives units of: $m * \frac{\epsilon}{m} = \epsilon$. This should have the same units as thermal energy ($k_B T$), therefore T has units of ϵ / k_B . The ideal gas law is $P = N k_B T / V$. $k_B T$ is energy, which has units of ϵ , V is in σ^3 and N is the total number of particles which has no units. Therefore P has units of ϵ / σ^3 .

2 Methods

In this section, the implementation of the described theory in a simulation will be discussed.

2.1 Numerical integration methods

In MD simulations, the equations of motion are solved approximately, since they are impossible to solve analytically. The easiest way to do this is with numerical integration. The idea is to make time discrete instead of continuous, and calculate the position of the particles for every time step.

2.1.1 Euler method

The most straight-forward way to solve the equation of motion is by only considering the first-order term:

$$\mathbf{x}_{n+1} = \mathbf{x}_n + \mathbf{v}_n dt$$

and

$$\mathbf{v}_{n+1} = \mathbf{v}_n + \frac{1}{m} \mathbf{F}(\mathbf{x}_n) dt$$

Even though this method, called the Euler method, does not conserve energy, it is still implemented to be later tested against the Verlet algorithm, explained in the next section.

2.1.2 Verlet method

An improvement upon the Euler method is the Verlet algorithm. This algorithm conserves energy and takes into account higher orders of h . The algorithm works by first calculating $\mathbf{x}(t + dt)$. Taking the Taylor expansion of $\mathbf{x}(t + dt)$ gives:

$$\mathbf{x}(t + dt) = \mathbf{x}(t) + \mathbf{v}(t)dt + \frac{(dt)^2}{2m} \mathbf{F}(\mathbf{x}(t)) + \mathcal{O}((dt)^3) \quad (2)$$

Where $\dot{\mathbf{x}}(t)$ has been replaced by $\mathbf{v}(t)$ and $\ddot{\mathbf{x}}(t)$ has been replaced by $\frac{1}{m} \mathbf{F}(\mathbf{x}(t))$ as told by Newton's second law. An equation for \mathbf{v} is needed, therefore we take the Taylor expansion as well: $\mathbf{v}(t + dt) = \mathbf{v}(t) + \dot{\mathbf{v}}(t)dt + \frac{(dt)^2}{2} \ddot{\mathbf{v}}(t) + \mathcal{O}((dt)^3)$. $\ddot{\mathbf{v}}$ can be found by using the definition for derivatives again:

$$\ddot{\mathbf{v}}(t) = \frac{1}{dt} [\mathbf{F}(\mathbf{x}(t + dt)) - \mathbf{F}(\mathbf{x}(t))] / m$$

Finally we obtain:

$$\mathbf{v}(t + dt) = \mathbf{v}(t) + \frac{dt}{2m} [\mathbf{F}(\mathbf{x}(t + dt)) + \mathbf{F}(\mathbf{x}(t))] + \mathcal{O}((dt)^3) \quad (3)$$

To execute this algorithm, first $\mathbf{x}(t + dt)$ is calculated with equation 2. Then, $\mathbf{F}(t + dt)$ is calculated with the potentials. Lastly, using the stored value for $\mathbf{F}(t)$ and the calculated value $\mathbf{F}(t + dt)$, $\mathbf{v}(t + dt)$ is calculated. This process repeats for the desired number of time steps.

By preserving the discretized energy, the total energy cannot drift away. It will rather oscillate around the correct value, which is not the case for the Euler method.

2.2 Boundary conditions

In order to limit the size of the simulation, three dimensional box of some fixed size L is used with periodic boundary conditions. Particles that exit this box will re-enter it at the opposite side with the same velocity. This mimics the behaviour of an infinitely-sized simulation.

2.3 Minimal image convention

Theoretically, the simulation contains an infinite number of particles which all interact with one another. However, this is impractical to implement. Therefore, the interaction potential is truncated at some point. Fortunately, the Lennard-Jones potential decays rather fast with distance. Box size L will always be significantly larger than the inter-atomic distance. Therefore, even though each particle i interacts with an infinite number of copies of the particles in the box, we do not have to calculate all interactions. In considering a particle and all its copies, only the closest copy (or original) will be accounted for. This is called the *minimum image convention*.

Python allows us to write it as $(x_i - x_j + L/2) \% L - L/2$. The first two values in Table 2 (0 and $L/2$) are trivial. If the distance between the particles is L , if distance $x_i - x_j = L$, one of the particles should already have looped back, therefore the modulo distance should be 0. If $x_i = 0$ at $x_i - x_j = 3L/4$, then the other particle is $L/4$ away from being at L where x_i is (since L is the same as 0). A distance of $L/4$ is the same as $-L/4$ as $x_i - x_j = x_j - x_i$. (The distance from i to j is the same as from j to i .)

$x_i - x_j$	0	$L/2$	L	$L/4$	$3L/4$
$(\Delta x_{ij} + L/2) \% L - L/2$	0	$L/2$	0	$L/4$	$-L/4$

Table 2: Distances between the particles vs. the modulo distances.

2.4 Initial conditions

The basic input parameters for each simulation are ρ and T which determine the size of the simulation and the initial velocities of the particles.

2.4.1 Face-centered cubic lattice

For particles starting too close to each other, the r^{-12} term will have huge contributions to the potential energy which will yield unphysical velocities. In order to mitigate this, atoms will be put on a regular grid. Argon are placed in a face-centered cubic (fcc) lattice (Figure 2 shows part of the FCC lattice), which is regular i.e. it repeats itself. Each repeating unit consists of 4 atoms with the following coordinates:

$$[x, y, z] = [0, 0, 0], [0, 0.5a, 0.5a], [0.5a, 0, 0.5a], [0.5a, 0.5a, 0]$$

Where a is the lattice constant. By choosing our volume L^3 to have $3 \times 3 \times 3$ units, the total number of atoms should be $N = 108$. The total length of the box L can be

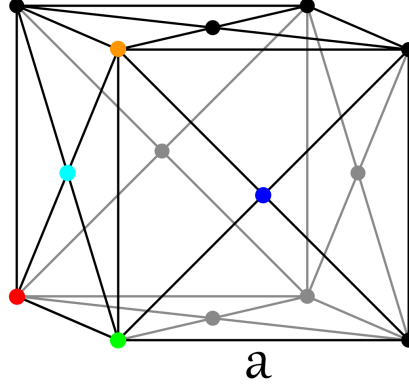


Figure 2: FCC lattice. If the red point is taken as the origin, the four coloured dots (green, blue, cyan, orange) are the four smallest distances to the origin. a denotes the lattice constant.

determined from the input density through:

$$L = \left(\frac{N}{\rho} \right)^{1/3}$$

2.4.2 Temperature

The temperature is set by drawing velocities for x, y and z from the Maxwell velocity distribution:

$$p(v_x) \sim e^{-mv_x^2/2k_B T}$$

In our unitless system, this results in velocities drawn from a Gaussian distribution with a mean of 0 and a variance $\sigma^2 = T$ (with T in natural units).

2.4.3 Velocity relaxation

When starting the simulation, the system is not in equilibrium yet which results in a not-conserved total energy. If the simulation is allowed to run sufficiently long, the system will "relax" by itself, however this can take very long. After relaxation, the kinetic energy of the system will be $E_{kin}^{target} = (N - 1) \frac{3}{2} k_B T$ (the total momentum in the system is conserved, leaving only $N-1$ independent degrees of freedom). In order to speed up the process, the system is allowed to evolve for a number of steps after which all velocities are rescaled by a factor λ :

$$\mathbf{v}_i \rightarrow \lambda \mathbf{v}_i$$

λ is chosen such that $E_{kin}^{target} = \lambda^2 E_{kin}^{current}$, which would set the current kinetic energy of the system exactly to the value E_{kin}^{target} . The kinetic energy $E_{kin}^{current} = \frac{1}{2} \sum_i m v_i^2$,

so λ must be:

$$\lambda = \sqrt{\frac{(N-1)3k_B T}{\sum_i m v_i^2}}$$

This rescaling is repeated a number of times until the temperature has converged.

2.5 Observing the simulation

In order to gauge the performance of the simulation, and validate its result, multiple quantities are measured. The results (pressure, pair correlation) are determined after the system has been relaxed and is therefore in equilibrium.

2.5.1 Pair correlation

At each step in time, a histogram $n(r, t)$ is constructed of the distances r between particles. At the end of the simulation, these histograms are averaged over time (after relaxation), yielding $\langle n(r) \rangle$ and appropriately scaled in order to obtain the pair correlation function $g(r)$:

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r}$$

with V the volume of the simulation, N the number of particles and Δr the size of a bin. This pair correlation function is a way to represent distances between particles in some state and can be used to determine the state of matter. Distinct peaks mean that particles are often found at some fixed distance from each other, which is expected in a lattice. In a gas, the velocity of particles is too high to be significantly affected by the attractive r^{-6} term. For $r > \sigma$, where the r^{12} no longer dominates, the gas is distributed homogeneously, and $g(r)$ should be constant. The scaling of $g(r)$ leads to $g(r) \approx 1$. In this simulation, we only consider three states: gas, liquid and solid.

2.5.2 Pressure

The pressure can be calculated with:

$$\frac{P}{k_B T \rho} = 1 - \frac{1}{3Nk_B T} \left\langle \frac{1}{2} \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r_{ij})}{\partial r} \right\rangle$$

With r_{ij} denoting the distance between particle i and j , i.e. $r_{ij} = |\mathbf{x}_j - \mathbf{x}_i|$.

3 Results

For these results, the Verlet method is used by default as this conserves the total energy and leads to more accurate results. A comparison with the Euler method is discussed in paragraph 3.5. Three sets of simulation parameters (ρ , T) have been provided which lead to the different states of matter (see Table 3). These will be used

as the default parameters for our results as they show different behaviour. Simulation evolution of these three states is shown in Figure 3.

State	ρ [n.u.]	T [n.u.]
Gas	0.3	3
Liquid	0.8	1
Solid	1.2	0.5

Table 3: Simulation parameters ρ and T in natural units for which the the resulting state of matter has been provided.

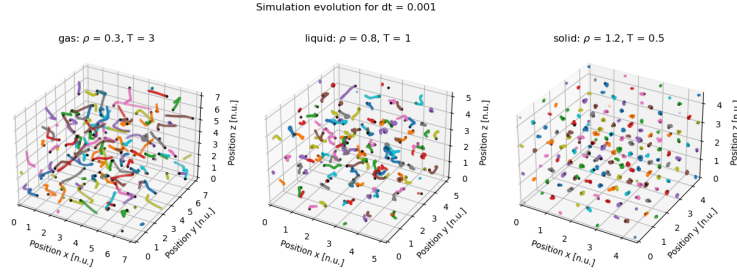


Figure 3: Last 500 steps for three states of matter of Argon.

3.1 Energy conservation

In order to achieve logical and accurate results, the total energy of the system should be conserved. After velocity relaxation, the total energy should stay constant throughout the simulation. Before rescaling the velocities, the simulation is allowed to run for X steps before the first rescaling takes place. Afterwards, Y steps are performed between each rescaling of the velocities. Theoretically, it is best to let the simulation run for as long as possible before rescaling in order to let the kinetic energy drift as much as possible. However, this makes simulations incredibly long and inefficient. During experimentation it was found that the liquid and solid phases are relatively easy to relax, with $X = 50$, $Y = 50$ being enough. However, the gas phase still drifts in this case (see Appendix Figure 12). Gas benefits from a large X and Y since the energy drifts slowly due to little interaction between particles. For $dt = 0.001$, it has been found that $X = 300$, $Y = 75$ are adequate to relax even the gas phase. The measured E_{kin} needs to be within 5% of the target energy $E_{kin-target}$ in order for the system to be "relaxed".

Figure 4 shows the evolution of the potential, kinetic and total energy of the system for the three default states. It can be seen that the total energy is virtually constant after the system is deemed relaxed. The gas phase does have slight drift, but it is deemed insignificant. The combination of the faster movement of particles in the gas phase and the very steep r^{12} term of the potential leads to the possibility of ob-

taining forces that are too high. This problem can be mitigated by decreasing dt , but this would increase the number of necessary timesteps, so it is not done.

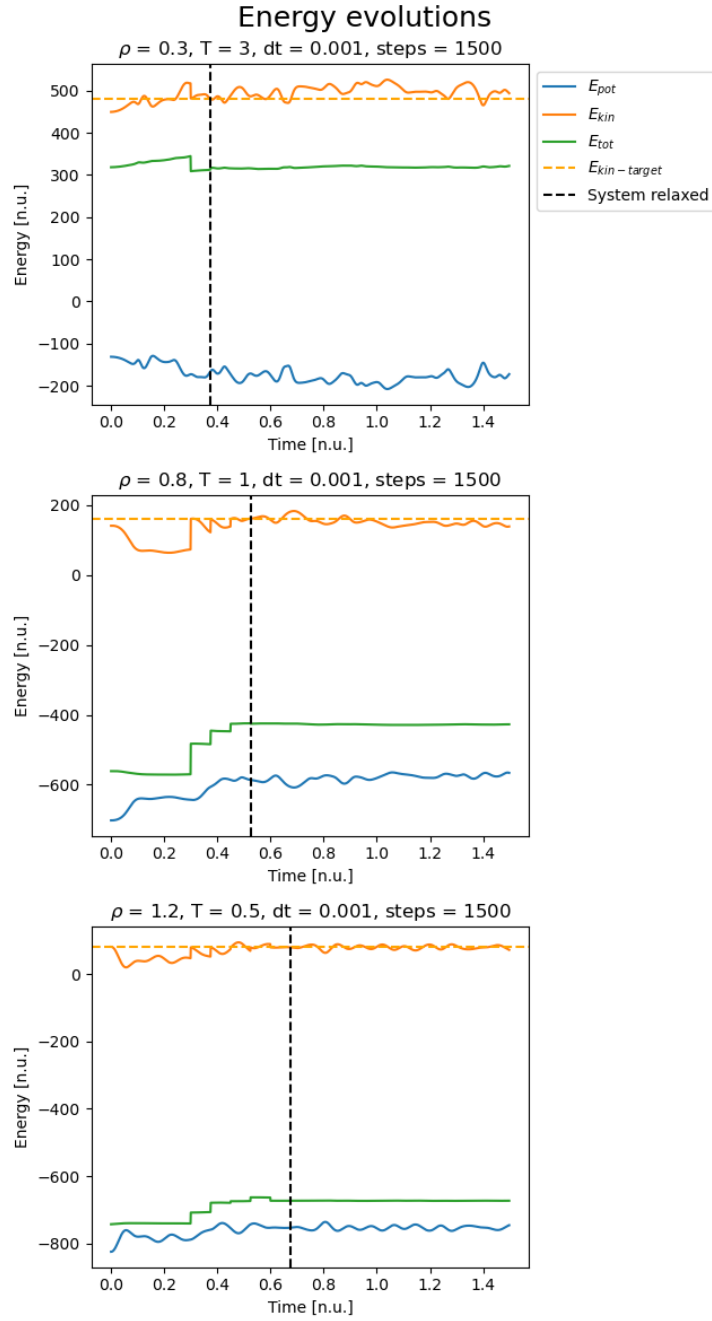


Figure 4: Energy evolution for the three default parameter sets. From top to bottom: gas, liquid, solid. Dashed black line shows the time as which the system has been deemed "relaxed". Quantities like pressure and pair-correlation are determined after this time.

3.2 Pair correlation

The pair correlation function ($g(r)$) is different for the three states of matter (see Figure 5). The solid phase has clear peaks at discrete distances which correspond to the distances between particles in an fcc lattice. The distance between unit cells is denoted a and is expressed in terms of ρ and N :

$$a = \frac{L}{3} = \frac{1}{3} \left(\frac{N}{\rho} \right)^{1/3}$$

The 4 smallest distances from Figure 2 are:

- red-cyan: $a/\sqrt{2}$
- red-green: a
- red-blue: $\sqrt{3/2}a$
- red-orange: $\sqrt{2}a$

For the default solid, with $\rho = 1.2$, we get the following distances: 1.06, 1.49, 1.84 and 2.12, which indeed matches the peaks seen in Figure 5. In the liquid phase, two peaks are seen around distances 1.1 and 2.2, which matches the minimum of the Lennard-Jones potential (and its first multiple). It seems that the liquid state forms a very loose cubic grid with a characteristic distance of 1.1. In the gas phase a single peak is present at 1.1, similar to a liquid. $g(r)$ then levels out to 1 as expected.

These three states can be discerned with the following criteria:

- Gas: 1 peak
- Liquid: 2 peaks
- Solid: ≥ 3 peaks

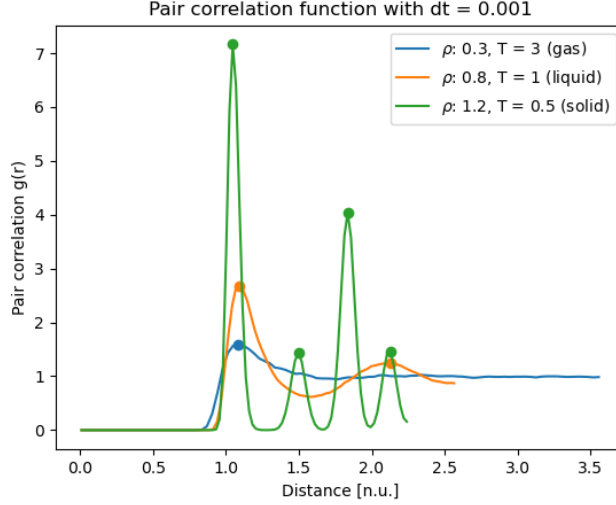


Figure 5: Pair correlation functions $g(r)$ for the three default states. Circular dots represent the identified peaks used to determine the state.

3.3 Pressure

The pressures for the systems has been determined by running 10 simulations for each state with relaxation parameters as determined previously for most accurate result. Each simulation has $dt = 0.001$ and runs for 1500 steps in total (including relaxation). Table 4 shows the pressures calculated by the simulation, both in natural units and in bar.

State	Pressure [n.u.]	Pressure [bar]
Gas	1.00 ± 0.02	4.19 ± 0.08
Liquid	0.8 ± 0.1	3.35 ± 0.42
Solid	8.68 ± 0.08	36.38 ± 0.36

Table 4: 10 sims, dt 0.001, 2000 steps, Verlet, 100 init relax, 25 relax steps

The Ideal gas law can be written as:

$$P = nk_B T \quad (4)$$

Where P is the pressure, n is the number density of the molecules and T is the temperature. The number density is the total number of molecules in a certain volume. Since $N = \frac{m}{\mu m_u}$, equation 4 can be written as

$$P = \frac{1}{V} \frac{m}{\mu m_u} k_B T = \frac{k_B}{\mu m_u} \rho T$$

Where μm_u is the mass of an Argon atom in kg and ρ is the density. If P is calculated with this equation for the input values for the gas simulation ($\rho = 0.3$, $T = 3$), a value of $P = 0.9$ (n.u.) is obtained. So, the simulation calculates a pressure that is 11% higher than the actual value. Possibly, this is due to the small peak of the gas phase at 1.2 seen in Figure 5. This small tendency of particles to cluster in the gas phase could lead to a deviation from the theoretical prediction.

In order to validate the simulation further, a few test cases have been run to compare to known literature values. The simulation is run for multiple values of T and ρ . The resulting pressure is compared to the pressure displayed in Figure 8 in a paper from A. B. Kaplun and A. B. Meshalkin [2]. In the paper, they calculate the pressure as a function of density and temperature via equations from thermodynamics.

Input ρ [kg/m ³]	Input T [K]	Output P [MPa]	Literature P [MPa]
500	300	33.60	31
500	250	27.81	26
1000	160	27.16	21
900	150	21.55	10
525	160	14.44	8

Table 5: Validation of the simulation by comparing the outputted pressure to pressure predicted by pressure. (5 Verlet simulations, $dt = 0.001$, timesteps = 1000)

Table 5 shows that simulated pressure values are quite similar to literature values when "far away" from the critical point. However, when closer to the critical point, the simulation starts predicting pressure values that are higher than the theoretical values.

3.4 Triple point of Argon

In order to find the triple point of simulated argon, a large phase space needs to be checked. At lower densities and temperatures, the simulation starts to behave weirdly:

- The system relaxes very slow, taking about 10 seconds.
- At these values, the particles tend to cluster together in parts of the simulation (this can be seen in Figure 6).

In order to obtain relaxation, dt was set to 0.01 and 2500 steps were taken. These values also reproduce the results previously obtained for the three default states, with the only difference being that the simulation looks much more chaotic.

A range of ρ and T values has been checked and the resulting state has determined. Figure 7 shows an overview of the phase space. The point $\rho = 0.16 \pm 0.03$, $T = 0.8 \pm 0.1$ is taken to be the triple point. Error margins are taken to be half the distance between the grid points. The pressure at this point is 0.21 ± 0.01 [n.u.].

The actual triple point of Argon is at 83K, 69[3] kPa and corresponds to a lattice constant a of 546 pm[1]. The triple point found with the simulation has values (in SI

Simulation evolution for $dt = 0.01$
liquid: $\rho = 0.16$, $T = 0.8$

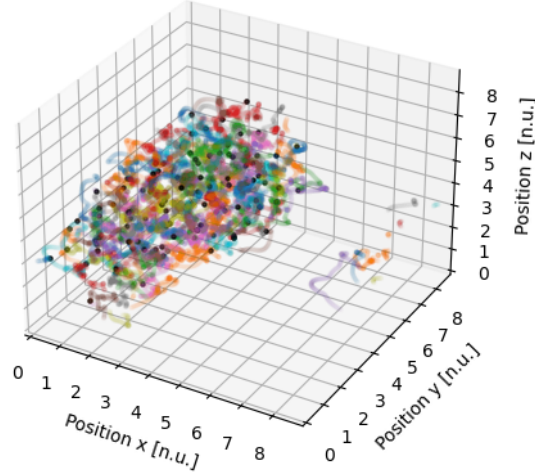


Figure 6: Simulation evolution at the found triple point.

units): $T = 1.0 \pm 0.1 \times 10^2$, $a = 995^{+72}_{-55}$ and a pressure of 8.7 ± 0.4 kPa (the latter is totally off).

The likely reason for the discrepancy between the true triple point and the triple point we have found is the method of determining the state. Simply counting peaks works well for clearly distinct states where the structures differ. But near the triple point, $g(r)$ becomes a blend of multiple states as seen in Figure 8 and it's not immediately clear whether this is a liquid or a solid. A different method of determining the state, like taking the distance between peaks into account, would likely improve the triple point.

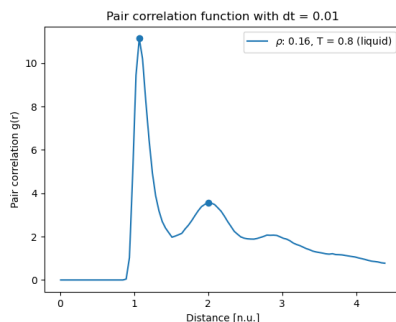


Figure 8: The pair correlation function $g(r)$ for the triple point found ($\rho = 0.16, T = 0.8$).

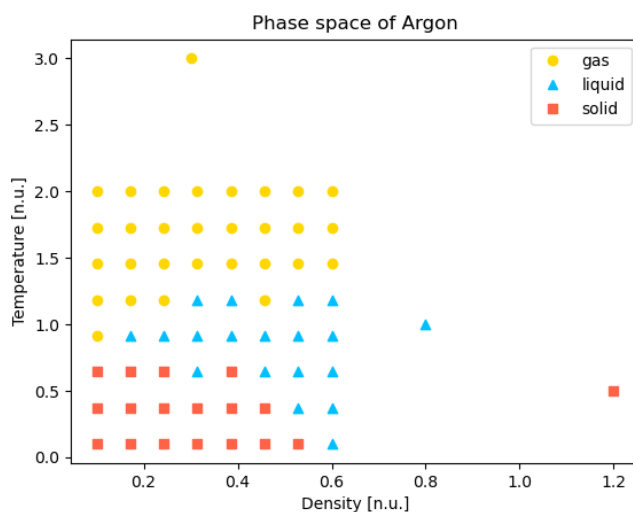


Figure 7: The state of argon as a function of density ρ and temperature T in natural units. $dt = 0.01$, 2500 steps. $\rho = 0.16 \pm 0.06$, $T = 0.8 \pm 0.2$ is taken to be the triple point (second column, 4th row)

3.5 Euler vs Verlet

The Euler method does not generally conserve energy, especially when compared to the Verlet method, see in Figure ???. This refusal to properly "relax" and conserve energy affects the measured pressure of the system. Table 6 shows that all pressures are higher than expected. Decreasing dt generally increases accuracy of the simulation, as a smaller dt is less prone to produce large forces that are unrealistic. This

results in the dt of the Euler-simulation having to be much smaller to get accurate pressure results. This in turn will cause the program to run much longer, which is generally not considered optimal.

State	Pressure [n.u.]
Gas	1.10 +/- 0.02
Liquid	1.4 +/- 0.1
Solid	11.0 +/- 0.2

Table 6: 10 sims, dt 0.001, 2000 steps, Euler

Figure ?? shows the pair correlation in the gas and solid phase obtained from the simulation utilising the Euler method. For the atoms in the gas phase, it can be seen that the particles are not uniformly distributed, there seems to be a large peak at $r \approx 1$ (n.u.). This (as well as the pair correlation for the atoms in solid phase) seems to resemble the pair distribution function of gas obtained with the Verlet method. This means that the structure of molecules gets predicted to acceptable extend with the Euler method.

However, there is no advantage to using the Euler method as it is not faster than the Verlet method, and yields less accurate results.

4 Summary

A molecular dynamics simulation of Argon has been created using periodic boundaries and an initial fcc lattice with 108 atoms. Two methods were used to evolve the system: Euler and Verlet. The Verlet method is preferred as it conserves total energy. Particles are initially placed in a fcc lattice with velocities drawn from a Gaussian distribution so that the total kinetic energy matches the expected value. The system is allowed to run and then forced into equilibrium by repeatedly rescaling velocities to keep the kinetic energy at the desired value.

The pair correlation is plotted in Figure 5 and match up well with theory. The calculated pressures match up quite well with hydrodynamic equations. However, when approaching the critical point between gas and liquid, the simulated values start to deviate more. The triple point has been identified at $\rho = 0.16 \pm 0.03$, $T = 0.8 \pm 0.1$, but this does not fully line up with theory.

The Euler method does not inherently conserve total energy, and so yields inaccurate pressure results. However, the pair-correlation function does resemble the Verlet results.

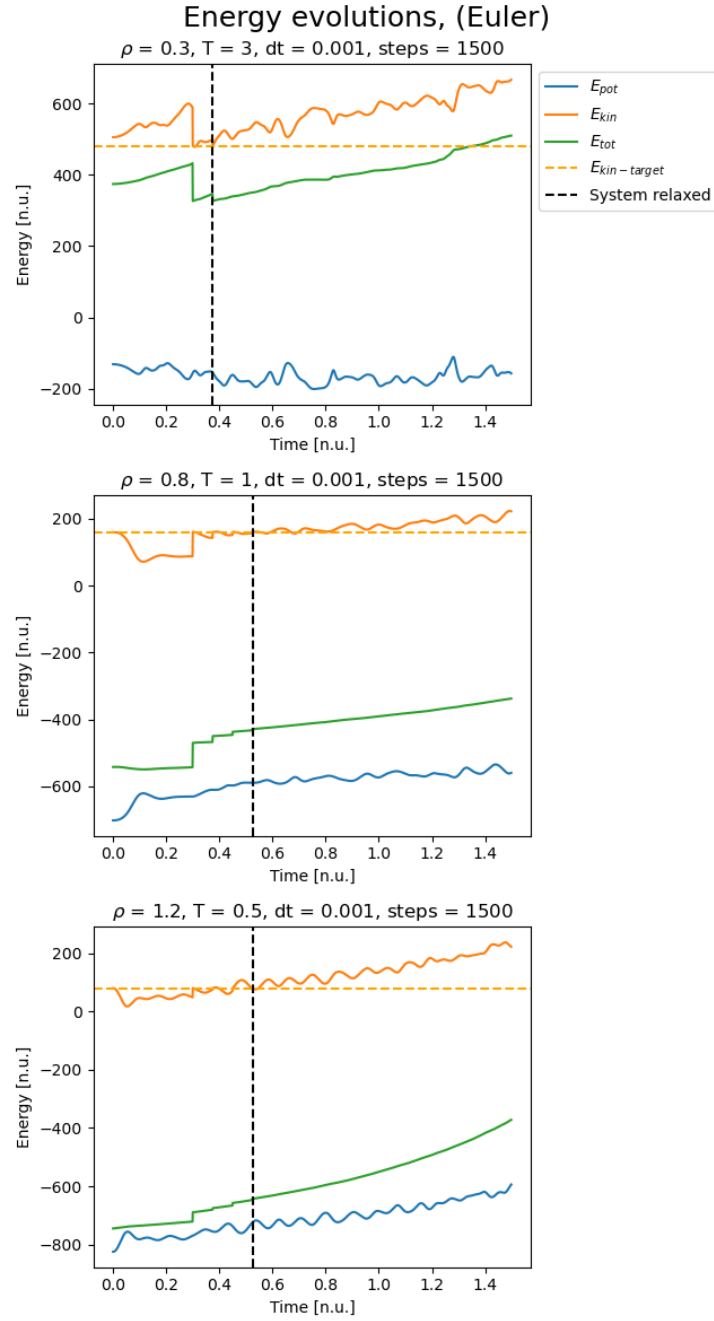


Figure 9: The energy plots for the simulation utilising the Euler method. The top plot shows the energies for the atoms in the gas phase, the middle plot in the liquid phase and the bottom plot in the solid phase.

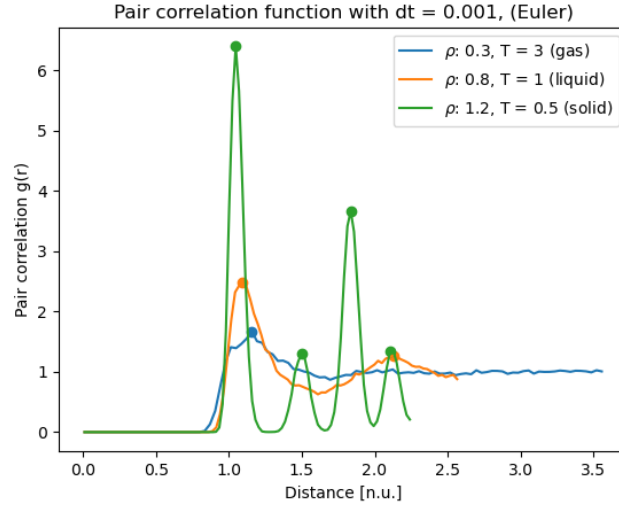


Figure 10: Pair correlation function for the gas (upper plot) and solid (lower plot) simulation. (Euler method, 1 simulation, $dt = 0.001$, 2500 timesteps)

5 Appendix

Simulation evolution for $dt = 0.01$
liquid: $\rho = 0.16, T = 0.8$

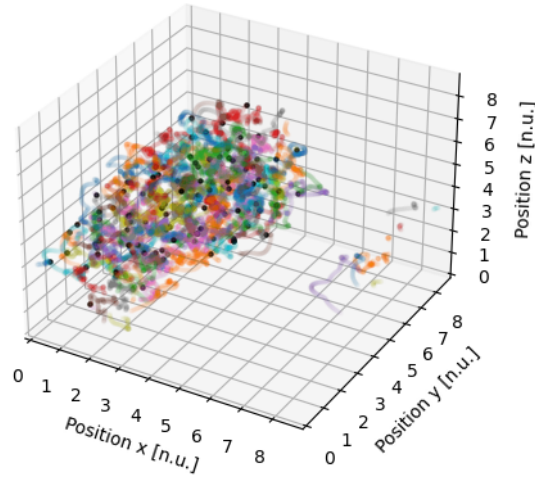


Figure 11: Positions around

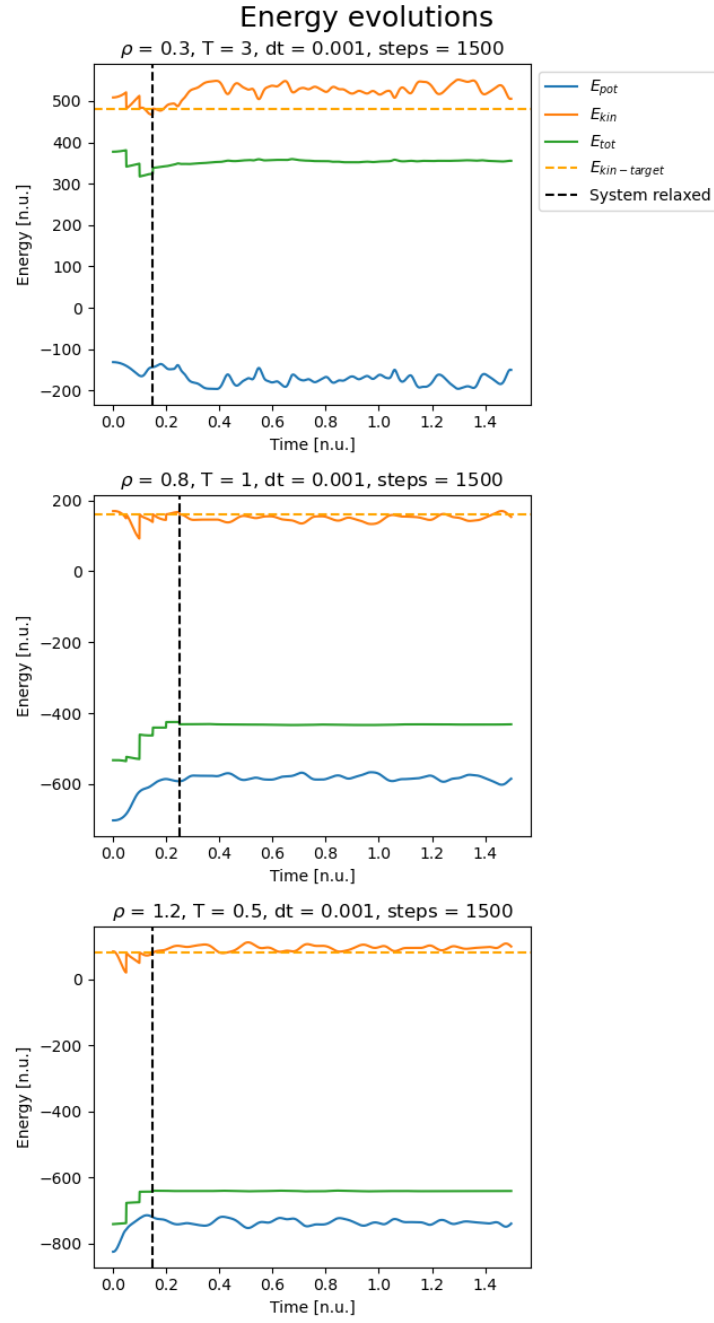


Figure 12: Energy evolution for $X = 50, Y = 50$

References

- [1] John W Arblaster. *Selected values of the crystallographic properties of elements*. ASM International, 2018.
- [2] Alexandr Borisovich Kaplun and Arkadiy Borisovich Meshalkin. Thermodynamic validation of the form of unified equation of state for liquid and gas. *High Temperature*, 41(3):319–326, 2003.
- [3] David R Lide. *CRC handbook of chemistry and physics*, volume 85. CRC press, 2004.
- [4] Aneesur Rahman. Correlations in the motion of atoms in liquid argon. *Physical review*, 136(2A):A405, 1964.
- [5] TimeStep89. Graph of the lennard-jones potential: interaction energy as a function of the particle distance. https://commons.wikimedia.org/wiki/File:Graph_of_Lennard-Jones_potential.png, 2020.