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Project 1: Molecular Dynamics with Argon

1 Abstract

We simulate Argon particles in gas, liquid, and solid phases to examine their particle dynamics. Using the Lennard-Jones potential for potential energy and Newtonian dynamics for kinetic energy, we set 108 Argon particles in a FCC lattice comprised of 3x3x3 identical unit cells. We record the total energy of the system and position of the particles, and calculate the pair-correlation function and diffusion for each phase.

2 Introduction

Computational simulations bridge theoretical equations and explanations with experimental observations. In this project, we incorporate various physically motivated equations for the movement and interaction of atomic particles at different phases. We assign our particles as Argon, a noble gas which behaves well as a singular point mass instead of a compound, and use parameters appropriate for that element. These particles interact with each other following the Lennard-Jones potential, given as

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

Otherwise the atoms move classically with Newtonian equations.

Argon has a melting point of 83.8K and a boiling point of 87.3K. Its phase can also be described by the density of the sample. We manipulate both to specify the phase state of the Argon atoms, which is explained in further detail in Section 3.2. We are interested in the difference of observables between phases, including the pair-correlation function. This measures the distribution of particles based on distance, or how many particles are a given distance from a reference point, averaged over time. For $n(r)$ particles a distance Δr (bin size) from a reference point r, and N total particles in a volume V, the pair-correlation function $g(r)$ is

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

We also measure the diffusion of the system over time as the average difference between the original position and its current position. Finally, we are interested in following the positions of the atoms and the total energy of the system throughout the simulation.

3 Methods

3.1 Units

Before we can begin, we recognize the scales used in this simulation are prone to rounding errors. To combat this we adjust the units of position and energy to reflect constants in Equation 1, σ and ϵ respectively, transforming these variables to be dimensionless. Taking this further, we find units of time to be $(\frac{m\sigma^2}{\epsilon})^{1/2}$. This effectively eliminates m and k_B from original equations. Now Equation 1 reads

$$U(r) = 4(r^{-12} - r^{-6}) \tag{3}$$

As we introduce more equations, we acknowledge their original form and note the replacement with modified units.

Phase	Temperature	Density
Solid	0.5	1.2
Liquid	1.0	0.8
Gas	3.0	0.3

Table 1: Defining phase with dimensionless units of temperature and density

3.2 Initial Conditions

The particles inside the simulation space are placed on a FCC lattice to reflect how solid Argon behaves. The lattice is comprised of $3 \times 3 \times 3$ unit cells with defined length L each containing 4 Argon atoms. The positions of these 4 original atoms are copied into each unit cell to have a set distribution throughout the lattice. We set L based on the density required for a given phase. The temperature is set by choosing specific velocities for all particles corresponding to a Gaussian distribution given as:

$$e^{-mv^2_{x,y,z}/(2k_BT)}$$

These velocities are unique for each of the 108 particles, and not copies between unit cells. With dimensionless units of temperature and density, the phases are defined by Table 1. We run the simulation for 10,000 time steps, with each time step as $\Delta t = 0.004$.

3.3 Running the Simulation

It is difficult to predict how the system will evolve after these initial states. We therefore let the simulation run until the system reaches an equilibrium, after which all velocities can be readjusted by a certain factor to correspond to a given temperature. This factor is:

$$\lambda = \sqrt{\frac{(N-1)3k_BT}{\sum_i mv_i^2}}$$

With modified dimensionless units the equation becomes

$$\lambda = \sqrt{\frac{(N-1)3T}{\sum_i v_i^2}} \tag{4}$$

This means results for the observables are generally unreliable before the simulation is in equilibrium and adjusted. The two vertical dashed lines in Figure 1 indicate the interval in which the rescaling takes place. It is clear that the rescaling successfully sets λ to one by $t = 5000$.
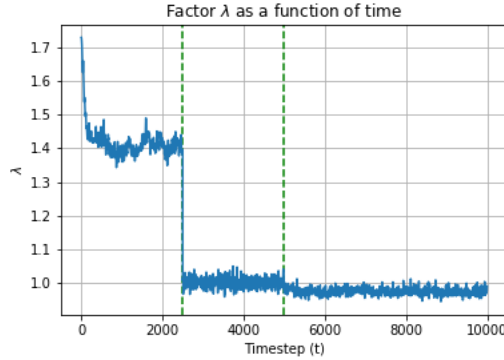

Figure 1: Rescaling factor λ reaches equilibrium of 1.0 by $t = 5000$.

4 Results

4.1 Total Energy

The total energy is the sum of the kinetic energy and the potential energy, where the potential energy is represented by the Lennard-Jones Potential and the kinetic energy is calculated with Newtonian dynamics. We take care to not count the potential twice for each pair. The total energy should be constant for all phases after the velocities have been rescaled, completed by $t = 5000$. We see this is the case in Figure 2 although there is some fluctuation. The total energy for Argon gas, Figure 2a, is positive (in dimensionless units) while that of liquid and solid argon, Figures 2b and 2c, are negative. This reflects a higher kinetic energy in gas and higher potential energy in liquid and solid form.
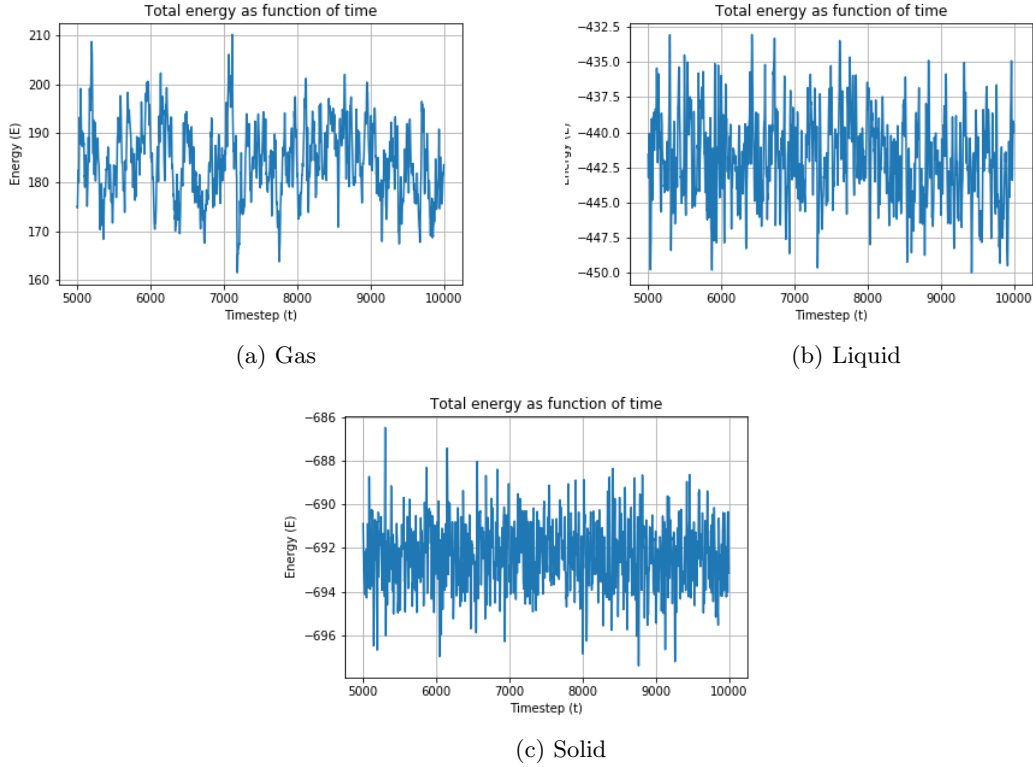

(a) Gas

(b) Liquid

(c) Solid

Figure 2: Total energy of system over time.

4.2 Positions

We also plot the positions of the 108 particles, which is admittedly somewhat chaotic. Figure 3a shows gas particles moving all over the lattice, especially following the pink and grey lines. Figure 3b has clear patterns, with liquid particles keeping a similar y-position and moving back and forth on the x-axis. This is easy to follow with the orange, brown, green, pink, and gray particles. Examining the solid state in Figure 3c shows the particles all followed the same diagonal path and kept the same distance from each other. One can interpret this as the solid as a whole moving in a diagonal path on the xy-plane (the z-axis is not shown but can be assumed to also demonstrate solid movement).
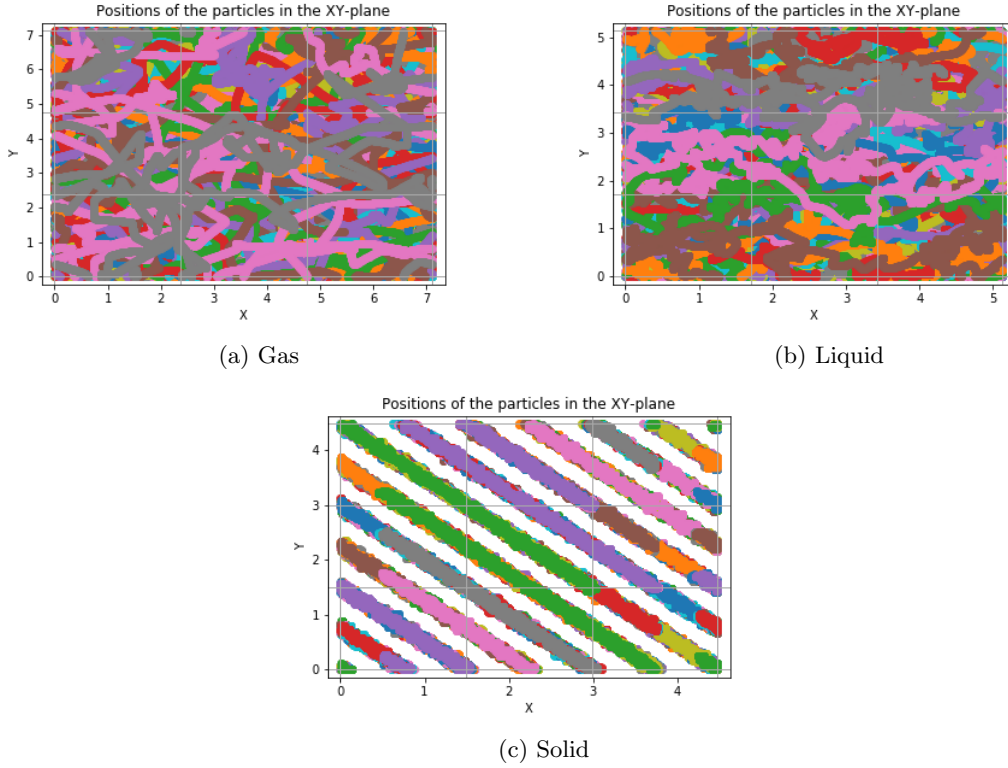

(a) Gas

(b) Liquid

(c) Solid

Figure 3: Position of particles on xy-plane over time

4.3 Pair-Correlation Function

The pair correlation function for each phase is shown in Figure 4 where we see a sharp increase at $r = 1$. This is expected as particle pairs will not be found closer due to the Lennard-Jones potential's repulsion. In Figure 4a we see a somewhat constant probability of finding a particle pair with distance between $r = 2$ and $r = 4$. Because the Argon gas is not as bound to a certain position, a particle pair can easily be at any of these distance values. The same cannot be said for liquid or solid forms, where a more rigid structure is enforced and set distances are preferred. In fact, particles in a solid can only be found at specific distances in the lattice which is demonstrated in Figure 4c.
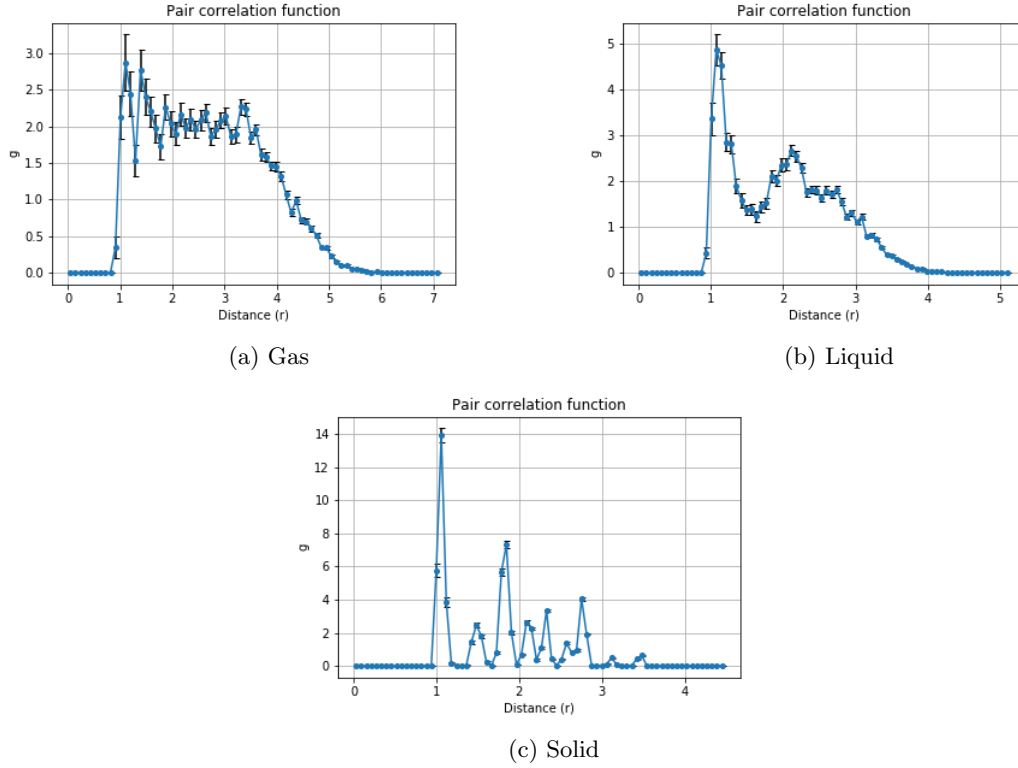

(a) Gas

(b) Liquid

(c) Solid

Figure 4: Pair-correlation functions.

4.4 Diffusion

Finally we observe diffusion of the system at different phases in Figure 5. These values were calculated using a bootstrap method, where we re-sampled the data 100 times for each time step. This creates a distribution from which we can calculate an average and standard deviation for each time step.

As can be expected, the gas state demonstrates the most diffusion, and liquid and solid states less so. In Figure 5b we see diffusion increase after time step $t = 2000$. The particles are generally moving away from their original position at this time, which is also shown in Figure 3b as the particles move back and forth in the box (although the particles can still be some z distance away from the original position, which is not shown in the xy-plane). We can also compare the position and diffusion in the solid case. All of the particles move farther or closer to their original point as the entire solid moves.
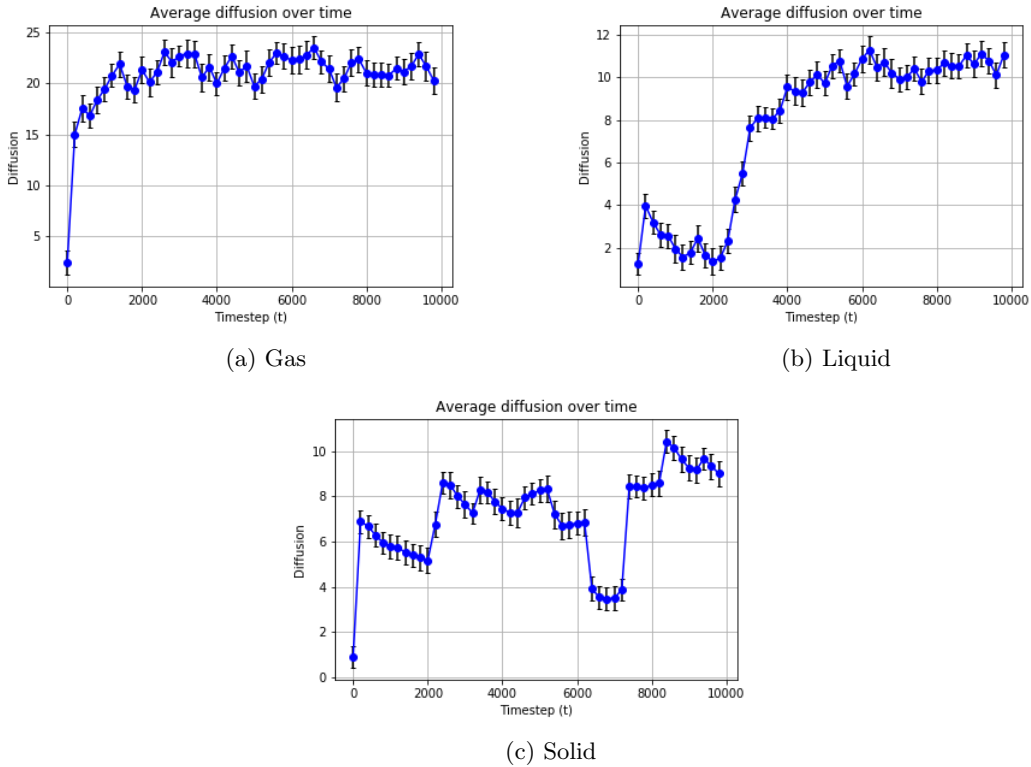

(a) Gas

(b) Liquid

(c) Solid

Figure 5: Diffusion of particles over time.

5 Conclusion

We successfully created a simulation of Argon particles following Newtonian dynamics and the Lennard-Jones potential for the three phase states. As expected, the gas example shows high kinetic energy, a large range of positions with high diffusion, and a consistent pair-correlation function. The liquid simulation demonstrates a higher potential energy, with positions and diffusion of particles changing together, and a more constricted pair-correlation function. Finally, the solid Argon follows common understanding of a rigid lattice structure. It has the largest potential energy, fairly precise values in the pair-correlation function, and position of particles moving together with uniform diffusion.

Future work includes more observables, including pressure and specific heat of the system. Additionally, one can look at the temperature dependence of the observables for different phases. In order to improve accuracy, the simulation can be run on the GPU to simulate more particles in less computational time.

References

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[2] Verlet, L. (1967). Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Physical Review, 159*(1), 98-103.