

Modelling Molecular Dynamics of Argon

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Abstract—In this paper a computational model is proposed in order to simulate the molecular dynamics of Argon atoms, from which several measurable (material) properties can be extracted. In this model we focussed on determining the specific heat, diffusion coefficient and a measure for the pressure for a given density and temperature. We found the model to be effective and to largely agree with values from literature or to show correct physical behaviour.

Index Terms—Molecular dynamics, Computational Physics, Argon, Pressure, Specific Heat, Diffusion Coefficient

I. INTRODUCTION

IN this paper a method to simulate the molecular dynamics of Argon is proposed. By simulating the microscopic interaction we hope to gain insight in the connection between these interactions and the macroscopic properties of the entire system. The benefit of the molecular dynamic approach used over the also commonly used alternative, the Monte Carlo approach, is that it is easier to determine dynamic properties of the collection of Argon atoms like the pressure, diffusion coefficient and the specific heat. These quantities will be determined for given densities and temperatures across solid, liquid and gas phases. Before we start explaining the computation method of the simulations we will give some of the basic assumptions we used in our model. The interaction energy of two Argon atoms is described by the Lennard-Jones potential. Since the Lennard-Jones potential in SI units can contribute to a longer computation time, we have chosen to use the following expression in reduced units for the Lennard-Jones potential in our simulations:

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

In Figure 1 the Lennard-Jones potential from Equation 1 is plotted.

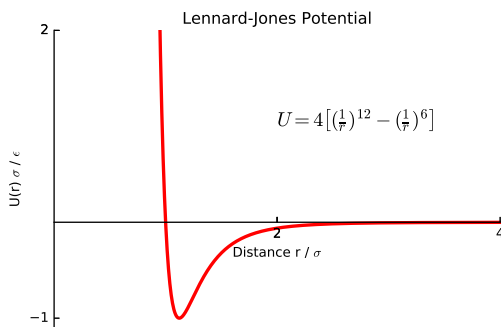


Fig. 1: The Lennard-Jones potential according to Equation 1.

From the Lennard-Jones potential the forces acting on an individual Argon atom j can be calculated by summing over the interactions with all other atoms:

$$\vec{F}_j = - \sum_{i \neq j} \frac{\partial U(r_i)}{\partial r_i} \hat{r}_i \quad (2)$$

The initial position of the Argon atoms are arranged in a FCC structure, see Figure 2 for a 3D plot of the initial positions of the Argon atoms for $n = 108$ particles.

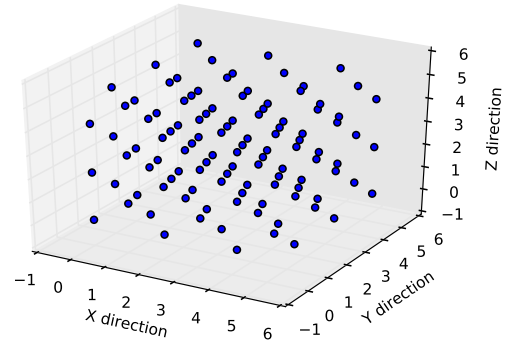


Fig. 2: The initial positions of the Argon gas for $N = 108$ particles. This shows the correct FCC structure.

Another assumption we have made in our simulation is that the initial velocity of each Argon atom is normal distributed around zero, with a standard deviation $\sigma = 0.1$. We have done this in order to maintain a zero mean velocity of the atoms (since we want the container holding the Argon atoms to have a zero velocity). The velocity of the Argon atoms is related to the temperature, since a higher temperature is a result of a higher kinetic energy of the individual Argon atoms, we need to implement this relation in our simulation.

After the position and velocities are initialised, we keep iterating the following steps:

- 1st step: Calculating forces
- 2nd step: Update velocities
- 3rd step: Update positions

which is known as the Verlet/leap-frog algorithm.

II. THE COMPUTATION METHOD

IN this section the computation method for the molecular dynamics simulation is explained in detail.

In the Introduction we started with an Equation for the forces on each Argon atom (see Equation 2). We started by evaluating the differential of the Lennard-Jones potential and implementing the correct \hat{r} . The result is:

$$\vec{F} = - \sum_{i \neq j} \left[\frac{48}{r^{13}} - \frac{24}{r^7} \right] \frac{\vec{r}}{|r|}. \quad (3)$$

Before we can calculate the updated velocities and positions we will explain in some more detail the relation between the temperature and the velocity used in our simulation. As mentioned before we want a zero mean velocity of the ensemble, which means that we are dealing with a stagnant medium. We obtained this by a normal distributed velocity field with a zero mean velocity. Since the number of particles is finite, this still results in a non-zero mean velocity. In order to compensate for this we subtract the mean velocity from the velocity field. Another criteria which the velocity needs to satisfy is the kinetic energy relation of the ensemble to the thermal energy in the system, in reduced units:

$$T = \frac{1}{2} (v_x^2 + v_y^2 + v_z^2) \quad (4)$$

When the criteria in Equation 4 is met, the Verlet/leap-frog algorithm can start. Since we start in a rather inconvenient initial position, namely an FCC-structure, it is better to let the algorithm run for several cycles. In this 'start-up' phase of the computation the temperature is forced back to the desired temperature as given in the initial condition. After a reasonable amount of cycles the system is in equilibrium, from that moment on the start-up phase is finished and the simulation can start. See Figure 3 to see the system reach its equilibrium.

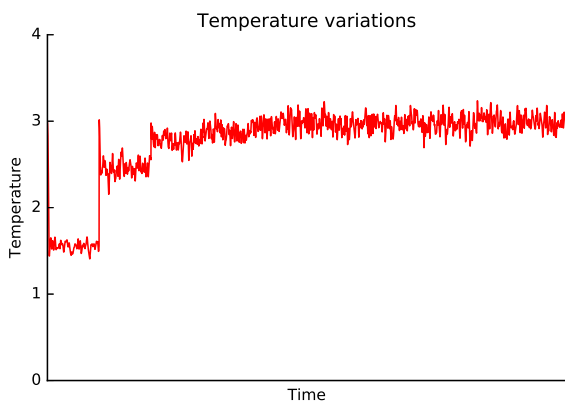


Fig. 3: The temperature is forced back to the desired temperature given in the initial conditions. In this simulation the temperature is forced four-times back to the desired temperature (in this case $T = 3$). After this it is clearly visible that the temperature is in a stable state.

III. MEASURABLE QUANTITIES

IN order to test our simulation we can extract physical quantities which we can compare to their literature values. If these values correspond, it is likely that our simulation properly describes the physical behaviour of Argon atoms.

A. Pressure

A first quantity to examine is the pressure of the Argon atoms. From statistical mechanics one can derive the virial equation for a measure of the pressure, sometimes called the compressibility factor, from now on we will refer to this measure as just the pressure [2]:

$$\frac{P}{nk_bT} = 1 - \frac{1}{3Nk_BT} \left\langle \sum_i \sum_{i>j} r_{ij} \frac{\partial U(r)}{\partial r_{ij}} \right\rangle_{cut-off} - \frac{2\pi N}{3k_bTV} \int_{r_{cut-off}}^{\infty} r^3 \frac{\partial U(r)}{\partial r} g(r) dr \quad (5)$$

The pair correlation function in Equation 5 $g(r)$ is approximately 1 for large $r_{cut-off}$. This allows us to rewrite Equation 5 as:

$$\frac{P}{nk_bT} = 1 - \frac{1}{3Nk_BT} \left\langle \sum_i \sum_{i>j} r_{ij} \frac{\partial U(r)}{\partial r_{ij}} \right\rangle_{cut-off} + \frac{2\pi N}{3k_bTV} \left[\frac{48}{9} r_{cut-off}^{-9} - \frac{24}{3} r_{cut-off}^{-3} \right] \quad (6)$$

B. Specific heat

Another interesting physical quantity to measure is the specific heat for a fixed volume, c_v . The specific heat can be calculated from the Lebowitz' formula [2]

$$\frac{\langle \delta k^2 \rangle}{\langle k \rangle^2} = \frac{2}{3N} \left(1 - \frac{3N}{2c_v} \right) \quad (7)$$

Rewriting Equation 7 results in:

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

Equation 8 is the specific heat for the entire system. The specific heat per atom is simply c_v/N .

C. Diffusion Coefficient

Since the position and momentum of the individual particles are being tracked, the average migration of the interacting particles can be easily extracted in the form of a diffusion coefficient. This coefficient can be defined as:

$$D = \frac{\langle r^2 \rangle}{t} \quad (9)$$

Where r is the nett distance travelled by a single particle and t the time in which that travel took place.

The values of the diffusion coefficient D should give an indication of the phase of the system. In the solid phase, this coefficient should be near zero. Furthermore, the gas phase should give a significantly higher value of D compared to the liquid phase.

IV. RESULTS AND VERIFICATION

IN this section the results from the simulation will be discussed and compared to values found in literature. For a range of initial conditions, which we have chosen to match with some values in Verlet [1], we obtained the following results shown in Table I.

TABLE I: Results obtained from our simulation with amount of particles $N = 864$. Time step size $h = 0.004$, equilibrium time $\tau_{eq} = 10$ and total timespan of $\tau = 100$. With ρ and T_0 the set density and temperature. \bar{T} the average measured temperature, T_σ the variance of that temperature. P the quantity found from Equation 5 and P_ϵ the corresponding error. C_v the found specific heat per particle and $C_{v,\epsilon}$ its corresponding error. All values are in reduced units.

ρ	T_0	\bar{T}	T_σ	P	P_ϵ	C_v	$C_{v,\epsilon}$
0.88	1.10	1.1048	0.1238	3.4600	0.0445	2.6699	0.4674
0.88	0.94	0.9472	0.0991	2.8384	0.0446	2.6070	0.4306
0.88	0.59	0.5894	0.0330	-4.0077	0.0167	3.0677	1.0258
0.85	2.89	2.8698	0.1875	4.3659	0.0256	2.1784	0.2091
0.85	1.21	1.2395	0.1059	3.1135	0.0371	2.4432	0.2877
0.85	1.13	1.1064	0.1166	2.7235	0.0429	2.4547	0.3148
0.45	1.55	1.5412	0.2363	0.5417	0.0270	1.8094	0.1067
0.4	1.42	1.4239	0.2350	0.3826	0.0263	1.8262	0.1202
0.35	1.62	1.6108	0.3070	0.5744	0.0206	1.7552	0.0763
0.35	1.42	1.4184	0.3392	0.3904	0.0286	1.7809	0.1411

Some of the results Verlet obtained in his paper in 1967 are shown in Table II [1]:

TABLE II: The results L.Verlet obtained in 1967 with his molecular dynamics model fo 864 Argon atoms [1]. Here ρ is the density, T the temperature and P the pressure. All values are in reduced units.

ρ	T	P
0.88	1.095	3.48
0.88	0.94	2.72
0.88	0.591	-0.18
0.85	2.889	4.36
0.85	1.214	3.06
0.85	1.128	2.78
0.45	1.552	0.75
0.4	1.424	0.38
0.35	1.620	0.58
0.35	1.418	0.40

If we compare the results, we see some values are in agreement, within the error. Some results are just outside the error range, but can be considered in agreement since the temperatures are not identical. For the values $\rho = 0.88, T = 0.591, P = -0.18$ and for $\rho = 0.45, T = 1.552, P = 0.75$ the results do not match.

In Table III our results for the diffusion coefficients are shown. We have chosen the density and temperature, such that they match a solid, liquid and gas phase of Argon [2].

TABLE III: Results obtained from our simulation with amount of particles $N = 864$. Time step size $h = 0.004$, equilibrium time $\tau_{eq} = 10$ and total timespan of $\tau = 100$. With ρ and T_0 the set density and temperature. With \bar{T} the average measured temperature, T_σ the variance of that temperature. With D the diffusion coefficient and D_ϵ the corresponding error. All values are in reduced units.

ρ	T_0	\bar{T}	T_σ	D	D_ϵ
1.2	0.5	0.4986	0.0047	3.2167	0.141
0.8	1.0	1.0080	0.1008	344.93	18.1
0.3	3.0	2.9828	0.1809	4491.4	122

V. DISCUSSION

FOR our results of the specific heat we do not have any experimental values from literature. In order to validate our results we took a look at the asymptotic case in which there was hardly any interaction between the Argon atoms. We did this by simulating a very low density gas. From statistical mechanics we should expect the specific heat for a single Argon atom to be equal to $3/2$. Our simulation resulted $C_v = 1.5014 \pm 0.0005$.

The results for the diffusion coefficient seem valid, since we would expect a low diffusion coefficient for a solid and a relative high diffusion coefficient for a gas and liquid to be somewhere in between. We observe that the diffusion coefficient increases by two orders of magnitude when changing the phase from solid to liquid and another order of magnitude when changing from a liquid to a gaseous phase, as can be seen in III. This is exactly the behaviour we would expect.

The results for the pressure generally correspond well with the results obtained by Verlet, even though we have approximated the pair-correlation function $g(r) = 1$. Two results do not match up when comparing Table I with Table II. In one we find a very large negative pressure, we suspect this is due to a phase change of the system towards a solid. Given our limited amount of time we could not have examined this further. For our second deviation with Verlet's results we do not have a explanation. We see no reason why our result should be invalid, except for the fact it does not agree with the result Verlet obtained.

VI. CONCLUSION

OUR computational model for the molecular dynamics of Argon, simple as it is, corresponds pretty well with an existing model created by L. Verlet. Besides the fact we did not calculate the diffusion coefficient in SI units, it did show correct physical behaviour. Again, for the specific heat we did not compute any values in SI units, but in the asymptotic case we did find the correct results as predicted from theory. In conclusion we can say that this computational model is capable of predicting the behaviour of Argon molecular dynamics accurately and can predict the right material properties.

REFERENCES

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