Analysis of argon gas using Molecular Dynamics simulations

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We studied common properties of argon gas using molecular dynamics simulations. We compared our results with the iconic paper by Verlet (Verlet, 1967). We find that our method behaves similarly, giving confidence in our method. We then studied phase transitions by using color maps of pressure and correlation function as functions of temperature and density. We found the correlation function gives the best measure of phase transitions, while pressure shows a strong transition between two unknown states giving rise to a plateau of low pressure next to a region with a gradient.

Introduction

Molecular dynamics has long been a method for studying the physical properties of materials. Dating back to the 60s where it was developed in the footprints of Monte Carlo simulations, it has grown into a field of study on its own with many computer packages performing such simulations. This work will focus on the Verlet paper (Verlet, 1967) which we will largely reproduce using modern computers. For comparison, we use a simple retail computer to run these simulations. In our simulations we will have N = 729 particles moving in a three-dimensional box, subject to the Lennard-Jones potential, see equation (1). The particles are simulated in a cubic box with side length l with periodic boundary conditions, implying that when they hit the top wall, they arrive from the bottom wall and vice versa for all dimensions.

$$U(r) = 4((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6) \tag{1}$$

Here σ is a measure for the intermolecular distance, in our case σ = 3.405Å. For this work we will make use of dimensionless equations where we set $x' = \frac{x}{\sigma}$, $t' = t(\frac{\epsilon}{m\sigma^2})^{1/2}$, $E' = \frac{E}{\epsilon}$ and rescale all other physical quantities accordinly to this, using the values $\frac{\epsilon}{k_B}$ = 119.8K.

For the evolution steps we will use Velocity-Verlet algorithm (Thijssen, 2007), described as follows:

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

$$\mathbf{v}(t + h) = \mathbf{v}(t) + \frac{h}{2}(\mathbf{F}(\mathbf{x}(t + h) + \mathbf{F}(\mathbf{x}(t))) \tag{3}$$

As time step we use through this work h = 0.004. For further details regarding the method we refer to the Verlet paper, including the usage of dimensionless units.

Differences

We have decided to not include a cut-off distance. In the original paper a cut-off distance of r_{cutoff} = 2.5σ is chosen, beyond which no forces are calculated anymore. In our case we will consider *all* particles when calculating forces. Furthermore, we use N = 729 particles, rather than N = 864 particles due to initialization settings. Additionally, we will focus on slightly different physical quantities. We will focus on pressure, temperature, compressibility factor - as did the original paper - but we will also consider the partition function and average displacement of particles.

Method

We have built a Python code on which we will simulate N = 729 particles moving in a three-dimensional periodic box. We initialize the system by creating a grid of N = n^3 particles, where we pick n = 9, along the entire volume, equally spaced (taking into account periodic boundary conditions) - thus we start with a primitive cubic crystal. At each iteration the force derived from equation (1) is calculated as shown in equation (4):

$$F(r) = 4(-(\frac{12}{r^{13}}) + (\frac{6}{r^7})) \tag{4}$$

Using this equation, together with equations (2) and (3) we can determine the location of each particle in the next iteration.

Initialization

The initial positions of the atoms chosen in the vertices of a simple cubic system, and the initial velocities are distributed using a normal distribution $e^{-3v^2/2T^2}$. Before measuring the quantities we equilibrate the system by letting it run for 10 steps, and then we apply a reassignment of the velocities according to equation (5) and repeat 200 times for a total of 2000 steps.

$$\mathbf{v}_i \to \lambda\mathbf{v}_i = \sqrt{\frac{(N - 1)3T_0}{\sum_i v_i^2}}\mathbf{v}_i \tag{5}$$

Here the rescaling factor λ is the total kinetic energy in the system as desired by the initial temperature T_0 divided by the total kinetic energy in the system as calculated directly. This rescaling of the velocities allows us to fix the actual temperature in spite of a sub-optimal set of initial positions of the particles. After having rescaled two hundred times we can be quite sure that our system is in equilibrium and the actual temperature close enough to the desired temperature. After that we let the system evolve without interference for 2000 time steps, during all of which we measure all the physical properties we are interested in.

Physical measurements

In order the measure the temperature, we will use equation (6), where in each dimension the temperature contributes $\frac{T}{2}$ (in dimensionless units) to the kinetic energy. The factor (N-1) comes from the fact that the sum of all velocities is conserved (it adds up to zero), which reducdes a degree of freedom. The factor d stands for the dimension. In order to calculate the the pressure, we use the virial theorem, see equation (7).

$$T = 2 * \frac{E_{kin}}{(d(N-1))} \tag{6}$$

$$P = \frac{1}{V}(NT + \frac{\sum_{i<j} r_{ij} f_{ij}}{3}) \tag{7}$$

We are also interested in the compressibility factor which is defined as $Z = \frac{p}{\rho T}$ in dimensionless units.

Besides these physical quantities, there is also the pair correlation function which tells us more information about the local structure of the model. As described in (Thijssen, 2007) is a normalised function of all the inter atomic distances.

$$g(r) = \frac{V}{N(N-1)} \left[\frac{\langle n(r) \rangle}{4\pi r^2 \Delta r} \right] \tag{8}$$

with $\langle n(r) \rangle$ the number of particles in the range $[r, r + \Delta r]$ averaged over time. In the case of a solid we would expect peaks at regular intervals, with the Fourier transform of this histogram giving the lattice constant at its strongest frequency. We can furthermore obtain more information about the phase of the system by looking qualitatively at the average displacement of all the particles $d(t) = [|r_0 - r(t)|.]$ with respect to the initial position r_0.

Estimating errors

We may estimate the error in our calculations of the pressure and temperature by using the Bootstrap method. Our 1000 time steps each produce a value for the temperature and pressure. However, these values are correlated: the pressure now will not be very much different from the pressure in the previous time step. We still wish to give a quick and simple estimate of the error using equation (9). In order to do this, we resample our 1000 data points randomly by picking 100 data points (we may same the same data point multiple times). This removes the correlation and thus we get a classical standard deviation.

$$\sigma = \sqrt{< A^2 > - < A >^2} \tag{9}$$

Results

First we will compare our results with that of Velvet. For this we will compare his list of compressibility factors with ours, see table 1

Table 1
Comparison of simulation runs between the Verlet paper and our code. ρ is the particle density, T is the desired temperature, Z is the compressibility factor defined as $Z = \frac{p}{\rho T}$. Notice that the actual temperatures were all within a standard deviation of the desired temperatures.

ρ	T	Z_{Verlet}	$Z_{TUDelft}$	$\sigma(Z_{TUDelft})$
0.88	1.095	3.48	3.53	0.15
0.88	0.940	2.72	2.99	0.17
0.88	0.591	-0.18	-0.05	0.17
0.85	2.889	4.36	4.50	0.14
0.85	2.202	4.20	4.28	0.15
0.85	1.214	3.06	3.15	0.15
0.85	1.128	2.78	2.87	0.15
0.85	0.880	1.64	1.84	0.11
0.85	0.782	0.98	1.00	0.15
0.85	0.786	0.99	1.23	0.16
0.85	0.760	0.78	0.90	0.17
0.85	0.719	0.36	0.36	0.18
0.85	0.658	-0.20	-0.15	0.12
0.85	0.591	-1.20	-1.10	0.14
0.75	2.849	3.10	3.16	0.12
0.75	1.071	0.89	0.80	0.12
0.75	0.881	-0.12	0.01	0.15
0.65	1.585	1.25	1.35	0.11
0.5426	1.404	0.57	0.53	0.14
0.5	1.360	3.40	0.43	0.10
0.45	4.625	1.68	1.68	0.08
0.45	1.552	0.75	0.59	0.13
0.35	1.418	0.40	0.39	0.13

We can see that, safe for six values $((\rho, T) = (0.88, 0.940)$, $(0.85, 2.202)$, $(0.85, 0.88)$, $(0.85, 0.786)$, $(0.5, 1.360)$, $(0.45, 1.552))$, all our results are within a standard deviation from Verlet's results. This is even slightly better than expected according to a normal distribution. Thus we may conclude that our method and Verlet's method behave similarly. Notice, however, that for $(\rho, T) = (0.5, 1.360)$ we get entirely different results. We also did runs on $(\rho, T) = (0.5, 1.350)$ and $(\rho, T) = (0.5, 1.370)$, but we get similar values $(Z = 0.37 \pm 0.09$ and $Z = 0.41 \pm 0.14$
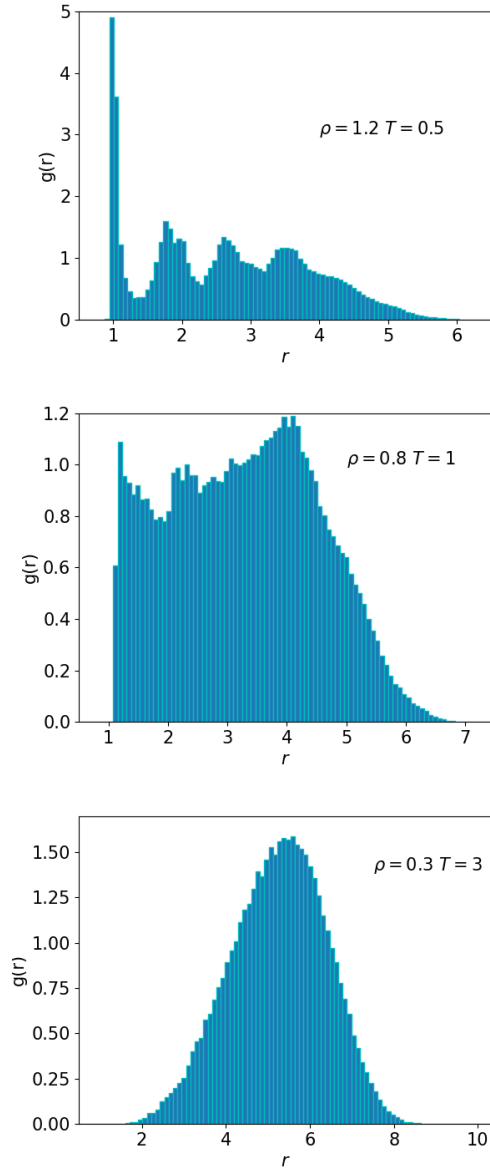
Figure 1. Correlation function corresponding to each of the cases with the parameter ρ and T as shown for $N = 729$. The three phases can be distinguished by the quantitative shape of the function with solid, liquid and gas as top, middle and bottom distributions correspondingly.

Figure 2. Normalized atomic displacement averaged over all particles as a function of time. The same parameters as in fig 1 for the three phases are used.

respectively). Most likely Verlet's result is simply several standard deviations from its actual value.

Now we are interested in being able to characterize the different phases of the system with respect to the parameters, for this end we will inspect at both macroscopic and microscopic properties. The correlation function proves very useful in allowing us to distinguish between each different phase. In fig. 1 we see for three different cases how the shape of the func-
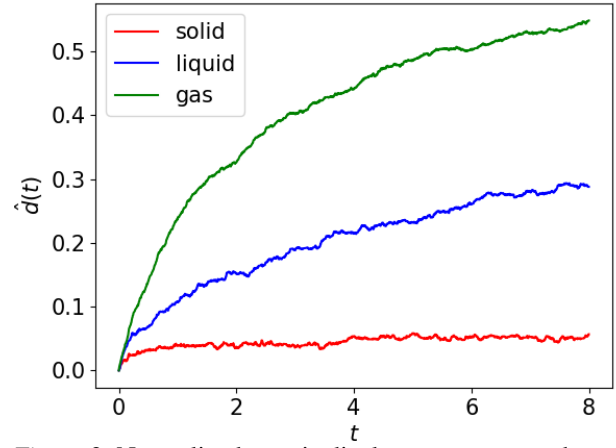
tions changes drastically. Its remarkable how a great deal of understating of the atomic behaviour can be obtained by looking at the function. For a solid (top) we see how the periodicity in the arrangement of the atoms is observed in the peaks of the correlation function, where the first sharp line corresponds to the inter atomic distance in the lattice. For a liquid (middle) we can see how the distribution resembles a plateau indicating how the there is a uniform distribution of all the atoms and their velocities through the space. In contrast with the gas phase (bottom) where the characteristic shape shows a Gaussian distribution in the atoms around the center of the box, as expected of non-interacting particles.

Inspired by the results shown by the correlation function we continue analysing how the particles behave in each one of the phases. To continue we look at the average displacement $\hat{d}(t) = \frac{d(t)}{l}$. The extra factor is added because the number of particles is kept constant through each of the simulations, thus density changes are achieved through varying the volume of the box $V = (\frac{N}{l})^{1/3}$ meaning that in order to compare the displacement over different densities we must normalize over the length of our box. The results are shown in fig. 2 were the great difference in magnitude tells average behaviour for each phase. With these results in mind now we are interested in characterizing a bigger picture of the system, and especially in focusing in the comparison between microscopic and macroscopic measurable quantities. To do see we change the parameters ρ and T and look at the averaged pressure and at the max displacement achieved over 2000 time steps. The results can be seen in fig. 4 where the $log(P)$ and a normalized maximized displacement are shown for 400 points in fig. 4. The top color map shows the pressure gives a very
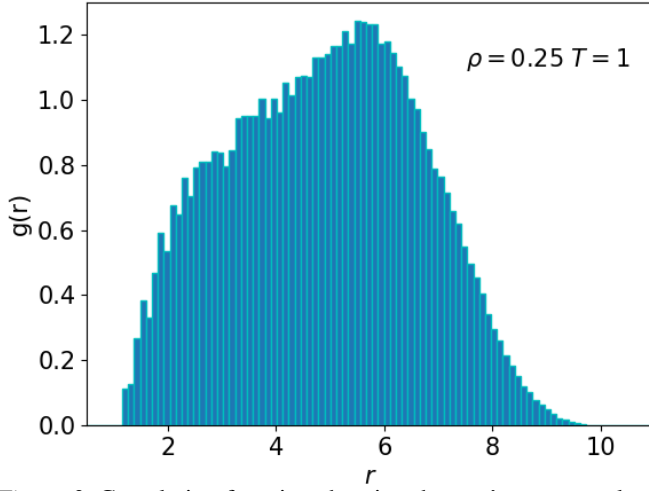
Figure 3. Correlation function showing that we're at a mostly gaseous state. The parameters $(\rho, T) = (0.25, 1)$ are taken to be in the dark plateau figure **??** (top).

predictable result as we would expect, that is; increasing density and temperature always produces an increase in pressure. However its remarkable to say that there appears to be a sharp transition in the increase of the values in P when the densities are low and the temperature increases, perhaps signaling a change of phase from gas to solid. The bottom color map shows the maximum normalized displacements where as well very predictable results are obtained, we can see a clear correlation with displacement and temperature. Moreover we can see a dark region for dense and cold systems which corresponds to a solid, where the sharp change in the value as the temperature increases is a indicator of a phase transition. Overall, the results allow for a good comparison between both displacement and pressure, as we can see how both quantities are not directly correlated, reminding us of how macroscopic and microscopic quantities contain very different information about a physical system.

Further analysis of the dark plateau in the pressure color map shows that it is not a solid, see figure 3 but rather a gas. It seems, then, that we are dealing with a different kind of phase transition. Perhaps a second order phase transition. The full details of this are unknown to us, but would benefit future research.

Conclusion

We have shown, using Verlet's work as our starting point, that we can reproduce his work and expand upon it by providing more measurements over the parameter space in which
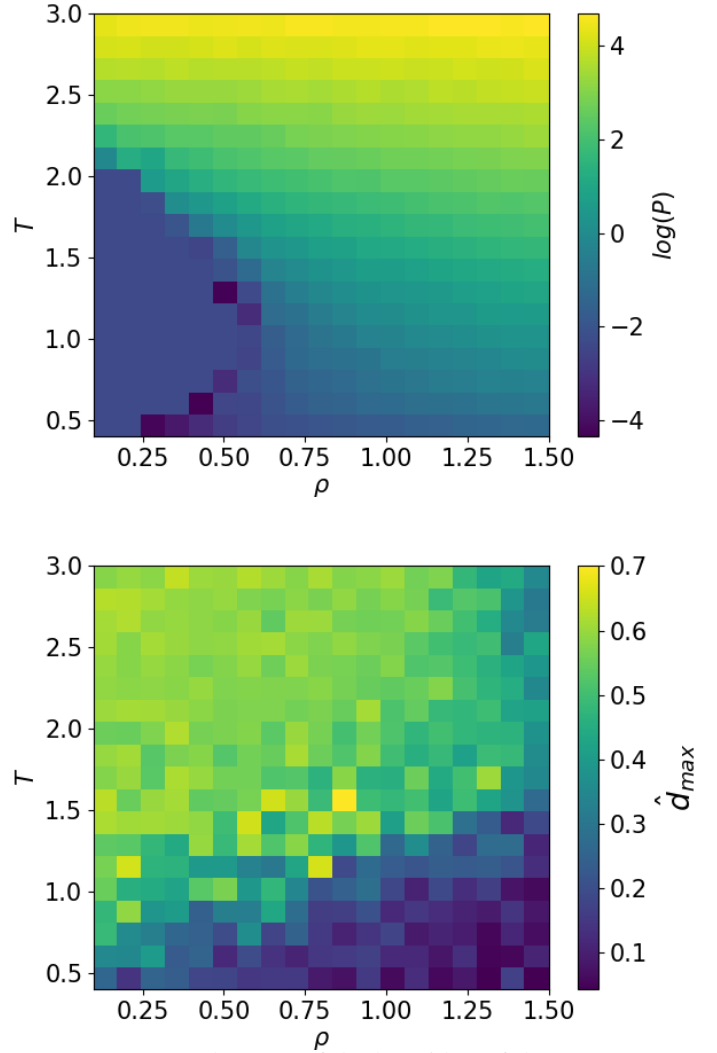

Figure 4. (Top) Color map of the logarithm of the pressure averaged over all iterations. (Bottom) Color map of the maximum absolute value of the displacement reached through the evolution time. The number of points in the map is 400, where each axis is equally divided in 20 and a number of particles $N = 342$ is used.

phase transitions become visible. While the color map on correlation function is the best measure for phases, the color map on pressure shows an interesting plateau of low pressure amidst a gradient. We do not know where this plateau comes from, it may be related to a second order phase transition in the gaseous system. Notice also that the correlation function alone is not enough to distinguish easily between gas and liquid states, so the histograms will remain useful.

References

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