

Molecular dynamics simulation for a system of 864 argon particles

First project of Computational Physics

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ABSTRACT

This study shows the physical characteristics of the element argon for different temperatures and densities. The quantities are a result of a Molecular Dynamics (MD) simulation. This simulation is computed using the velocity-Verlet algorithm. The physical quantities that are studied include the correlation function, heat capacity, pressure and diffusion constant. Some quantities show a rapid change in value at the phase transition of argon, from the gas to the solid phase. For the heat capacity values predicted by the ideal gas law (for the gas phase) and by the Dulong-Petit law (for the solid phase) are found. The pressure in the gas phase is seen to deviate from the ideal gas law because of the attractions and repulsions that are introduced between the atoms. The correlation function also displays distinct features for the liquid, gas and solid phase. Finally, observations of the diffusion behaviour show a distinct cross-over from the ballistic behaviour for times smaller than the collision time, to the diffusive regime for times larger than the collision time. This project is the first assignment of the course Computational Physics, given by J.M. Thijssen at the University of Technology Delft.

Key words. Molecular dynamics, Argon, Lennard-Jones interactions, Computational physics

1. Introduction

In this report the results of a molecular dynamics (MD) simulation of argon particles using the Verlet algorithm is presented. MD is a method mostly used for studying classical many-particle systems. Here the system is determined by the equations of motion and develops over a period of time. At the core of the theory behind molecular dynamics simulation lies the notion of ergodicity: ensemble averages necessary to calculate physical quantities can be approximated by time averages which are easy to calculate from simulations. Values of physical quantities, dynamical phenomena and relaxation of systems far from equilibrium can be studied using the MD method.

This study focuses on the interaction between mono-atomic particles, in this case argon. These particles do not possess any internal degrees of freedom and their interaction is assumed to be pairwise and only dependent on the pair distances. The calculated forces can then be used, together with a proper initial setup, to solve the equations of motion. Using the MD method the solution of the equations of motion describes the time evolution of a real system. Of course, this method is an approximation and errors occur due to different reasons, which are described shortly.

- This study focuses on the classical description and does not consider quantum mechanical effects. The reason for this is that quantum effects make the system significantly more difficult but do not contribute to the goal of this project. The neglect of these effects results in for example not exactly known forces between particles and therefore contributes to the error of the system.
- The system size of the simulation is much smaller than that of an experimental system. To get around the boundary of the system, periodic boundary conditions are used to approximate an infinitely large system.

- The simulation cannot run infinitely, so the time average is evaluated over a finite time (and therefore a finite number of integration steps).
- The algorithm that is used in this study is numerical and becomes more accurate with smaller integration time steps. Obviously, smaller time steps results in a slower simulation process and a choice need to be made between the time step and duration of the simulation.

These processes of the MD method need to be considered when programming the simulation. The relation between speed and accuracy needs to be considered. To check whether the accuracy is of the right level, results can be compared with available literature.

2. Theory

In this study the behaviour of argon is simulated. Argon is a mono-atomic molecule and has therefore no internal degrees of freedom, so the only important degrees of freedom in the system are the particle positions and momenta.

The interactions between the particles are assumed to be pairwise and only dependent on the separation distance between each pair. In this simulation, the Lennard-Jones potential is chosen to describe these pairwise interactions:

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

For argon, the values for the parameters in the Lennard-Jones potential are given as $\epsilon/k_B = 119.8$ K and $\sigma = 3.405$ Å.

The molecular dynamics simulation consists of an initialisation step, which is described in detail in the Methods section, and the actual simulation of the particle trajectories. To integrate

the equations of motion of the system numerically, the velocity Verlet algorithm is used. It evaluates velocities and positions at the same time instances using:

$$\mathbf{r}(t+h) = \mathbf{r}(t) + h\mathbf{v}(t) + h^2\mathbf{F}(t)/2 \quad (2)$$

$$\mathbf{v}(t+h) = \mathbf{v}(t) + h[\mathbf{F}(t+h) + \mathbf{F}(t)]/2 \quad (3)$$

From the simulated particle trajectories and momenta certain physical quantities can be calculated. In this study the correlation time (which is important to know to estimate the error statistics), specific heat capacity, the pressure, the correlation function and the diffusion characteristics were determined from the simulation results.

2.1. Error term

The Verlet algorithm is a second order algorithm. Like all mid-point integration methods it has an error term which is of the second order. This is a significant improvement in comparison to the standard Euler method which has a first order error term.

2.2. Correlation time

The correlation time is estimated from the auto-correlation function $R(t, \tau)$, which is defined as:

$$R(t, \tau) = \left\langle \frac{1}{N} \sum_{i=1}^N \mathbf{r}_i(t) \cdot \mathbf{r}_i(t + \tau) \right\rangle \quad (4)$$

where the angle brackets indicate an ensemble average. Commonly, the auto-correlation is assumed to be time-invariant (only depending on the lag τ) and modelled by an exponentially decaying function:

$$R(\tau) = R(0)e^{-\tau/\tau_c} \quad (5)$$

The decay time τ_c is then called the correlation time of the system and indicates what amount of time it takes for the system to randomize. It is also an indication for the time separation necessary between two times in the simulation to be able to assume that the simulation results are independent.

2.3. Heat capacity

The heat capacity per particle can be calculated in this micro-canonical system from the fluctuations in the kinetic energy, using a formula derived by Lebowitz. This formula is given by

$$c_V = \frac{3\langle K \rangle^2}{2\langle K \rangle^2 - 3N\langle K^2 \rangle} \quad (6)$$

For solids, the Dulong-Petit law predicts the following value for the specific heat capacity:

$$c_V = 3k_B \quad (7)$$

while the ideal gas model predicts the following value for the specific heat capacity of mono-atomic gases:

$$c_V = \frac{3}{2}k_B \quad (8)$$

Table 1. Natural units used in this report. The values of all units are derived from properties of argon.

quantity	property	value
mass	argon mass m	$6.69 \cdot 10^{-26}$ kg
energy	potential well depth ϵ	$1.65 \cdot 10^{-21}$ J
distance	equilibrium distance σ	$3.41 \cdot 10^{-10}$ m
time	$\tau = (m\sigma^2/\epsilon)^{1/2}$	$2.17 \cdot 10^{-12}$ s
temperature	ϵ/k_B	119.8 K
pressure	ϵ/σ^3	$41.6 \cdot 10^6$ Pa
diffusion constant	σ^2/τ	$5.36 \cdot 10^{-8}$ m ² / s

2.4. Pressure

The virial theorem can be employed to calculate the pressure of the system. Pressure is then given by

$$\frac{P}{nk_B T} = 1 + \frac{1}{3Nk_B T} \left\langle \sum_{\langle ij \rangle} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle \quad (9)$$

where the sum over the virials is taken over all pairs $\langle ij \rangle$ and averaged over time. Note that in the case the virial correction term is zero, the ideal gas equation of state is recovered.

2.5. Correlation function

The correlation function can be calculated from a separation distance histogram $n(r)$ by the following formula:

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

where Δr is the bin width used to calculate the histogram.

2.6. Diffusion

Finally, the diffusion of particles in the simulation can be studied and the diffusion constant can be obtained. For times smaller than the average collision time between particles, the variance in the traveled distance is expected to behave ballistically like

$$\langle \Delta x^2 \rangle = \langle v^2 \rangle t^2 \quad (11)$$

For times larger than the average collision time, diffusion theory predicts that the variance in the traveled distance becomes linear in time. This is reflected in the following expression involving the diffusion coefficient D :

$$\langle \Delta x^2 \rangle = Dt \quad (12)$$

For solids the diffusion coefficient is expected to be very close to zero.

2.7. Units

Throughout this report natural units are used. The value of these units depends on the properties of argon and are given in table 1. If a quantity is specified without units, natural units are implied.

3. Methods

The MD simulation consists of three main stages:

- Initialisation
- Reaching equilibrium
- Production phase

These three stages will be explained in the following section.

3.1. Initialisation

To determine the initial positions of the atoms an fcc lattice (which tends to minimise the potential energy of an Lennard-Jones potential) is generated resulting in a $L \times L \times L$ system containing $4M^3$ particles where M determines the number of unit cells of the initial fcc lattice ($M = 1, 2, \dots$). Four particles are placed in each unit cell at location $(0,0,0)$, $(0.5,0,0)$, $(0,0.5,0)$ and $(0,0,0.5)$ relative to the origin of the unit cell.

The initial velocities are generated based on the desired temperature, using a Gaussian distribution for each of the components v_x , v_y and v_z . This distribution is then given as:

$$f(v_i) = \frac{e^{-\frac{mv_i^2}{2k_B T}}}{\sqrt{2\pi k_B T}} \quad (13)$$

for each component.

For all simulations, the following parameters are used:

- particle number $n = 864$
- number of unit cells in every direction $M = 6$
- linear system size $L = (n/\rho)^{1/3}$
- simulation time steps $h = 0.004 \tau$
- total simulation time $t = 110.0 \tau$
- equilibration time $t = 50.0 \tau$ (of which the first 40.0τ is used to force the system towards the desired temperature)

Between simulations, the following parameters are varied:

- atom density ρ
- desired temperature T

3.2. Reaching equilibrium

After initialisation the molecular dynamics simulation starts: the interaction forces are calculated and the equations of motion are integrated continuously. Note that in this study no cut-off was applied to the interaction potential as it proved not to be necessary in terms of simulation speed.

Initially, the system is given some time in which it can reach equilibrium. During this time no measurements are done on the system. In the beginning kinetic energy will be exchanged with the potential energy which alters the temperature of the system. To force the system towards an equilibrium of the desired temperature, the velocities are periodically rescaled (each 40 timesteps) so that the kinetic energy matches the desired temperature again. This rescaling procedure is repeatedly applied in the first 40.0τ of simulation time, after which the system is given an additional 10.0τ to reach the final equilibrium.

3.3. Production phase

When the system has reached equilibrium, the values required to eventually calculate the desired physical quantities are measured at every time step. This stage is called the production phase. To check the correctness of the system in equilibrium the total energy (which is conserved) is computed. An example is shown in figure 1. The results are saved in a file which allows for data processing at a later time.

3.3.1. Diffusion and auto-correlation

The diffusion distance and auto-correlation function have to be calculated relative to a certain time point in the simulation. As it is memory-intensive to record the positions of all particles in

every time step, the averages used in determining these quantities have to be calculated during the simulation itself, which means that the starting time point must be selected during simulation. This starting time point is reset twice in order to obtain three different realizations for the diffusion distance and auto-correlation function per simulation.

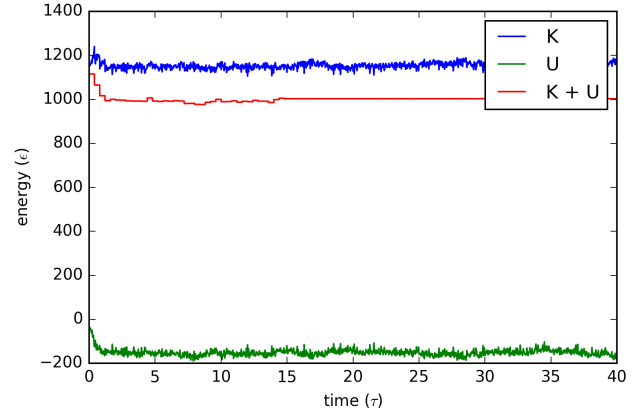


Fig. 1. Plot of the development of the kinetic energy K and the potential energy U during simulation. In the first 15τ of simulation time the velocity rescaling procedure is periodically executed to force the system into an equilibrium with a certain temperature (in this case $T = 3.0$). After this initial phase the total energy $K + U$ is conserved, affirming the correctness of the simulation algorithm.

To give an illustration (figure 2) of the argon particles moving through a certain volume, a simple simulation is computed that shows the particles in the volume after a certain amount of time.

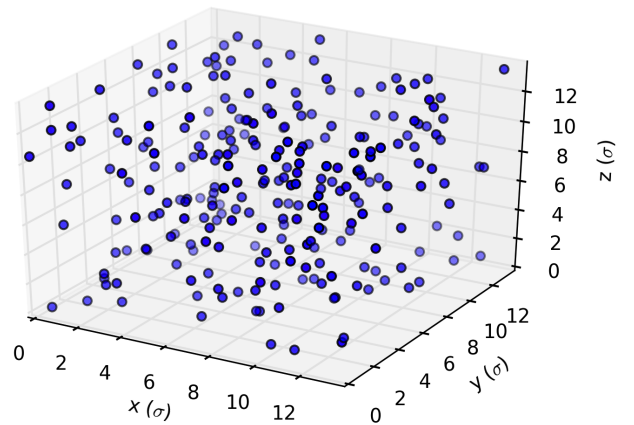


Fig. 2. Exemplary 3D visualisation of a simulated system of argon atoms. In this case 256 argon atoms were simulated in the gas phase with $T = 3.0$ and $\rho = 0.1$

3.4. Error estimation

To estimate the error in the final calculated physical quantities of interest, the simulation time in the production phase is chopped up into time intervals of 5τ , which is larger than the correlation time τ_c in all simulations (see the results section). This means it may be expected that the behaviour of the system is randomized between subsequent time intervals and quantities calculated

from averages over these time intervals are distributed independently. From this distribution of quantities the mean value for the quantity is estimated as well as the standard deviation, which may be used as an error estimate.

4. Results

In this research the dynamics of a simulated argon gas was studied for 22 different densities, ranging from $\rho = 0.02$ to $\rho = 2.0$, and 15 temperatures, ranging from $T = 0.5$ to $T = 4.0$. This makes for a total of 330 different simulations which took about 10 minutes each to complete on a 3.3 GHz processor. Four simulations could be run in parallel on four processor cores, resulting in a total processing time of about 14 hours. In this section the physical quantities obtained from these simulations will be presented, along with their interpretations.

4.1. Correlation time

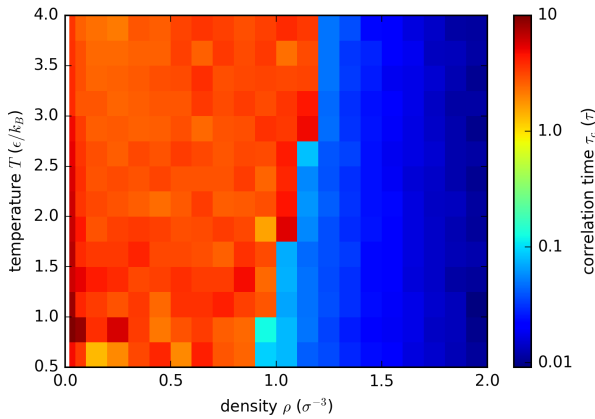


Fig. 3. Correlation time as a function of temperature and density. Note the logarithmic scale;

In figure 3 a sharp change can be seen at the phase transition from liquid/gas to solid. The correlation time almost never exceeds $\tau_c < 5\tau$, which means that the system can almost always be assumed to behave statistically independently after 5τ . This result is used in estimating the error in the following quantities (see methods section). Figure 4 shows clearly that the correlation drops exponentially with a constant factor for different simulations under gaseous circumstances. In figure 5 the same three plots are shown for solid circumstances. Here the value also decays exponentially, but to a constant instead of zero.

4.2. Specific heat

Figure 6 shows the specific heat as a function of the temperature and the density. In this plot a clear distinction can be made between the solid and the gas phase. In the solid phase the specific heat is approximately equal to $3k_B$ as predicted by the Dulong-Petit law. In the gas phase it is approximately $\frac{3}{2}k_B$ which is predicted by the ideal gas model. In figure 7 the errors in the estimation of the specific heat can be seen. This error was calculated from the standard deviation of the specific heat calculated from 12 non-overlapping, uncorrelated time intervals per simulation. What should be noted is that the error in the measurement sharply increases with an increase in density and is much less related to an increase in temperature.

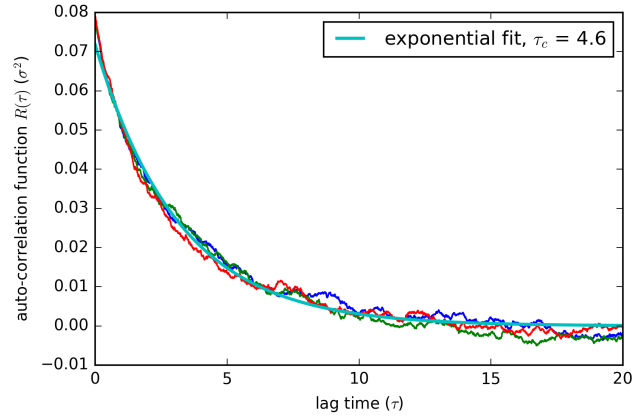


Fig. 4. Plot of three realisations the auto-correlation function under gaseous conditions ($T = 3.0$, $\rho = 0.2$). The data has been fitted to an exponential decay.

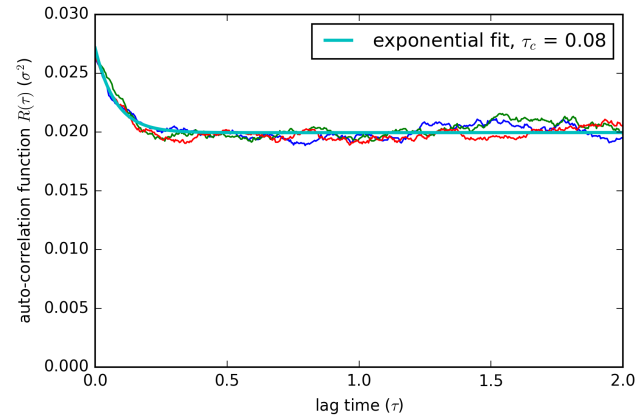


Fig. 5. Plot of three realisations of the auto-correlation function under solid conditions ($T = 0.5$, $\rho = 1.0$). The data has been fitted to an exponential decay on top of a linear baseline for the auto-correlation.

4.3. Pressure

In figure 8 a plot of the density as a function of the temperature and density is shown. In general the pressure increases with temperature and density, as would be expected. A sharp phase transition can not be seen in the pressure between the gas/liquid and the solid phase, but pressures are generally much higher in the solid phase than in the gas phase. What is remarkable is that the error in the pressure seems to be directly dependent on the phase. This error can be seen in figure 9. The error is the highest when the argon is still a solid but approaching the phase change.

For the gas phase the results can be compared to the ideal gas law, which is shown in figure 10. The pairwise potential introduces a deviation in the pressure from the ideal gas law values: attractive interactions cause a lower pressure at low temperatures while repulsions cause a higher pressure at high temperatures.

4.4. Correlation function

Figure 11 shows the correlation function as a function of the separation distance for the three different phases. The solid phase shows clear peaks at the distance of the cells. When the ar-

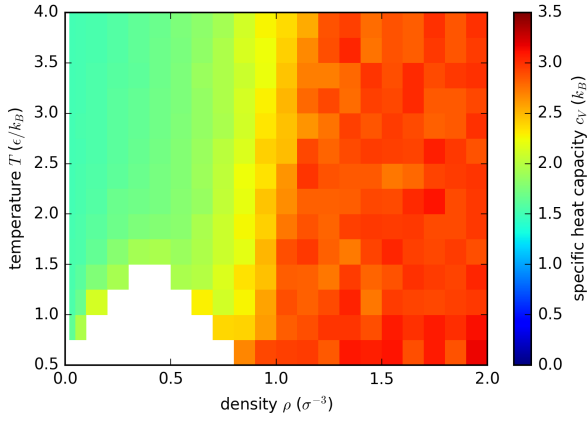


Fig. 6. Specific heat capacity as a function of temperature and density. Values for c_V with an abnormally high standard deviation (> 0.3) are removed

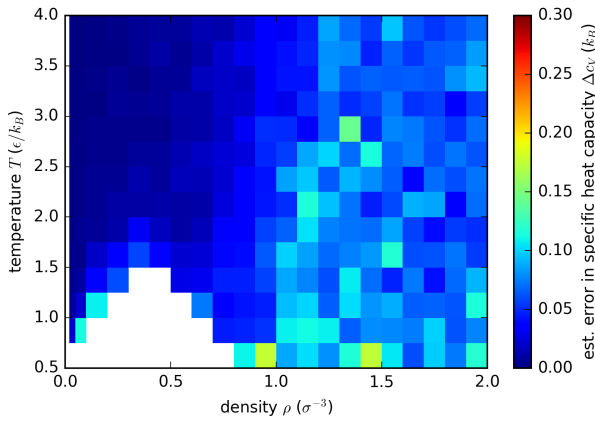


Fig. 7. Estimated errors in the specific heat capacity as a function of temperature and density. Values for c_V with an abnormally high standard deviation (> 0.3) are filtered out. For the gas phase, this error is on the order of $\sim 0.01 k_B$, while for the solid phase the error is an order of magnitude larger ($\sim 0.1 k_B$).

gon makes the transition to a fluid, the correlation function still achieves maximum values at the integer distances, but also has a finite value in between these peaks. When the gas evaporates to the gaseous regime, the correlation function is independent of the separation distance, as long as this distance is larger than the repulsion distance.

4.5. Diffusion

In figure 12 three different realisations of the diffusion distance are shown for the low density gaseous regime, generated from three non-overlapping periods of the same simulation. For small times, the simulated diffusion distance closely follows the parabola predicted by the ballistic trajectories of the particles at $t = 0$. For larger times the cross-over into the linear diffusive regime can be clearly distinguished. Under these conditions, the diffusion constant is estimated to be $D = 36.1 \pm 0.2$.

In figure 13 three different realisations of the diffusion distance are shown for the high density solid regime, generated from three non-overlapping periods of the same simulation. The collision time is now so small that the particles are constantly

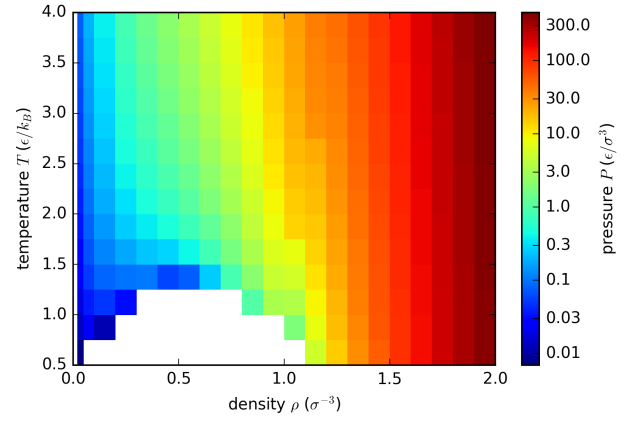


Fig. 8. Pressure as a function of temperature and density. Negative values for P are removed.

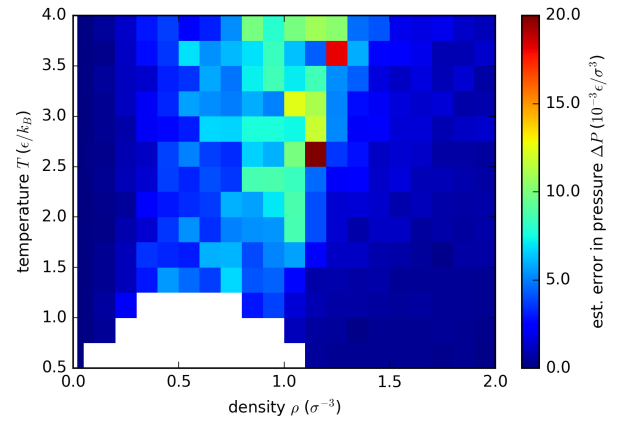


Fig. 9. Estimated errors in the pressure as a function of temperature and density. Negative values for P are removed.

colliding, confining them to a very small region around their initial position. The diffusion constant is very close to zero in this situation. The periodic behaviour, which is of similar frequency content in all three realisations, can be explained from lattice vibrations.

In figure 14 the phase transition is shown by plotting the diffusion coefficient for different densities as a function of temperature. In general, the diffusion coefficient increases as a function of temperature. For higher densities, a sharp transition between the solid phase where $D \approx 0$ and the liquid or gas phase where $D > 0$ can be seen as the temperature increases. This transition temperature increases with density. This same plot is also shown as a 2d plot in figure 15.

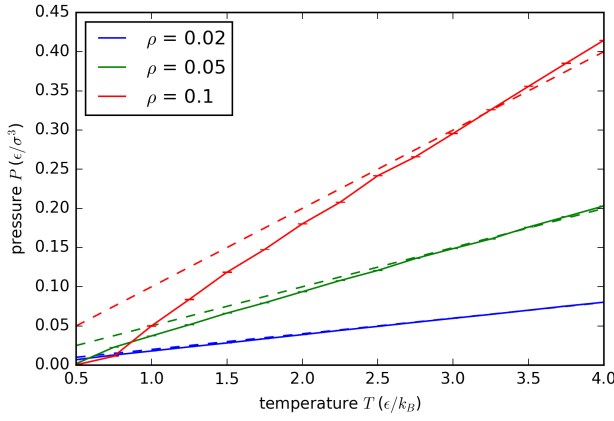


Fig. 10. Pressure as a function of temperature in the gas phase for different densities. Solid lines indicate the simulated pressures while the dashed lines indicate the value of the pressure as predicted by the ideal gas law. It can be seen that the pairwise attraction between particles at low temperatures causes a decrease in pressure as compared to the ideal gas law, while the hard core repulsions cause an increase in pressure at high temperatures.

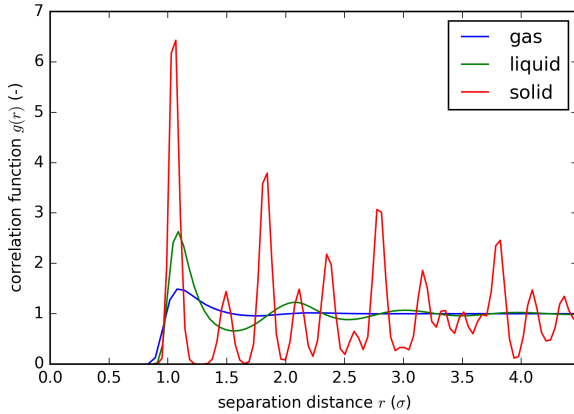


Fig. 11. Correlation function for the gas phase ($T = 3.0, \rho = 0.3$), liquid phase ($T = 1.0, \rho = 0.8$) and solid phase ($T = 0.5, \rho = 1.2$).

5. Conclusions

From the results of the simulations it can be seen that for argon a simple computer model can show specific information about the behaviour of this element in different configurations. Although approximations of the forces, algorithm and environment enlarge the error of the system, the MD simulation gives a lot of information to study this element.

In several plots a clear distinction can be made where the sample shifts from the solid phase to the gas phase. The points at which this phase transition occurs are in correspondence with earlier simulations of the argon system and experimental results (see figure 17). From these experimental results it may also be explained why the extraction of quantities often failed in the low-density, low-temperature regime, as this is the regime where the gas and liquid phases coexist.

Density, heat capacity, correlation function and diffusion coefficient change rapidly at this phase transition. The liquid phase is hard to identify but the correlation function clearly shows it may also be encountered in simulations.

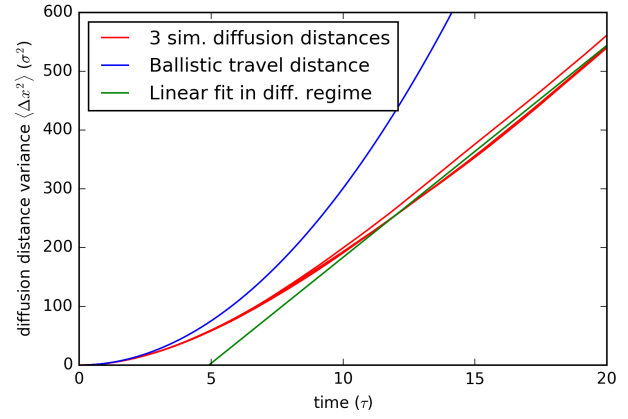


Fig. 12. Particle diffusion in the low density gaseous regime for $T = 1.0$ and $\rho = 0.02$.

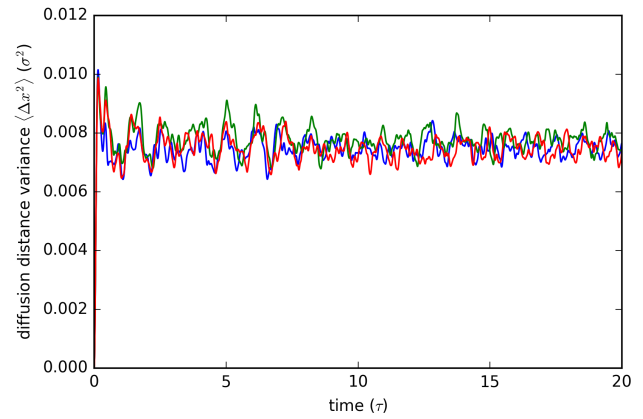


Fig. 13. Particle diffusion in the high density solid regime for $T = 0.5$ and $\rho = 1.2$.

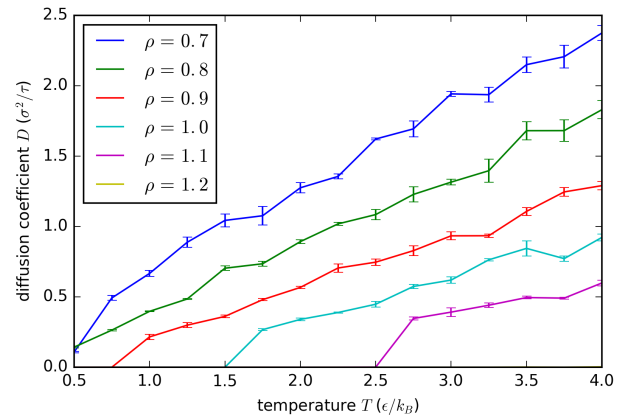


Fig. 14. Estimated diffusion coefficients as a function of temperature, plotted for various densities.

A feature which is also shown in the results is the increase in the temperature at which the phase shift occurs at different densities. At higher densities the gas will stay in the solid phase for a longer time. In the plot of the correlation distance it can be seen that the phase shift occurs at almost 0.5 at a density of 0.8. For a density of 1.2 however, the temperature needs to be 2.9.

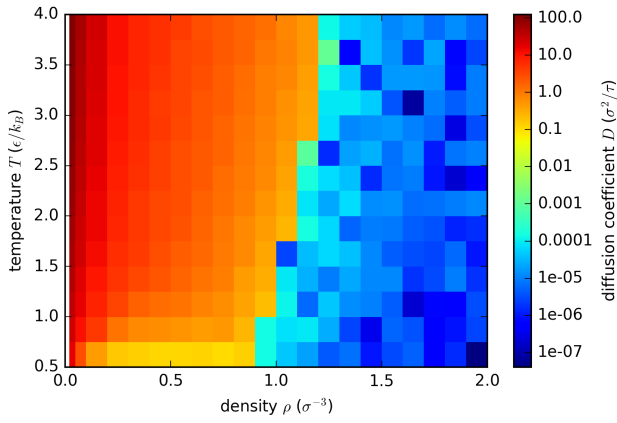


Fig. 15. Colour plot of the estimated diffusion coefficients as a function of temperature and density.

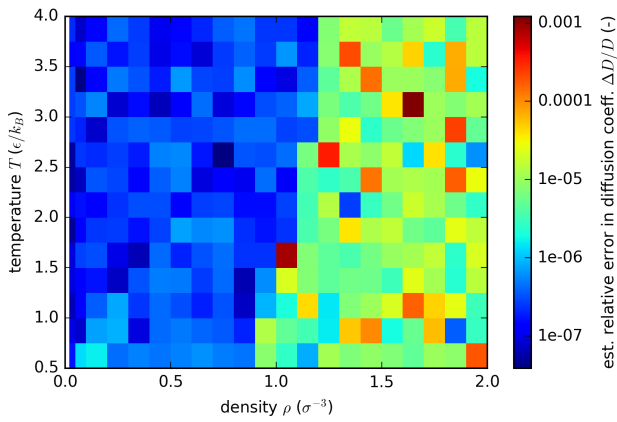


Fig. 16. Colour plot of the relative errors in the estimated diffusion coefficients as a function of temperature and density.

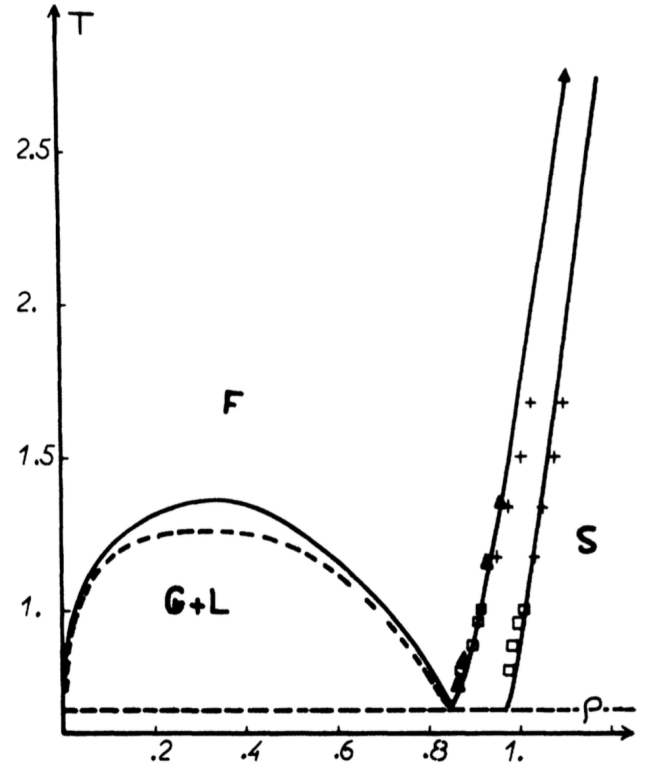


Fig. 17. Coexistence curve for a Lennard-Jones system with temperatures and densities in natural units. The solid line gives the theoretical results by Hansen and Verlet (2). The dashed line gives an argon gas-liquid coexistence line that was obtained experimentally. The circles and crosses indicate various experimental results for the melting point of argon while the triangles indicate the melting point predicted by a rule-of-thumb (more information in the reference). Taken from (2).

References

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