

# Molecular Dynamic Simulation of Argon Atoms using the Verlet Algorithm

*L. de Wilde (4246853), S.K. Rosenstand (1358065)*

## Abstract

Molecular dynamics simulations for argon atoms have been performed in the micro-canonical and canonical ensemble. The pair interactions between the atoms are approximated with the Lennard-Jones potential. The verlet algorithm is used to update positions and velocities after each time step and the pair correlation function, pressure and heat capacity have been calculated. The calculated values correspond well to the values found in the literature.

## 1 Introduction

Molecular dynamic simulations are a widely used tool to study behaviour of molecular systems. In molecular dynamic simulations, the atomic trajectories are computed over time. In this project this simulation technique is used to get a better understanding of the properties of a argon gas with the Lennard-Jones potential as the interaction potential.

Argon molecules are neutral and mono-atomic and behave approximately as hard spheres that attract each other through van der Waals forces. The Lennard-Jones potential (Eq. (1)) is a good approximation for such pairwise interaction between atoms. The Lennard-Jones potential approximates the hard core repulsion with the  $r^{-12}$  term and the van der Waals attraction with the  $r^{-6}$  term. The parameters of the Lennard-Jones potential are  $\sigma$  describing the hard core radius and  $\epsilon$  describing the depth of the potential well.

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

The force on each particle can be determined from the potential as:

$$F_i = \sum_{j=1, j \neq i}^N -\nabla U_{LJ}(|r_i - r_j|). \quad (2)$$

Knowing the force on each particle we simulate the argon atoms using the Verlet algorithm which will

be discussed in Section 2.2. By simulating the argon atoms we determine several physical quantities such as correlation function, pressure and specific heat as will be described in Section 3.

## 2 Methods

In molecular dynamic simulations, atomic trajectories are computed by numerically solving Newton's equations of motion  $m \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j \neq i} \mathbf{f}(\mathbf{r}_{ij})$ . The algorithm to simulate the molecular dynamics consist essentially of 3 steps [1]: Initialisation of position and velocity, simulation to equilibrium and continued simulation and extracting physical quantities.

We will consider a system with  $N = 864$  argon atoms in a cubic volume with sides  $L$ . Since 864 atoms is still a very small number of particles, periodic boundary conditions are imposed in all directions, a particle leaving the system at one side will appear from the opposite side. The system is then considered to have an infinite number of copies in all spatial directions with the exact same configuration, representing a small volume embedded in a infinite system[1]. In our simulation we will use the minimal image convention. In this way we assume the system is surrounded by identical systems and each particle will only interact with the nearest copy of the other particles.

In our simulation we will make use of natural units for argon with the depth of the Lennard-Jones potential well  $\epsilon = 1.6510^{-21}$  J as the unit of energy, the width of the potential well  $\sigma = 3.410^{-10}$  m

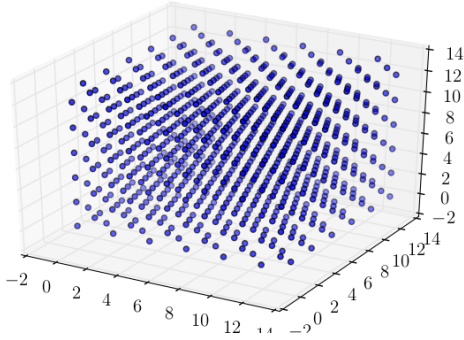


Fig. 1: Initial positions of the Argon atoms with  $N = 864$

as the unit of distance and the atomic mass  $m = 6.6910^{-26}$  kg of Argon as the unit of mass. We take time steps of  $\Delta t = 0.004 \sqrt{\frac{m\sigma^2}{\epsilon}}$  [1].

## 2.1 Initialisation

To set the initial positions of the atoms, random positioning can be used. However, this may result in significant overlap between the atoms resulting in a potential energy of infinity. Therefore a better initialisation method is the positioning of the atoms in a Face-centred cubic (FCC) lattice which is also the ground state configuration for an argon gas [1, 2]. A number of unit cells ( $m$ ) are stacked in the  $x, y, z$  directions Fig. 1 to build up a system of  $N$  particles.

The initial velocity components ( $x, y, z$  directions) are drawn from a Gaussian distribution corresponding to the Maxwell Boltzmann distribution

$$f(\mathbf{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[ -\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T} \right]. \quad (3)$$

To prevent the system as a whole from drifting, the total momentum is set to zero by subtracting the average speed in each direction from all the components in the same direction. The velocities are then rescaled to satisfy the equipartition theorem by multiplying all the speed components with a factor

$$\lambda = \sqrt{\frac{(N-1)3k_B T_D}{\sum_{i=1}^N m v_i^2}}. \quad (4)$$

Due to the setting of the total momentum to zero, the number of degrees of freedom are reduced with

3, therefore  $\lambda$  has a  $(N-1)$  term in the square root.

## 2.2 Simulation

During the simulation Newton's equations of motion are integrated numerically by the Verlet algorithm starting at the initial positions and velocities. The Verlet algorithm follows from Taylor expansions of the positions for  $r(t+dt)$  and  $r(t-dt)$ :

$$\begin{aligned} \mathbf{r}(t+dt) &= \mathbf{r}(t) + \mathbf{v}(t)dt + \frac{1}{2}\mathbf{a}(t)dt^2 \\ &\quad + \frac{1}{6}\frac{\partial^3 \mathbf{r}(t)}{\partial t^3}dt^3 + \mathcal{O}(dt^4) \\ \mathbf{r}(t-dt) &= \mathbf{r}(t) - \mathbf{v}(t)dt + \frac{1}{2}\mathbf{a}(t)dt^2 \\ &\quad - \frac{1}{6}\frac{\partial^3 \mathbf{r}(t)}{\partial t^3}dt^3 + \mathcal{O}(dt^4). \end{aligned} \quad (5)$$

Adding up these equations and by using  $\mathbf{v}(t) = \frac{\mathbf{r}(t+dt) - \mathbf{r}(t-dt)}{2dt}$  and  $\mathbf{a}(t) = -\frac{1}{m}\nabla V(\mathbf{r}(t)) = \frac{\mathbf{F}}{m}$ , results in the equations (Eq. (6)) for the velocity Verlet algorithm [3]. Using the velocity Verlet algorithm the positions and velocities are updated after every time step  $dt$ .

$$\begin{aligned} \mathbf{r}(t+dt) &= \mathbf{r}(t) + dt\mathbf{v}(t) + \frac{1}{2}\mathbf{F}(t)dt^2 + \mathcal{O}(dt^3) \\ \mathbf{v}(t+dt) &= \mathbf{v}(t) + dt\frac{\mathbf{F}(t+dt) + \mathbf{F}(t)}{2} + \mathcal{O}(dt^3) \end{aligned} \quad (6)$$

The force  $\mathbf{F}$ , on each atom is determined from the distance between atom pairs by the Lennard-Jones potential. Due to the periodic boundary conditions the system is surrounded by an infinite number of identical systems. For each atom only the nearest copy of the remaining particles is taken into account following the minimum image convention [1]. For large values of  $r$ , the Lennard-Jones potential becomes very small, therefore we take only atoms within a cut-off distance into account when performing the force calculation to reduce computation time. We take  $r_c = 3\sigma$ , similar values of  $r_c$  are used previously [1–3].

During the simulation the temperature can change due to the conversion of potential energy in kinetic energy. The system initialised as described in Section 2.1 will equilibrate in the beginning of the simulation to a difficult to predict final temperature  $T$  [1]. To control the temperature of the

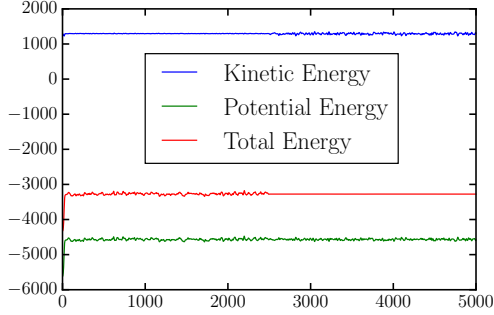


Fig. 2: Plot of the kinetic, potential and total Energy as a function of time at  $T = 1$  and  $\rho = 0.8$  with the thermostat turned off after 2500 time steps

system a thermostat is implemented; the temperature is kept at the desired temperature  $T_D$  during equilibration of the system by rescaling the velocity components at each step by a factor  $\lambda$  (Eq. (4)). After equilibration the temperature will fluctuate around a mean value close to the desired temperature.

### 2.3 Error Analysis

From the simulation several physical quantities are determined as the expectation value over time. The errors of physical quantities measured in the simulation can be calculated using the data-blocking method [1]. In this method the values of the physical quantity of interest are listed in a file. This file is then chopped in blocks that are larger than the correlation time but sufficiently small to have enough blocks. For each block the average is calculated: For blocks of size  $m$ , the  $j$ th block average is

$$\bar{a}_j = \frac{1}{m} \sum_{k=jm+1}^{m(j+1)} a_k. \quad (7)$$

The error can be calculated as the standard deviation  $\sigma$  of the uncorrelated blocks

$$\sigma^2 = \overline{A^2} - \bar{A}^2. \quad (8)$$

## 3 Results & Discussion

The simulation has been carried out for 5000 time steps, of which the first 2500 steps with the thermostat on. It can be seen in Fig. 2 that during this phase the kinetic energy is constant, due to the velocity rescalings at every step. Once the thermostat has been turned off at  $nt = 2500$ , the total energy remains constant, while the kinetic and potential energy fluctuate around a mean value. The system is then assumed to be at equilibrium, and we proceed to calculate several thermodynamic quantities: Correlation function, pressure and specific heat.

### 3.1 Correlation Function

The static pair correlation function is formally defined as

$$g(r_1, r_2) = \frac{V^2}{N! h^{3N} Z} \int_V e^{-\beta U_N(r_1, \dots, r_N)} d^3 r_3 \dots d^3 r_N, \quad (9)$$

with  $Z$  the partition function,  $h$  the Planck constant, and  $U$  the potential energy[1]. The pair correlation function is a measure of the average distance between particles and can be used to obtain accurate values of macroscopic thermodynamic quantities such as the pressure and potential energy as we will see in the following sections.

It is however much easier to calculate the correlation function from the simulation by considering it to be the number of atoms at a distance  $r$  from a given atom compared with the number for an ideal gas at the same density [2]. To determine the correlation function a histogram containing the number of particle pairs  $n(r)$  at distances in the range  $r \pm \Delta r/2$ , is calculated using

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

Here  $\Delta r$  is the width of the bins of the histogram and the factor  $4\pi r^2$  originates from spherical coordinates.

Fig. 3 shows the static pair correlation function for the system of argon atoms in different phases. Due to the hard core of the atoms the correlation function is  $g(r) = 0$  for  $r < \sigma$  for all phases. For the

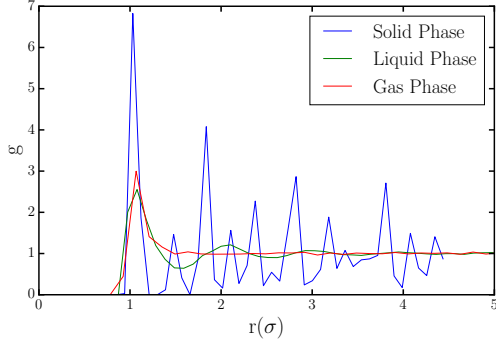


Fig. 3: Pair correlation function for Argon atoms in the gas phase ( $T = 3$ ,  $\rho = 0.3$ ), liquid phase ( $T = 1$ ,  $\rho = 0.8$ ) and solid phase ( $T = 0.3$ ,  $\rho = 1.2$ )

solid phase with  $T = 0.5$  and  $\rho = 1.2$ , we expect to find atoms at distances of the unit cell lengths corresponding to the FCC lattice. In the liquid phase with  $T = 1$  and  $\rho = 0.8$ , the atoms are allowed to move around much more and therefore the correlation function flattens out to a value of 1 for large  $r$ . For the gas phase with  $T = 3$  and  $\rho = 0.3$  the kinetic energy of the atoms is much higher and therefore the atoms are distributed even more randomly in space. Therefore the correlation function  $g(r) = 1$  for  $r > \sigma$ . In Fig. 3 we can indeed see the behaviour we would expect. The values for temperature and density for the different phases are from [1].

### 3.2 Pressure

The pressure is calculated from the virial expansion of the pressure (Eq. (11)) [1].

$$P = \frac{k_b T N}{V} \left[ 1 - \frac{1}{3Nk_b T} \left\langle \sum_i \frac{\partial U}{\partial r_i} \cdot r_i \right\rangle \right]. \quad (11)$$

In our simulation the potential energy consists only of the atom pair interactions. Therefore the average  $\langle \sum_i \frac{\partial U}{\partial r_i} \cdot r_i \rangle$  can be readily calculated by the sum over the forces as  $\langle \sum_i \sum_{j>i} F(r_{ij}) \cdot r_i \rangle$ . In this way the virial contribution to the pressure for all pair interactions with distance  $r < r_c$  can be calculated.

The contribution of pair interactions with distances  $r > r_c$  are not taken into account by calcu-

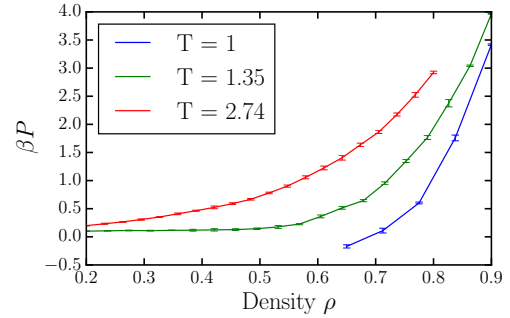


Fig. 4: Pressure as a function of density calculated for different values of the temperature

lating the virial contribution to the pressure. The value of each such pair interaction will be very small. However, because there are a lot of pair interactions with large distance in a system, they have a significant contribution to the pressure. Because all particles are identical and  $U$  only depends on the magnitude of these pair interactions, the virial correction for  $r > r_c$  can be analytically computed with an integral over  $r > r_c$  [1]. The virial contribution to the pressure then becomes

$$\begin{aligned} \frac{P}{nk_b T} = 1 - \frac{1}{3Nk_b T} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{\partial U(R)}{\partial r_{ij}} \right\rangle_{cut-off} \\ - \frac{2\pi N}{3k_b T V} \int_{r_c}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r) dr, \end{aligned} \quad (12)$$

with  $g(r)$  the correlation function Eq. (10). As we have seen in Section 3.1 large  $r$  the correlation goes to 1 therefore we assume in Eq. (12),  $g(r) \approx 1$  for  $r > r_c$ . Evaluating the integral then results in the following expression for the virial pressure:

$$\begin{aligned} \frac{P}{nk_b T} = 1 - \frac{1}{3Nk_b T} \left\langle \sum_i \sum_{j>i} r_{ij} F_{ij} \right\rangle_{cut-off} \\ - \frac{\pi N \epsilon}{6k_b T V} \left[ \frac{32\sigma^6}{r_c^3} - \frac{64\sigma^{12}}{3r_c^9} \right]. \end{aligned} \quad (13)$$

The pressure as a function of density is plotted for several temperatures in Fig. 4. The errors in the plot are obtained using Data-blocking as described in Section 2.3. In order to satisfy having blocks larger than the correlation time, blocks of  $m = 500$

are used. For a simulation of  $nt = 2500$ , there are only a few blocks. Due to limited computation time we did not make longer simulations.

For very low densities and high temperatures, argon is expected to behave approximately as an ideal gas. From the ideal gas law it follows that  $\beta P = \rho$ , which is the behaviour we see for the  $T = 2.74$  isotherm in Fig. 4 up to a density of  $\rho = 0.5$ . As the density increases the particles will be closer to each other and the repulsion term in the Lennard-Jones potential Eq. (1) becomes more important. The pressure then starts increasing much faster as a function of the density. For low temperatures it is more favourable for the atoms to be close together at the minimum of the potential well. Therefore at low densities and low temperatures the particles form clusters and the pressure can become negative.

### 3.3 Specific Heat

In the microcanonical ensemble ( $E, N, V$  fixed) the specific heat can be calculated using the fluctuations in the kinetic energy  $K$  [1, 4]:

$$\frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N} \left( 1 - \frac{3N}{2C_V} \right), \quad (14)$$

with  $N$  the number of particles in the system,  $C_V$  the heat capacity at constant volume,  $\langle \delta K^2 \rangle$  the standard deviation of the kinetic energy. For low densities and high pressure the argon gas can be approximated by the ideal gas law. The specific heat for the ideal gas is  $C_V = \frac{3}{2}k_b$ . Therefore we expect that in our simulation the specific heat goes to a value  $C_V \approx \frac{3}{2}$ . For low temperatures and high densities we expect our system to behave as a solid. In an Einstein solid, the system can be approximated by  $3N$  independent harmonic oscillators resulting in a heat capacity of  $C_V \approx 3Nk_b$ .

Values found for the specific heat can be found in Table 1. In Fig. 5 the specific heat vs temperature is plotted for several densities. For the case of high temperatures and low densities we find values for the specific heat close to the theoretical value of 1.5. For high densities, the specific heat approaches the value 3 but does not reach it. This can be explained by the fact that the specific heat for the Einstein model only holds for the limit  $T \Rightarrow \infty$ .

For high densities the errors are very large. The

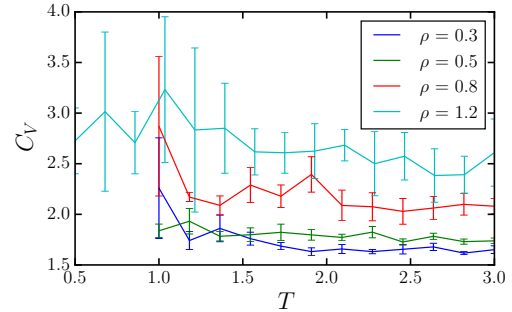


Fig. 5: Specific heat as a function of Temperature calculated for four different values of the particle density  $\rho$

errors are determined using Data-Blocking as in Section 2.3. For simulations with high density the correlation times and time till equilibration are very large. Due to limited computation time we let the system equilibrate in  $nt = 2500$  time steps and calculated the specific heat for  $nt = 2500$  time steps. We have taken sample sizes of 500 time steps to calculate the specific heat, which are too small to calculate the fluctuations in the kinetic energy. Therefore the errors in the specific heat could not be calculated reliably. One simulation run has been performed with  $nt = 10000$  of which the results can be found in the first row of Table 1.

### 3.4 Potential Energy

During the simulation the potential energy is calculated as the Lennard-Jones potential for all particle pairs with distances within the cut-off distance ( $r < r_c$ ). To correct the potential energy for the neglected tail of the potential energy, the correlation function can be used [1]. The tail of the potential energy can then be calculated analytically as:

$$\begin{aligned} \langle U \rangle_{r>r_c} &= 2\pi \frac{N(N-1)}{V} \int_{r_c}^{\infty} r^2 U(r) g(r) dr \\ &\approx 2\pi \frac{N(N-1)}{V} \left[ \frac{\sigma^6}{3r^3} - \frac{\sigma^{12}}{9r^9} \right]. \end{aligned} \quad (15)$$

Table 1 contains values for the potential energy calculated using Eq. (15) as well as the pressure (Eq. (13)) and specific heat (Eq. (14)) for several temperature and density values. Here  $T_D$  is the desired equilibrium temperature.

Tab. 1: Calculated temperature, pressure, potential energy and specific heat for different values of the density  $\rho$  and desired equilibrium temperature  $T_D$  for  $nt = 5000$  time steps and block size  $m = 500$ . The first row has been calculated using double the usual (simulation and equilibrium) time  $nt = 10000$  and block size  $m = 715$ .

$\rho(\frac{1}{\sigma^3})$	$T_D(\frac{\epsilon}{k_B})$	$T(\frac{\epsilon}{k_B})$	$\frac{\beta P}{\rho}$	$U(\epsilon)$	$C_V(\epsilon)$
1.20	0.5	$0.500 \pm 10^{-3}$	$25.6476 \pm 0.002$	$-7.0522 \pm 0.0003$	$3.03 \pm 0.24$
1.20	0.5	$0.295 \pm 10^{-4}$	$22.6020 \pm 0.0004$	$-7.3465 \pm 0.0002$	$2.80 \pm 0.38$
0.88	1.0	$1.014 \pm 0.005$	$3.13 \pm 0.05$	$-5.613 \pm 0.009$	$2.87 \pm 0.66$
0.80	1.0	$1.004 \pm 0.002$	$1.279 \pm 0.028$	$-5.217 \pm 0.004$	$2.46 \pm 0.21$
0.70	1.0	$0.998 \pm 0.001$	$0.062 \pm 0.035$	$-4.613 \pm 0.005$	$2.22 \pm 0.19$
0.30	3.0	$3.037 \pm 0.007$	$1.11 \pm 0.03$	$-1.623 \pm 0.013$	$1.64 \pm 0.03$

## 4 Conclusion

In the molecular dynamics simulation for a system of argon atoms behave approximately as a ideal gas for low densities and high pressure and as a solid for high densities. The thermodynamic quantities such as correlation function, pressure, specific heat and potential energy are calculated at equilibrium correspond with those found in the literature [1, 3, 5] for both computer simulations and real experiments. The code used can be easily extended to study several more thermodynamic identities at equilibrium for example diffusion.

- [5] A Rahman. “Correlation in the Motion of Atoms in Liquid Argon”. In: *Physical Review* 136.2A (1964), pp. 405–411. ISSN: 0031-899X. DOI: 10.1103/PhysRev.136.A405.

## References

- [1] J. Thijssen. *Computational Physics*. Cambridge University Press, 2007. ISBN: 9780521833462.
- [2] M. P. Allen and D. J. Tildesley. *Computer Simulation of Liquids*. New York, NY, USA: Clarendon Press, 1987. ISBN: 0-19-855375-7.
- [3] Loup Verlet. “Compute Experiments on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules”. In: *Physical Review* 159.1 (1967), pp. 98–103.
- [4] J. L. Lebowitz, J. K. Percus, and L. Verlet. “Ensemble Dependence of Fluctuations with Application to Machine Computations”. In: *Phys. Rev.* 153 (1 Jan. 1967), pp. 250–254. DOI: 10.1103/PhysRev.153.250. URL: <http://link.aps.org/doi/10.1103/PhysRev.153.250>.