The heat capacity, pressure, correlation function and diffusion constant of Argon using a molecular dynamics simulation

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Abstract

A molecular dynamics simulation of an Argon gas in a cubic box with periodic boundary conditions is presented. The Argon atoms are initialized in the ground state for $T = 0$ and the initial velocities are generated from the Maxwell distribution. Using the velocity Verlet algorithm, the time evolution of the Argon gas is computed and various physical quantities (heat capacity, pressure, correlation function and the diffusion constant) are studied as a function of the temperature and density.

1 Introduction

Due to a large number of particles it is often not practical to study many-body systems analytically. Molecular dynamics is a technique to study classical many-body systems [1]. By numerically integrating Newton's equation of motion, the behavior of the system as it moves around in phase space can be studied. Drawbacks are that due to the scaling of the interactions between the particles the simulation is computationally intensive for a large number of particles. An advantage is that it is also possible to investigate non equilibrium behavior, such as relaxation times, by initialising the system far from equilibrium.

A molecular dynamics simulation of Argon is often used as a reference model for other substances. Argon has no electrical multipole moments making it relatively simple to model the interaction.

In his famous 1967 paper, Loup Verlet [2] presented "computer experiments" simulating the motion of 864 interacting Argon atoms. The quadratic scaling of interaction pairs and the large amount of data the simulation produces makes it an excellent candidate to explore the different aspects of the field of computational physics. The system comprises of 864 Argon atom, enclosed in a cube of length L with periodic boundary conditions. The Argon atoms are represented as point particles interacting only pairwise via the Lennard-Jones potential.

2 Theoretical model

The system consists of a cubic box, containing 864 Argon atoms. We assume periodic boundary conditions, meaning when a particle moves past a boundary, the box size is added/subtracted to/from the relevant coordinate of the particle (i.e. what goes out at one end, comes in at the other). When considering the distances between two particles, the minimum image convention [1] is used. The Argon atoms interact via the Lennard-Jones potential.

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

This potential has a minimum of $-\epsilon$ at $r = 2^{1/6}\sigma$ and crosses zero at $r = \sigma$. The optimal values for ϵ/k_B and σ are in the case of Argon atoms 119.8 and $3.405 \mathring{A}$ respectively. The repulsive part of the potential models the Pauli exclusion principle and the attractive part models the dipole-dipole interaction due to electron dispersion. The system is initialized in the ground state for $T = 0$, which corresponds to a fcc lattice. The reason for this decision is that randomly generating the positions could result in a situation where two or more particles have almost the same position resulting in a very large energy. The temperature of the system after a few time steps would then be very far from the temperature the system was initialised in. The velocities are generated from the Maxwell distribution by drawing each component of
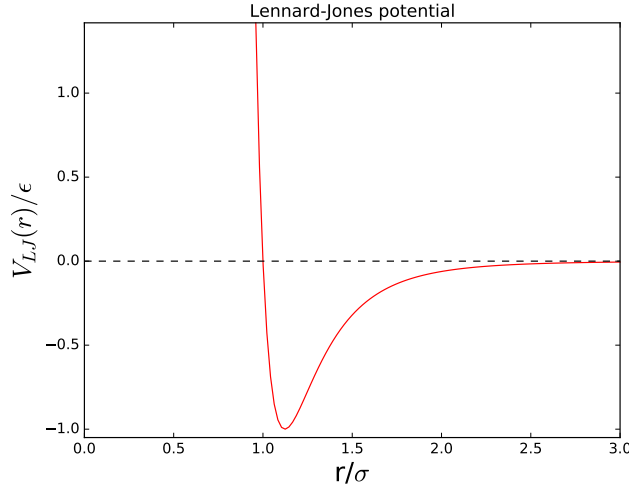
Figure 1: The Lennard-Jones potential plotted in dimensionless units.

the velocity from a Gaussian distribution.

$$f(v_i) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(\frac{-mv_i^2}{2k_B T}\right) \qquad (2)$$

Once the coordinates and momenta have been initialized, the time evolution of the system is evaluated using the velocity-Verlet algorithm, resulting in a local numerical error of $\mathcal{O}(h^3)$, where h is the timestep of the simulation. Physical quantities in this paper are calculated either in the microcanonical (specific heat-capacity) or the canonical ensemble (pressure, diffusion coefficient and correlation function). In order to a get a system in the canonical ensemble, one can rescale the momenta such that the system stays close to the desired temperature. As the initialized system is usually not in equilibrium, it is important to first let the system reach equilibrium before physical quantities are computed. In order to determine if the system has reached equilibrium changes in the kinetic energy are monitored for the microcanonical ensemble and changes in the total energy are monitored for the canonical ensemble. In an effort to cut down computing time, one can define a cut-off range r_c such that for particles with distance greater than this r_c their influence on each other is negligible, and thus not computing the forces decreasing computation cost.

The heat capacity is calculated in the microcanonical ensemble using the Lebowitz formula.

$$\frac{C_v}{N} = \frac{3k_B < K >^2}{2 < K >^2 - 3N < \delta K^2 >} \qquad (3)$$

In this formula $\langle K \rangle$ is the total kinetic energy of the system and $\langle \delta K^2 \rangle$ is the variance of this energy.

The virial theorem is used to calculate the pressure of the system. Due to the cut-off distance– which in case none is explicitly implemented, is equal to the maximum possible distance between particles in the system – we must compensate by adding an integral over the rest of space.

$$\frac{P}{nk_B T} = 1 - \frac{1}{3Nk_B T} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{\partial U}{\partial r_{ij}} \right\rangle_{r_c} - \frac{2\pi N}{3k_B TV} \int_{r_c}^{\infty} \frac{\partial U}{\partial r} g(r) dr \qquad (4)$$

In the integral in the equation above the correlation is approximated by it's asymptotic value, $g(r) = 1$ for large r. Consequently the integral can be evaluated analytically.

The correlation function gives information about the average distance between the particles.

$$g(r) = \frac{2V}{N(N-1)} \left[\frac{< n(r) >}{4\pi r^2 \Delta r}\right] \qquad (5)$$

In this equation $n(r)$ gives the number of particle pairs with separation within range $[r, r + \Delta r]$.

When the system has reached equilibrium, at a certain time step the positions of the particles are taken as the initial positions for which the displacement for each particle for future times is computed. These displacements are averaged over all the particles and can then be plotted as a function of time. For a free particle, a constant velocity implies that the mean squared distance $\langle x^2 \rangle$ is proportional to t^2. In the gas phase the particles behave approximately as free particles for short times because the interaction is weak for a low density. For large times the particles in the gas phase will have interacted and the system is in the diffusive regime, it is expected that diffusion occurs in a linear fashion, in particular: $\langle x^2 \rangle = 6Dt$. Thus for the gas phase, the squared distance is expected to behave quadratically in time for short times and after some time linearly. A fluid should show diffusive behavior from the start because the higher density leads

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to significant interaction meaning that the particles never behave as free particles. In the solid phase, we expect no diffusion to occur whatsoever, as the Argon atoms should have no net displacement, but instead just vibrate around their equilibrium positions.

3   Results

All physical quantities are calculated in reduced units. The Argon mass is chosen as the unit mass, σ as the unit distance and $\tau = \left(m\sigma^2 / \epsilon \right)^{1/2}$ as the unit time. Further the computation of the physical quantities is delayed until the system is in equilibrium. A time step of $h = 0.004$ is determined to be a good balance between computational efficiency and errors and this timestep is used for the computation of all the physical quantities. A larger time step leads to instability due to the fact that a particle can 'jump' over the minimum of the Lennard-Jones potential in one time step.

Several values of the density and temperature have been selected and the corresponding phase and physical quantities with errors are shown in table 1.
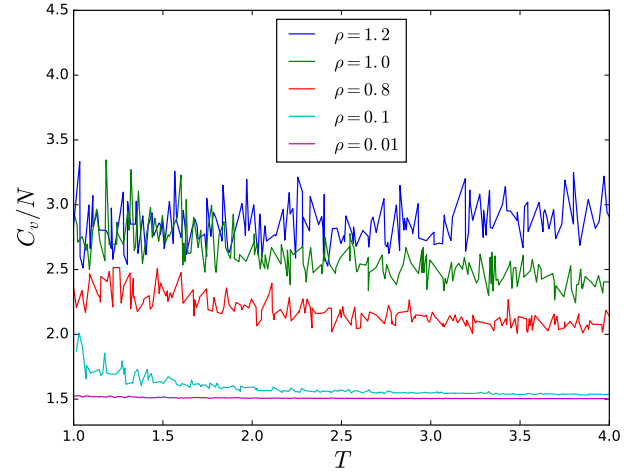

Figure 2: The intensive specific heat capacity is plotted as a function of temperature. Data with uncertainty of measured C_v larger than 0.3 and error in temperature larger than 0.005 have been left out. Upper bound of the errors from $\rho = 0.01$ to 1.2 respectively: 0.3, 0.3, 0.2, 0.2, 0.008

ρ	T	phase	C_v/N	P	D
0.01	3	gas	1.5052(1)	0.9988(2)	32.6(9)
0.3	3	gas	1.645(2)	1.113(5)	1.119(2)
0.8	1	liquid	2.41(7)	1.26(3)	0.0679(5)
1.2	0.5	solid	2.99(3)	25.498(2)	–

Table 1: The table shows the physical quantities including errors for a selection of densities and temperatures. Errors in the temperature are of order 1/10000 for the simulations done in the canonical ensemble.

The heat capacity is calculated in the microcanonical ensemble using the Lebowitz formula. Initially the velocities are rescaled so that the temperature of the system will start to fluctuate around some set temperature once the rescaling is stopped. Using this approach the heat capacity is investigated as a function of the temperature with fixed densities and as a function of density with fixed temperatures . In figure 2 the intensive specific heat capacity is plotted versus temperature for constant densities. The simulation was run for $\tau = 40$, with rescaling of the temperatures until equilibrium was reached. For low densities the fluctuations in the heat capacity are small. At these low densities the particles barely interact with each
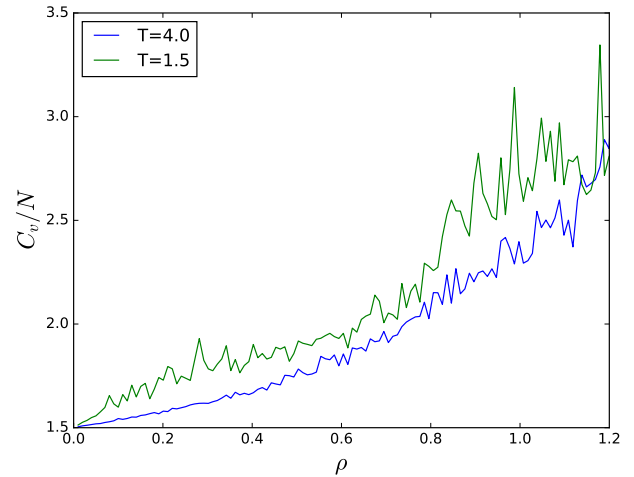

Figure 3: The intensive specific heat capacity is plotted as a function of density. Upper bound of the errors for $T = 4.0$ and $T = 1.5$ are 0.24 and 0.43 respectively.
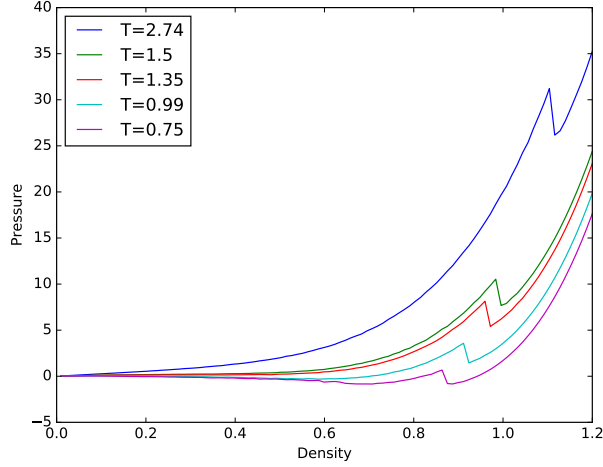
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Figure 4: The pressure is plotted as a function of the density for different temperatures around the critical temperature.

Figure 5: A zoom-in of figure 1 for $T = 1.5$, $T = 1.35$ and $T = 0.99$. It can be seen that for $T = 1.35$ the pressure becomes flattened and that for $T = 0.99$ the pressure becomes negative.

other, making the ideal gas law approximation more exact. This can be observed in figure 2 for $\rho = 0.01$, for which the heat capacity retains a constant value of approximately the ideal gas value $3/2$. For higher densities the system exhibits large fluctuations in the heat capacity, accompanied by large measured errors. It is suspected that this is caused by the following process. At high densities some of the particles form groups in the liquid or solid phase while the other part of the particles remain in the gas or liquid phase respectively. The latter mentioned particles have a larger kinetic energy compared to the other group. These fast particles collide with the condensed groups and break them apart. During this process the potential energy of the particles that were broken apart is increased giving a large fluctuation in the kinetic energy. In the Lebowitz formula it is then seen that this can result in a jump of the intensive specific heat. The reverse process also takes place where 'loose' particles condense into groups giving a large fluctuation in the heat capacity. In figure 3 the intensive specific heat capacity is plotted versus density for constant temperatures. For low densities, the system is in the ideal gas regime for which the intensive specific heat capacity is equal to $3/2$. In figure 3 both curves pass approximately through $3/2$ as $\rho \to 0$. For high densities it is observed that the intensive specific heat capacity approaches the dimensionless Dulong-Petit value of 3.
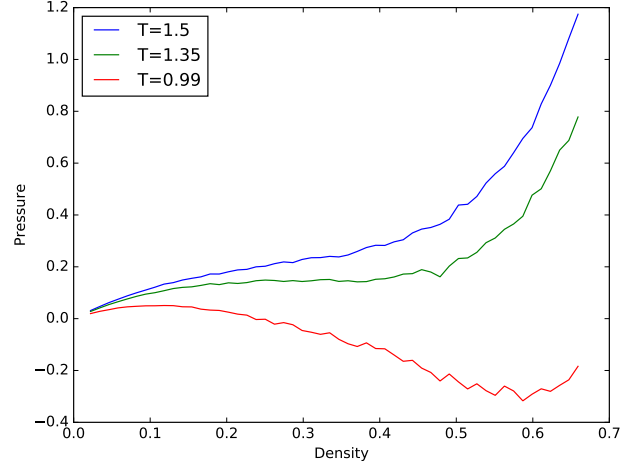
The pressure is calculated in the canonical ensemble using the virial theorem. The canonical ensemble is modeled by rescaling the velocities of the particles every 20 times steps. The pressure is plotted as a function of density for fixed temperatures. For low densities, the interaction potential of the particles is negligible, resulting in ideal gas behavior. Indeed in figure 4 it can be seen that the pressure isotherms go to zero for $\rho \to 0$. As expected, higher temperatures result in higher pressures. When the density is increased it is observed that either the pressure goes up or down depending on the temperature of the system (see close up in figure 5). The regions of negative pressure suggest coexistence of multiple phases. The simulation is not capable of representing this regime accurately. Two groups of particles form, one group consists of a condensed structure and the other group are gaseous particles. With periodic boundary conditions homogeneity is assumed which clearly does not apply. If the simulated box is repeated in all directions a secondary lattice structure – formed by condensed groups– would appear. The simulation fails to reflect a physical system resulting in a non-physical quantity, namely a negative equilibrium pressure. In figure 5 it can be seen that the slope flattens for $T = 1.35$ indicating that this is approximately the critical temperature for a phase transition. Indeed from [3] in the phase diagram it can be seen that around approximately $1.35 \cdot 119.8 \approx 162K$ this flattening is measured. As the density is further increased the pressure
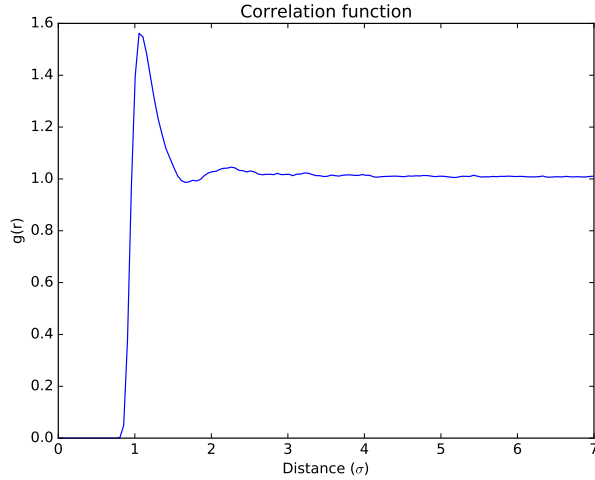
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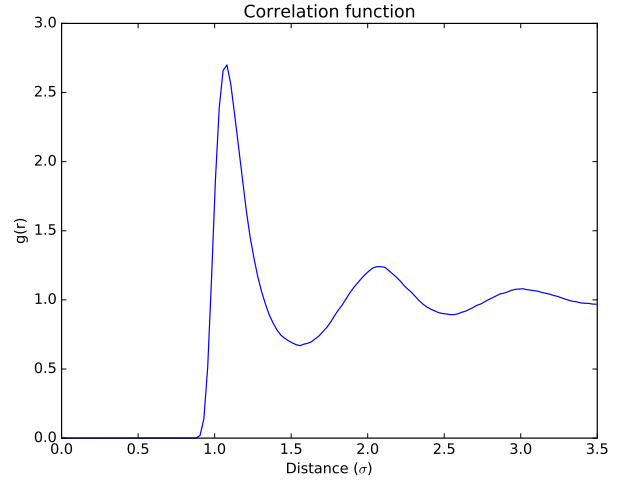Figure 6: The correlation function is plotted for gaseous Argon; $\rho = 0.3$, $T = 3$.

Figure 7: The correlation function is plotted for liquid Argon; $\rho = 0.8$, $T = 1$.

increases. The $1/r^{12}$ term in the Lennard-Jones potential starts to dominate, leading to repulsion, explaining the rise in pressure. At higher densities, a discontinuity in the pressure occurs indicating a phase transition to the solid phase. As expected, the density at which this phase transition occurs becomes larger when the temperature is higher because the tendency of the particles to escape the potential well due to their kinetic energy becomes higher. When the system is transitioning to the solid phase the particles are no longer able to move out of their wells giving a negative jump in the pressure.

The correlation function is calculated in the canonical ensemble. Figures 6-8 show the correlation function in the gas, liquid and solid phase respectively. The correlation function for the gas phase is plotted in figure 6. Due to the strong repulsive part of the Lennard-Jones potential, the distance between two Argon atoms can only become slightly smaller than $\sqrt[6]{2}\sigma \approx 1.22\sigma$. This explains why the correlation function is zero up to a value of approximately 1.22 . Argon atoms that are a distance 1.22σ apart are in the minimum of each others potentials. The Argon atoms prefer this configuration explaining the large peak in the correlation function near $r = 1.22\sigma$. Following this reasoning another peak is expected at $r = 2 \cdot 1.22\sigma$. Indeed figure 6 shows that the correlation function has a small bump at $r = 2.44$. Higher order bumps are present but barely visible.

The correlation function for the gas phase is plotted for a relative high temperature, the particles move fast and the bumping pattern disappears quickly because the particles are relatively free. Figure 7 shows the correlation function for the liquid phase. It is observed that the shape is similar to that of the gas phase, however the peaks expected at 1.22 ; $2 \cdot 1.22$; $3 \cdot 1.22$, ... are much better visible than in the gas phase. The particles are less free in the liquid phase and the bumping pattern persists over a longer range. Finally figure 8 shows the correlation function for the solid phase. In this phase the particles form a fcc lattice and only oscillate around their equilibrium positions. For the density of 1.2 it can be calculated that the lattice constant is approximately equal to $a = 1.5$. From the fcc structure we expect to see peaks around integer multiples of $a/\sqrt{2}$, a , $\sqrt{2}a$, $\sqrt{3}a$ etc. These positions correspond to the equilibrium positions of the vibrations of the atoms. Due to finite temperature the peaks spread out around these values.

When the system has reached equilibrium, at a certain time step the positions of the particles are taken as the initial positions for which the displacement for each particle for future times is computed. These displacements are averaged over all the particles and are then plotted in figure 9 for the different phases of Argon. For the gas phase also a close-up for small times is provided. In the gas phase, the particles are far apart, suppressing the influence of the interaction po-
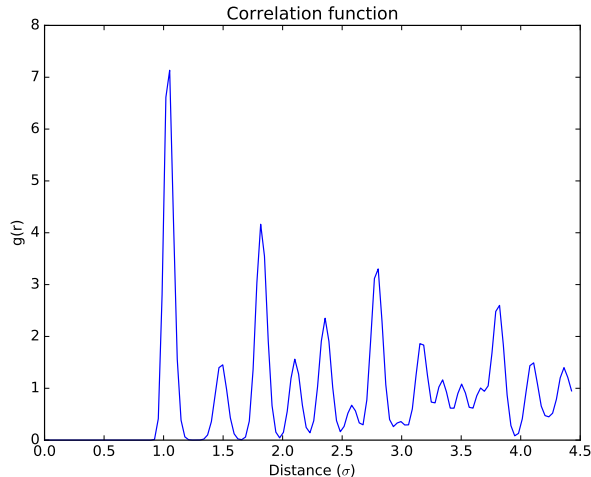
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Figure 8: The correlation function is plotted for solid Argon; $\rho = 1.2$, $T = 0.5$

tential. This means that for small times the particles behave in a ballistic manner explaining the quadratic shape of the curve as seen in the close-up figure. After some time, the particles have interacted, upon which the system enters the diffusive regime. For a liquid, due to the close spacing of the particles, the system exhibits diffusive behavior from the start. For a solid, the particles are trapped in the wells of the interaction potential, vibrating due to their kinetic energy. This explains the constant nature of the displacement. The fluctuations in the displacement are observed to be relatively large (of order 20%). If the particles would move completely independent, these fluctuations would average out. As the particles are highly interacting ($\rho = 1.2$) the motion is correlated and large fluctuations appear.

4   Conclusion

In this paper a molecular dynamics simulation of Argon atoms enclosed in a cubic box with periodic boundary conditions has been processed, various physical quantities have been computed in the microcanonical ensemble (heat capacity) and canonical ensemble (pressure, correlation function and diffusion constant). For high temperatures, the results of the simulations of the pressure for low and high densities proved to be quite successful. At low densities we indeed see the pressure go to zero, while at high temperature the pressure steeply increases. For lower temperatures the atoms seemed to condense, which

–due to the nature of the model– resulted in unphysical behavior. A solution to this unfortunate drawback –largely due to the choice of periodic boundary conditions– would make an interesting improvement to the model. In the simulation of the heat capacity it was observed that for low densities the intensive specific heat capacity approached the ideal gas value of 1.5 and for high densities the Dulong-Petit value of 3 (see table 1). The behavior of the correlation could be well explained through physical reasoning. In the gas phase peaks occurred at integer multiples of the distance for which the potential is minimal, however these peak died out quickly compared to the liquid phase. In the solid phase the Argon atoms became localized resulting in peaks at specific positions. Tracking the displacement gave a good insight into the movement of particles through the box for the three different phases. In table 1 the differences in time scale of diffusion for the gas and liquid phases become clear. In the solid phase there is no diffusion because the Argon atoms become localised.

References

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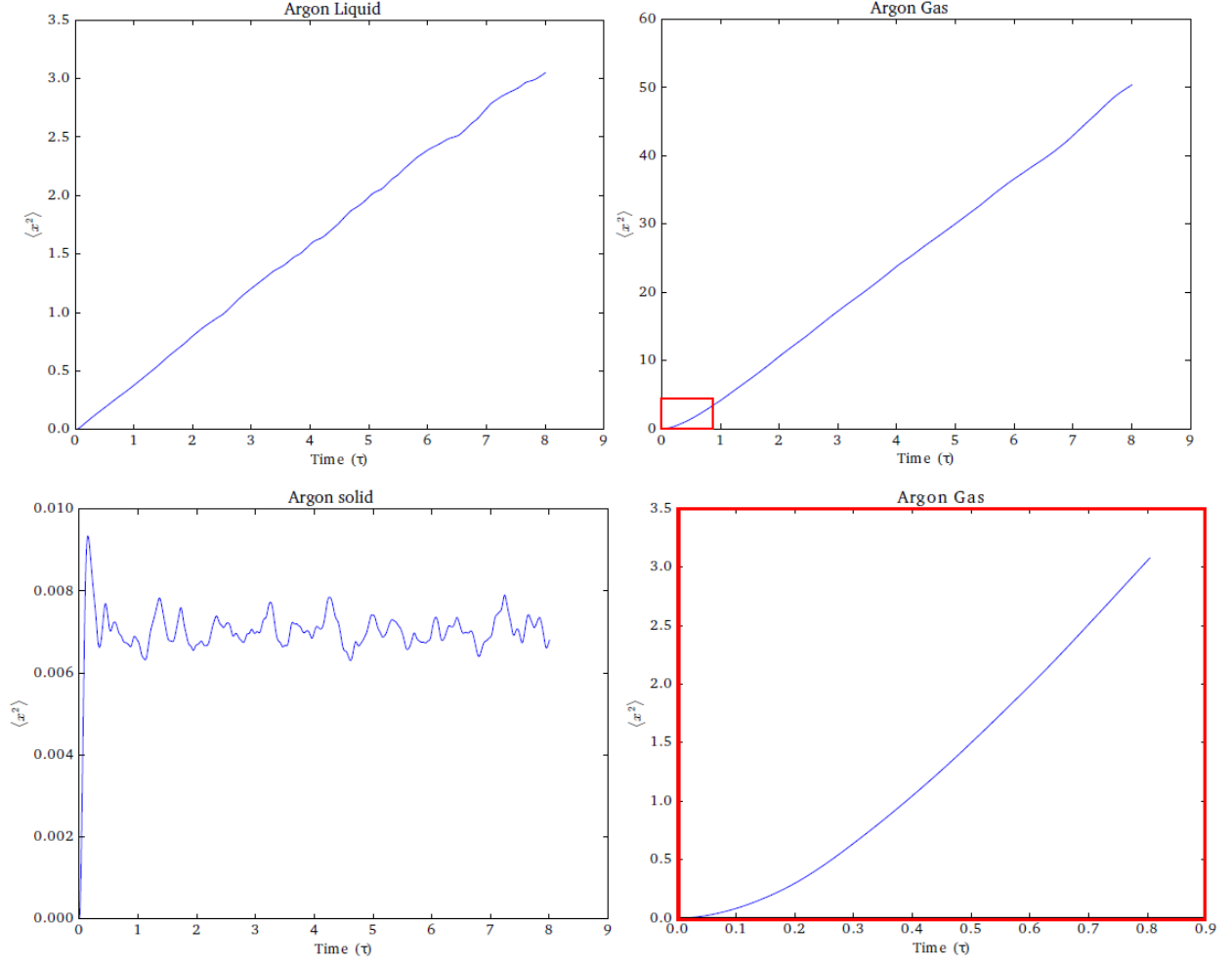
Figure 9: The average squared displacement of the Argon atoms is plotted as a function of time, demonstrating the self diffusion of Argon atoms in the solid, liquid and gas phase. Top left: liquid phase, $\rho = 0.8$, $T = 1$. Bottom left: solid phase, $\rho = 1.2$, $T = 0.5$. Top right: gaseous phase, $\rho = 0.3$, $T = 3$. Bottom right: close up of red captioned area in gaseous phase.