

Molecular Dynamics Model of Argon using the Verlet Algorithm

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In this paper the motion of argon atoms, interacting via the Lenard-Jones potential, is simulated using the velocity-Verlet algorithm. Using this simulation certain macroscopic quantities are determined. The specific heat found is not in agreement with literature which is probably caused by usage of the bootstrapping technique as this takes only one system realisation into account. The pressure does agree when taking the phase transition from liquid to solid into account, which happens at a slightly higher value, $(\rho, T) = (0.90, 1)$, than found in literature, $(0.88, 1)$. The pressure also suffers from the same bootstrapping issue. The calculated pair correlation functions are in agreement with those found in literature. The simulation run time scales quadratic with particle number and linear with the number of time steps.

Introduction

In the course Computational Physics (AP3082D) several physical problems need to be solved using computational methods. The first problem in the series is the modelling of an Argon atoms system. During the modelling the student is getting acquainted with the Python syntax and the physics behind the molecular dynamics in such a system. In order to calculate the dynamics of the particles in the system it was advised to use the velocity-Verlet algorithm as solving the Newton equations by Euler discrete integration is not sufficient.

Method

Non-dimensionalising

To simplify the problem and prevent working with very small values dimensionless units are used. The conversion from the dimensional to dimensionless units can be found in Table 1. For Argon: $\sigma = 3.405\text{\AA}$ and $\epsilon = k_B 119.8\text{K}$. Thijssen (2007)

Table 1

Dimensionless (dl) units as calculated from real units.

r_{dl}	E_{dl}	t_{dl}	v_{dl}	T_{dl}	E_{dl}^{kin}
\updownarrow	\updownarrow	\updownarrow	\updownarrow	\updownarrow	\updownarrow
$r\sigma^{-1}$	$E\epsilon^{-1}$	$t\sqrt{\frac{\epsilon}{m\sigma^2}}$	$v\sqrt{\frac{m}{\epsilon}}$	$k_B T\epsilon^{-1}$	$v_{dl}^2/2$

In the rest of the paper only these dimensionless units will be used unless explicitly stated otherwise. Therefore the subscript 'dl' is omitted from here on.

Particle interactions

The particle interactions are determined by the initial location and speed of the particles combined with the inter-

action potential, which is the Coulomb potential. In a non-dimensional form, this is given by:

$$U_{ij} = 4 \left\{ \left(\frac{1}{r_{ij}} \right)^{12} - \left(\frac{1}{r_{ij}} \right)^6 \right\} \quad (1)$$

in which r_{ij} is the distance between the interacting particles i and j .

As it is not possible to calculate the interactions in infinite space, the calculations are done for a finite box of sides L which is repeated periodically in space (for all three dimensions). This is done by setting periodic boundary conditions. The interactions due to the Coulomb potential for two particles needs to be calculated for the smallest distance between these particles, hence the distance to nearest particle or virtual particle copy. In figure 1 it can be seen that the smallest distance between two particles is not necessarily inside one box.

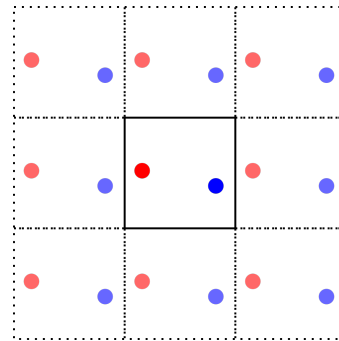


Figure 1. Simple sketch of the periodic boundary conditions for two particles in the box. The smallest distance between the two particles is for the two particles in neighbouring boxes (the original and a copy). Wimmer (2018)

In formula form the smallest distance between a particle i and j is given by:

$$\begin{aligned} |x_i - x_j| &< L/2 &\rightarrow x'_j &= x_j, \\ x_i - x_j &> L/2 &\rightarrow x'_j &= x_j - L, \\ x_i - x_j &> -L/2 &\rightarrow x'_j &= x_j + L \end{aligned} \quad (2)$$

where x_i , x_j and x'_j are the x-coordinates of particle i , j and the virtual copy of j closest to i , and L is the box side length. For the other dimensions x can be substituted with y and z . The smallest distance between interacting particles is:

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

Propagation in time

The time evolution of the particles propagation is evaluated by applying the velocity-Verlet algorithm. Thijssen (2007) The reason for this is that the velocity-Verlet algorithm conserves the energy of the system better than the Euler integration of the Newton equations. According to the velocity-Verlet algorithm:

$$\begin{aligned} \tilde{v}(t) &= \tilde{v}(t) + h\vec{F}(t)/2, \\ \vec{r}(t+h) &= \vec{r}(t) + h\tilde{v}(t), \\ \tilde{v}(t+h) &= \tilde{v}(t) + h\vec{F}(t+h)/2 \end{aligned} \quad (4)$$

Here \tilde{v} is used to improve efficiency, since the force of the previous iteration can be used. Hence, only one force calculation per iteration is needed instead of two. The time step is set to $h = 0.04$ as this is suggested to be optimal by Thijssen (2007). The force can be calculated from the inter particle potential in the following way:

$$\vec{F}(\vec{r}) = -\nabla U(\vec{r}) = -\frac{dU}{dr} \frac{\vec{r}}{r} \quad (5)$$

where U is the potential as given by eq. 1.

Initial conditions & feedback

A Maxwell distribution for the temperature is needed. This is provided by picking the initial position and velocity of the particles from a Gaussian distribution. The energy exchange between kinetic and potential energy due to the interactions between the particles when the system goes towards equilibrium cannot be predicted easily. Therefore the velocities of the particles are scaled in such a way that the kinetic energy satisfies the equipartition theorem. The scaling factor needed to do so is given by λ :

$$\lambda = \sqrt{\frac{3(N-1)T}{2E_{kin}}} \quad (6)$$

The necessity of re-scaling the temperature of the system is evaluated once the system has reached equilibrium. To determine if the system is in equilibrium, the mean free path

is used together with the kinetic energy present in the system to determine the amount of interactions. The interaction number can be calculated in the following way:

$$n_{int} = \frac{\pi}{L^3 \sqrt{2E_{kin}/N}} \quad (7)$$

In the derivation we have taken the 'size' of a particle to be σ , hence in dimensionless units this equals 1. We assume that if, on average, every particle has had one 'collision', equilibrium has been reached. Temperature re-scaling is applied when in this equilibrium state the temperature is not within a standard deviation of the system temperature. This is repeated until the system temperature corresponds to the temperature that was set in the simulation. Once the system has reached this pre-set temperature, the measurement of the system starts. The number of data points wanted in this measurement is denoted by N_{Eq} and will be given in the results section.

Specific heat

The fluctuations of the kinetic energy of the system are used to calculate the specific heat. This relation is derived by Lebowitz et al. (1967) and is adapted to:

$$C_V = \frac{2}{3N} - \frac{\langle \delta K^2 \rangle}{\langle K \rangle^2} \quad (8)$$

in which N is the number of particles in the system, K is the kinetic energy and δK is the fluctuation in kinetic energy. In order to get a measure for the specific heat which is independent of the number of particles in the system, the expression for C_V is additionally divided by N . The results for the specific heat will be compared with the findings of Lebowitz et al. (1967).

Pressure

The pressure in the system is given in Thijssen (2007) and in its dimensionless form:

$$P = 1 + \frac{1}{3N} \left\langle \sum_{i=1}^N \vec{r}_i \cdot \vec{F}_i \right\rangle \quad (9)$$

in which \vec{F}_i is the total interaction force on particle i , \vec{r}_i is the distance to particle i from the origin and N is the number of particles in the system. The average depicted is the ensemble average, but as it is a dynamic system, the time average can be used instead. Thijssen (2007) The results for the pressure will be compared with the findings of Thijssen (2007).

Pair correlation

The pair correlation function is given in Thijssen (2007) by:

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

here r denotes the inter particle distance, $\langle n(r) \rangle$ the time average of the amount of particles at distance r within an interval Δr . The pair correlation will be looked at for three distinct phases: solid ($T = 0.5, \rho = 1.2$), liquid ($T = 1.0, \rho = 0.8$) and gas ($T = 3.0, \rho = 0.3$). Thijssen (2007) The pair correlation function will be compared with literature for $T = 1.06$, $\rho = 0.827$, which is the triple point of argon. Thijssen (2007)

Bootstrapping

The averages in equations 8 and 9 are determined by the bootstrapping technique. For a given data set $\{d_t\}$ consisting of M data points over time, the bootstrapping technique randomly picks M data points from this set. From these randomly picked M data points the quantity Q is calculated in the same manner as it would have been calculated from the original data set. This process is repeated k times for the same data set $\{d_t\}$. The k different values of Q are then used to determine the (time) average and standard deviation of Q . The k is denoted by N_{BS} in the results.

Results

The results about to be shown are all from simulations with the following settings unless stated otherwise.

Table 2

Settings used in simulations, where N is the number of particles in the system, h the time step, N_{Eq} the number of equilibrium data points and N_{BS} the number of bootstrap sequences.

N	h	N_{Eq}	N_{BS}
864	0.04	2000	1000

These settings are chosen to be able to compare the simulation results with literature.

Energy conservation & temperature correction

The system has to be in equilibrium and satisfying the equipartition theorem before results can be shown.

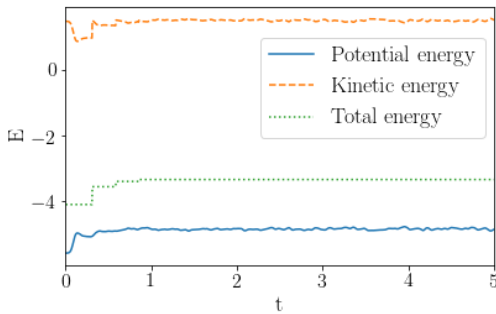


Figure 2. The potential, kinetic and total energy in the system over time. After $t = 0.95$ the scaling corrections have lead to the equilibrium satisfying the equipartition theorem.

In figure 2 can be seen that after scaling the particle velocities in the system three times, the mentioned conditions are met. It also shows that the total energy is conserved as it should be. The corresponding temperature behaviour is shown in figure 3.

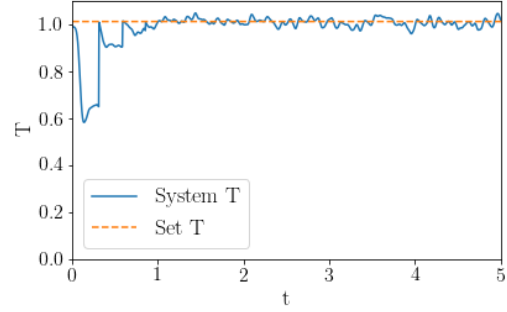


Figure 3. The temperature of the system and the wanted, set temperature. The temperature of the system stabilises towards the wanted temperature due to the corrections and reaching the wanted system state.

From this plot it is clear that the system stabilises towards the desired temperature by performing multiple (correction) scalings of the calculated temperature and once this is achieved the scaling stops.

Pair correlation & phases

The pair correlation function is determined for the triple point of Argon ($T = 1.06, \rho = 0.827$) and shown in figure 4. Comparing this to the result in Thijssen (2007) for the same state of the system, the result differs by a factor of π but has the same shape.

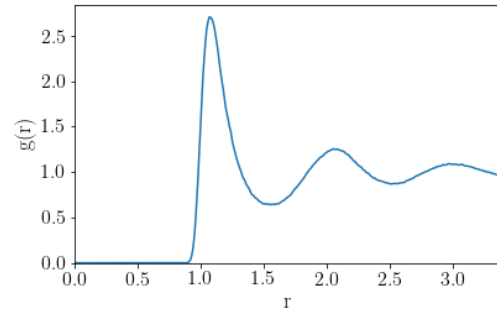


Figure 4. The pair correlation function at the triple point of argon ($T = 1.06, \rho = 0.827$) for a simulation with $N = 256$.

For the solid ($T = 0.5, \rho = 1.2$), liquid ($T = 1.0, \rho = 0.8$) and gas phase ($T = 3.0, \rho = 0.3$) the pair correlation functions can be seen in figure 5. The results are as expected. For the solid phase a clear discrete lattice can be seen. For the gas phase, after an initial peak due to the core repulsion, the pair

correlation function is flat. The liquid phase is somewhere in between the gas and solid phase.

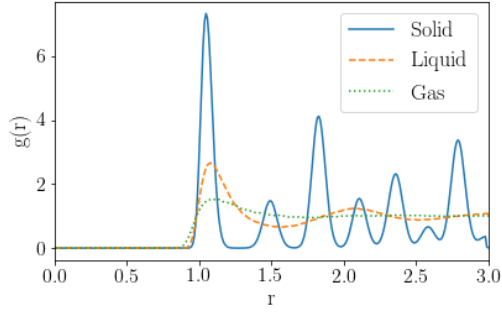


Figure 5. The pair-correlation functions for three phases, solid ($T = 0.5$, $\rho = 1.2$), liquid ($T = 1.0$, $\rho = 0.8$) and gas ($T = 3.0$, $\rho = 0.3$) with $N = 256$.

Macroscopic properties

Specific heat. In table 3 the simulated specific heat and the corresponding standard deviation is shown.

Table 3

Realised system temperature and specific heat with its corresponding standard deviation. ρ^{set} , T^{set} are input variables.

ρ^{set}	T^{set}	T^{sim}	C_v^{sim}	$\sigma_{C_v}^{sim}$
0.85	2.89	2.89	2.29	0.04
	2.20	2.22	2.35	0.04
	1.21	1.20	2.61	0.06
	1.13	1.12	2.70	0.06
	0.88	0.88	2.47	0.05
0.75	2.84	2.88	2.00	0.02
	0.827	0.82	2.24	0.03
0.45	4.62	4.63	1.70	0.01
	2.93	2.93	1.73	0.01
	1.71	1.71	1.74	0.01
	1.51	1.51	1.90	0.02

In general there seems to be a disagreement between the C_v values found and the values given by Lebowitz et al. (1967) as they differ by up to 0.4 for some states. The disagreement mentioned could be due to two different causes. Firstly Lebowitz et al. (1967) do not provide any indication of the standard deviation of their found values, besides, they determined C_v in three different ways, which gives results differing by up to 0.2.

Secondly, there seems to be a problem in the way the bootstrap method is applied. The specific heat for complete new simulations does not seem to be reflected by the values found in only one simulation. A reason could be that every simulation is a very specific realisation, and only a sub-part

of the total possible realisations is used in our results, since we bootstrap over one realisation only. This results in low standard deviations. In order to substantiate this claim, the simulation is done for a twice as large $N_{Eq} = 4000$ as well to see if this had any effect on the standard deviations. This did not yield any better results, hence the concern about the bootstrap method stays valid. This is based on the suspicion that the data in a realisation is not independent.

Pressure. In table 4 the pressure and the corresponding standard deviation is shown.

Table 4

Realised system temperature and pressure with its corresponding standard deviation ρ^{set} , T^{set} are input variables.

ρ^{set}	T^{set}	T^{sim}	P^{sim}	σ_P^{sim}
0.90	1.00	0.99	2.485	0.014
0.88	1.00	1.01	0.994	0.018
0.80	1.00	1.00	1.012	0.015
0.70	1.00	1.00	1.002	0.012

For $\rho = 0.88$ the simulation is a factor 3 off compared to Thijssen (2007). By setting ρ to 0.90 the pressure value makes a sudden jump. The pair correlation functions indicate that $\rho = 0.88$, $T = 1$ corresponds to the liquid phase and $\rho = 0.90$, $T = 1$ to the solid phase and thus a phase transition. Looking at a phase diagram of argon this transition is present indeed. Grams et al. (2005) Hence a small deviation from certain system properties can result in completely different properties. This, together with the discussed flaw in the implementation of the bootstrapping technique, could be the reason why the simulated pressure values are not within three standard deviations from the values in Thijssen (2007).

Software performance

Apart from the output given by the written software, the performance is an important feature as well. The run time is measured for different number of particles in the system. As

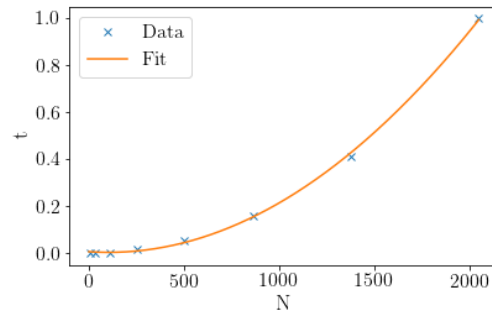


Figure 6. Number of particles N versus run time t . The run time is normalised with respect to the maximum run time measured. The data is fitted with a second order polynomial.

can be seen in figure 6, the run time has a quadratic behaviour with respect to the number of particles in the system. Errors are not presented in the plot since the run time differences are very small and dominated by externally set parameters, like processor performance, which cannot be controlled. To give an indication of the absolute run time: 864 particles and 3000 time steps takes approximately 10 minutes. The scaling with time steps is linear.

Conclusion

From the results it can be concluded that the simulation software generates a physical system which conserves the total energy and gives output similar but not in full correspondence to the output given in the literature mentioned. In the case of the specific heat the uncertainties of the reference values in Lebowitz et al. (1967) are not known. Therefore it could be that the specific heat presented in this report disagrees in a less extent than currently thought. The deviation of the simulated pressure from the result presented in Thijssen (2007) is partly caused by the presence of a phase transition close to $\rho = 0.88$, $T = 1$. Overall, it is thought that these discrepancies are most likely caused by the application of the bootstrapping technique, while the data, on which this is applied, is not independent.

Reflection on cooperation

In general cooperation went well and quite a bit was learned along the way. It was noticed that it is important to first make a solid plan before the programming starts. In this plan there should be well defined tasks which can

be made independently. For this we used a ‘to-do’ list application, but in the future we would like to start using the issue feature on Git. Besides that we were able to resolve the encountered problems together after discussing them. As for the workload, this was distributed as evenly as possible. During the intense week together the foundations were laid for a correct simulation after which the rest of the work to be done was divided per macroscopic quantity between each other. During the entire project results were discussed and code was checked by each other. To give an overview of the specific distribution:

Together: foundations of the simulation including: velocity-Verlet, fcc lattice, periodic boundary conditions, temperature correction and initial speed.

Tom: specific heat and pressure.

Vincent: specific heat and pair correlation.

References

- Grams, M., Stasicki, B., & Toennies, P. (2005, 12). Production and characterization of micron-sized filaments of solid argon. , *Vol. 76*, 123904-1.
- Lebowitz, J. L., Percus, J. K., & Verlet, L. (1967). Ensemble dependence of fluctuations with application to machine calculations. *Phys. Rev.*, 153(1), 250–254.
- Thijssen, J. (2007). *Computational physics, 2nd edition*. Cambridge University Press.
- Wimmer, M. (2018). *Course notes, project 1: Molecular dynamics*. Retrieved from gitlab.kwant-project.org/computational_physics_18/course_notes