

Molecular Dynamics simulation of Argon atoms

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November 7, 2021

Abstract

Using the velocity varlet algorithm and the lambda algorithm we are able to simulate argon in three different states accurately.

Introduction

The behaviour of two interacting particles is well understood. Classically, the way to solve such problems for arbitrary potential has been known for centuries. However, when we consider three particles, things become very complicated very quickly: no closed-form solution exists for this problem, even classically. This is problematic, since at our human scale, all objects are made up of incredible amounts of interacting particles. This means we cannot hope to possibly find exact solutions for the behaviour of a gas of interacting particles, for instance, and we must resort to using statistical physics.

However, all hope is not yet lost: where calculus fails, numerical analysis succeeds. By using a computer to numerically integrate the equations of motion for many-body problems, we can approximately calculate the behaviour of such systems, theoretically to arbitrary precision. We will explore this method by using it to study the dynamics of a system of argon atoms in a box with periodic boundary conditions, with the end goal of finding the pair correlation function (a measure of how frequently certain particle-particle distances appear) and pressure of the system for the gas, liquid and solid phases of argon. But to do this, we must first figure out the rules under which our system operates.

1 Theory

To simulate the behaviour of a collection of argon atoms, we need to figure out how the atoms interact: the interaction will define almost all the properties of the system, after all. Atom-atom interactions are typically dictated by two effects. Firstly, even though atoms are electrically neutral, the displacement between the nucleus and the electron cloud creates a dipole moment, causing an attractive force between particles at long range. However, at short range, the

Pauli exclusion principle causes the atoms to repel each other. The combination of these effects is typically modelled by the Lennard-Jones potential [1],

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

where r is the distance from the source of the potential, ϵ has units of energy and is called the interaction energy, and σ has units of length and is called the interaction length. The first term in the potential models the short-range repulsion, and the second term models the long-range attraction.

Now, in principle, if we know the values of ϵ , σ , and the mass of argon m , we can calculate the path of each particle i by adding up the potentials created by the other particles and integrating Newton's second law:

$$\frac{d^2 \mathbf{x}_i}{dt^2} = -\frac{1}{m} \nabla_i \sum_{j \neq i} U_j(r_{ij}) \quad (2)$$

But this is inefficient. For argon, the values of ϵ , σ and m are [2]:

$$\epsilon = 1.654 \cdot 10^{-21} \text{ J}, \quad \sigma = 3.405 \cdot 10^{-10} \text{ m}, \quad m = 6.6 \cdot 10^{-26} \text{ kg} \quad (3)$$

Working with such small values in a simulation is cumbersome and prone to rounding errors. This is why we will make a change of variables:

$$\tilde{\mathbf{x}} = \frac{\mathbf{x}}{\sigma}, \quad \tilde{U} = \frac{U}{\epsilon}, \quad \tilde{t} = t / \sqrt{\frac{m\sigma^2}{\epsilon}} \quad (4)$$

Since energy has units $\text{kg m}^2 \text{s}^{-2}$, these new variables are dimensionless quantities: they are dimensionless length, dimensionless energy and dimensionless time, respectively. The dimensionless potential is now given by:

$$\tilde{U}(\tilde{r}) = 4(\tilde{r}^{-12} - \tilde{r}^{-6}) \quad (5)$$

And the equations of motion become:

$$\frac{d^2 \tilde{\mathbf{x}}_i}{d\tilde{t}^2} = -\tilde{\nabla}_i \sum_{j \neq i} \tilde{U}_j(\tilde{r}_{ij}) \quad (6)$$

This is much better: when calculating in terms of these quantities, all numbers will be close to order 1, which is much simpler to work with. There are other quantities we will use in dimensionless form: all quantities we will use and their definitions are given in Table 1.

We can find that the dimensionless force exerted by one particle is given by:

$$\tilde{\mathbf{F}}(\tilde{\mathbf{r}}) = -\tilde{\nabla} \tilde{U}(\tilde{r}) = 24(2\tilde{r}^{-14} - \tilde{r}^{-8})\tilde{\mathbf{r}} \equiv \tilde{f}(\tilde{r})\tilde{\mathbf{r}}, \quad (7)$$

where we call $\tilde{f}(\tilde{r})$ the dimensionless force prefactor. This definition will come in handy later on.

Length	$\tilde{L} = L/\sigma$
Energy	$\tilde{E} = E/\epsilon$
Time	$\tilde{t} = t/\sqrt{\frac{m\sigma^2}{\epsilon}}$
Velocity	$\tilde{v} = v/\sqrt{\frac{\epsilon}{m}}$
Force	$\tilde{F} = \sigma F/\epsilon$
Density	$\tilde{\rho} = \sigma^3 \rho/m$
Temperature	$\tilde{T} = k_B T/\epsilon$
Pressure	$\tilde{P} = \sigma^3 P/\epsilon$

Table 1: Definitions of all dimensionless quantities used in this report. Here, k_B is Boltzmann’s constant.

2 Methods

From this point onward, we will suppress tildes for ease of notation: all quantities are dimensionless unless otherwise stated.

Now that the necessary theoretical framework is set up, we can describe how we will build our simulation model. We will put a number of Argon atoms n in a cubic box with sides L and periodic boundary conditions, and give them starting velocities. The periodic boundary conditions mean that any particle that reaches an edge of the box will reemerge at the opposite edge. However, just giving them random starting positions and velocities would be a bad idea, for two reasons. Firstly, we want to study the system at equilibrium at specific densities and temperatures, so we want our initial conditions to depend on these quantities. Secondly, for arbitrary initial conditions, the system can take an extremely long time to reach equilibrium, possibly even billions of years if we are unlucky. Therefore, we need to set favorable initial conditions that we know are close to equilibrium.

We guess that setting the atoms in a face-centered cubic (FCC) lattice should be close to equilibrium. Such a lattice is shown in Figure 1. Let b be the length of the sides of the cube in the figure. Then the unit cell contains four atoms, with locations given by:

$$\mathbf{r}_0 = (0, 0, 0) , \quad \mathbf{r}_1 = \left(\frac{b}{2}, \frac{b}{2}, 0\right) , \quad \mathbf{r}_2 = \left(\frac{b}{2}, 0, \frac{b}{2}\right) , \quad \mathbf{r}_3 = \left(0, \frac{b}{2}, \frac{b}{2}\right) , \quad (8)$$

and the positions of all atoms can be found by displacing these positions by vectors of the form (bi, bj, bk) , where i, j and k are integers. So for this simulation, if the box that contains the atoms has sides L , we take the initial positions of the atoms to form a FCC lattice with $a = \frac{L}{a}$: this way, the system will contain a^3 unit cells, and thus $N = 4a^3$ atoms, and they will effectively feel an infinite FCC lattice around them due to the periodic boundary conditions.

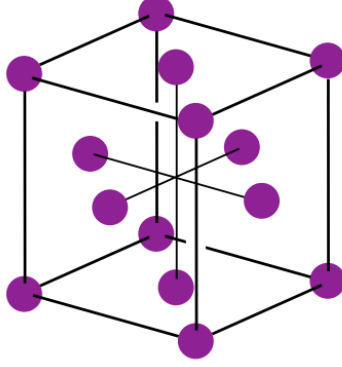


Figure 1: A piece of a face-centered cubic lattice [1].

Now, we need to couple this to the density. In dimensionful quantities, the density of this system is given by:

$$\rho = \frac{mN}{L^3}$$

So in dimensionless quantities it becomes:

$$\rho = \frac{N}{L^3} \quad (9)$$

So if ρ and a are given, we can calculate the box side length L we need with:

$$L = a \sqrt[3]{\frac{4}{\rho}} \quad (10)$$

In our simulation, we used $a = 3$.

Now that we have our initial positions, we move on to the velocities. The way to get close to equilibrium here is to simply randomly generate our initial velocities using a Maxwell-Boltzmann distribution for each component of the velocity. In dimensionful quantities, this distribution is of the form [1]:

$$p(v_x) \sim e^{-mv_x^2/(2k_B T)} ,$$

and the same holds for v_y and v_z . In dimensionless units, this simply becomes:

$$p(v_x) \sim e^{-v_x^2/(2T)} ,$$

which is a Gaussian distribution with mean 0 and variance T .

Now, we need to figure out how position and velocity evolve. The particles must be able to interact with each other through the periodic boundary conditions, but there lies a problem: how do we determine if two particles need to interact directly or through the walls? The answer is called the minimal image convention: we imagine each particle has 26 images in boxes surrounding the central box (all together forming a cube of 27 boxes), and other particles only interact with the image that is closest to them. We can decompose this problem into the individual dimensions of the position, and the x-component of the distance between two particles \mathbf{r}_{ij} is given as follows:

$$\begin{cases} x_{ij} = x_i - x_j & \text{if } -\frac{L}{2} \leq x_i - x_j \leq \frac{L}{2} \\ x_{ij} = x_i - x_j - L & \text{if } \frac{L}{2} \leq x_i - x_j \leq L \\ x_{ij} = x_i - x_j + L & \text{if } -L \leq x_i - x_j \leq -\frac{L}{2} \end{cases} \quad (11)$$

And similar equations for y_{ij} and z_{ij} . This can all be summarized in the expression:

$$\mathbf{r}_{ij} = (\mathbf{r}_i - \mathbf{r}_j + \frac{L}{2}) \bmod L - \frac{L}{2}, \quad (12)$$

where mod stands for modulo.

Now that we know this, we can calculate the forces with equation 7, and integrate the equation of motion:

$$\frac{d^2 \mathbf{x}_i}{dt^2} = - \sum_{j \neq i} \mathbf{F}_i(\mathbf{r}_{ij}) \quad (13)$$

To ensure energy is conserved, we use the Velocity Verlet algorithm to integrate this [1]:

$$\begin{cases} \mathbf{x}(t+h) = \mathbf{x}(t) + h\mathbf{v}(t) + \frac{h^2}{2}\mathbf{F}(\mathbf{x}(t)) \\ \mathbf{v}(t+h) = \mathbf{v}(t) + \frac{h}{2}(\mathbf{F}(\mathbf{x}(t+h)) + \mathbf{F}(\mathbf{x}(t))) \end{cases} \quad (14)$$

In our simulation, we used $h = 0.005$ as our time step length.

We are almost ready to run the system now, but there is one problem. We are close to equilibrium, but not quite close enough. This means we help the system with the lambda algorithm. In dimensionless units, the equipartition theorem implies that the total kinetic energy of the system should be given by:

$$\overline{E_{kin}} = \frac{3}{2}(N-1)T \quad (15)$$

And the actual kinetic energy of our system is given by:

$$K = \frac{1}{2} \sum_i \mathbf{v}_i^2 \quad (16)$$

So if we define a quantity λ :

$$\lambda = \sqrt{\frac{E_{kin}}{K}} \quad (17)$$

we can force a set of velocities to have the correct kinetic energy by multiplying them with their λ . This means we can force the system to go to equilibrium faster by periodically multiplying all velocities with λ . So before we do the real simulation, we repeat this algorithm until λ is small enough (< 0.01 for us).

Now, we want to calculate the pair correlation function, the fingerprint of each phase of argon, defined by [1]:

$$g(r) = \frac{2L^3 \langle n(r) \rangle}{N(N-1)4\pi r^2 \Delta r} \quad (18)$$

where $n(r)$ is the number of atom pairs within distances between r and $r + \Delta r$. We also want to calculate the pressure, given in dimensionless units by [1]:

$$P = \rho(T + \frac{1}{3N} \langle \frac{1}{2} \sum_i \sum_{j>i} r_{ij}^2 f(r_{ij}) \rangle) \quad (19)$$

The averages are over timesteps and over different simulations.

From [1] we have been given that a dimensionless density of 0.3 with a dimensionless temperature of 3 gives a gaseous state. A dimensionless density of 0.8 with a dimensionless temperature of 1 gives a liquid state. And finally, a dimensionless density of 1.2 with a dimensionless temperature of 0.5 gives a solid state. These are the three different states that will be investigated in our simulation.

3 Results

Looking at figures 2, 3 and 4 it can be seen that the simulation conserves the total energy very well. As you go from gas to liquid one can also see that all the energies decrease, and then when you go from liquid to solid they all decrease again. This is to be expected from this change of state.

Looking at figures 5, 6 and 7 it can be seen that Lambda fluctuates closely around 1 for all 3 states. This means that the calculated value of the kinetic energy, given by equation 15, and the experimental value of the kinetic energy,

given by equation 16 stay close.

Looking at figure 8 it can be seen that most distances are at one interaction length. As is expected from a gas the rest of the distances are very homogeneously spread. This homogeneity ends after an interaction length of about 3.5, where the pair correlation function starts to decrease. The cause of this decrease is most likely the implementation of the nearest window principle, meaning that larger distances are cut off. Figure 9 the homogeneity that was seen for the gas is gone and we see two definite peaks. This indicates more organization in the distance of the atoms thus most likely the liquid retains more of the initial lattice shape than the gas does. Figure 10 shows definite peaks and thus a much better organization of the atom distances. As is to be expected the solid state retains most of the original lattice shape and thus has this organization.

Table 4 shows that the values of the pressure that we get experimentally do not fluctuate very much, as the standard deviations are low compared to the actual values. The error in measurement is also very small, this is because a lot of measurements were taken, exactly $10 \cdot 10000$, the number of simulations times the number of time steps.

Using table 1 we can convert the dimensionless pressure in 4 to pressure with dimension, then we compare it to actual values given by [3]. Converting the dimensionless pressure gives $4.02 \cdot 10^7$ Pa for the given gas state at 359 K and 502 kg/m^3 , $4.19 \cdot 10^7$ Pa for the given liquid state at 120 K and 1337 kg/m^3 and $3.60 \cdot 10^8$ Pa for the given solid state at 60 K and 2006 kg/m^3 . [3] does not give the pressure at the exact same density and temperature combinations, however at the closest ones we get that the order of magnitude only differs by at most 1. For gas we get the value $4.8 \cdot 10^6$ Pa at a temperature of 150.69 K and density of 535.6 kg/m^3 . For liquid we get $4.59 \cdot 10^7$ K and 943.7 kg/m^3 . For solid [3] does not have any values.

4 Conclusion

It can be concluded that the simulation works well. Firstly, it conserves the total energy very well, as can be seen by figures 2, 3 and 4. Secondly, the experimental kinetic energy is very close to the energy in equilibrium that is to be expected, as can be seen by figures 5, 6 and 7. The slight fluctuations can be seen as the slight fluctuations of the system around the equilibrium as is to be expected. Thirdly, figures 8, 9, 10 show that there is a definite increase of the organization of the atom distances as you go from gas so solid, as is to be expected. Lastly, the values for the pressures for each combination of temperature and density are of the same order of magnitude as the pressure values one would actually receive in for those combinations.

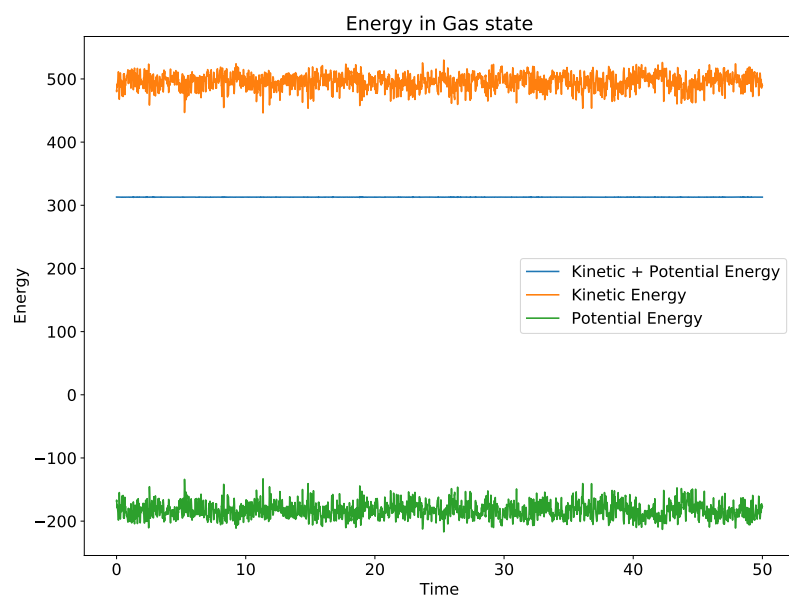


Figure 2: The dimensionless kinetic, potential and total energy of the atoms in a gas state over dimensionless time using the dimensionless temperature 3 and dimensionless density 0.3.

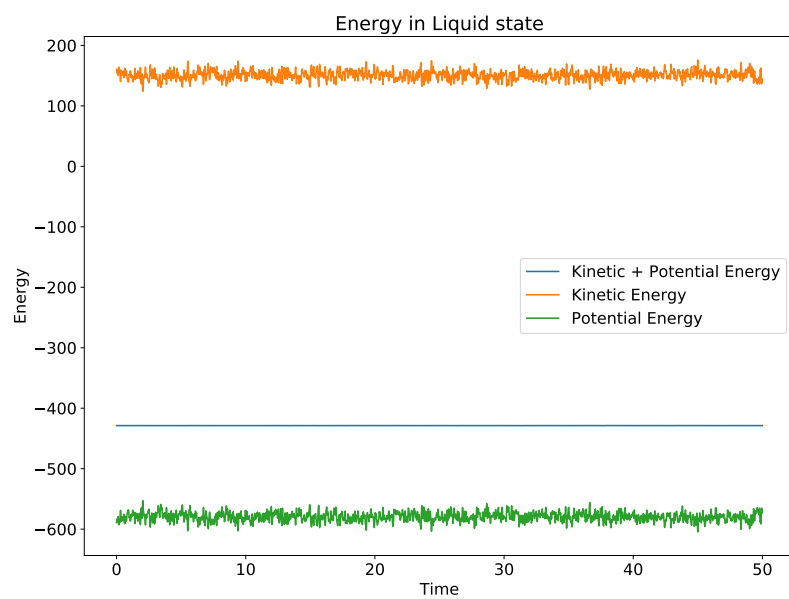


Figure 3: The dimensionless kinetic, potential and total energy of the atoms in a liquid state over dimensionless time using the dimensionless temperature 1 and dimensionless density 0.8.

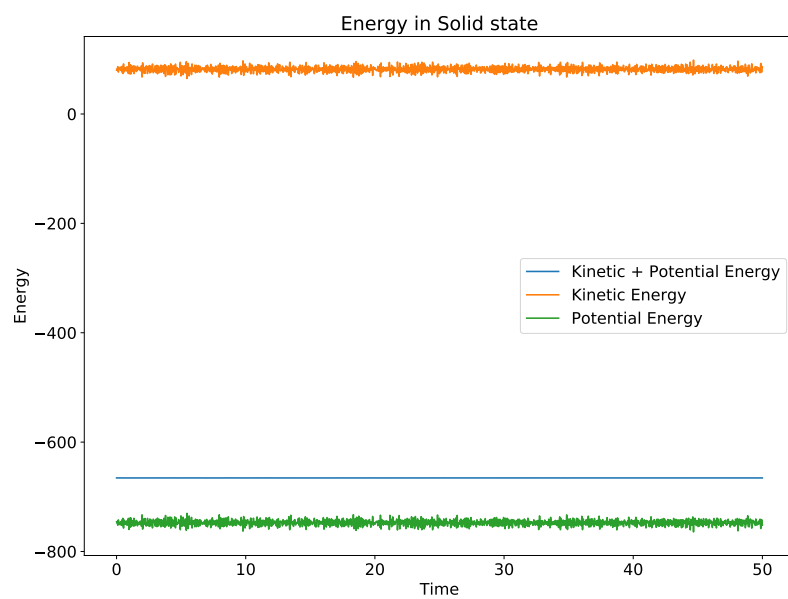


Figure 4: The dimensionless kinetic, potential and total energy of the atoms in a solid state over dimensionless time using the dimensionless temperature 0.5 and dimensionless density 1.2.

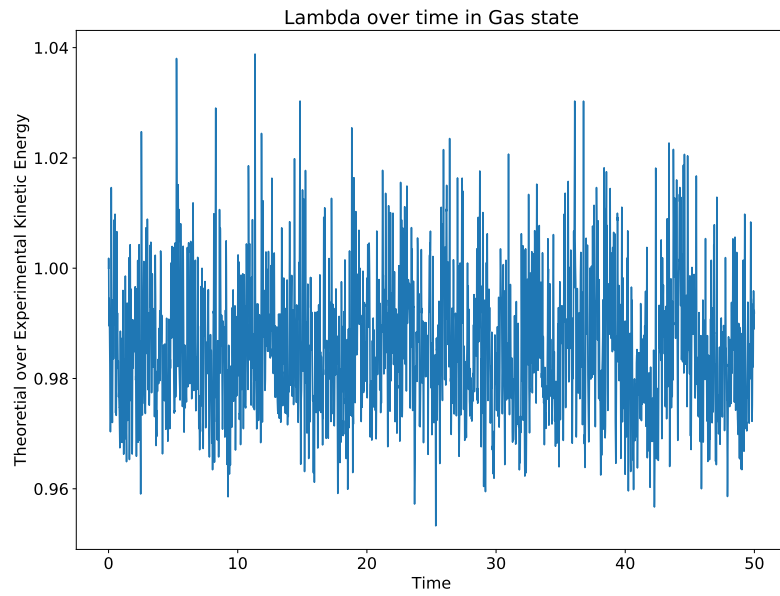


Figure 5: Lambda of the atoms in a gas state over dimensionless time using the dimensionless temperature 3 and dimensionless density 0.3.

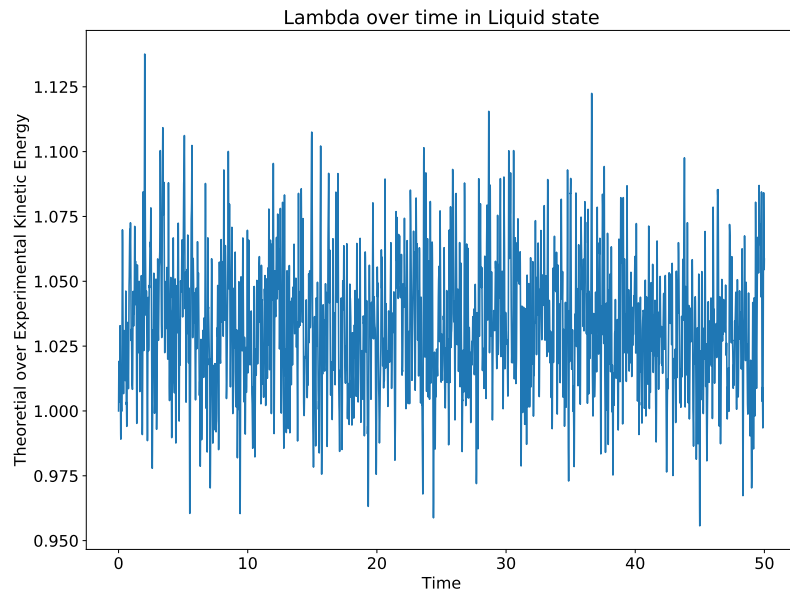


Figure 6: Lambda of the atoms in a liquid state over dimensionless time using the dimensionless temperature 1 and dimensionless density 0.8.

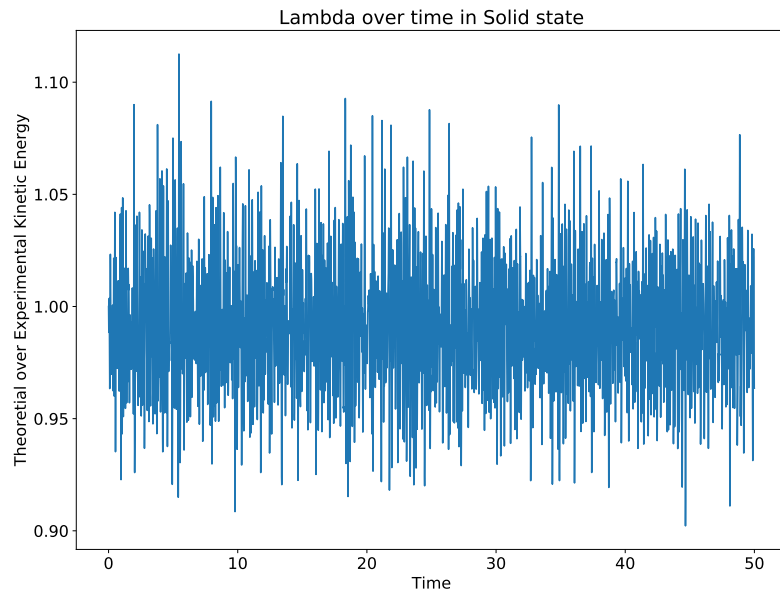


Figure 7: Lambda of the atoms in a solid state over dimensionless time using the dimensionless temperature 0.5 and dimensionless density 1.2.

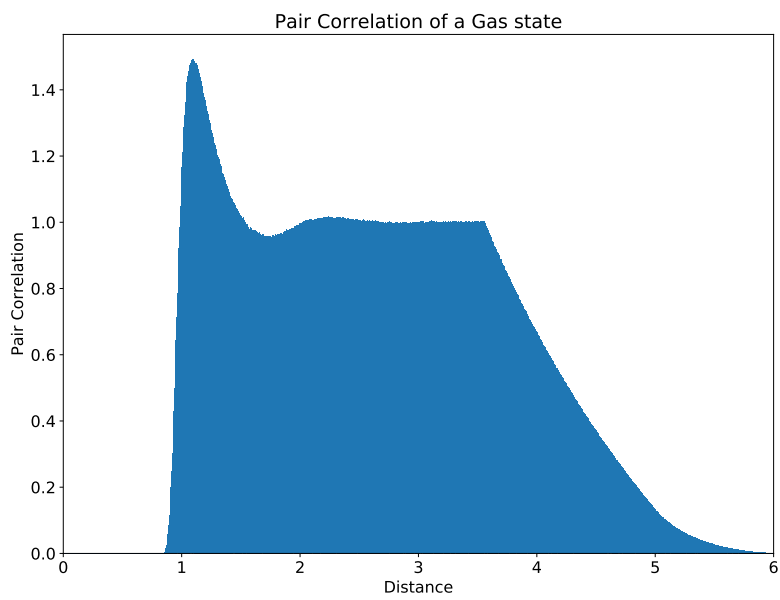


Figure 8: Pair correlation function of the atoms in a gas state using the dimensionless temperature 3 and dimensionless density 0.3.

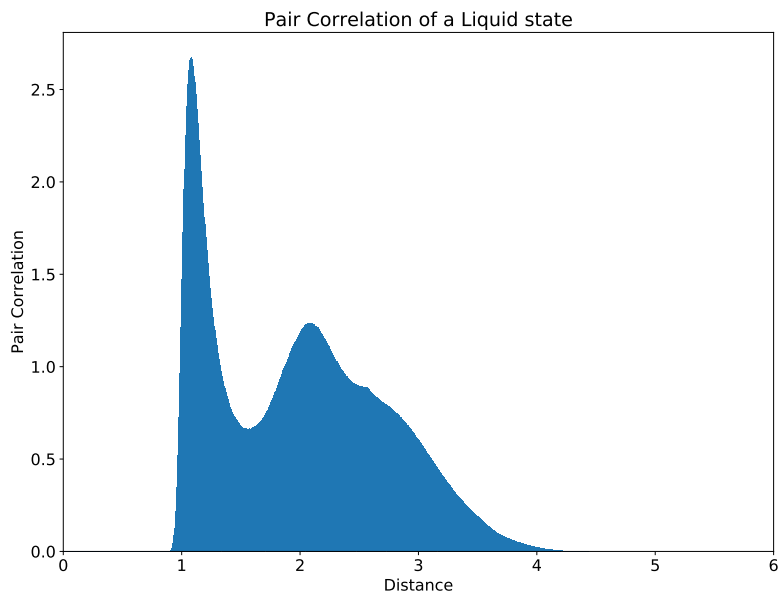


Figure 9: Pair correlation function of the atoms in a liquid state using the dimensionless temperature 1 and dimensionless density 0.8.

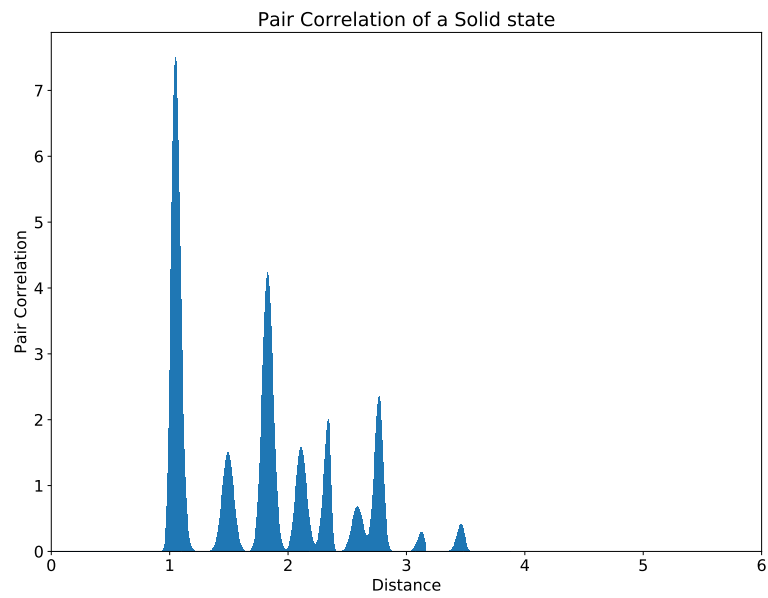


Figure 10: Pair correlation function of the atoms in a solid state using the dimensionless temperature 0.5 and dimensionless density 1.2.

State	Average Pressure	Standard Deviation	Measurement Error
Gas $\rho = 0.3, T = 3$	0.96	0.092	0.00029
Liquid $\rho = 0.8, T = 1$	1.0	0.18	0.00058
Solid $\rho = 1.2, T = 0.5$	8.6	0.14	0.00046

Table 2: Values of the dimensionless pressures that were calculated at different states with their error

References

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- [3] Engineering ToolBox, (2018). Argon - Density and Specific Weight. [online] Available at: https://www.engineeringtoolbox.com/argon-density-specific-weight-temperature-pressure-d_2089.html [Accessed Day Mo. Year].