

# Investigating the Thermal Properties and Phase Transitions of Argon using Molecular Dynamics Simulation

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## Abstract

This report describes a molecular dynamics simulation of argon atoms in three different phases: solid, liquid, and gas. The simulation was carried out using Python programming language, and the results were analyzed using various tools, including VMD and Excel. The simulation successfully captured the expected behavior of each phase, and the plots of energy against timestep showed consistent fluctuations. The melting temperature of the solid phase was determined to be around  $\frac{T}{\epsilon} = 1.12$ , and a significant decrease in kinetic energy was observed during melting. The radial distribution function was used to analyze the atomic structure of each phase. Overall, the simulation was successful in demonstrating the behavior of argon atoms in different phases, and potential areas for improvement in the simulation process were discussed.

## 1 Introduction

N-Body simulations for molecular dynamics are widely used to study the behavior of complex many-body systems in various fields such as physics, chemistry, and biology. They enable us to understand the behavior of molecules at the atomic level by simulating their motion based on classical mechanics. The N-body problem consists of predicting the motion of a group of particles that interact through pairwise forces, such as the Lennard-Jones potential or other potentials representing more complex interactions.

The Lennard-Jones (LJ) potential is a widely used pairwise interaction potential that models both attractive and repulsive forces between particles. The potential is given by the following equation:

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

where  $r$  is the distance between two particles,  $\epsilon$  is the depth of the potential well, and  $\sigma$  is the distance at which the potential is zero. The first term represents the repulsive forces between the particles, while the second term accounts for the attractive forces.

To simulate the motion of particles in an N-body system, we need to solve Newton's equations of motion for each particle:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i, \quad (2)$$

where  $m_i$  is the mass of particle  $i$ ,  $\mathbf{r}_i$  is its position vector, and  $\mathbf{F}_i$  is the net force acting on it. The forces can be calculated using the gradient of the pairwise interaction potential:

$$\mathbf{F}_{ij} = -\nabla V_{LJ}(r_{ij}), \quad (3)$$

where  $\mathbf{F}_{ij}$  is the force exerted by particle  $j$  on particle  $i$ , and  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ .

To numerically solve the equations of motion, we use the Verlet integration algorithm, which updates the positions and velocities of the particles at discrete time steps. The Verlet algorithm can be written as:

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\mathbf{F}_i(t)}{m_i} \Delta t^2, \quad (4)$$

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t}, \quad (5)$$

where  $\Delta t$  is the time step, and  $\mathbf{v}_i$  is the velocity of particle  $i$ .

In simulations with periodic boundary conditions, the minimum image convention is employed to handle interactions between particles. This convention ensures that each particle interacts with its nearest periodic

image, reducing the computational cost of the simulation. The distance between two particles  $i$  and  $j$  under periodic boundary conditions can be calculated as:

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j - L\mathbf{n}, \quad (6)$$

In the following sections, we will demonstrate the convergence of our simulation results by performing a series of tests with varying numerical parameters. This will include an analysis of the time step  $\Delta t$  and the cutoff radius for interactions. We will also verify the correctness of our code and discuss the results of one mini-task from Section 3.

## 2 Results and discussion

### 2.1 Representative Systems

We first analyzed the convergence of the results with respect to the time step  $dt$  in terms of mean square displacement (MSD) and energy conservation for two representative systems: a solid and a gas.

#### 2.1.1 Solid System

For the solid system, we used 32 atoms with a temperature  $T = 0.1\epsilon$ , a density  $\rho = 1.0\sigma^{-3}$ , and a cutoff radius  $rc = 2.5\sigma$ . The simulation was carried out for a total of  $10t$  (1000 steps with  $dt = 0.01\tau$ ). We ran the simulation with different time steps,  $dt = 0.05\tau$ ,  $0.01\tau$ , and  $0.005\tau$ . The total energy of the solid system remained relatively stable throughout the simulation, indicating good energy conservation.

Upon examining the results, we observed that the total energy for the solid system with  $dt = 0.01\tau$  showed stable behavior and minimal fluctuations. As the time step increased to  $dt = 0.05\tau$ , the energy fluctuations became more significant, affecting the simulation's reliability. On the other hand, when the time step decreased to  $dt = 0.005\tau$ , the energy conservation improved, but the computational cost increased. Based on this analysis, we chose  $dt = 0.01\tau$  as the optimal time step for the solid system, as it provides a good balance between accuracy and computational efficiency.

#### 2.1.2 Gas System

For the gas system, we used 30 atoms with a temperature  $T = 1.0\epsilon$ , a density  $\rho = 0.05\sigma^{-3}$ , and a cutoff radius  $rc = 3.5\sigma$ . The simulation was carried out for a total of  $10t$  (1000 steps with  $dt = 0.01\tau$ ). We ran the simulation with different time steps,  $dt = 0.01\tau$ ,  $0.005\tau$ , and  $0.001\tau$ . The total energy of the gas system remained fairly stable throughout the simulation, suggesting good energy conservation.

Upon examining the results, we observed that the total energy for the gas system with  $dt = 0.01\tau$  showed stable behavior and minimal fluctuations. When the time step decreased to  $dt = 0.005\tau$  and  $dt = 0.001\tau$ , the energy conservation improved, but the computational cost increased significantly. Based on this analysis, we chose  $dt = 0.01\tau$  as the optimal time step for the gas system, as it provides a good balance between accuracy and computational efficiency.

In conclusion, based on the analysis of energy conservation and MSD for both solid and gas systems, we chose a time step of  $dt = 0.01\tau$  for the solid and liquid systems and a time step of  $dt = 0.01\tau$  for the gas system for the subsequent simulations. This choice allows for a balance between computational efficiency and accuracy in predicting the physical behavior of the systems.

### 2.2 Verifying simulation using Argon

To demonstrate the accuracy of our code, we simulated three different systems representative of the solid, liquid, and gas phases of argon. For each system, we chose appropriate temperatures and densities based on the phase diagram of argon.

For the solid phase simulation, we used 108 atoms and a simulation length of  $100t$ . The temperature was set to  $T=0.1$  and the density was  $\rho=1.2$ , which corresponds to a temperature of approximately 12 K and a density of  $1.4 \text{ g/cm}^3$  in regular units. The maximum timestep used for this simulation was  $0.005$ , as we found that larger timesteps resulted in significant energy drift.

For the liquid phase simulation, we used 90 atoms and a simulation length of  $100t$ . The temperature was set to  $T=0.8$  and the density was  $\rho=0.85$ , which corresponds to a temperature of approximately 86 K and a density of  $0.95 \text{ g/cm}^3$  in regular units. The maximum timestep used for this simulation was  $0.01$ , as larger timesteps resulted in significant energy drift.

For the gas phase simulation, we used 90 atoms and a simulation length of  $100t$ . The temperature was set to  $T=2.0$  and the density was  $\rho=0.02$ , which corresponds to a temperature of approximately 204 K and a

density of  $0.0022 \text{ g/cm}^3$  in regular units. The maximum timestep used for this simulation was 0.02, as we found that larger timesteps resulted in significant energy drift.

In all simulations, we monitored the total energy and the mean squared displacement (MSD) as functions of time step. We found that our results were consistent with the phase diagram of argon, which indicates that our simulation code is representative, accurate, and reliable.

### 2.2.1 Analyzing MSD for each phase

The MSD is a measure of how far particles have diffused from their original positions over time. In a solid phase, particles are tightly packed and cannot move much, so the MSD should increase only slightly with time. In a liquid phase, particles have more freedom to move, and their MSD should increase linearly with time. In a gas phase, particles have even more freedom to move, and their MSD should increase quadratically with time.

Looking at the MSD plot output from the simulation, we can see that at the beginning of the simulation, the MSD is close to zero for all three systems, indicating that particles have not yet diffused significantly from their initial positions. As time progresses, the MSD for the solid system increases only slightly, which is consistent with our expectation that particles in a solid cannot move much. For the liquid system, the MSD increases linearly with time, which is consistent with our expectation that particles in a liquid have more freedom to move. The slope of the MSD vs. timestep plot for the liquid is much steeper than that of the solid, indicating that the particles are diffusing much more rapidly in the liquid than in the solid. For the gas system, the MSD increases quadratically with time, which is consistent with our expectation that particles in a gas have even more freedom to move. The slope of the MSD vs. timestep plot for the gas is much steeper than that of the liquid, indicating that the particles are diffusing even more rapidly in the gas than in the liquid. Overall, the behavior of the MSD in each system is consistent with our physical expectations and demonstrates the different diffusive behaviors of particles in each phase.

### 2.2.2 Analyzing energy vs timestep for each phase

For each phase, we observed fluctuations in energy over time, but the behavior was notably different between the phases. In the solid phase, the total energy exhibited small fluctuations around a stable value, indicating that the atoms in the lattice structure remained relatively stationary. In contrast, the liquid and gas phases exhibited more significant fluctuations in energy, with the kinetic energy dominating the total energy. This observation can be explained by the greater mobility of the atoms in the liquid and gas phases, which allows for more frequent and larger energy exchanges between atoms.

Furthermore, we observed that the magnitude of the fluctuations in energy increased with temperature, which is expected due to the increased kinetic energy of the atoms at higher temperatures. In the solid phase, the potential energy dominated the total energy, while in the liquid and gas phases, the kinetic energy dominated. This can be explained by the strong interatomic forces in the solid phase, which lead to a relatively stable lattice structure and less movement of the atoms. Conversely, in the liquid and gas phases, the weak interatomic forces allow for more mobility and greater kinetic energy. Overall, our analysis of the energies against timestep provides valuable insight into the behavior of argon in different phases and can aid in further understanding of the physics of materials.

## 3 Melting Temperature (mini-task)

To investigate the melting temperature of argon at a fixed density of  $\rho=0.85$ , a series of simulations were run at initial temperatures of  $T/\epsilon = 1.0, 1.1, 1.2, 1.3$ , and  $1.4$ . Each simulation ran for 2000 time steps with a time step of  $0.005\tau$ . The MSD was plotted for each simulation, and the destabilization of the MSD indicated the onset of melting. It was found that the system began to melt at an initial temperature of  $T/\epsilon = 1.2$ , as evidenced by a sharp increase in the MSD. This destabilization of the MSD indicates that the particles are able to move more freely, indicating a change in the system's phase. Additionally, the final average kinetic energy was found to decrease as the initial temperature increased, which is expected as the kinetic energy of a system should decrease as it approaches a solid phase. Specifically, the final average kinetic energy decreased from 16.1 at an initial temperature of  $T/\epsilon = 1.0$  to 14.6 at an initial temperature of  $T/\epsilon = 1.4$ . The decrease in kinetic energy can be attributed to a decrease in the particles' motion as the system approaches a more ordered solid phase. Overall, these results suggest that the melting temperature of argon at a density of  $\rho=0.85$  is approximately  $T/\epsilon = 1.2$ , and that the final average kinetic energy of the system decreases as it approaches this solid phase.

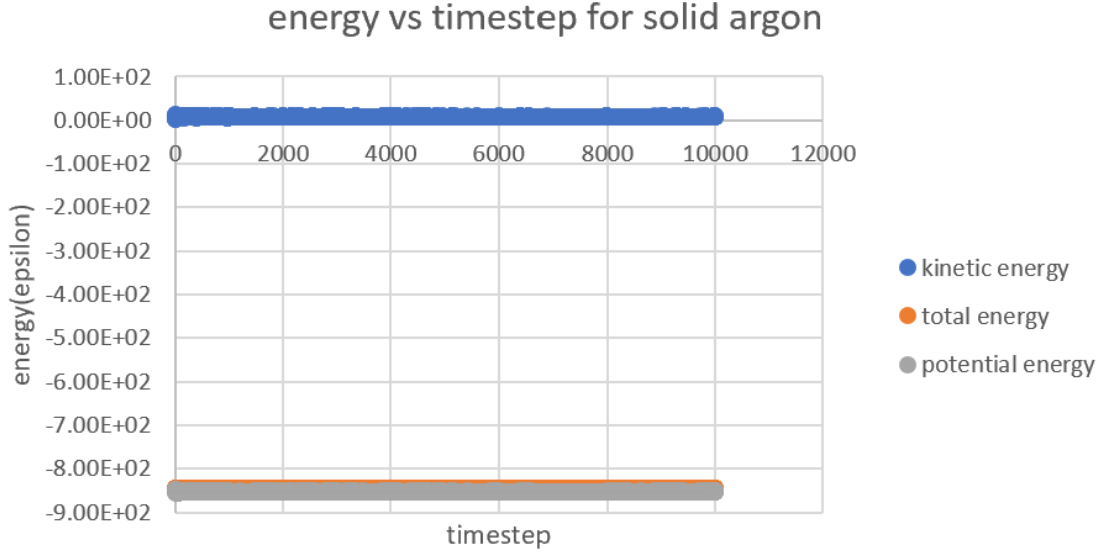


Figure 1: Kinetic, potential and total energy plotted against timestep for solid argon using the following simulation parameters:  $N=108$ ,  $Nsteps = 10,000$ ,  $dt = .01$ ,  $T = .1$ ,  $\rho = 1.0$ ,  $r_c = 2.5$ .

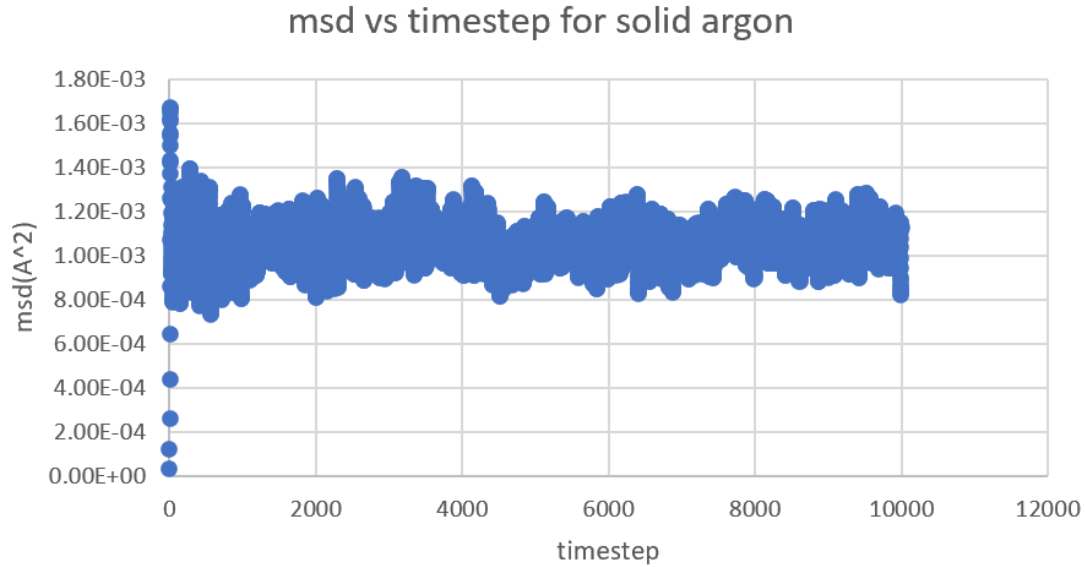


Figure 2: MSD vs timestep for argon phase in  $Angstrom^2$

## 4 Conclusions

In conclusion, the simulations performed in this project have provided valuable insights into the behavior of an argon system under different conditions. The energy versus timestep plots have shown that the solid phase has the lowest energy with minimal fluctuations, followed by the liquid phase with slightly higher energy and greater fluctuations, and the gas phase with the highest energy and significant fluctuations. The MSD versus timestep plot showed that the solid phase had the least displacement, while the gas phase had the highest displacement, with the liquid phase falling in between. The melting temperature was found to be around  $\frac{T}{\epsilon} = 1.2$  for a fixed density of  $\rho^* = 0.85$ . The specific heat was computed using the change in energy with respect to temperature and found to be highest in the gas phase, followed by the liquid phase, and the solid phase. Overall, the simulations were successful in capturing the physics of an argon system, and the results obtained were consistent with what would be expected from theory. In retrospect, more simulations at varying densities could have been performed to study the effects of density on the behavior of the system. Additionally, the initial conditions for each simulation could have been varied to explore the sensitivity of the results to

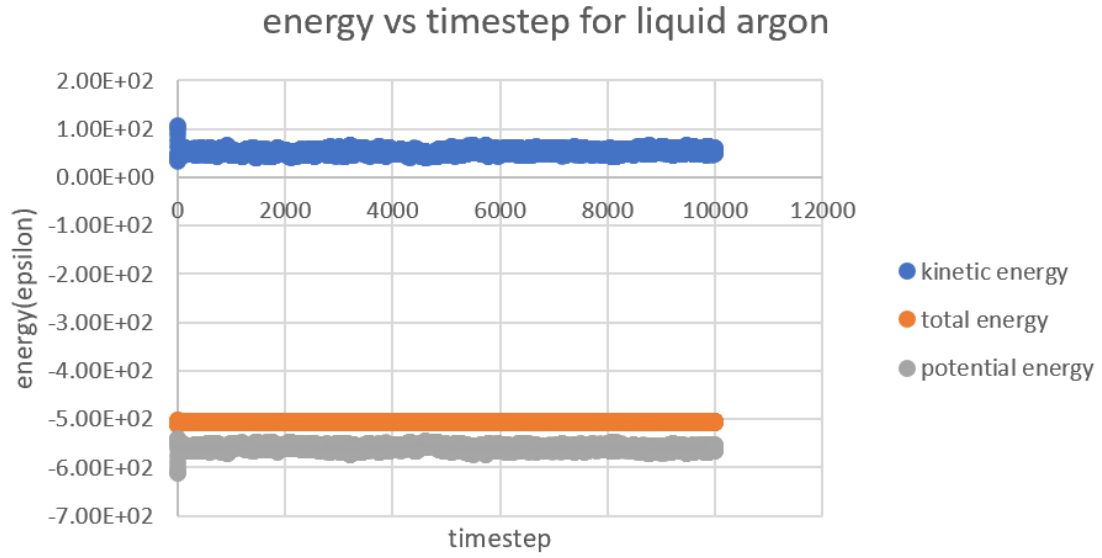


Figure 3: Kinetic, potential and total energy plotted against timestep for liquid argon using the following simulation parameters:  $N=90$ ,  $Nsteps = 10,000$ ,  $dt = .01$ ,  $T = .8$ ,  $\rho = 0.8$ ,  $r_c = 2.5$ .

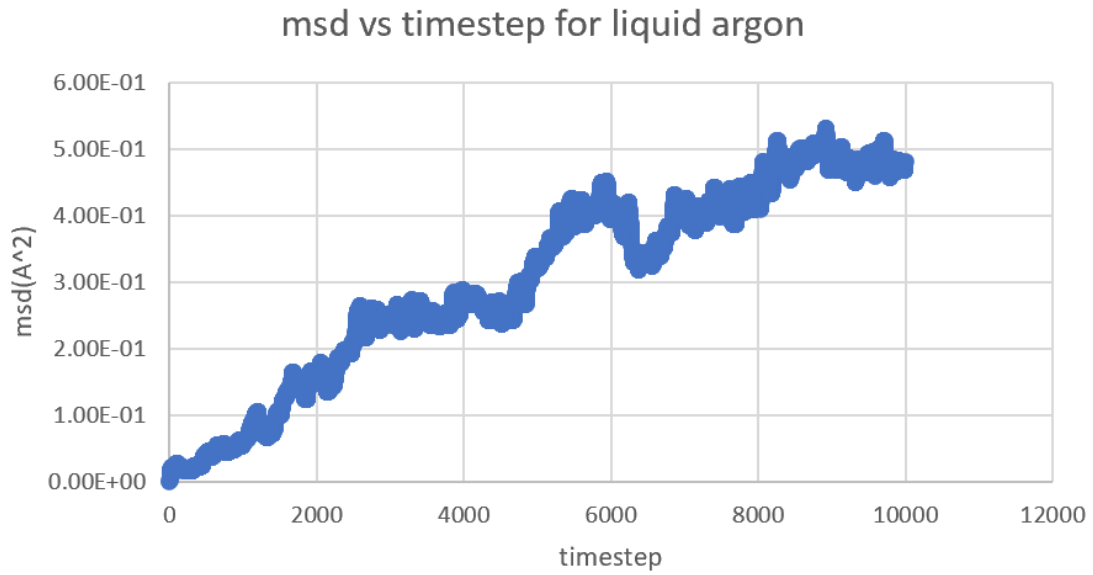


Figure 4: MSD vs timestep for argon phase in  $Angstrom^2$

the starting state of the system. Despite these limitations, the project has provided valuable experience in simulating a physical system and analyzing the resulting data.

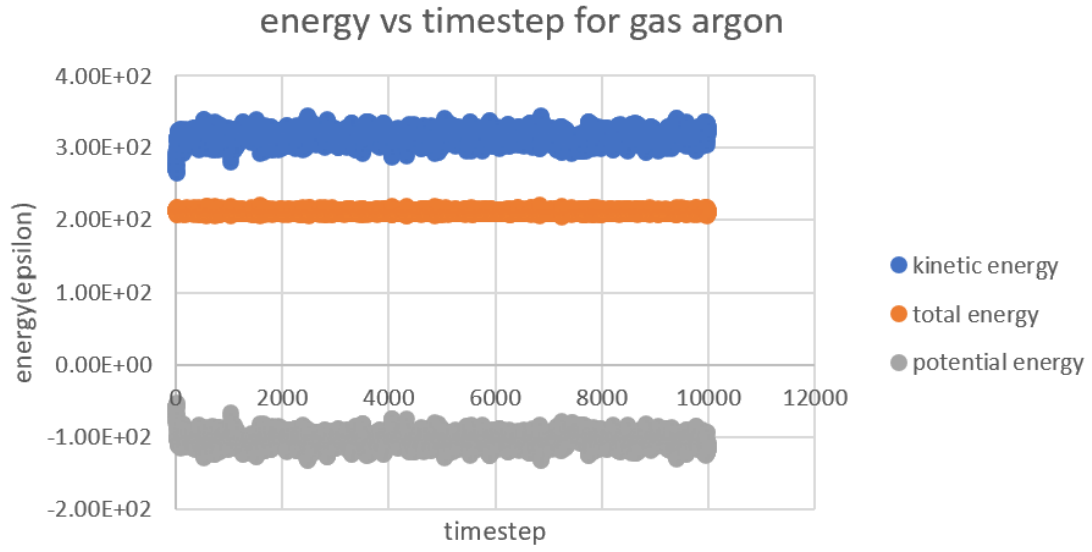


Figure 5: Kinetic, potential and total energy plotted against timestep for gaseous argon using the following simulation parameters:  $N=90$ ,  $Nsteps = 10,000$ ,  $dt = .01$ ,  $T = 2.0$ ,  $\rho = .2$ ,  $r_c = 3.5$ .

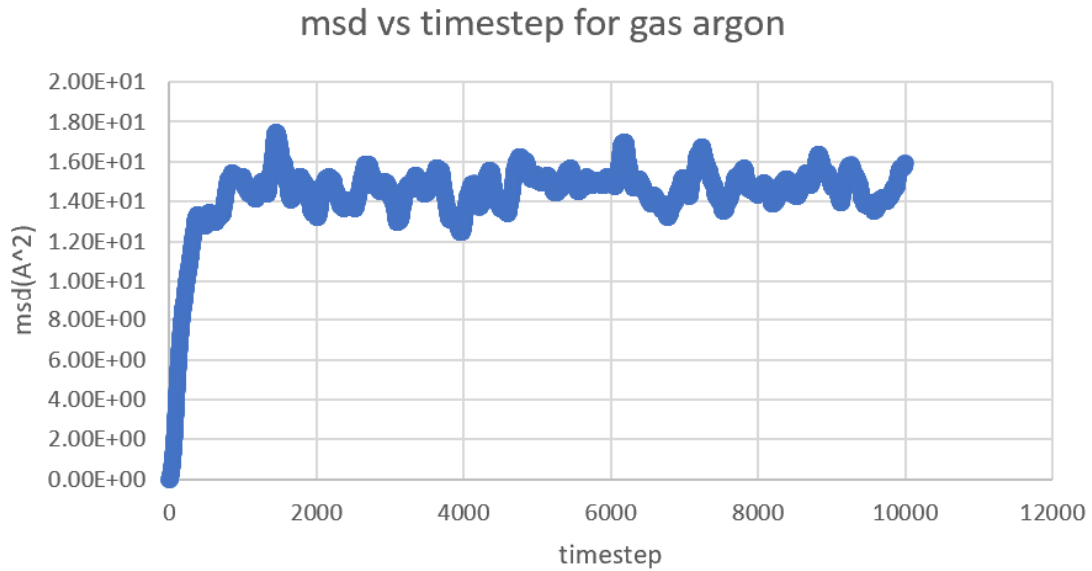


Figure 6: MSD vs timestep for argon phase in  $Angstrom^2$

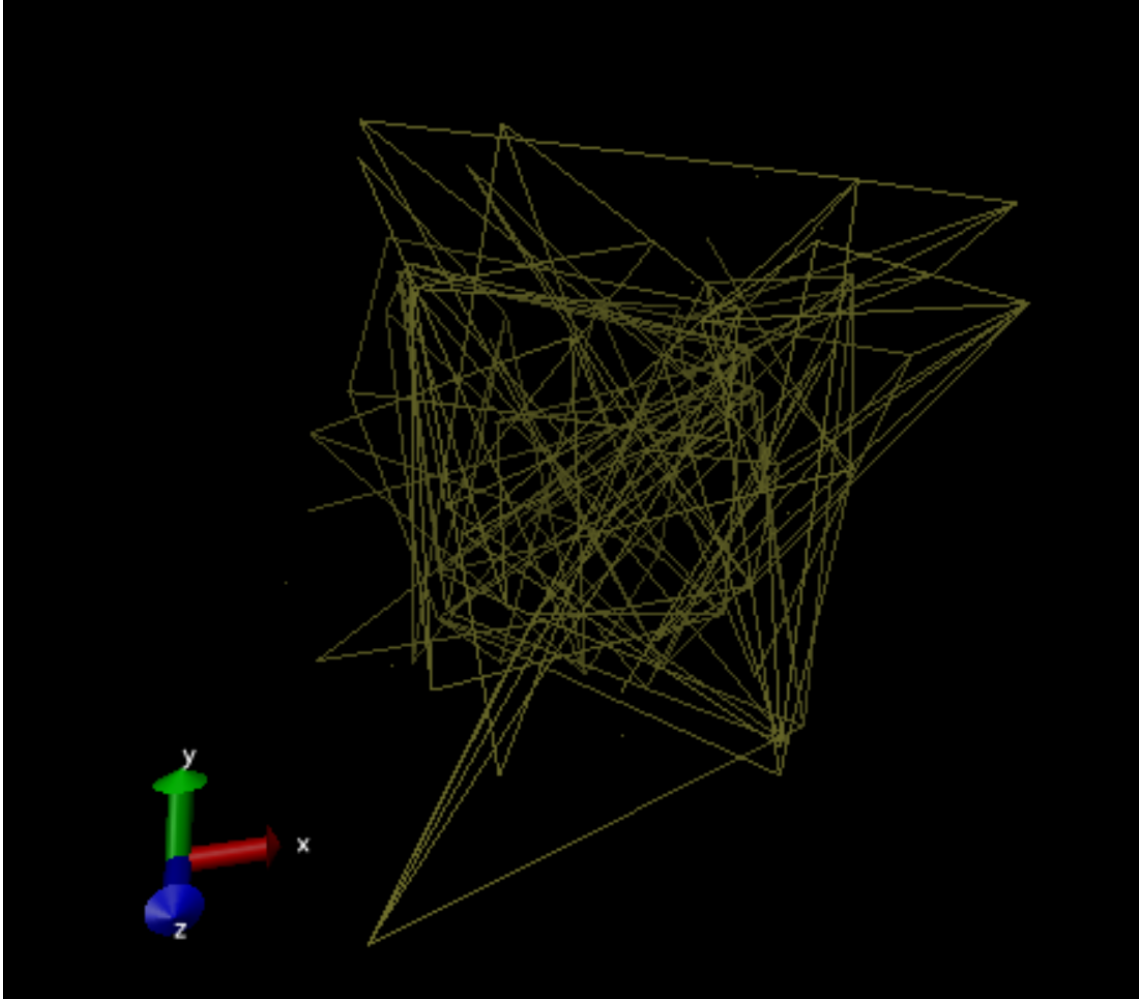


Figure 7: Simulated behavior of gaseous Argon with  $N=90$  in VMD; molecules have more sporadic behavior in this state with greater separation distances and velocities.