Molecular Dynamics Simulation of Argon in the Canonical and Microcanonical Ensemble

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The molecular dynamics (MD) method allows us to simulate the interaction of particles in a system by solving their equations of motion. In this way, we can numerically determine various physical quantities. Here, we simulate an Argon gas consisting of 864 particles that interact via a Lennard-Jones potential. We use the Verlet algorithm to calculate the positions and momenta at subsequent timesteps. Once the system reaches equilibrium, we evaluate the energy, pair correlation function, pressure and heat capacity. Furthermore, we characterize the diffusive behavior of the system for different phases. We find that most quantities behave as predicted by theory.

I. INTRODUCTION

To solve any classical physics problem, it is in principle sufficient to solve the relevant equations of motion. In theory, this is a relatively simple procedure. However, in practice the system size usually demands great computational power to do so. Therefore, in many problems physicists resort to macroscopic descriptions of the system and are just interested in statistical averages of experimental results. Still, we would like to be able to confirm that we find similar values for these quantities when we simulate the system. In this sense, we can use numerical simulations to form a bridge between theory and laboratory experiments.

A striking example of a classical physics problem that can be simulated is the many-body problem of interacting particles. More specifically, this model can be used to describe the interaction between molecules. This problem can be modeled by a set of coupled differential equations that can be solved numerically by a computer. It was only in 1964 that Loup Verlet used the now so called molecular dynamics (MD) method for the first time[1]. Over the years, it has become an important technique for the study of fluids and solids.

In the MD method the trajectories of single particles are calculated and from this a range of thermodynamic quantities can be extracted. In general, we consider a volume V in which N particles interact with each other. Typically, the Lennard-Jones potential is chosen to describe this interaction. The equations of motion can be solved numerically and by fixing specific variables the behavior of the system in different ensembles can be studied. If we conserve the total energy E and fix the particle number N and the total volume V, we study the microcanonical (NVE) ensemble. Another often studied ensemble is the canonical (NVT) ensemble, in which, instead of the total energy, the kinetic energy is fixed. Usually, this is done by implementing a thermostat, which fixes the temperature of the system. However, we can fix any other variables we like, enabling us to study a variety of ensembles such as the isothermal-isobaric (NPT) ensemble or the isoenthalpic-isobaric (NPH) ensemble.

In this paper, we use the MD method to simulate an Argon (Ar) gas of several hundred particles. We solve the equations of motion and extract several relevant thermodynamic quantities. In section II, we lay out the theoretical framework of those quantities. We discuss their relevance and the theoretical predictions of their values. In section III, we lay out the model of the computational simulation. We discuss the design of the model, including matters like the algorithm, the choice of potential function and the initialization method. In section IV, we present the results of our simulation. We relate our results to the predictions from section II. Finally, in section V, we conclude this paper.

II. THEORETICAL FRAMEWORK

Once we have succeeded in creating a stable simulation of the system, we want to be able to extract physical observables from the system. Here, we shortly discuss four physical parameters of the system.

A. Pair correlation function

The pair correlation function (or radial distribution function) $g(r)$ describes how the particle density $N/V(\rho)$ varies with the distance r. It is a measure of the probability of finding a particle a distance r away from a reference particle. Usually, the pair correlation function is normalized with respect to an ideal gas, where all particle pairs are completely uncorrelated. It is determined by sorting the distances between all particles into a histogram[2]. Mathematically, this is expressed as

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

where r denotes the distance and $\langle n(r) \rangle$ denotes the number of particles in the spherical shell $4\pi r^2 \Delta r$. The pair correlation function provides valuable information about the phase of the system. When the system is in the gas phase, $g(r)$ should go to one for large r, since every next

shell should contain approximately the same amount of particles. For smaller r $g(r)$ should show a single large peak. In both a liquid and solid, $g(r)$ should also decay to one for large r. In the case of a liquid, this decay is typically quite smooth, with a few smooth peaks for smaller r. In a solid, where the particles reside on a evenly spaced lattice, $g(r)$ typically shows big peaks before decaying to one.

B. Pressure

The pressure of the system can be calculated using the virial theorem. However, since we usually use a cutoff when calculating the pairwise interactions, we need to correct for this[2]. Thus, we obtain

$$
\frac{P}{nk_BT} = 1 - \frac{1}{3Nk_BT} \left\langle \sum_i \sum_{j<i} r_{ij} \frac{\partial U(R)}{\partial r_{ij}} \right\rangle_{co} \\
- \frac{2\pi N}{3k_BTV} \int_{r_{co}}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r)dr, \quad (2)
$$

where the first term on the right hand side represents the ideal gas equation of state, the second term the virial correction and the last term the correction for the cutoff distance r_{co}.

Intuitively, we would expect the pressure of the system to increase with increasing particle density. Additionally, we expect higher pressures for higher temperatures. However, for certain specific values of the density and temperature, we could be close to a phase transition. In those regions, the above reasoning does not hold. Typical results can be presented in a diagram showing multiple isotherms for varying density.

C. Heat capacity

In the NVE ensemble and in the absence of angular rotational and vibrational modes the fluctuations in kinetic energy can be related to the specific heat[3] as

$$
C_V^{NVE} = \frac{3N}{2} \frac{1}{1 - \frac{3N}{2} \frac{\langle \delta K^2 \rangle}{\langle K \rangle^2}}, \quad (3)
$$

where $\langle \delta K^2 \rangle$ denotes the variation in kinetic energy K and $\langle K \rangle^2$ represents the average kinetic energy squared. When the variations in the kinetic energy K go to zero, the heat capacity goes to $3Nk_B/2$. Thus, the heat capacity per particle should equal $3k_B/2$, similar to that of an ideal gas. We expect the gaseous system to approach the heat capacity of an ideal gas for a very large number of particles, since $\langle K \rangle \sim N$ and $\langle \delta K^2 \rangle \sim \sqrt{N}$. For a solid, we can consider the system as being made up of $3N$ independent harmonic oscillators (3 for each spatial

dimension) and when we recall that each harmonic oscillator has an average energy of k_BT, we find that a solid should have a specific heat capacity $C_V = 3Nk_B$. In this case, the specific heat per particle should equal $3k_B$.

In the NVT ensemble, the heat capacity can be evaluated as[4]

$$
C_V^{NVT} = \frac{\langle \delta V^2 \rangle}{T^2} + \frac{3N}{2}, \quad (4)
$$

where $\langle \delta V^2 \rangle$ is the variance of the potential energy and T is the temperature. Here, we also see that when the fluctuations of the potential energy go to zero, we should find that $C_V = 3k_B/2$.

D. Diffusion

There are many ways to describe the diffusive behavior of particles in a gas, liquid or solid. A general approach is solving the Langevin equation assuming that no external force is present[5]. To quantify the diffusive behavior of the system, we are interested in the mean squared displacement $\langle x^2(t) \rangle$. Without losing generality, we can distinguish two regimes: the ballistic regime and the diffusive regime. For short times t, when particles have not moved far enough to collide with each other, we expect that

$$
\langle x^2(t) \rangle \sim t^2. \quad (5)
$$

This is the ballistic regime. For large t, when the effect of collisions is already absorbed in the mean squared displacement, we expect that

$$
\langle x^2(t) \rangle \sim Dt, \quad (6)
$$

where D denotes the diffusion coefficient. This is the diffusive regime. The diffusion coefficient should reflect in which phase the system is. For a gas $D > 1$, for a liquid $D \sim 10^{-1}$ and for a solid $D \sim 0$, meaning that there occurs no diffusion of particles in a solid, since each particle is bound to its lattice site.

III. MODEL

This section attempts to set out the method used to compute the trajectories of all the particles which will allow the computation of the aforementioned observables.

A. Verlet's algorithm

To update the positions and momenta for every timestep, we use the Verlet algorithm. It is very stable with respect to errors due to the finite numerical precision of the simulation[2]. The algorithm is defined as

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}\Delta t + \frac{\mathbf{F}(t)}{2m}\Delta t^2 + \mathcal{O}\left(\Delta t^3\right) \qquad (7)$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{\Delta t}{2m}\left[\mathbf{F}(t + \Delta t) + \mathbf{F}(t)\right] + \mathcal{O}\left(\Delta t^3\right).$$

Although this algorithm is stable, it takes $\mathcal{O}(N^2)$ calculations per time step to calculate all contributions to the force, since we use a pair-interaction potential. Another problem is formed by the boundary conditions. Here, we will assume periodic boundary conditions (PBC). We discuss our approach to these matters below.

To derive Verlet's algorithm, we Taylor expand $\mathbf{r}(t + \Delta t)$ in Δt to find

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \left.\frac{d\mathbf{r}}{dt}\right|_t \Delta t + \frac{1}{2}\left.\frac{d^2\mathbf{r}}{dt^2}\right|_t \Delta t^2 + \mathcal{O}(t^3). \quad (8)$$

Substituting the velocity and the force in equation 8, we find equation 7 up to order Δt^2. The velocity equation requires some additional work. Taylor expanding the velocity gives

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{\mathbf{F}(t)}{m}\Delta t + \frac{1}{2}\left.\frac{d^2\mathbf{v}}{dt^2}\right|_t \Delta t^2 + \mathcal{O}(\Delta t^3). \quad (9)$$

However, calculating the second derivative of the velocity would require an extra computational step. To avoid this, we Taylor expand $v(t)$ to obtain

$$\mathbf{v}(t) = \mathbf{v}(t + \Delta t) - \frac{\mathbf{F}(t - \Delta t)}{m}\Delta t + \frac{1}{2}\left.\frac{d^2\mathbf{v}}{dt^2}\right|_{t + \Delta t}\Delta t^2 + \mathcal{O}(\Delta t^3). \quad (10)$$

Combining 9 and 10, we find

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{\Delta t}{2m}\left[\mathbf{F}(t + \Delta t) + \mathbf{F}(t)\right] + \frac{\Delta t^2}{4}\left[\left.\frac{d^2\mathbf{v}}{dt^2}\right|_t - \left.\frac{d^2\mathbf{v}}{dt^2}\right|_{t + \Delta t}\right] + \mathcal{O}\left(\Delta t^3\right). \quad (11)$$

The third term on the right hand side is of the order Δt^3, and we can thus ignore it. We then obtained the velocity part of the Verlet algorithm.

B.   Boundary conditions

We assume PBCs on the edges of the system. To this end, we periodically extend the system in all three directions. This has as a consequence that we have to take into account an infinite number of interactions. To avoid this, we only take into account the nearest copy for each particle in the system. This is called the minimum image convention and is depicted in figure 1.
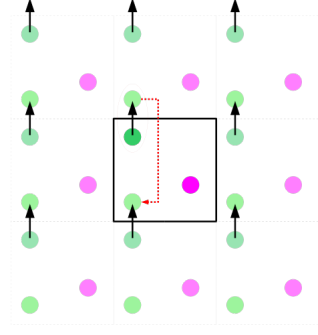

FIG. 1.   Minimum image convention.   Figure taken from en.wikipedia.org/wiki/Periodic_boundary_conditions

C.   Lennard-Jones Potential

We model the interaction between the Argon molecules with the Lennard-Jones (L-J) potential. Thus, we take into account only pairwise interactions depending on the distance between the molecules $|\mathbf{r}_i - \mathbf{r}_j|$. The Lennard-Jones potential is given by

$$V_{LJ}(r) = \epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - 2\left(\frac{\sigma}{r}\right)^6\right], \qquad (12)$$

and is depicted in figure 2. The repulsive behavior at short range is taken into account by the r^{-12} term. Physically, this term models the Pauli repulsion due to overlapping electron orbitals at short distances. The attractive behavior at longer distances is modeled by the r^{-6} term. This is the Vanderwaals interaction. The parameters ϵ and σ determine respectively the depth of the potential well and the distance at which the potential is minimal. For Argon, experiments have shown that $\epsilon = 1.65 \times 10^{-21}\,J$ and $\sigma = 3.82 \times 10^{-10}m$.

The lowest energy configuration for an infinite number of particles described by the Lennard-Jones potential is a hexagonal close-packed lattice (HCP). The lowest free energy arrangement is the cubic close-packed or face-centered cubic (FCC) lattice.
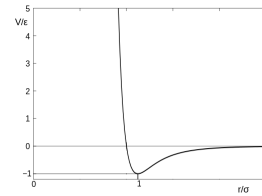

FIG. 2.   The Lennard-Jones potential plotted as function of the intermolecular distance.   Figure taken from en.wikipedia.org/wiki/Lennard-Jones_potential.

From this interaction potential, the intermolecular force can be simply calculated. The force on a molecule

i is given by

$$\mathbf{F}_i = \sum_{j=1,j\neq i}^{N} \mathbf{F}_{ij} = \sum_{j=1,j\neq i}^{N} -\nabla_{\mathbf{r}_i} V_{LJ}\left(|\mathbf{r}_i - \mathbf{r}_j|\right). \quad (13)$$

Exploiting Newton's third law ($\mathbf{F}_{ij} = -\mathbf{F}_{ji}$) reduces the number of computations that need to be done with a factor 2.

D. Initialization

Considering equation 7 we note that the positions and momenta of the particles at each discrete point in time are dependent on the previous positions and momenta. This forces us to assign an initial position and momentum to each particle. We want to make small time steps as this will increase the precision of our simulation. However, due to computational limitations, this means that the total simulation time is limited. We therefore want the system to start close to an equilibrium state. Otherwise, the number of timesteps, that need to be calculated before the system reaches equilibrium, is unreasonably big. For Argon simulated with a Lennard-Jones potential the FCC lattice, which is shown in figure 3, is an equilibrium configuration. The unit cell of the FCC lattice has sides a, which is related to the density as $\rho = 4/a^3$. The initial positions are set to be the coordinates of the primitive unit cells that make up the total lattice.

The initial momenta are drawn from the Maxwell-Boltzmann distribution for the momentum vector:

$$P(p_x, p_y, p_z) = (2\pi m k_B T)^{-\frac{3}{2}} \exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{2m k_B T}\right] \quad (14)$$

Instead of drawing out N vectors, we draw out $3N$ scalars, that we then use to create N vectors.
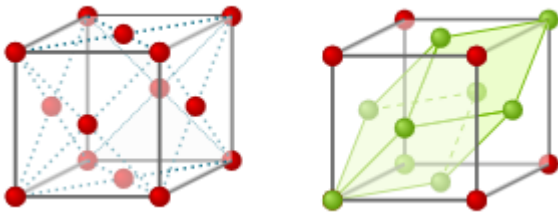

FIG. 3. The FCC lattice. The left figure depicts the conventional unit cell; the right figure the primitive unit cell. In the simulation, the primitive unit cell is used. Figure taken from http://www.physics-in- a-nutshell.com/article/11

Furthermore, we need to define the physical parameters of the system. For reasons of simplicity we use natural units. Thus, m, ϵ, σ and k_B equal to 1. As a consequence, the length, particle density, temperature and time scales change. Length is defined in units of

TABLE I. Natural units with their corresponding values for Argon.

	symbol	reduced value		value
position pot. min.	σ	1	⇔	0.382 nm
depth of potential	ϵ	1	⇔	10.3 meV
mass of particle	m	1	⇔	6.63×10^{-26} kg
temperature	T	1	⇔	119.8 K
time	τ	$\sqrt{\frac{m\sigma^2}{\epsilon}} = 1$	⇔	$2.42ps$

σ. The particle density is then defined in units of $1/\sigma^3$. Temperatures are measured in units of $\epsilon/k_B = 120K$ and time is measured in $\tau = \sqrt{m\sigma^2/\epsilon} = 2.4$ ps. A clear overview of the natural values and their corresponding physical values is given in table I.

Finally, we need to define the timestep. It is important that the time step is much smaller than the time in which a particle can cover a distance σ. Otherwise, two particles can end up in each others hard core repulsion zone, which will cause the force to blow up. Quantitatively, we need to choose a timestep t_{step} such that $t_{step} \ll \sigma/v$. The most probable speed drawn from a Maxwell-Boltzmann distribution is given as $v = \sqrt{2k_B T/m}$, which reduces to $v = \sqrt{2}$ in natural units. We thus find that $t_{step} \ll 1/\sqrt{2}$. In fact, the actual value of t_{step} is not very important as long as it is small enough, although a value that is superfluously small is a waste of computation power. Earlier work[1] uses $t_{step} = 0.016 \times \tau$. Here, we use $t_{step} = 0.004 \times \tau$.

E. Averages & error estimation

During the simulation, we will want to be able to determine average values of physical quantities. Also, we want to be able to bound the error associated with the average values. We can determine the ensemble average $\langle A \rangle = \frac{1}{N}\sum_{i=1}^{N} A_i$ of the physical quantity A as the average over multiple independent simulations of the system. In practice, the time average $\overline{A} = \frac{1}{N}\sum_{i=1}^{N} A_i$ converges to the ensemble average for long enough times. This is thus a convenient way to evaluate the average since the system does not need to be brought to equilibrium multiple times. Note that 'time' here does not necessarily represent the physical time. From this, we can estimate the variance as

$$\sigma^2 = \overline{A^2} - \overline{A}^2. \quad (15)$$

However, if the subsequent samples A are correlated in time, this procedure does not produce reliable results. Therefore, we need to divide up the data in blocks that are longer than the correlation time of the data. This length can be obtained from calculating the correlation time, but can also be found through trial and error. Also, we need to take care to have enough blocks to calculate the average and standard deviation reliably. This procedure is called data-blocking.

IV. RESULTS & DISCUSSION

We simulate the system in natural units and for $N = 864$, unless specified otherwise. Below, we present our results. First, we consider the energy, which functions as a stability check of the simulation. Then, we consider several physical quantities.

A. Energy

In order to check whether the simulation is physically sound, we plot the energy over time. In the NVE ensemble, the total energy should be (approximately) constant. Figure 4 shows the energy of the system over time. We observe small fluctuations of the potential and kinetic energy, while the total energy is conserved. Also, we can clearly see that the system needs some timesteps to reach equilibrium. This is valuable information, since it tells us not to consider those timesteps when we calculate the physical quantities of the system.
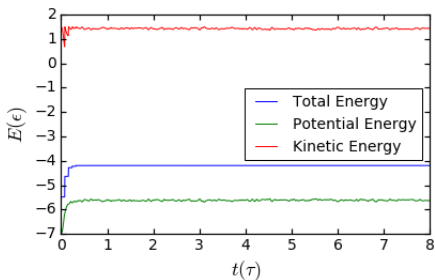

FIG. 4. The total, kinetic and potential energy for $T = 1$ and $a = 1.5$ ($\rho \simeq 1.19$)

B. Pair correlation function

We calculate the correlation function for different values of the temperature and density. These values were chosen such that the system was clearly in the gas, liquid or solid phase. Figure 5 shows typical plots for the correlation function of the system in the gas, liquid and solid phase. The blue line corresponds to the gas phase. We observe one large peak after which the correlation function decays swiftly to one. This is typical behavior for a gas as discussed in section II. The green and red lines show typical liquid and solid behavior. The graph for the solid shows multiple peaks, which is in agreement with the periodicity of the lattice. This results confirm our predictions from section II. Moreover, they give us confidence that the simulation works correctly and that we can reliably distinguish the different phases of the system.
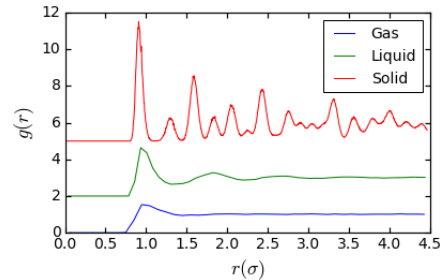

FIG. 5. The correlation function for $N = 4000$ in a gaseous phase $(T = 2.5, a = 2$ $(\rho = 0.5))$, liquid phase $(T = 1, a = 1.5$ $(\rho \simeq 1.19))$ and the solid phase $(T = 1, a = 1.3$ $(\rho \simeq 1.82))$. For reasons of clarity, the graphs corresponding to the liquid and solid have offset 2 and 5 respectively.

C. Pressure

We evaluate equation 2 with $g(r) = 1$ for $r > r_{co}$, which is a good approximation. Following earlier work[1], we calculate the pressure for the isotherms $T = 1$, $T = 1.35$ and $T = 2.74$. Figure 6 shows the results. For $T = 1$, we observe - in agreement with earlier work[1] - a negative pressure for lower densities. At this temperature, the gas wants to condense and so exerts a net inward force in the systems' 'walls'. When increasing the density, this behavior disappears and the pressure starts to rise rapidly with the density.
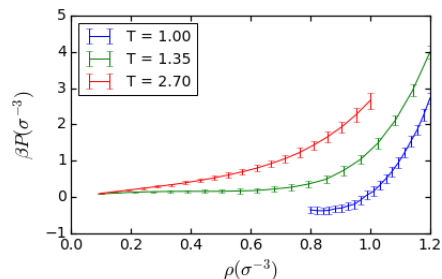

FIG. 6. The pressure for $T = 1$, $T = 1.35$ and $T = 2.70$.

D. Heat capacity

We calculate the heat capacity in the NVE ensemble using equation 3. Figure 7 shows the results for different temperatures and for different densities. For lower unit cell size, we nicely see that the heat capacity assumes the proper value of 3. Here, the system is in the solid phase. When increasing temperature, it decays towards 3/2, although it fails to actually reach it. This is because the system will not become a gas at such low temperatures. For larger unit cell sizes the heat capacity

converges to 3/2 much more quickly since it is already in the gas phase. Also, it is worth noting that the error is reasonably small.
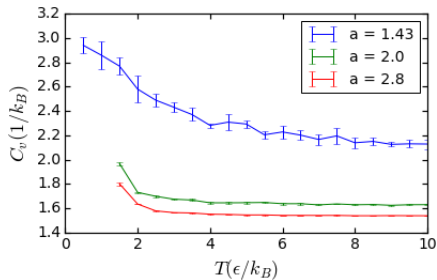

FIG. 7. The heat capacity in the NVE ensemble for a solid $(a = 1.43 \ (\rho = 1.37))$ and two gases $(a = 2.0 \ (\rho = 0.5); a = 2.8 \ (\rho = 0.18))$.

For the NVT ensemble, we find a heat capacity that is constantly 3/2 except for fluctuations on the order of 10^{-2}. It seems to be independent of temperature and density. For a solid this seems to be a problem since we expect a value of 3. Similarly we do not expect the heat capacity of the gas phase to be so close to 3/2 since there are interactions between the particles.

E. Diffusion

We determine the diffusion coefficient D for different phases by evaluating the mean-squared displacement at different times after the system has reached equilibrium. Considering equation 6, it seems natural to fit a linear regression to the data of the mean-squared displacement in order to determine the diffusion constant D and its corresponding autocovariance. Figures 8a and 8b show the results for the gaseous phase. The linear regression lines are only slightly off for small times. This is due to the ballistic movement of the particles. After a short time, we enter the diffusive limit. For a very dilute gas this effect is more pronounced since the average distance between particles is much larger. As such it takes more timesteps before the particles have made their first collisions. For a liquid, this behavior is the same, but now the diffusion is much slower, as shown in figure 8c.

Figure 8d shows the mean-squared displacement of a gas against the time squared for short times. Again performing a linear regression confirms that the mean-squared displacement indeed scales as t^2, which implies that the system is in the ballistic limit. Figure 8e shows the mean-squared displacement of a particle in the solid phase. As can be seen, the mean-squared displacement reaches a small value almost immediately after which it fluctuates around a constant value. This is as expected since the particles behave as harmonic oscillators fixed to their lattice sites.
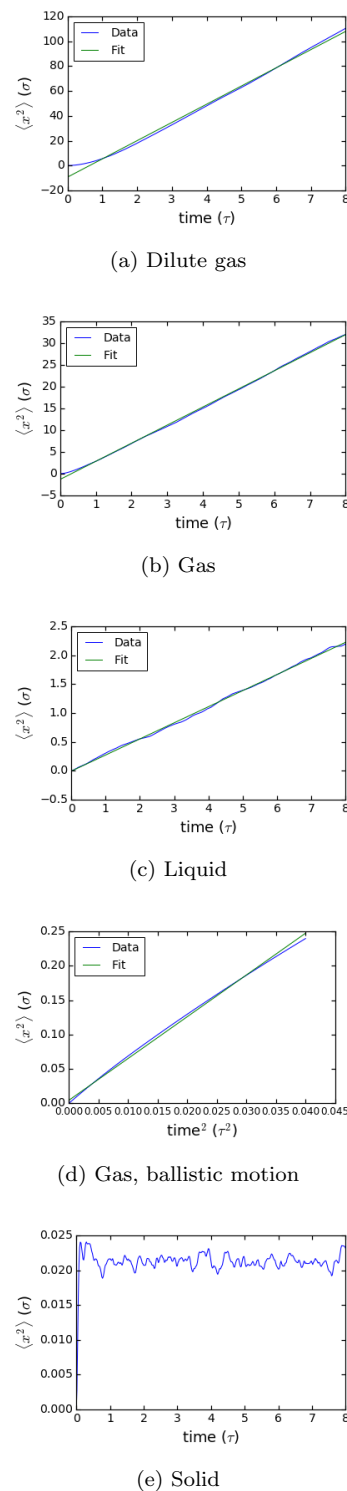

(a) Dilute gas

(b) Gas

(c) Liquid

(d) Gas, ballistic motion

(e) Solid

FIG. 8. The mean-squared displacement for various phases. (a) A dilute gas $(T = 2.5, a = 3 \ (\rho \simeq 0.15))$. Note that it takes the system relatively long to go from the ballistic regime to the diffusive regime. $D = 1.46 \times 10^1 \pm 2.4 \times 10^{-3}$. (b) A gas $(T = 2.5, a = 2 \ (\rho = 0.5))$. $D = 4.2 \times 10^0 \pm 2.5 \times 10^{-5}$ (c) A liquid $(T = 1, a = 1.5 \ (\rho \simeq 1.19))$. $D = 2.8 \times 10^1 \pm 2.5 \times 10^{-7}$ (d) A gas $(T = 2.5, a = 3 \ (\rho \simeq 0.15))$. Here, we zoomed in on the ballistic regime. Note that the horizontal axis shows time squared (τ^2). (e) A solid $(T = 2.5, a = 1.3 \ (\rho \simeq 1.82))$. $D \sim 0$.

V. CONCLUSION

We have examined the properties of an Argon gas using the MD method. By evaluating the pair correlation function, we were able to distinguish the gas and the solid phase of the system. The gas solidifies at low temperature and high density, which could clearly be observed from the form of the correlation function. Also, we could distinguish the liquid phase from the gas phase reasonably well. Pressure calculations of various isotherms result in typical phase diagrams that correspond again reasonably well with earlier work[1]. The heat capacity in the NVE ensemble equals approximately 3 for low temperature and high density. However, it then quickly starts to decrease to $3/2$, which is the predicted value for an ideal gas. A reasonable explanation for the fact that the heat capacity does not always quite reach $3/2$ is that it depends on the fluctuations in the kinetic energy, that -

for a finite system - are not zero. Finally, we find that the diffusive behavior of the system can be neatly characterized for the gas, liquid and solid phase. Thus, we conclude that the MD method is reasonably successful at simulating an Argon gas consisting of 864 particles.

To improve this simulation, future work could focus on using longer simulation times and longer datablocking lengths to reduce the errors in the system. Also, simulating with more particles should reduce the variance of most physical quantities. In particular, the heat capacity calculation should benefit from this. However, this demands much more computational power.

To extend the analysis of the Argon system, more quantities and ensembles could be taken into account. The grand canonical, NPH and NPT ensemble could be considered. Furthermore, the behavior of the system around critical phase transitions could be investigated. Finally, other molecules with internal degrees of freedom could be considered.

[1] Loup Verlet. Computer experiments on classical fluids. i. thermodynamical properties of lennard-jones molecules. *Physical Review Letters*, 159(1), 1967.

[2] J.M. Thijssen. *Computational Physics*. Cambridge University Press, Cambridge, United Kingdom, 1999.

[3] J. L. Lebowitz, J. K. Percus, and L. Verlet. Ensemble dependence of fluctuations with application to machine computations. *Phys. Rev.*, 153:250–254, Jan 1967.

[4] D.J. Tildesley M.P. Allen. *Computer simulation of liquids*. Oxford University Press, Oxford, United Kingdom, 1987.

[5] Jos Thijssen. Lecture notes in advanced statistical mechanics, September 2014.