Molecular Dynamics Simulation for Argon atoms

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Abstract—This project aims to develop a molecular dynamics simulation of Argon particles. Different simulations are performed with variations of the temperature and the density of the system. The simulations were done to compute the thermodynamic properties of *heat capacity*, *pair correlation function* and *pressure*. The results obtained closely resemble the experimental reference material, proving that the simulation built on the Lennard-Jones potential is a suitable approximation for an Argon system.

Keywords—*Lennard-Jones potential, Molecular Dynamics, Thermodynamics, Argon*

I. INTRODUCTION

Molecular dynamics is a sub-field of computational physics which address the problem of many interacting atoms and molecules. In molecular dynamics, the equations of motion for the particles are solved using Newton equations straightforwardly using numerical algorithms.

The aim of molecular dynamics simulations is to predict the behaviour of gases, liquids and solids (and systems in other phases, like liquid crystals) by calculating physical quantities such as the pressure, correlation function, density, as statistical averages over a restricted set of states. The system moves in phase space along its physical trajectory as determined by the equations of motion. In general the systems that can be simulated are always much smaller than realistic systems, however this method over a considerable amount of particles exhibit very reliable results. Through this project we simulated a system at a predefined temperature and density.

The report is divided in two main sections named: *Molecular Dynamics Simulation* and *Results and Discussion*. First, we are going to explain all the methodology and know how of developing a molecular dynamics simulation and afterwards the results will be discussed based on the different thermodynamic properties.

II. MOLECULAR DYNAMICS SIMULATION

A. Equations of motion

The classical Molecular Dynamics(MD) simulations are based on integrating Newton's equations of motion for the particles which build up the investigated system:

$$m\frac{d^2r_i}{dt^2} = F_i(r_1, r_2, ..., r_N) \quad i = 1, 2, ..., N \qquad (1)$$

Here r_i are the position vectors and F_i are the forces acting upon the N particles of the system. In this case the force is derived from a potential, in our case the Lennard Jones

potential which will be explained in the next subsection. However, this potential functions, $U(r_1, r_2, ..., r_N)$ always represent the potential energy of the system for the specific geometric arrangement of the particles. In all cases the forces are computed as following:

$$F_i(r_1, r_2, ..., r_n) = -\nabla_{r_i} U(r_1, r_2, ..., r_n) \qquad (2)$$

This form implies the conservation of the total energy $E = E_{kin} + U$, where E_{kin} is the instantaneous kinetic energy. In the absence of external forces, the potential can be represented in the simplest case as a sum of pairwise interactions:

$$U = \sum_{i=1}^{N} \sum_{j>i}^{N} U(r_{ij}) \qquad (3)$$

where $r_{ij} = r_i - r_j$, and the condition $j > i$ prevents the double counting of the particle pairs. The forces acting on the particle are composed in such case of the individual interactions with the rest of the particles:

$$F_i = \sum_{j\neq i}^{N} f_{ij}, \quad f_{ij} = -\frac{dU(r_{ij})}{dr_{ij}} \cdot \frac{\vec{r}_{ij}}{r_{ij}} \qquad (4)$$

According to Newton's third law, $f_{ij} = -f_{ji}$. The computational effort to solve the set of equations of motion Equation 1 is $\mathcal{O}(N^2)$ and is mainly associated with the evaluation of forces. Therefore, for tractable computations the forces should be expressed analytically. To further reduce the computational effort the potential can be cut off at some limiting separation (for $r_{ij} > r_{\text{cut-off}}$) beyond which the potential becomes negligible.

Next, the model for interaction is discussed.

B. Interaction Model

The Lennard-Jones potential is one of the most famous pair potentials for Van der Waals systems, it is defined as[1]:

$$U_{LJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right], \qquad (5)$$

where ϵ is an energy parameter that governs the strength of the interaction, and σ is a distance parameter that defines the length scale, since $U(\sigma) = 0$.

The term proportional to r_{ij}^{-12}, dominating at short distances, models the repulsion due to the non-bonded overlap of the electronic orbitals, namely due to the Pauli exclusion Principle.

The attractive term proportional to r_{ij}^{-6} dominates at large distances and it models the van der Waals dispersion forces caused by the dipole-dipole interactions due to fluctuating

dipoles. These weak forces provide the bonding character of closed-shell systems, such as Argon.

The inter-particle forces arising from such potential Equation 5 can be computed using Equation 2 and can be expressed as:

$$f_{ij} = \frac{48\epsilon}{r_{ij}^2} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \frac{1}{2} \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \vec{r}_{ij} \qquad (6)$$

A downside of this model is the fact that atoms are treated as classical objects, which is suitable in the case of closed-shell system. However, the Lennard-Jones potential is totally inadequate for open shell systems, in which strong localized bonds are formed. By closed and open shell systems we make reference to whether the valence shell is/isn't completely filled with electrons. Open shell molecules are more difficult to study computationally [2].

C. Boundary and Initial conditions

In order for the computational experiment to yield realistic results, realistic boundary and initial conditions are necessary. This Section will discuss the choices made for computing Argon particles, and the consequences that they bring.

1) Boundary conditions: In order to simulate the bulk of a fluid or solid, many particles should be taken into account. However, due to the fact that the computation of the force scales with N^2, a good equilibrium should be found.

In this experiment, the bulk of the particles is simulated by inducing Periodic Boundary Conditions (PBC). In short, this boundary conditions implies that there are 26 boxes of the same size surrounding the computational domain, and mimicking the particle position and speed in each box. This greatly increases the behaviour of the gas, as there is no interaction with a wall, and implicitly more particles are simulated.

The consequence of this condition is that these particles in other boxes have to be taken into account when computing the force interaction. The particle does not only interact with each partner j in the system cell but also with the images of particle j in all the copies of the system. In principle a infinite number of interactions has to be summed over. One way of overcoming this problem is finding the nearest neighbour of each particle (which can be outside of the computational domain) based on the fact that the force decays with the distance, and that the particles which are not the nearest neighbour have a negligible influence on the particle for which the force is computed. Therefore each infinite sum over all the copies is replaced by a single term.

Often it is possible to cut the interactions off at a distance $r_{\text{cut-off}}$ smaller than 3σ. In that case the forces do not have to be calculated for all pairs. However all the pairs are needed to check whether their separation is larger than $r_{\text{cut-off}}$. This cut-off distance has consequences when calculating thermodynamic properties, which will be discussed in the next subsection.

2) Initial conditions: In order to evaluate the thermodynamic quantities, the system has to be initialized in a certain condition. In these experiments, the density (ρ) and the temperature (T) were chosen beforehand and the system is set into the state determined by those values of ρ and T.

For the initialization of the position the particles, a FCC structure was chosen, because it is the ground state configuration for noble gases like argon [3]. According to the desired density, the distance between all particles was scaled to acquire the desired density.

The initial velocities were randomly chosen from a Maxwell Distribution of speed, with zero mean and variance $\sqrt{kT/m}$, with k the Boltzmann constant and m the mass of the particle, in order to approximate the desired temperature of the system. In order to enforce zero mean momentum, the mean of the momenta of the system is subtracted from each particle.

It has been found that after this initialization, the average kinetic energy tends to change over the first timesteps. In order to be able to compute the thermodynamic quantities, the system has to be stationary, i.e. the mean kinetic and potential energy should not move. In order to make the system converge to this stationary state, and in order to enforce the right temperature, the momenta are scaled as follows:

$$p_i \rightarrow p_i \sqrt{\frac{3/2(N-1)kT}{E_{\text{kin}}}}. \qquad (7)$$

D. Reduced Units

One important step in developing a Molecular Dynamics simulation is transforming all the magnitudes are into reduced units or dimensionless magnitudes, because, among other reasons, enable:

1) the possibility to work with numerical values of the order of unity, instead of the typically very small values associated with the atomic scale.
2) the simplification of the equations of motion, due to the absorption of the parameters defining the model into the units.
3) the possibility of scaling the results for a whole class of systems described by the same model.

A table with the reduced units can be found in Table I

TABLE I: Basic Units for liquid Argon

Physical quantity	Unit	Value for Ar
length	σ	3.4×10^{-10}m
energy	ϵ	1.65×10^{-21}J
mass	m	6.69×10^{-26}kg
time	$\sigma \, (m/\epsilon)^{1/2}$	2.17×10^{-12}s
temperature	ϵ/k	120K
force	ϵ/σ	4.85×10^{-12}N
pressure	ϵ/σ^3	4.20×10^7 Nm^2

E. Investigated thermodynamic properties

Considering the temperature T and density ρ as independent variables, the total energy and the pressure, as well as the heat capacity and the correlation function can be readily expressed.

The energy and the pressure provide the link between the microscopic and macroscopic level. It should be noted that, however, that in MD simulation the energy is constant, rather than the temperature.

This section discusses the investigated thermodynamic properties, and how to these are computed.

1) Kinetic and Potential Energy: After the units reduction, the Kinetic and Potential Energy are:

$$E_{kin} = \frac{1}{2} \sum_{i=1}^{N} v_i^2 \qquad (8)$$

$$U = 4 \sum_{i<j}^{N} \left(r_{ij}^{-12} - r_{ij}^{-6} \right) \qquad (9)$$

2) Temperature: Since each translational degree of freedom contributes to the total kinetic energy by $kT/2$, the temperature of the system may be defined by:

$$T = \frac{2E_{kin}}{k(3N-3)} \qquad (10)$$

The denominator corresponds with taking all the particles and also considering that already three degree of freedom have been removed by doing the averaging over the momentum to make it zero.

This computation is done once the system have reach the equilibrium, with the kinetic energy result from the Verlet algorithm [4].

3) Heat Capacity: The heat capacity in the canonical ensemble, at constant volume is defined as:

$$C_v = \left(\frac{\partial E}{\partial T} \right)_{N,V} \qquad (11)$$

Using the expression that the $E = -\frac{\partial lnZ}{\partial \beta}$ the heat capacity can be related with the root mean square fluctuation of energy:

$$C_v = \frac{1}{kT^2} \left(<E^2> - <E>^2 \right) \qquad (12)$$

However, in the microcanonical ensemble, the total energy is fixed therefore its fluctuation vanishes all the times. However, this amount can be calculated also from the fluctuation of the kinetic energy by the Lebowitz formula [5]:

$$\frac{<\delta E_{kin}^2>}{<E_{kin}>^2} = \frac{2}{3N} \left(1 - \frac{3N}{2C_v} \right) \qquad (13)$$

4) Correlation Function: Correlation functions describe how microscopic variables, such as spin and density, at different positions are related. More specifically, the correlation function quantifies how microscopic variables co-vary with one another on average across space and time.

This function contains information about the local structure of the fluid. For isotropic systems the correlation function only depends on the distance $\Delta r = |\vec{r} - \vec{r'}|$.

The correlation function is determined by keeping track of the numbers of particles $n(r)$ for every interval $[i\Delta r, (i+1)\Delta r]$. The expression used to compute the pair correlation function is [6]:

$$g(r) = \frac{2V}{N(N-1)} \left[\frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \right] \qquad (14)$$

5) Pressure: The pressure can readily be computed applying the virial theorem [7]:

$$\frac{\beta P}{n} = 1 - \frac{\beta}{3N} \left\langle \sum_{i=1}^{N} \vec{r}_{ij} \nabla_i U_N(r) \right\rangle \qquad (15)$$

where $\langle ... \rangle$ denotes the usual ensemble average.

However, this average is taken over all the particle pairs, not only the ones within the cut-off distance. In order to make up for this discrepancy, the expression for the potential energy has to be corrected.

$$\langle U \rangle = \langle U \rangle_{\text{cut-0ff}} + 2\pi \frac{N(N-1)}{V} \int_{r_{\text{cut-off}}}^{\infty} r^2 U(r) g(r) dr \quad (16)$$

Where $\langle ... \rangle_{\text{cut-off}}$ is the average restricted to pairs with separations smaller than the $r_{\text{cut-off}}$. For large r, the correlation function is often approximated by its asymptotic value 1.

Consequently the virial equation for the pressure should be corrected as well, yielding as [6]:

$$\begin{aligned} \frac{P}{\rho kT} = 1 - &\frac{1}{3NkT} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r)}{\partial r_{ij}} \right\rangle_{\text{cut-off}} \\ - &\frac{2\pi N}{3kTV} \int_{r_{\text{cut-off}}}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r) \mathrm{d}r \end{aligned} \qquad (17)$$

F. Algorithm

The algorithm that has been developed for simulating the Leonard-Jones liquid, has been globally described in Algorithm 1.

The main steps in the algorithm are:

1) *Initialize position:* The position will be initialized in a FCC lattice, dependent of the density ρ.
2) *Initialize velocity:* All the initialized particles will be given a random velocity in the $x-$, $y-$ and $z-$ direction taken from the Maxwell distribution of speed. After this, the average velocity is set to 0 in order to not have a moving box.
3) *Verlet Velocity algorithm:* The Verlet Velocity algorithm is used to integrate Newton's equation of motion for the particles.
4) *Scale momentum:* Scale the momentum to get a desired temperature, done according to Equation 7.
5) *Caclulate Forces:* The forces on each particle are calcuated according to Equation 4.
6) *Calculate Virial* Calculates the virial term from Equation 17. Because $\frac{\partial U}{\partial r}$ is computed during the force algorithm, one should use this information to be able to calculate the virial term cheaply.

7) *Particle distribution* The particle distribution is calcu-
lated from the distance between all the particle pairs.
Because the distance is computed in order to find the
force on each particle pair, one should compute n within
the force algorithm in order to do it cheaply.

Algorithm 1 General set-up of the code

Require: T and ρ given
1: Initialize position
2: Initialize velocity
3: **for** i in $N_{\text{timespteps}}$ **do**
4:     First-half Verlet Velocity step
5:     Calculate Forces
6:     Second-half Verlet Velocity step
7:     Calculate Kinetic Energy
8:     **if** $i \leq N_{\text{thermostat}}$ and $i \pmod{10} == 0$ **then**
9:         Scale momentum
10:     **end if**
11:     **if** $i > N_{\text{thermostat}}$ **then**
12:         Calculate Virial
13:         Calculate particle distribution (n)
14:     **end if**
15: **end for**
16:
17: **return** Kinetic Energy, Virial, n

The most time-consuming component of an MD calculation
concerns the evaluation of forces, since the force on 1 particle
is dependent on all other particles, so computing the force on
all particles scales with N^2.

For the integration of the velocities and accelerations we
use the Verlet Algorithm considering the speed at mid-interval
$v\left(t + \Delta t/2\right)$. The system of equations used are:

$$
\begin{aligned}
v\left(t + \Delta t/2\right) &= v(t) + \Delta t/2 \; a(t) \\
r\left(t + \Delta t/2\right) &= r(t) + \Delta t/2 \; v\left(t + \Delta t/2\right) \\
a\left(t + \Delta t\right) &= \frac{F\left(r\left(t + \Delta t\right)\right)}{m} \\
v\left(t + \Delta t\right) &= v\left(t + \Delta t/2\right) + \Delta t/2 \; a\left(t + \Delta t\right)
\end{aligned}
\tag{18}
$$

Expressing the speed at mid-interval has several advantages,
like:

- conservation of energy
- high stability
- low memory requirements

The error per integration step is the order Δt^4 [6].

III. RESULTS AND DISCUSSION

A. Energy conservation

Since the force between the particles is a central force,
that is, the interaction only depends on the distance between
the particles and not on the path taken by the particle, is a
conservative force. This fact implies that the force can be
rewritten as minus the gradient of certain potential, in this case
the Lennard Jones potential (Equation 5) and consequently the

total energy has to remain constant. The total energy is given
by the sum of the Kinetic energy and the potential energy due
to all the particles in each time step:

$$
E = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 + V(r)
\tag{19}
$$

Therefore this an important requisite that our system has to
fulfill in order to be correctly described.

Figure 1 shows the kinetic, potential and total energy of
the system over 350 timesteps: In this figure it can be seen
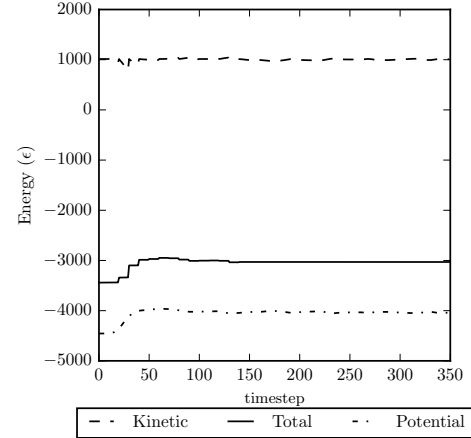

Fig. 1: The total, kinetic and potential energy during the first
300 timesteps of a simulation

that the system is not stable in at the start, the total energy
fluctuates with time. The big jump in kinetic energy around
the 30th timestep is due to the velocity scaling. The time that
the energy takes in relaxing is of the order of $\tau = \sigma\left(m/\epsilon\right)^{1/2}$
[6] which the value is shown in Table I. That is why is good
time steps is 10^{-14}s which in units of the relaxation time (τ)
is 0.004τ. After around 150 timesteps, the system seems to
be in equilibrium, where the total energy does not fluctuate
anymore.

B. Equilibrium properties

After the system has reached it's equilibrium, thermody-
namic properties can be deduced from the statistical ensemble
of the system. The investigated thermodynamic properties
that are going to be discussed are: Heat capacity, the pair
correlation function and the pressure.

1) Heat capacity: The heat capacity has been investigated
as a proof of concept. We wanted to show that it is possible to
calculate the heat capacity with the use of statistical mechanics
as a way of checking the program; if the expected extremes
of $C_v = 3NkT$ and $C_v = 3/2NkT$ are reached in the solid
and the gas phase respectively, we know our system would be
valid. Table II shows the results from these two extremes. T_D
is the desired temperature, to which the momenta are scaled
(see Equation 7).

TABLE II: Heat Capacity and Temperature for a solid and a gas

	Solid		Gas	
	$\rho = 0.88$	$T_D = 0.01$	$\rho = 0.01$	$T_D = 5$
C_v/N	3.066 ± 0.122		1.500 ± 0.0326	
T	$9.8943 \times 10^{-3} \pm 7 \times 10^{-3}$		5.0114 ± 0.0006	

From Table II it can be seen that the expected values for C_v/N are met, but with a relatively large uncertainty. This uncertainty comes from the fact that the heat capacity has to be deduced not only from a statistical ensemble, but from the variance of the ensemble. To deduce the errors in this calculation, one has to take the variance of the variance into account. With a limited amount of data points, this causes the relatively high error in the measurement.

2) Correlation function: The correlation function describes the structure of the system, in terms of how many particles there are at a distance r of each other. In the case of a solid, where the particles are regularly distributed in the lattice, it is expected to find narrow peaks for the correlation function.
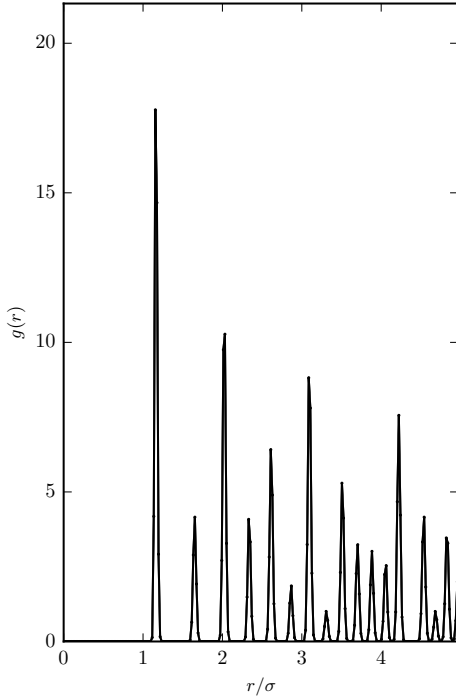

Fig. 2: Correlation function for a solid configuration ($T_D = 0.01$, $\rho = 0.88$ in reduced units)

Figure 2 shows this correlation function for a solid Argon at $T_D = 0.01$ and $\rho = 0.88$. As can be seen, before $r/\sigma = 1$ there are no particles present, after that there are narrow peaks. This 0 before $r/\sigma = 1$ is expected because $r/\sigma = 1$ is the 0 of the Lennard-Jones potential, if a particle comes closer, there is a strong repulsion force. The high narrow peaks

imply that the particles that are close don't move much, they are vibrating in their spot in the lattice, like in a solid. The first peak corresponds to the minimum of the Lennard-Jones potential, which is located at $r/\sigma = 2^{1/6}$. The error of this calculation was found to be in the order of 0.01.

Figure 3 shows this correlation function for liquid argon. In a liquid, the particles are assembled into a quasi random configuration with the same equilibrium distance as the solid. Again, no particles are expected before $r/\sigma = 1$ because of the repulsion forces due to the Pauli exclusion principle. The random configuration makes it so that the correlation function does not describe sharp peaks like in the solid case, but rather shows a peak at $r/\sigma = 2^{1/6}$, and after that varies around 1. This variation around 1 shows that the liquid is not completely random, but close to the atom the liquid is still structured. At larger distances this structure vanishes as $g(r)$ tends to 1. The error of this calculation was found to be in the order of 0.006.
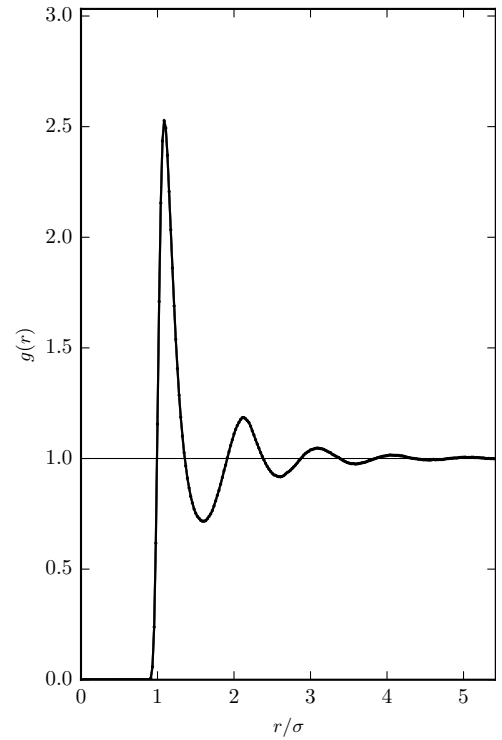

Fig. 3: Correlation function for a liquid configuration($T_D = 0.7833$, $\rho = 0.6775$ in reduced units)

It can be observed that the peaks of a solid are of higher amplitude than the case of a liquid and this can be readily explained because of the fact that the first one has a higher density and consequently is more probable to find more particles between the same intervals. Furthermore as part of the same idea, it is expected then, that the peaks of the solid are more narrow than for the liquids counting on the fact that both systems have the same amount of particles.

Regarding the approximation made in the pressure calculation, the pair correlation function is assumed to be $g(r) = 1$ after the cut-off distance of $r/\sigma = 3$. From Figure 3 it can be

seen that this is a good approximation for liquid because it fluctuates lightly around 1, but for the solid this might induce an error in the calculation.

3) Pressure: In order to describe the behaviour of the system at different temperatures and different density, isotherms for the relation between P/kT and density ρ have been shown in Figure 4, where isotherms at $T = 1.25$, 1.35, 2.74 are shown. Experimental data from [8] has been included to validate the M.D. simulation. It can be seen from Figure 4 that the simulation performed complies with experimental data at $T = 1.35$.

From [9] we have learned that the critical point for Argon is at $T = 1.25063$, and the isothermic line at $T = 1.25$ shows behaviour of an isotherm very close to this temperature. We see that it is lower than the critical temperature by it's initial rise in P/kT, dropping slightly before rising quickly. The initial rise can be seen from $\rho = 0.1 - 0.2$, dropping slightly from $\rho = 0.2 - 0.5$ and rising quickly afterwards. At the critical temperature, the first and second derivative of the pressure are 0 at a certain density. The graph of $T = 1.25$ shows behaviour close to this behaviour.

For temperatures above the critical temperature, the gas cannot be liquefied, regardless of pressure. Therefore, the isotherm at $T = 2.74$, it is expected to behave like a gas, regardless of density. At low densities, it is expected to behave like an ideal gas. This can be seen in the region of $\rho = 0.1 - 0.2$, where the pressure increases linearly with density.

The statistical errors were in the order of 10^{-3}.

IV. Conclusion

This project of Molecular Dynamics has brought useful insights of how to compute the main physical magnitudes of a system which involves many interacting particles in a finite space. Through the developing of the methodology that uses a Lennard-Jones potential, the Verlet velocity algorithm and periodic boundary conditions, we were able to create a simulation which produces results that resemble literature closely. Consequently we were able to deduce from this simulation a heat capacity, pair correlation function and isotherms for P/kT.

The errors of these properties are taken from a statistical treatment of these properties and from the assumption made in the computation of the integral beyond the cut-off distance. This did not introduce significant errors.

Therefore, the main results posted here are reproducible and consequently robust.

Acknowledgment

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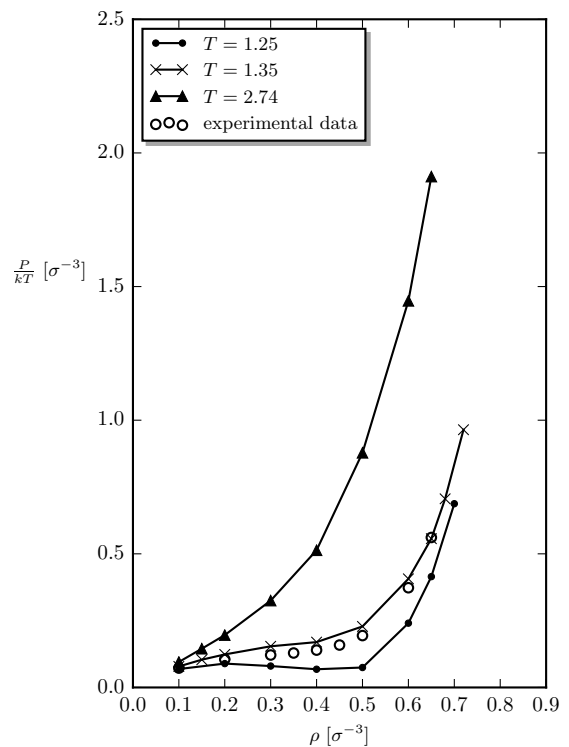

Fig. 4: Isotherms around the Argon critical temperature at: T=1.25063 ([9] in reduced units. The statistical errors were of order 10^{-3}. Experimental data at $T = 1.35$ from [8]

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