

A thermodynamic assessment of the molecular dynamic behaviour of argon within a finite volume with periodic conditions

G.I.L. van Oudenaren (4344650) and H.C.E. van den Brink (4367820)

(Dated: 27 March 2019)

In this report an thermodynamic assessment of the molecular dynamic behaviour of argon is examined. This is done by numerically solving Newton's equation of motion using the 'Leapfrog' numerical integration method for different initial temperatures and densities. Due to computation limitations we simulate $N = 864$ argon atoms in a box and apply periodic boundary conditions to replicate large scale behaviour. When comparing our results with the data from Verlets original paper we observed comparable outcomes, which is an indication that our simulation is adequate.

I. INTRODUCTION

In this project we perform a molecular dynamics simulation of argon. Argon is a relatively simple element to simulate because it is a noble gas, meaning it is inert to other atoms and molecules so it does not actively bond with its neighbours. Because atoms are small and the world is large it's hard to simulate a macroscopic amount of argon atoms used limited computational means. Therefore we simulate a workable number of particles in a box and apply periodic boundary conditions in order to simulate the behaviour of a much larger system.

This system is being set-up and simulated in Python, only making use of the essential scientific packages (NumPy, SciPy, Matplotlib). This report will seek to explain what properties have been simulated, under what conditions and how.

II. THEORY

Because of argon's inertness its interactions with itself can be described by the rather simple Lennard-Jones potential. This potential containing an attractive and repulsive component can be described as follows:

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

with interatomic distance r and fitting parameters σ for length and ϵ for energy. These were determined to be $\sigma = 3.405 \text{ \AA}$ and $\epsilon/k_B = 119.8 \text{ K}$ according to¹.

From the potential, we can calculate the interatomic force by taking the gradient:

$$F(r) = -\nabla U(r) \quad (2)$$

This means that the only information required to set up and solve the equations of motion is the interatomic distance r . We do run into one problem, however. Since we are solving this system using periodic boundary conditions (also meaning that when a particle leaves one surface, it re-enters on the opposite side), we need a way of calculating the distance to every other particle taking these boundary conditions into account.

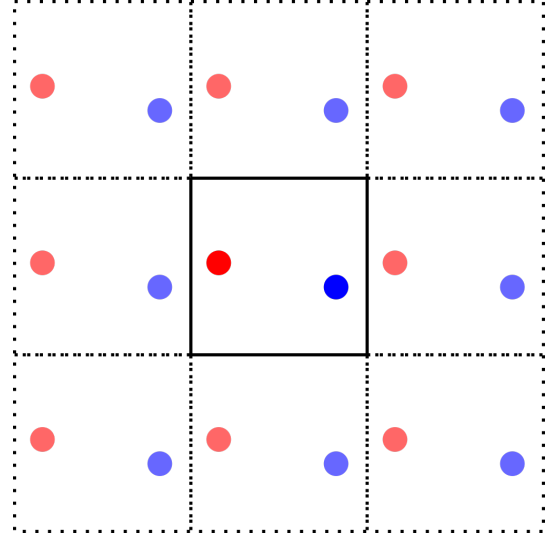


FIG. 1: Two particles and their closest image projections

This problem is solved by the minimum image convention. We want to minimize

$$r_{ij} = \sqrt{(x_i - x'_j)^2 + (y_i - y'_j)^2 + (z_i - z'_j)^2} \quad (3)$$

in which x_i , y_i and z_i are the coordinates of particle i and

$$x'_j = \begin{cases} x_j - L \\ x_j \\ x_j + L \end{cases} \quad (4)$$

Where x'_j is the minimum of the three options, x_j is the actual position of particle j (idem for y'_j and z'_j) and L is the width of the box. Fortunately, this comparison can

be reduced to a single expression:

$$x'_j = (x_i - x_j + L/2) \% L - L/2 \quad (5)$$

The implication of this statement is that the maximum distance that particles can act on each other is $L/2$.

III. UNITS

Because working on atomic scale involves incredibly small length and timescales it does not make sense to work in SI units. Therefore, we need to convert our units to dimensionless quantities. The first step is that the length is normalised by σ , using this we find that the dimensionless Lennard-Jones potential can be expressed as follows:

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

Using the fact that simulation consists of an mono-atomic gas we set the mass $m_{Ar} = 1$. This makes that the equation of motion can be written as follows:

$$\frac{d^2 \tilde{\mathbf{x}}}{d\tilde{t}^2} = \frac{1}{\sigma} \frac{d^2 \mathbf{x}}{dt^2} = -\frac{1}{\sigma} \nabla U(\tilde{r}) = -\frac{\epsilon}{\sigma^2} \tilde{\nabla} \tilde{U}(\tilde{r}) \quad (7)$$

If we normalise the time by a factor $\sigma^{-1} \sqrt{\epsilon}$ the dimensionless time is found. Using these relations we can describe the system of N particles as follows, the force on particle i is given by the sum of all forces acting on particle i due to the other particles. Newton's equation of motion in dimensionless units for particle i is given by:

$$\frac{d^2 \tilde{\mathbf{x}}_i}{d\tilde{t}^2} = - \sum_{i \neq j} \tilde{\nabla} \tilde{U}(|\tilde{\mathbf{x}}_i - \tilde{\mathbf{x}}_j|) \quad (8)$$

This system of equations has to be solved taking into account the initial positions of the particles in an FCC lattice of which the distances between the particles is determined by an arbitrary density ρ .

IV. INTEGRATORS

A. Verlet

Verlet integration is a method which is used to solve Newton's equation of motion.

$$\mathbf{x}(t+h) = \mathbf{x}(t) + h\mathbf{v}(t) + \frac{h^2}{2} \mathbf{F}(\mathbf{x}(t)) \quad (9)$$

Taylor expand in \mathbf{v} :

$$\mathbf{v}(t+h) = \mathbf{v}(t) + h\dot{\mathbf{v}}(t) + \frac{h^2}{2} \ddot{\mathbf{v}}(t) + \mathcal{O}(h^3) \quad (10)$$

Taylor expand in \mathbf{v} again:

$$\dot{\mathbf{v}}(t+h) = \dot{\mathbf{v}}(t) + h\ddot{\mathbf{v}} + \mathcal{O}(h^2) \quad (11)$$

and thus $\ddot{\mathbf{v}} = \frac{1}{h}(\mathbf{F}(\mathbf{x}(t+h)) - \mathbf{F}(\mathbf{x}(t)))$, from which it then follows that

$$\begin{aligned} \mathbf{x}(t+h) &= \mathbf{x}(t) + h\mathbf{v}(t) + \frac{h^2}{2} \mathbf{F}(\mathbf{x}(t)) \\ \mathbf{v}(t+h) &= \mathbf{v}(t) + \frac{h}{2}(\mathbf{F}(\mathbf{x}(t+h)) + \mathbf{F}(\mathbf{x}(t))) \end{aligned} \quad (12)$$

Which is the final form of equations that will be used in the simulation.

B. Leapfrog

The Leapfrog method operates on slightly different principles. Compared to the Euler method, where $\mathbf{x}(t+h) = \mathbf{x}(t) + h\mathbf{v}(t)$ the leapfrog instead hops between calculating position and velocity. This would look like:

$$x_{n+1} = x_n + hv_{n+1/2} \quad (13)$$

and

$$v_{n+3/2} = v_{n+1/2} + hF(x_{n+1}) \quad (14)$$

The difference is that in Euler algorithm you use the new value of position, not the old in order to calculate your force and thus velocity.

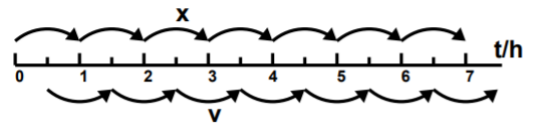


FIG. 2: A visualisation of the leapfrog algorithm.²

Like the velocity Verlet method, the Leapfrog method is also a second order integrator, making it more accurate than the first order Euler method.

V. OBSERVABLES

In this report two observables are examined, the temperature and the pressure. Here the temperature is calculated by the equipartition theorem. The pressure is calculated with the virial theorem.

A. Temperature

The temperature is a macroscopic observable which is directly related to the average kinetic energy of the particles in the system. For an system which does not exchange heat with its environment it is constant, thus the average kinetic energy of the particles is also a constant. The velocity distribution of these particles in a gas is given by the Maxwell-Boltzmann velocity distribution. The distribution for a three dimensional gas in dimensionless units is given by the following expression:

$$f(v) = 4\pi \left(\frac{T_0}{2\pi T} \right)^{\frac{3}{2}} v^2 e^{-\frac{v^2}{2} \frac{T_0}{T}} \quad (15)$$

Where $T_0 = \epsilon/k_B = 119.8$ K Using this relation one can calculate the mean squared velocity which is commonly known as the equipartition theorem.

$$\frac{1}{2} \langle v^2 \rangle = \frac{3}{2} \frac{T}{T_0} \quad (16)$$

Using this relation one can isolate the variable T , which gives an expression for the temperature.

B. Pressure

To calculate the pressure the virial theorem is used. This states for a given state of a system, described by the positions of the particles the pressure can be calculated by:

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N} \left\langle \sum_i \mathbf{r}_i \nabla_i V_N(R) \right\rangle_T \quad (17)$$

Where $\langle \dots \rangle_T$ denotes a time average and $\beta = 1/k_B T$.

VI. PHASE BEHAVIOUR

In order to asses the phase of the system, we can make use of the radial distribution function. The radial distribution function (RDF) is defined as follows:

$$g(r) = \frac{2}{\rho(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \quad (18)$$

With global system density ρ , total number of particles N , radius r and binsize Δr . What the RDF tells us what the average amount of particles are within the volume of the spherical shell with inner radius r and outer radius $r + \Delta r$. The expectation value is calculated by calculating the radial distributions for all particles, and taking the average. The shape of RDF is telling for which phase the

material presently is in. Typical RDFs are show in figure 3.

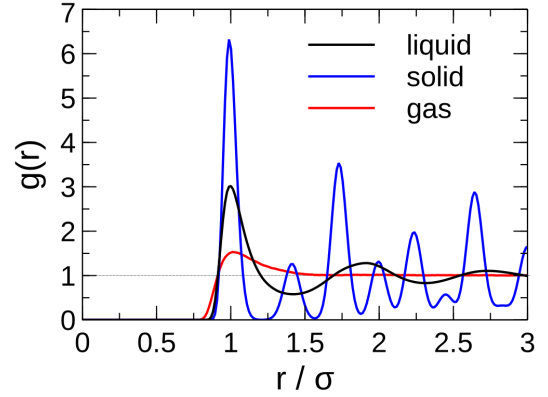


FIG. 3: Typical radial distribution function for different phases.

For a solid, there are distinct peaks at set distances from the origin. These correspond to the structure of an FCC lattice, which is how argon is distributed in solid phase. The liquid phase has an initial peak, and then oscillates around and converges to a constant while the gaseous phase only has an initial bump and then almost immediately converges to a constant.

VII. RESULTS

To illustrate the abilities of our simulation we will first show a number of plots of the various properties of the system we calculated. Our simulations used $N = 864$ particles. Figure 4 shows the velocity distribution. The histogram of velocities of the particles in the system fits the theoretically predicted Maxwell-Boltzmann distribution very well.

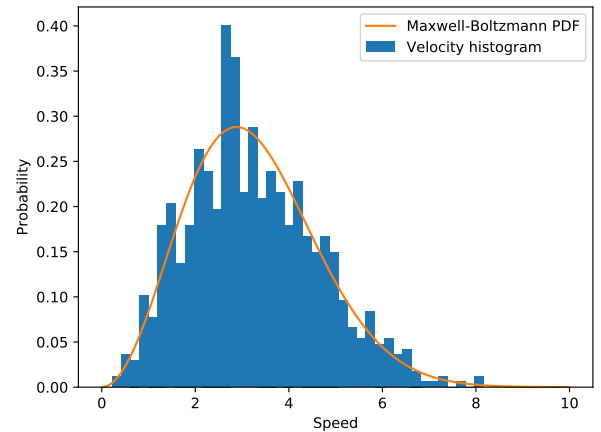


FIG. 4: Histogram of system velocities versus the MBD function at the set temperature.

Figure 5 shows the radial distribution function plot for three different temperatures corresponding to three different phases. There is clear distinction between the characteristic shapes of the different functions, and we can clearly recognize the characteristic functions shown in Figure 3.

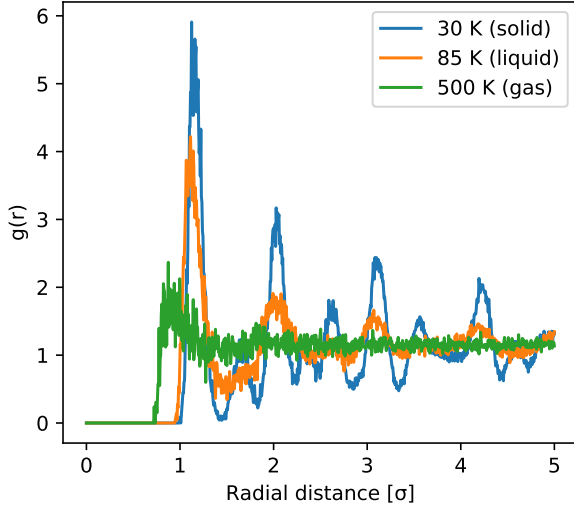


FIG. 5: Radial distribution functions for three temperatures, normalized by their mean. ($\rho = 0.88$)

An energy, temperature and pressure plot is shown in Figure 6. Errorbars ($\pm\sigma$) calculated using bootstrapping are denoted in red.

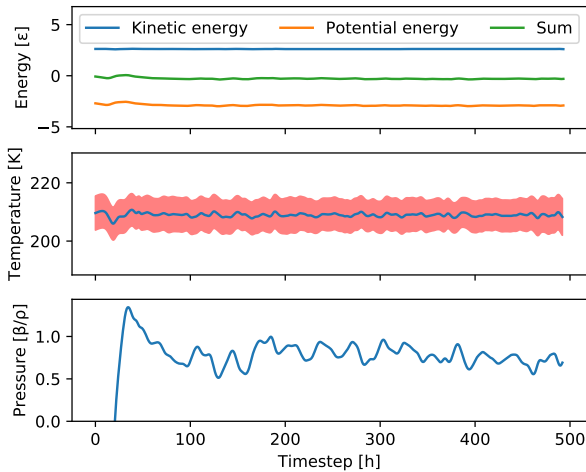


FIG. 6: Energy, temperature and pressure plot . ($\rho = 0.45$, $T = 208.9K$)

VIII. COMPARISON WITH VERLET'S PAPER

In order to test the output of our system, we compared it with a selection of the values given in the original Verlet paper.³ The Verlet values and our values are given in Table I, with Verlet's indicated with subscript V . As can be seen, most values match those found by Verlet. This leads us to believe our simulation works sufficiently well enough.

TABLE I

ρ	T	T_V	$\langle\beta P/\rho\rangle$	$\langle\beta P/\rho\rangle_V$	U	U_V
0,880	1,094	1,095	2,850	3,480	-5,980	-5,660
0,880	0,940	0,940	2,470	2,720	-6,060	-5,840
0,850	0,785	0,782	1,060	0,980	-6,016	-6,040
0,850	0,792	0,786	0,847	0,990	-6,060	-6,050
0,750	1,068	1,071	0,983	0,890	-5,113	-5,170
0,750	0,827	0,827	-0,513	-0,540	-5,346	-5,380
0,450	4,622	4,625	1,656	1,680	-2,275	-2,220
0,450	1,736	1,744	0,776	0,740	-2,897	-2,980

IX. CONCLUSION

The goal of this research was to examine the dynamic behaviour of an simulated argon gas containing N particles in a box with periodic boundary conditions. The simulation was initialised using different initial speeds and densities. When the system was converged the temperature and pressure was calculated using the equipartition- and virial theorem. Also the phase of the system was examined by calculating the radial density function, here there was a clear distinction between the gas, liquid or solid state.

Finally, using Verlet's original paper we checked whether or not our system behaves as it should. Comparing our Verlet's data with ours we saw that the data is comparable which is an indication our code is indeed reliable.

$$-\frac{\hbar^2}{2m}\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

¹J. Thijssen, *Computational Physics*, 2nd ed. (Cambridge University Press, 2007).

²P. Young, "Leapfrog (verlet) and other "symplectic" methods for integrating newton's equations of motion," (2014).

³L. Verlet, "Computer "experiments" on classical fluids. i. thermodynamical properties of lennard-jones molecules," *Phys. Rev.* **159**, 98–103 (1967).

X. COLLABORATION

We feel we both had an equal contribution to the final project, which is also reflected in the amount of git commits both of us made. Most of the time, we had brainstorm sessions while programming together and other times we worked apart and made clear appointments for when we wanted our milestones to be met. We think the collaboration went well, and our work flow definitely improved throughout the project (especially regarding the technical skills like using python and git) which leads us to believe we can start the next project off even better!