

Molecular Dynamics Simulation of Argon

MATTEO DOMENIGHINI 4512154

ANDRÉ MELO 4519302

Delft University of Technology

Abstract

The aim of this report is to present the results obtained using a molecular dynamics simulation. The interaction between particles is represented by the Lennard-Jones potential and is therefore particularly suited to describe the behavior of an Argon gas. Through the simulation it was possible to extrapolate the numerical values for some relevant thermodynamic quantities such as pressure, correlation function, specific heat and diffusion coefficient. These values are compared to the results obtained by Verlet [1], which are taken as reference in order to verify the accuracy of our simulation.

I. INTRODUCTION

Molecular dynamics is a computer simulation method which calculate the time dependent behaviour of a molecular system. The evolution of the system over time is based on Newton's equation of motion, where the intermolecular forces are modelled in this case with a Lennard-Jones potential. The particles are located in a cubic domain of size $V = L \times L \times L$, where L is calculated based on the considered density. The simulation considers periodic boundary condition and implements them using the nearest image convention. The presented results are calculated considering 864 atoms and updating the system for 10000 time steps unless otherwise stated. In the following sections we discuss the methods used in the simulation more in detail and present the results, comparing them to those obtained by Verlet [1].

II. METHODS

Equations of Motion

In the following discussion we adopt the convention used by Verlet [1] and Thijssen [2], in which $\epsilon = 1$, $\sigma = 1$, $m = 1$ and $k_B = 1$. ϵ and σ are the experimental constants of the Lennard-Jones potential, representing respectively the depth of the potential well and the distance at which the potential is zero, m is the mass of the argon atoms and k_B is the Boltzmann constant. The Lennard-Jones potential acting between two particles i and j can be written in the

form:

$$V(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

Using the above specified convention, this equation becomes

$$V(r_{ij}) = 4 \left(r_{ij}^{-12} - r_{ij}^{-6} \right) \quad (2)$$

The force resulting from the Lennard-Jones potential is therefore given by

$$\mathbf{F}(r_{ij}) = 24r_{ij} \left(2r_{ij}^{-14} - r_{ij}^{-8} \right) \quad (3)$$

The potential and the force are illustrated in Figure 1.

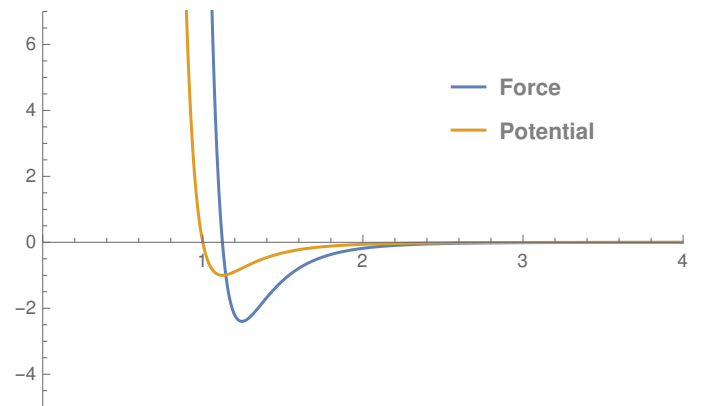


Figure 1: Lennard-Jones potential and force (natural units).

If we consider a specific particle i , the resultant of the forces is given by the sum over all the remaining particles

of the above expression. Using Newton's law of motion we can write

$$\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij} = m \mathbf{a}_i \quad (4)$$

We should note that since we chose m to be equal to 1, the total force acting on an atom is equal to its acceleration. Considering every pair of particles when calculating the total force requires $\mathcal{O}(n^2)$ steps, which becomes very computationally taxing when dealing with a high particle number. Since equation (3) behaves like r^{-8} at large distances, the contribution of particles such that $r_{ij} > 3\sigma$ is negligible and therefore not taken into account in the simulation.

The equations of motion are integrated using *Verlet's algorithm*. This algorithm is part of a broader class of algorithms called *symplectic integrators*, which are time reversible and therefore allow for the conservation of energy. It is to be noted that for long times, arithmetic error may still lead to an energy drift, since the error scales as $\mathcal{O}(h^2)$, where h is the adopted time step. The leap-frog variant of the algorithm consists in updating the positions and velocities of the particles through the following equations:

$$\mathbf{v}\left(t + \frac{h}{2}\right) = \mathbf{v}\left(t - \frac{h}{2}\right) + \mathbf{a}(t)h \quad (5)$$

$$\mathbf{r}(t+h) = \mathbf{r}(t) + \mathbf{v}\left(t + \frac{h}{2}\right)h \quad (6)$$

For more information on *Verlet's algorithm* and its implementation, see chapter 8.2 of Thijssen [2].

The time step chosen in the simulation is $h = 0.004\tau$, where $\tau = (m\sigma/\epsilon)^{1/2}$. Following the convention outlined before we set $h = 1$. In SI units h is roughly equal to 10^{-14} s.

To keep the particles from escaping the cubic domain, periodic conditions are implemented using the nearest im-

age convention, where inter-atomic distance is calculated with the equation

$$r_{ij} = \min_{\mathbf{n}} |\mathbf{r}_i - \mathbf{r}_j - n_{\mu} L_{\mu}| \quad (7)$$

where the components of n_{μ} take on the values $0, \pm 1$.

Initialization

The parameters set in the simulation are temperature (T) and density (ρ). The initial velocities are randomly generated from the Maxwell-Boltzmann distribution and the total momentum of the system is kept at zero by subtracting the average momentum from each component of the particles' velocities.

To initialize the simulation, the argon atoms are placed in an FCC lattice. This lattice can be divided in unit cells containing 4 atoms each; since the domain is cubic with M unit cells per unit length, there is a total of $N = 4M^3$ atoms. Choosing $M = 6$ bears $N = 864$, which is the number of particles taken into account in the simulation. As the simulation starts, the systems drift towards equilibrium, causing a change in the kinetic energy and consequently in the temperature. In order to maintain the temperature to a value close to the given one a virtual thermostat is introduced, which rescales the velocities after a fixed number of time steps. The thermostat applies the following transformation:

$$\mathbf{v}_i(t) \rightarrow \lambda \mathbf{v}_i(t) \quad (8)$$

$$\lambda = \sqrt{\frac{(N-1)3k_B T_0}{\sum_i m v_i^2}} \quad (9)$$

where T_0 is the set temperature.

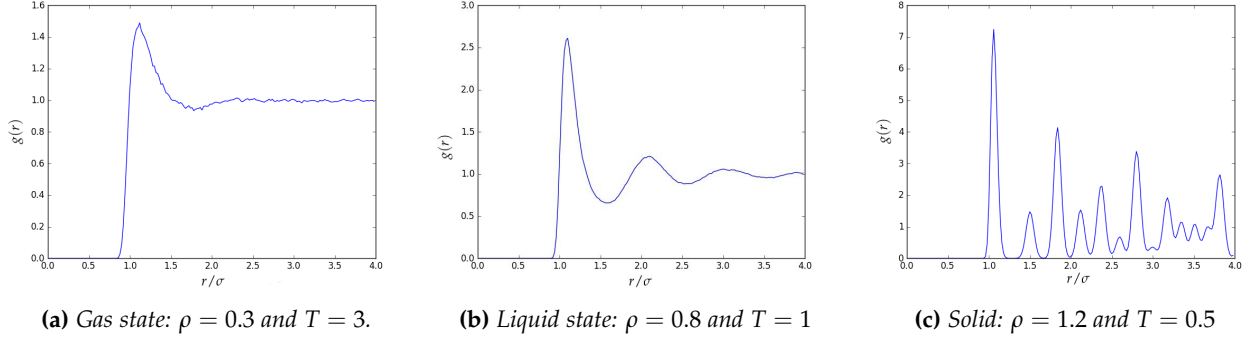


Figure 2: Pair correlation functions for different phases.

III. THERMODYNAMIC QUANTITIES

ρ	T	T_r	U/N	$\frac{\beta P}{\rho}$	C_v/N
0.30	1.5	1.7(1)	0.0615(6)	0.65(3)	1.70(6)
0.30	2	2.005(8)	0.9166(4)	0.91(2)	1.67(5)
0.30	2.5	2.547(7)	1.6909(3)	1.06(2)	1.64(4)
0.30	3	3.02(1)	2.53694(4)	1.17(2)	1.59(2)
0.45	1.0	1.08(2)	-1.819(1)	0.07(8)	1.9(1)
0.45	1.5	1.518(8)	-0.7178(5)	0.70(5)	1.8(1)
0.45	2	2.027(8)	0.2059(5)	1.09(4)	1.8(1)
0.45	2.5	2.520(6)	1.0799(3)	1.34(3)	1.7(2)
0.45	3	2.954(6)	1.8298(2)	1.47(3)	1.80(8)
0.60	1	0.994(3)	-2.7126(4)	-0.10(8)	2.0(2)
0.60	1.5	1.479(8)	-1.7498(1)	1.05(5)	1.9(1)
0.60	2	2.005(9)	-0.7354(2)	1.67(5)	1.9(2)
0.60	2.5	2.56(1)	0.3142(1)	1.96(3)	1.8(1)
0.60	3	3.022(6)	1.1776(2)	2.14(3)	1.9(2)
0.80	1	0.999(5)	-4.0326(1)	1.76(6)	2.1(1)
0.80	1.5	1.295(6)	-2.8827(2)	3.04(4)	2.0(2)
0.80	2	2.002(8)	-1.7428(2)	3.57(4)	2.2(4)
0.80	2.5	2.51(1)	-0.62238(1)	3.79(5)	2.0(2)
0.80	3	2.963(9)	0.3391(1)	3.88(4)	2.2(1)
1.00	0.5	0.4904(7)	-6.9779(2)	0.53(1)	3.1(1)
1.00	1	1.003(2)	-5.5474(1)	4.30(2)	2.8(6)
1.00	1.5	1.502(9)	-4.1263(2)	5.55(9)	3.1(9)
1.00	2	1.98(1)	-2.1596(2)	7.94(8)	2.3(3)
1.00	2.5	2.494(8)	-0.7352(2)	7.67(4)	2.4(3)
1.00	3	2.98(1)	0.5083(2)	7.44(6)	2.3(2)
1.20	0.5	0.4946(7)	-6.76797(3)	27.17(5)	3.5(8)
1.20	1	0.9914(6)	-5.34922(3)	17.43(1)	3.2(8)
1.20	1.5	1.504(2)	-3.88876(5)	14.04(3)	3.5(7)
1.20	2	1.988(2)	-2.53047(6)	12.39(3)	2.9(6)
1.20	2.5	2.541(5)	-0.9688(1)	11.28(4)	2.8(2)
1.20	3	3.056(8)	0.4829(1)	10.59(4)	2.8(5)

Table 1: Thermodynamic quantities obtained through the simulation. ρ is the density, T is the set temperature, T_r is the actual temperature attained at equilibrium, U/N is the energy per particle, $\frac{\beta P}{\rho}$ is the compressibility and C_v/N the specific heat per particle.

I. Pair Correlation Function

The pair correlation function $g(r)$ gives us information on the average distribution of the atoms with respect to a test particle. Since the distribution of the atoms is a consequence of the interactions taking place in the gas, the pair correlation function characterizes a system based on the nature of its forces.

In order to calculate $g(r)$, the distance between particles is recorded periodically in a file. These distances are averaged over time and collected in a histogram. The data is then normalized by the number of particles and volume considered. The resulting expression is

$$g(r) = \frac{2V}{N(N-1)} \left[\frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \right] \quad (10)$$

In Figure 3a, Figure 3b and Figure 3c the correlation functions for respectively gas, liquid and solid phases are plotted. The chosen values for ρ and T representing the various phases are taken from Thijssen [2]. The graphs give us some important information regarding the interaction. For the three phases there are no particles up to $r = \sigma$, as expected from equations (2) and (3): at distances lower than σ the potential becomes highly repulsive. It is also possible to clearly see a peak shortly after σ : this is due to the attractive interaction of the Lennard-Jones potential in which a potential well of depth ϵ is present (see Figure 1). In the gaseous and liquid phases, the correlation function tends to 1 at long distances, indicating chaotic movement in the substance. This asymptotic behaviour is attained much faster in the gaseous phase than in the liquid state, meaning that the interaction between particles is quite weak due to long inter-atomic distances. In the solid phase, the peaks are well defined and the function

doesn't tend to any particular value. This is due to the fact that in a solid the atoms tend to vibrate around their equilibrium positions. It is to be noted that while the atoms are located in a FCC lattice, it is hard to find a periodicity in the peaks of the correlation function because the latter is based on spherical symmetry, which is different from the symmetries of the lattice.

II. Energy

The energy of the system is calculated as the sum of the potential and kinetic energy for all the particles in the system. Since the simulations makes use of a cut-off distance, it is necessary to compensate for said cut-off by introducing a correction term that accounts for long range interactions. The expression for the potential energy becomes

$$\langle V \rangle = \langle V \rangle_{r < r_c} + 2\pi\rho(N-1) \int_{r_c}^{\infty} r^2 V(r) g(r) dr \quad (11)$$

From the previous section, $g(r)$ can be approximated to 1. The values obtained through the simulation are plotted in Figure 4 and show that in the gaseous phase the energy increases linearly with temperature. Furthermore we see that the slope of these curves is approximately 1.71, which close to the result expected from the kinetic theory of gases for an ideal gas:

$$E = \frac{3}{2} N k_B T$$

The numerical values of the energy can be found in Table 1 and are reasonably close to the ones found by Verlet [1]

The values obtained through this equation are reported in Table 1 and plotted in Figure 6; they are not too far from the results obtained by Verlet when considering low densities and high temperatures. The deviations become more significant at high densities and low temperature, probably because of the error caused by approximating the correlation function. A more detailed comparison with the values obtained by Verlet is carried out in Appendix B.

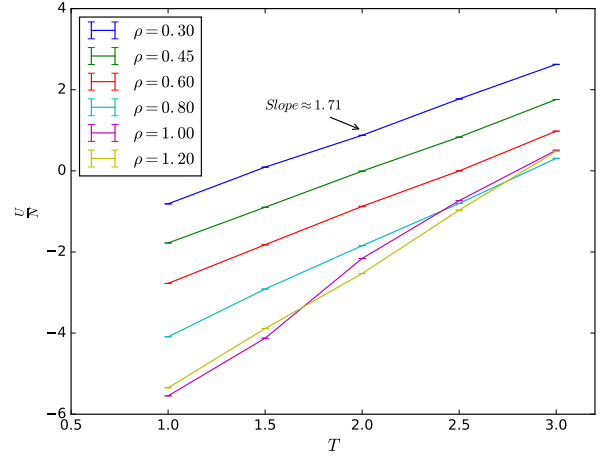


Figure 4: The energy per particle U/N as a function of temperature T for various isochores.

III. Compressibility

The compressibility is calculated using the virial theorem. Analogously to what happened for the energy, the introduction of a cut-off distance in the force and potential calculations requires the addition of a correction term, so that the equation for the pressure takes the form:

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

$g(r)$ can again be taken as equal to 1 so that

$$\frac{2\pi N}{3k_B T V} \int_{r_c}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r) dr = 8\epsilon \left(\frac{\sigma^6}{r_c^3} - \frac{2\sigma^{12}}{3r_c^9} \right)$$

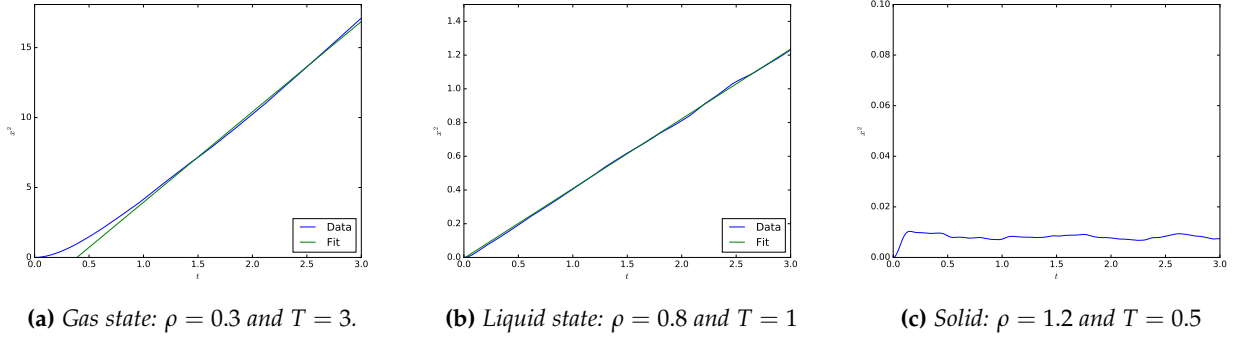


Figure 5: Mean squared displacement for different phases.

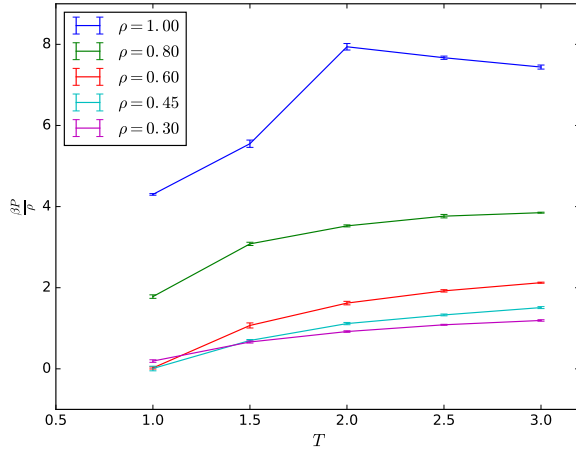


Figure 6: Compressibility as a function of the temperature for various isochores.

IV. Specific Heat

The calculation of the specific heat is calculated using Lebowitz's formula:

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N} \left(1 - \frac{3N}{2C_v} \right) \quad (12)$$

In the simulation the thermostat is used a fixed number of times until the kinetic energy becomes stable and is then switched off in order to calculate the specific heat from fluctuations in the energy of the system. The results obtained are reported in Table 1.

It's interesting to note that in that the gaseous phase (low densities and high temperature, namely $\rho = 0.3$,

$T = 3$) the specific heat attains values close to 1.5, which is expected result for the ideal gas result.

For higher densities and lower temperatures we see that the capacity reaches values close to 3, in accordance with the Dulong-Petit law.

V. Diffusion Coefficient

For times smaller than the typical collision time the behaviour of the system is ballistic:

$$\langle x^2(t) \rangle \propto t^2$$

For later times the movement crosses over to a diffusive behaviour:

$$\langle x^2(t) \rangle = Dt \quad (13)$$

Where the proportionality constant D is called the diffusion constant.

The diffusion constant can be calculated without any additional computational load. At each iteration a matrix containing the displacement of each particle is saved. After running the main simulation, a processing routine sums these displacements and averages them over all the particles to obtain the function $\langle x^2(t) \rangle$. Subsequently the results are fitted to a straight line. Note that by using this approach we avoid dealing with the periodic boundary conditions as well as any extra steps during the simulation.

In order to study the diffusive behaviour of the system the mean squared displacement was plotted for the values of ρ and T taken from Thijssen [2] corresponding to the gas, liquid and solid phase.

The plots are shown in Figure 5.

For the gaseous phase the ballistic behaviour is very noticeable until approximately $t = 1$. For the liquid phase the transition to the ballistic regime is unnoticeable and the function immediately becomes linear. This is to be expected, since the typical collision times for a liquid are much smaller than those of a gas. In the case of the solid we see that displacement remains approximately constant, which is to be expected in a solid phase.

In order to find D the results for the gas and liquid were fitted to a straight line. In case of the gas only points after $t = 1.5$ were considered in the fit.

The results are gathered in Table 2

Phase	ρ	T	D
Gas	0.3	1.5	6.1342(6)
Liquid	0.8	1.0	0.4134(4)

Table 2: Diffusion constants obtained through a linear fit to $\langle x^2(t) \rangle$

The diffusion constant in the gas is approximately 12 times larger than the liquid's, which is in agreement with the intuition that a particle in a gas has much more freedom to 'roam' than in a liquid, where the particles are more densely packed.

IV. CONCLUSION

A. APPENDIX - DATA BLOCKING

In order to calculate the error of the physical quantities a process known as data-blocking (see Thijssen [2] sec 7.4) was used. Assuming we are interested in calculating the value of a quantity A the program records its value at each iteration. A post-processing routine then divides the sequence of values A_k in blocks of size m and the averages of A are calculated within each block. For blocks of size m the j th block average is then given by:

$$\bar{A}_j = \frac{1}{m} \sum_{k=jm+1}^{m(j+1)} A_k \quad (14)$$

Provided that a large number of blocks is used and that m is chosen such that it represents a time larger than the typical correlation time of the system then the samples can be considered independent and the error can be calculated reliably as the standard deviation of the sequence \bar{A}_j .

For this simulation in particular a value of $m = 250$ was chosen. This was done by varying m over a large

range and determining at which point the error stopped fluctuating appreciably.

B. COMPARISON WITH VERLET

A more careful comparison with Verlet [1] was made for the compressibility. In Figure 7 the results obtained in the simulation were plotted alongside with Verlet's values. In general we see that the results are in agreement. There are however some deviations which can be attributed to the approximation $g(r) \approx 1$ for $r > r_c$.

In general we see that as we increase the density the deviation increases as well. This is because the approximation made loses its validity (as one can see through Figure 2). For fixed density the agreement of the results improves as we increase the temperature since the system becomes closer to a gaseous state and hence the approximation becomes better.

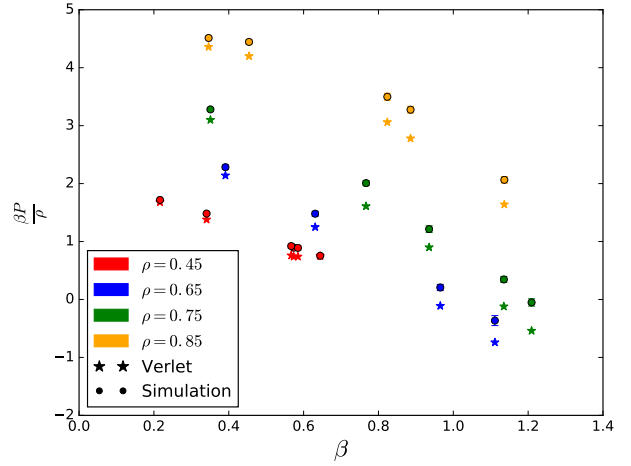


Figure 7: Comparison of values for compressibility with Verlet for different isochores.

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- [2] J.M.Thijssen, *Computational Physics*, Cambridge University Press, 2nd Edition, 2007.