Molecular Dynamics Simulation of Argon atoms

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Molecular dynamics simulation of Argon atoms is presented. Natural units and dimensionless calculation are implemented to obtain high approximate solutions. The evolution of the system in time is simulated using both Euler and Verlet methods. Using the results, observables such as pair correlation, specific heat, compressibility factor are calculated and compared to known values. The specific heat calculated was found to be $C_v = 0.41 \pm 2.75e^{-7}[J/kgK]$.

1 Introduction

Numerical dynamics of molecules are intensively studied to describe physical phenomena. Such phenomena are phase transitions, specific heat, pressure and pair correlation. Due to computational methods, one can observe the interaction between the particles and how they evolve in time. Phase transition can also be observed as the intensive variables of the system do change over time. At first, the Lennard-Jones potential is used for the potential energy. The reason for this potential is due to the minimal presence of quantum effects. The atoms used in this project are Argon atoms, since there have been numerous of studies and numerical results in order to compare the data with the literature.

2 Theory

2.1 Interactions of Argon Atoms

In order to simulate the phase transition of an Argon gas, it is crucial to study how single atoms interact with one another due the Lennard-Jones potential. As known, the Argon atom have a neutral charge density, which implies that there is no net force as a result of the coulomb interaction. This results in a displacement between the nucleus and the electrons, which gives rise to a small dipole moment. Both attraction and repulsing forces can be modelled with the Lennard-Jones potential:

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

where ϵ is the depth of the well, σ is the finite distance at which the inter-particle potential is zero, and r is the relative distance between two neighbouring atoms. Observe that the minus sign in front of the power r^{-6} is due to an attraction and the positive term is the repulsive term.

The numerical values of the relevant constants are given in SI units in the following table:

Table 1: *Numerical values for the relevant constants.*

Symbol	Value
k_B	$1,38 * 10^{-23}$ j
ϵ	$1.65 * 10^{-21}$ j
σ	$3.41 * 10^{-10}$ m
M_{Argon}	$6.68 * 10^{-26}$ kg

2.2 Dimensionless calculations

Because the constants are extremely small, the usage of SI units in the simulations will cause more errors during computation. It is convenient to introduce another set of units which will decrease the round-off errors and resulting in higher accuracy of numerical data. This requires to rewrite the expression for the Lennard-Jones potential in order to obtain natural units. This can be done by dividing $U(r)$ by ϵ, note

that ϵ has dimensions of energy so such transformation $\tilde{U} = \frac{U}{\epsilon}$ will indeed make the expression dimensionless. The same can be done the the distances by defining $\tilde{r} = \frac{r}{\sigma}$. The new expression for the potential then becomes

$$\tilde{U}(\tilde{r}) = \frac{U(\tilde{r})}{\epsilon} = 4(\tilde{r}^{-12} - \tilde{r}^{-6}). \qquad (2)$$

Once the expression for the potential is obtained in natural units, the equation of motion for each individual atom can be calculated using Newton's seconds law.

$$m\frac{d^2\vec{r_i}}{dt^2} = \sum_{i,j} \vec{F}(\vec{r_{ij}}) = -\nabla U(\vec{r}) \qquad (3)$$

where $\vec{r_i}$ is the position of the ith atom and $\vec{r_{ij}}$ is the relative distance between two atoms.
the gradient can be calculated as follows:

$$\nabla U(\vec{r}) = \frac{dU}{d\tilde{r}}\frac{\vec{\tilde{r}}}{\tilde{r}} = \left(-48\tilde{r}^{-14} + 24\tilde{r}^{-8} \right)\vec{\tilde{r}_{ij}}. \qquad (4)$$

Substituting 4 in 3 yields

$$m\frac{d^2\vec{r_i}}{dt^2} = \left(-48\tilde{r}^{-14} + 24\tilde{r}^{-8} \right)\vec{\tilde{r}_{ij}}. \qquad (5)$$

With this result, the motion of atoms can be calculated. In order to obtain a numerical solution two approximation methods will be used in this project. The Euler method and the Verlet algorithm.

There are several advantages of using dimensionless units. First, it speeds up the calculations and it can be easily checked what parameters contributes more or less to the outcomes. The same analogy is used to obtain time t and temperature T parameters:

$$t = \sqrt{\frac{m\sigma^2}{\epsilon}}\tilde{t} \qquad (6)$$

$$T = 119.8\tilde{T} \qquad (7)$$

2.3 Specific Heat

Since the total energy is fixed (micro canonical ensemble), the heat capacity can not be calculated from the fluctuations of the total energy values. However, since the kinetic energy fluctuates and does not have a constant value, the specific heat can be calculated.

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{\langle K^2 \rangle - \langle K \rangle^2}{\langle K \rangle^2} = \frac{2}{3N}(1 - \frac{3N}{2C_v}) \qquad (8)$$

where $\langle \delta K^2 \rangle$ is the fluctuation of the kinetic energy. This formulation was derived by Lebowitz [1] and in their paper they also derived an expression for the interaction part of the specific heat C^i, which will be used to compare the results of the simulation.

$$C^i = \frac{2}{3}C_v\frac{\beta^2}{N}(\langle \Phi^2 \rangle - \langle \Phi \rangle^2) \qquad (9)$$

Where Φ is the potential energy, $\beta = 1/k_bT$ and N total number of particles.

2.4 Virial theorem

Considering microscopic objects in our system, it does not seem obvious how to calculate quantities which contributes to macroscopic models. It is possible to calculate the pressure for our system consisting of atom using virial theorem, derived by Verlet [3].

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N}\left\langle \frac{1}{2}\sum_{i,j} r_{ij}\frac{\partial U}{\partial r_{ij}} \right\rangle. \qquad (10)$$

Where ρ is the density and r_{ij} the distance between particles

2.5 Pair Correlation Function

The pair correlation function allows systems with large objects to calculate the the probability of finding such system at a given location. It describes the density as a function of position for the whole system.

$$g(r) = \frac{2V\langle n(r) \rangle}{N(N-1)4\pi r^2\Delta r} \qquad (11)$$

The function takes different forms for different phase systems. Therefore this is a good measure to find the phase of the system. In solids there will be peaks at regular intervals due to the periodic structure of a solid lattice. In gas there is not much of a structure as the particle are more free to move about, making the function more smeared out. In liquids there is also not a regular structure of the particles especially in the long distances, therefore the function will have some peaks but not at regular intervals.

3 Computational method

It is not possible to simulate uncountably many Argon atoms. Since the simulation has finite dimensions, periodic boundary conditions are implemented. A finite box of length L is created, in which the atoms move according to the Lennard-Jones potential. The conditions then implies, that if a particle leaves the box at some coordinate, it re-enters on the opposite boundary with the same velocity. In a sense one has the original box of size L, and pastes additional images around that box, illustrated in Figure 1. The only interaction is the one between the closest neighbouring atoms, but now one has to take into account these images of the atoms as well.
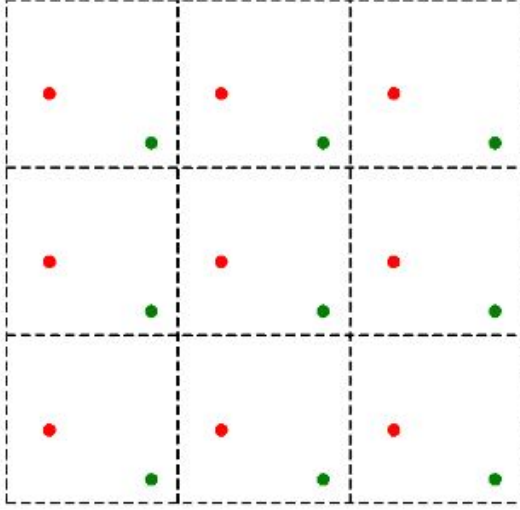
Figure 1: *Boundary conditions for the system. Observe that the closest particle might not be in the box.*

The initial state of the Argon atoms should distributed in a FCC lattice. Once the particles are distributed over the box, the next step is to assign initial velocities to each particles. This is done by using a Gaussian distribution with $\mu = 0$ and $\sigma = \sqrt{T}$. At this stage, all necessary information is known since the position and momenta vectors are calculated. The next step is to study how the system will evolve in time and what computational methods will be used to obtain correct values.

3.1 Euler method

Computational models are based on discrete input values, therefore the time evolution of the system will be a discrete approximation. Time steps for all particles are stored an an array and the Euler method is being applied on such array.

$$\vec{x}(t + h) = \vec{x}(t) + h\vec{v(t)} \qquad (12)$$

$$\vec{v}(t + h) = \vec{v}(t) + \frac{h}{m}\vec{F}(\vec{x}(t)) \qquad (13)$$

where $x(t))$ and $v(t)$ are the displacement and the velocity respectively. The accuracy of this method depends on the time step h which is a small but non vanishing constant. Using this method does not conserve the energy.

3.2 Verlet algorithm

A more accurate calculation is the Verlet method which takes a second Taylor order term into account around $t \pm h$.

$$\vec{x}(t + h) = \vec{x}(t) + h\vec{v(t)} + \frac{h^2}{2m}\vec{F}(\vec{x}(t)) \qquad (14)$$

$$\vec{v}(t + h) = \vec{v}(t) + \frac{h}{2m}\vec{F}(\vec{x}(t)) + \vec{F}(\vec{x}(t + h)) \qquad (15)$$

Using this method energy will be conserved and the approximation is higher since and an extra higher order term is added in addition to the linear differential stated in Euler's equations.

3.3 Velocities and temperature

When evaluating the velocities, fluctuations in kinetic energy should be avoided. Form equipartition theorem, kinetic energy and temperature are correlated at in the high temperature limit (classical limit).

$$U_{kin} = \frac{3}{2}(N - 1)k_B T \qquad (16)$$

The amount of energy in a system is equal to the degrees of freedom of all individual particles of the system. Since the variables are chosen to be unitless, we obtain for the rescaling velocity factor:

$$\lambda = \sqrt{\frac{3(N - 1)k_B T}{m \sum_i^N \|\vec{v_i}\|^2}} \qquad (17)$$

This factor results in a stable system and convergence of the temperature.

3.4 Block bootstrap

Running the simulation multiple times, will result in different expectation values. Since the molecular dynamics are not statistically independent, the fluctuations can not be calculated. Bootstrap method is used by taking N random points from the generated data and then computing the expectation value. Repeating this process n times will allow to calculate the variance for correlated data.

$$\sigma_A = \sqrt{\langle A^2 \rangle + \langle A \rangle^2} \qquad (18)$$

4 Results and Discussion

In this section the results from the simulations will be presented and discussed. The physical correctness of the simulation will be discussed in Section 4.1. Some observable, including the specific heat and compressibility, have been calculated from the simulations, these will be compared to values found in literature and discussed in Section 4.2. The performance will also be briefly discussed in Section 4.3.

4.1 Physical Correctness

For the simulation to make sense, it has to follow the laws of physics. One way to verify this, is to look at the energy of the system. From statistical physics it is known that microcanonical ensemble have to conserve the total energy. Which means that the sum of the kinetic and potential energy should remain constant over time.
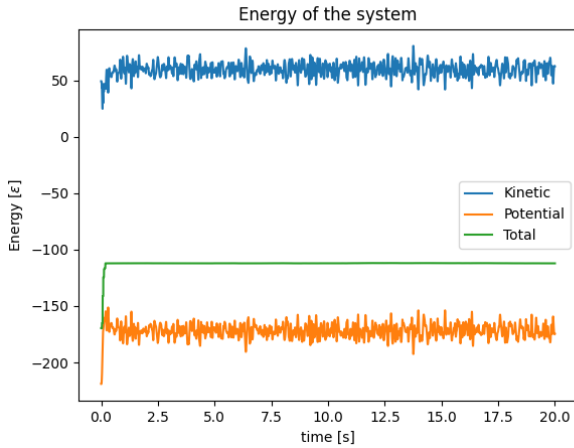

Figure 2: *The kinetic, potential and total energy of the system plotted over time. The energies are in units of ϵ. This is from a simulation with simulation parameters $\rho = 1$ and $T = 1$.*

From Figure 2 energies plotted over time can be seen. I shows that the kinetic and potential energy of the system fluctuate however the total energy remains constant over time which. At the beginning there is a spike of the total energy, this is because of the velocity rescaling, this is to ensure the simulation settles on the desired temperature. After this initialization phase the total energy remains constant over time.

4.2 Observables

To connect the simulation with real world properties of Argon, some observables have been calculated. This is again to verify the simulation. The observables that have been calculated and that will be discussed are the pair correlation function, the compressibillity and the specific heat.

4.2.1 Pair Correlation Function

One of the objectives of this paper was to study the phase transitions of the argon atoms. A good measure of this is the radial distribution function or pair correlation function. In essence this function gives the probability of finding a particle at a distance r from a reference particle.
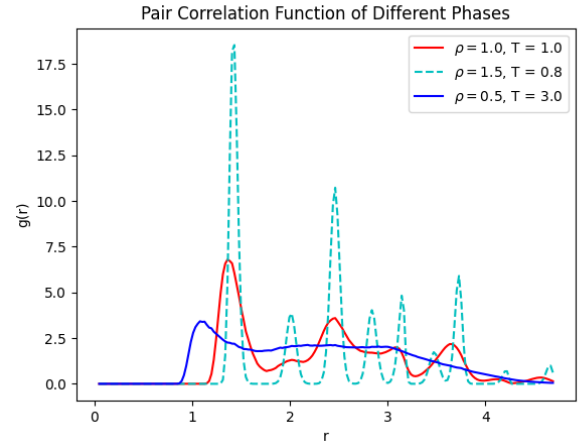

Figure 3: *Pair correlation function g(r) plotted for different temperatures and densities with number of particles $N_{particle} = 108$. The red line corresponds to a liquid Phase, the cyan dashed line a solid phase and the blue line a gas phase.*

In Figure 3 a clear distinctions between the phases of matter of argon is seen. When the density is taken to be large, which means that the atoms are quite tightly packed one would expect the material to be a Solid. Indeed in the dashed cyan line which corresponds to $\rho = 1.5$ and $T = 0.8$ it is noticed that the atoms are found at regular intervals. This is in correspondence with solids which have a regular and periodic structure. The atoms only move about their lattice positions, so they would have a high probability to be found at those positions. The gas phase, does not have a regular structure. This can be seen in the pair correlation function as not peaking at certain values but rather being smeared out. In Figure 3 this is phase would be the blue line. Liquid phases do not maintain a constant structure either especially in the long range, this is seen in the pair correlation function as their being a peak in the beginning and the subsequent peaks being more smeared out and at non regular intervals. This correspond to the red line in Figure 3.

4.2.2 Compressibility

Another observable which was looked at is the pressure, or rather the compressibility of the system. This quantity is calculated multiple time for different densities and temperatures. The values obtained were then compared to the Verlet paper [3]. This is shown in the following Figure.

From Figure 4, it can be seen that there is quite a good correspondence between the simulations done in this paper and the Verlet paper. I can be noted that overall the values obtained are higher than the values from Verlet. This might be because they have an extra correction term when calculating the compressibility, which takes into account the pressure of the tail of the
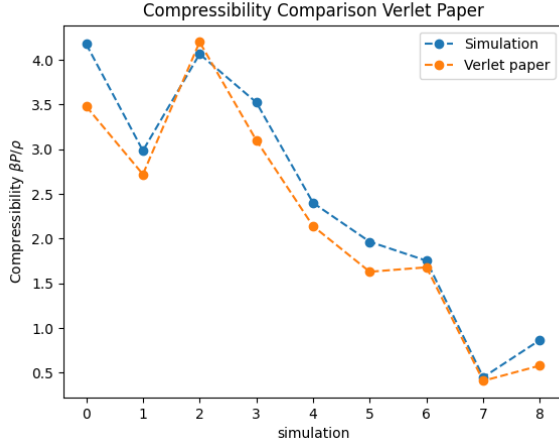
Figure 4: *A comparison between the compressibility values obtained from the simulations and the values in the Verlet paper. The simulations were done for different densities and temperatures, the table with the errors are in the appendix A.*

Figure 5: *The values for the interaction part of the specific obtained from the simulations plotted with the values from the Lebowitz paper. The full values of the simulation parameters rho and T are given in the appendix A.*

potential. This term has been not accounted for in the simulations of this paper

4.2.3 Specific Heat

The specific heat of the system was also calculated. This was done with the kinetic energy and the formula discussed in the methods section. By running the simulation, a specific heat of $C_v = 1.96$ with and error of 2.75e-7 is obtained. These values are with simulation parameters $\rho = 1$ and $T = 1$. The value is in dimensionless units, in order to go back to SI units, just multiply by k_b and divide by the mass. This gives a specific heat of $C_v = 0.41 \pm 2.75e^{-7}[J/kgK]$. The value for the specific heat of Argon in literature is $C_v = 0.312[J/kgK]$ [2] at constant volume. Which is in reasonable agreement with the values obtained in this paper.

To further research the specific heat further a comparison has been made to the Lebowitz Paper [1] where, they look at the interaction part of the specific heat C^i. In Figure 5 this comparison is shown.

The values obtained from the simulations in this paper match the values from Lebowitz quite well. These values however do depend on the number of time steps the simulation takes. It was noticed that for small number of time steps the values were matched more poorly to the values from Lebowitz than a large number of time steps .

4.3 Performance

The performance of the code is an important aspect. Even with periodic boundaries the number of atoms to be simulated can reach to high numbers and therefore slowing the simulation time down. When writing the
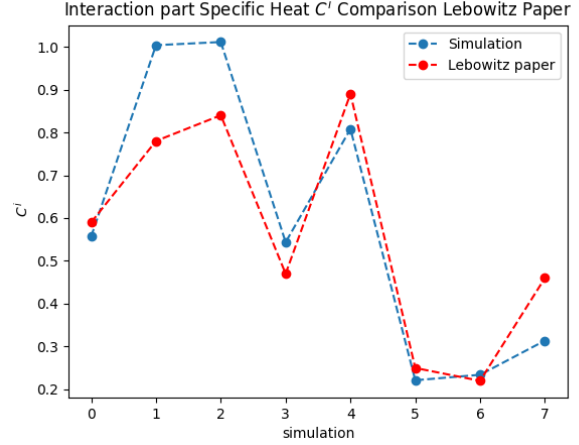
code, the number of for loops used had to be minimised. Instead numpy arrays were used to help speed up the simulation. Most notably, when calculating the forces of the particles and putting the atoms in the FCC lattice no for loop has been used . To see how to code reacts to number of particles the time needed has been recorded. This is shown in the Table below

Table 2: *The time it took for the simulation to complete for a certain amount of particles*

Number of particles	Time elapsed (s)
32	11.47
108	80.21
256	459.79

Since the atoms are in an FCC lattice the number of particles in the system depends on the unitcell. That is why these values for the number of particles have been chosen.

5 Conclusion

The molecular dynamics of Argon has been simulated and discussed in the previous sections. First the physical correctness has been studied. This was done by looking at the energy plotted over time. The total energy should remain constant to have conservation of energy. This is the case in Figure 2, which gives validation for the simulation concerning the energy conservation law. Trough this simulation the phase of Argon can be obtained. The pair correlation function that it calculates tells in what phase the argon is, shown in Figure 3. For a solid phase, the function will have peaks at regular intervals. For a gas phase, the function

will be smeared out. For a liquid phase, the function will have some peaks but not at regular intervals and more smeared out.

To link the simulation with real data, some observables were calculated. It was found for that the compressibilty was correctly obtained, this was verified by comparing the values obtained to the Verlet paper. The result of this comparison is seen in Figure 4. The specific heat was obtained to be $C_v = 1.96 \pm 2.75e^{-7}$ in dimensionless units. In SI units it was found to be $C_v = 0.41 \pm 2.75e^{-7}[J/kgK]$, which was compared to the value found in literature $C_v = 0.312[J/kgK]$. To further investigate the specific heat a comparison was made with the Lebowitz paper Figure 5. It was found that the interaction part of the specific heat that was obtained from the simulation matches the values from the paper. The performance was measured as the time needed to complete the simulation depending on the number of particles.

Bibliography

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[3] Loup Verlet. "Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules". In: *Phys. Rev.* 159 (1 July 1967), pp. 98–103. DOI: 10.1103/PhysRev.159.98. URL: https://link.aps.org/doi/10.1103/PhysRev.159.98.

A   Appendix A

Table 3: *List of the results for the compressibility $\beta P/\rho$ and the error of the simulations. The simulations were done for density ρ and temperature T according to the Verlet paper. The results of the Verlet paper are also presented here*

n	ρ	T	our $\beta P/\rho$	verlet $\beta P/\rho$	error $\beta P/\rho$
1	0.88	1.095	4.17	3.48	0.02
2	0.88	0.940	2.98	2.72	0.03
3	0.85	2.889	4.07	4.20	0.01
4	0.75	2.849	3.52	3.10	0.01
5	0.65	2.557	2.40	2.14	0.01
6	0.55	2.645	1.96	1.63	0.01
7	0.45	4.625	1.75	1.68	0.01
8	0.40	1.562	0.45	0.41	0.01
9	0.35	1.620	0.87	0.58	0.01

Table 4: *The values obtained for the interaction specific heat C^i for different densities and temperatures. These values have an accompanied error. The values from Lebowitz are included for comparison*

n	ρ	T	our C^i	Lebowitz C^i	error C^i 10^{-7}
1	0.85	2.89	0.56	0.59	5.1
2	0.85	2.20	1.00	0.78	7.2
3	0.85	1.21	1.01	0.84	6.5
4	0.75	2.84	0.54	0.47	4.7
5	0.75	0.827	0.80	0.89	6.4
6	0.45	4.62	0.22	0.25	3.1
7	0.45	2.93	0.23	0.22	2.4
8	0.45	1.71	0.31	0.46	2.9