

# COMPUTATIONAL PHYSICS

## Molecular Dynamics

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### 1 Introduction

Molecular systems consist of a large number of particles interacting with each other by some force. It is practically impossible to analytically determine properties of these complex systems, due to the amount of particles involved. To circumvent this problem we can use Molecular Dynamics (MD) simulations. Molecular dynamics is a computer simulation method for studying many-particle systems such as molecules and macroscopic systems such as gases, liquids and solids. With MD simulations, systems are evolved by solving the equations of motion numerically and computing particle trajectories. In this report we will be simulating a system of Argon atoms. Argon atoms behave approximately like hard spheres which interact with each other through weak van der Waals forces. They do not form any bonds and do not interact via Coulomb interaction, which simplifies the dynamics.

By comparing the inter-particle distance to de-Broglie wavelength (scale where particles behave quantum-mechanically) one can see that a completely classical description is justified. From the equipartition theorem  $E_{kin} = \frac{p^2}{2m} = \frac{3}{2}k_B T$  one finds the de-Broglie wavelength to be given by  $\lambda = \frac{h}{p} \rightarrow \lambda = \frac{h}{\sqrt{3mk_B T}}$ . At room temperature this corresponds to  $\lambda \approx 0.1\text{\AA}$ , which is negligible when compared to the typical distance of  $\sim 5\text{\AA}$  between argon atoms [1].

The interaction between two argon atoms can be approximated quite well by a Lennard-Jones potential function:

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

where  $r$  is the distance between the atoms,  $\epsilon = 1.65 \times 10^{-21}\text{J}$  is the strength of the potential energy, and  $\sigma = 3.4 \times 10^{-10}\text{m}$  is the value of  $r$  at which the energy is zero. Figure 1 shows a general sketch of the potential. The  $1/r^6$  force is due to a small displacement between the nucleus and the electron cloud which gives

rise to a small dipole moment. This results in a attractive dipole-dipole (van der Waals) interaction. Since argon atoms do not form molecules, there needs to be a repulsive force that becomes manifest for small inter-particle distances. A  $1/r^{12}$  repulsive potential is chosen to accommodate for that.

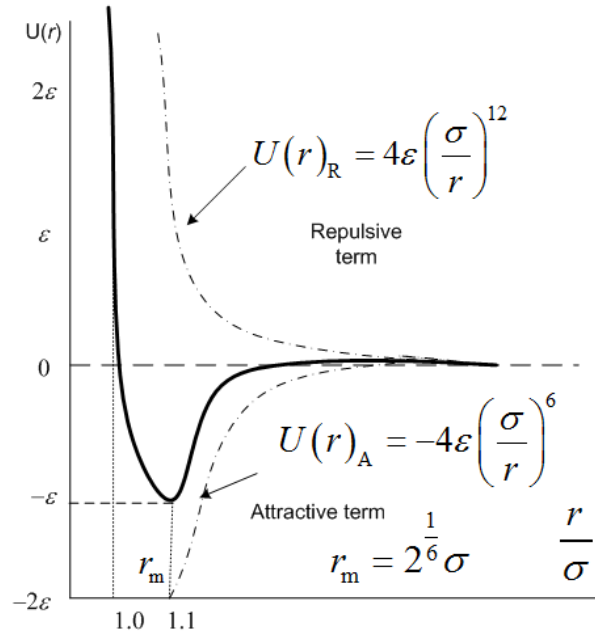


Figure 1. Lennard-Jones potential. Figure obtained from [2]

In this report we will simulate a system of argon atoms in its gas, liquid and solid phase. To check if the MD simulation does indeed provide the behavior of the different phases, we can calculate the pair correlation function which characterizes the phase of the argon system. We will then calculate a few canonical averages for each phase.

## 2 Methods

In our simulation a system of  $N = 108$  particles in a box with sides of finite length  $L$  is considered. Periodic boundary conditions are imposed in order to simulate an infinite system of Argon atoms. For convenience and also to prevent round-off errors we work with 'reduced units', where length is expressed in units of  $\sigma$ , energy in units of  $\epsilon$ , time in units of  $\tau = (\frac{m\sigma^2}{\epsilon})^{\frac{1}{2}} = 2.15 \cdot 10^{-12}s$  for Argon and temperature in units of  $\epsilon/k_B = 119.9K$ .

As we describe the system classically the time-evolution is governed by New-

ton's equation of motion (in reduced units):

$$\frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j \neq i} \mathbf{f}(r_{ij})$$

where the force is determined by the Lennard-Jones potential. For the interaction distance  $r_{ij}$  we use the minimum image convention, i.e. the distance within the box or the distance w.r.t. the image particle introduced by the periodic boundary conditions, whichever is shorter. We integrate by using the velocity-Verlet algorithm [3]:

$$\begin{aligned} \mathbf{r}(t + dt) &= \mathbf{r}(t) + \mathbf{v}(t)dt + \frac{\mathbf{f}}{2}dt^2 \\ \mathbf{v}(t + dt) &= \mathbf{v}(t) + \frac{\mathbf{f}(t + dt) + \mathbf{f}(t)}{2}dt \end{aligned}$$

thus the particles evolve in finite timesteps, where the time increment is set to  $dt = 0.004$ . With each timestep the  $\frac{N(N-1)}{2}$  interaction distances are computed, subsequently the forces and finally the particles' positions and velocities are updated.

The initial positions are set to a fcc lattice, which happens to be the ground state configuration for solid Argon. Moreover in this way we prevent the particles from being too close to each other, as otherwise the  $r^{-12}$  potential increases significantly forcing one to use smaller time increment, thus limiting computation time. The initial velocities are chosen from a Gaussian distribution such that a Maxwell-Boltzmann distribution  $e^{\frac{-mv^2}{k_B T}}$  is obtained with a given temperature. As the system equilibrates the temperature changes, hence in order to control the temperature of the system we rescale the velocities:

$$\mathbf{v} \longrightarrow \lambda \mathbf{v}$$

where from the equipartition theorem  $E_{kin} = (N - 1)\frac{3}{2}k_B T$  we find the rescaling factor:

$$\lambda = \sqrt{\frac{(N - 1)3k_B T}{\sum m v_i^2}}$$

The factor of  $(N - 1)$  is due to the constraint of conservation of momentum reducing the degrees of freedom.

In our simulation we run the system for 5000 timesteps amounting to a simulation time of  $20\tau$ . The system is allowed to come to equilibrium for 500 timesteps whereafter the system is rescaled for 2500 timesteps with a cycle of 20 timesteps. The remaining 2000 timesteps forms the production phase, from which

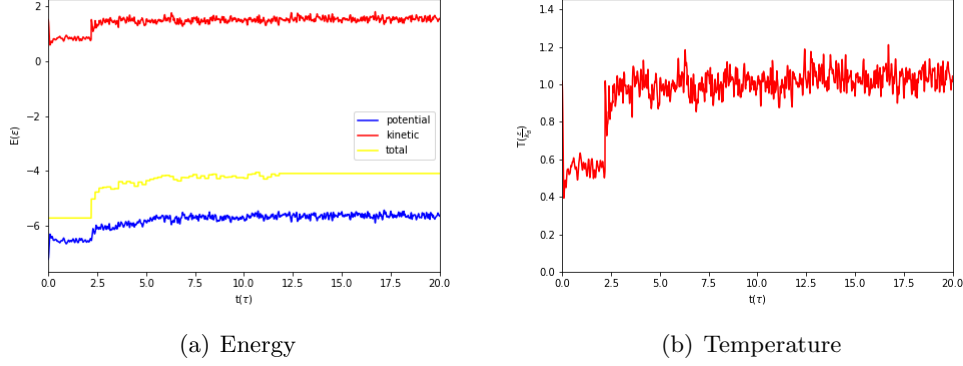


Figure 2. The temperature kinetic, potential and total energy extracted throughout the simulation (equilibration, rescaling and production phase) are shown.

we compute canonical averages and the pair correlation function. Throughout the simulation we extract the instantaneous temperature (again using the equipartition theorem), the potential and kinetic energy as shown in figure 2. The pair correlation function is made by creating a histogram of the number of pairs of particles  $n(r)$  with a separation distance  $r$ . In terms of  $n(r)$  the correlation function is given by:

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

where  $\Delta r$  is the bin size and  $V$  is the volume of the box.

Errors in averages are calculated by bootstrapping the extracted data points and treating them as independent datasets, hence computing the average for each dataset. The error is then given by:

$$\sigma_A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

For the propagation of errors we use the standard method:

$$\sigma_B = \sqrt{\left( \frac{dB}{dx} \right)^2 \sigma_x^2 + \left( \frac{dB}{dy} \right)^2 \sigma_y^2}$$

with  $B$  a variable dependent on  $x$  and  $y$ .

As a reference we use [5] to check our simulation. Setting the density  $\rho = 0.88 \frac{1}{\sigma^3}$  and  $T_0 = 1.0 \frac{\epsilon}{k_B}$  we find for the simulation temperature  $T = 0.954 \pm 2 \cdot 10^{-3} \frac{\epsilon}{k_B}$ , the compressibility  $Z = 2.46 \pm 8 \cdot 10^{-2}$  and the potential energy per particle  $U = -5.916 \pm 2 \cdot 10^{-3} \epsilon$ . These values correspond reasonably well with [5].

### 3 Results

In order to study Argon in different phases (solid, liquid and gas) we varied the density and temperature. Simulations were run with these parameters set to the values listed in table 1. The number of particles used was  $N = 256$ , the rescaling and production time was  $10\tau$  and a timestep of  $0.004\tau$  was used. Table 1 also lists some obtained canonical averages. Note that the temperature extracted from the

Table 1. Canonical averages found from simulation in different phases. The density  $\rho$  and temperature  $T_0$  are given as input parameters;  $T$  is the temperature,  $Z$  is the compressibility and  $U$  is the potential energy per particle determined by simulation.

phase	$\rho$	$T_0$	$T$	$Z$	$U$
solid	1.2	0.5	$0.4963 \pm 3 \cdot 10^{-4}$	$26.60 \pm 2 \cdot 10^{-2}$	$-7.2776 \pm 5 \cdot 10^{-4}$
liquid	0.8	1	$0.9934 \pm 6 \cdot 10^{-4}$	$1.443 \pm 6 \cdot 10^{-3}$	$-5.4365 \pm 9 \cdot 10^{-4}$
gas	0.3	3.0	$3.045 \pm 2 \cdot 10^{-3}$	$1.01 \pm 1 \cdot 10^{-2}$	$-1.706 \pm 3 \cdot 10^{-3}$

simulation is not exactly equal to the desired input temperature. Hence even after rescaling the temperature still fluctuates around its equilibrium value. Furthermore we observe that Argon behaves like an ideal gas in the gas phase, as then the compressibility is close to one. Finally we note the large potential energy (in the absolute sense) in the solid phase when compared to the other phases. This is to be expected, as the conversion of potential energy to kinetic energy is less when the positions of the particles are more rigid.

#### 3.1 Correlation function

The pair correlation function is made by keeping a histogram of the number of pairs of particles  $n(r)$  with a separation distance  $r$ . It gives an indication of the typical inter-particle distances. In terms of  $n(r)$  the correlation function is given by:

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

where  $\Delta r$  is the bin size and  $V$  is the volume of the box.

In figure 3 the correlation function obtained in the three different states of matter is shown. First of all we clearly observe sharp peaks in the solid phase, which reflects the fact that solid Argon configures into a fcc lattice. As the fcc lattice knows two typical distances, the first two peaks correspond to nearest neighbours, the second and third peak correspond to next-nearest neighbours etc. We further note that the first and largest peak is around  $r_m = 1.1\sigma$ , the particle

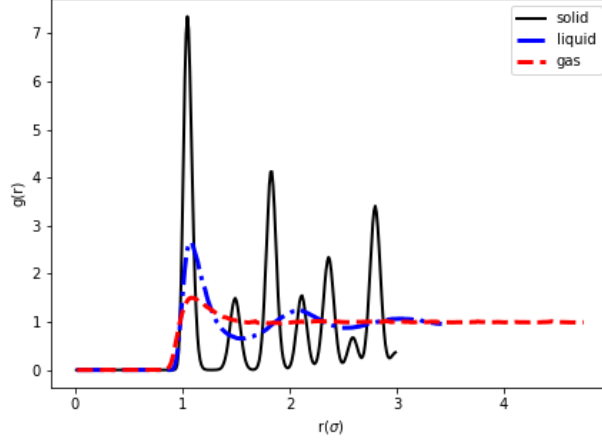


Figure 3. Pair number correlation function obtained from simulation in the three different phases: solid ( $\rho = 1.2$ ,  $T_0 = 0.5$ ), liquid ( $\rho = 0.8$ ,  $T_0 = 1$ ) and gas ( $\rho = 0.3$ ,  $T_0 = 3.0$ ).

distance where the Lennard-Jones potential is minimal. Distances smaller than  $r_m$  do not occur due to the repulsive term.

Though one can still observe some structure reminiscent of the fcc in the correlation function for the liquid and gas phase, it is clear that the pair distances between atoms are no longer uniform. Indeed, in the gas phase all distances (larger than  $r_m$ ) occur with almost equal frequency.

### 3.2 Diffusion

linear relation between msd and time indicates particles are subject to brownian motion. The diffusion constant satisfies  $msd = 6Dt$

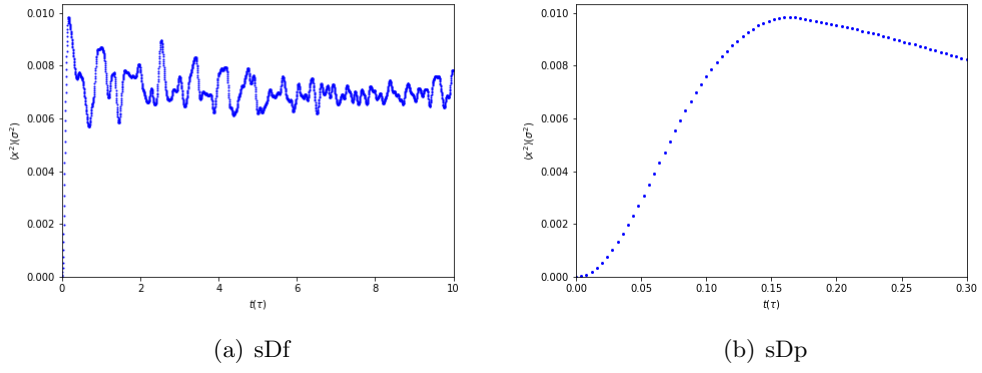


Figure 4. solid diff

solid diffusion. msd quadratic with time for particles in free flight. diffusion starts at collision time.

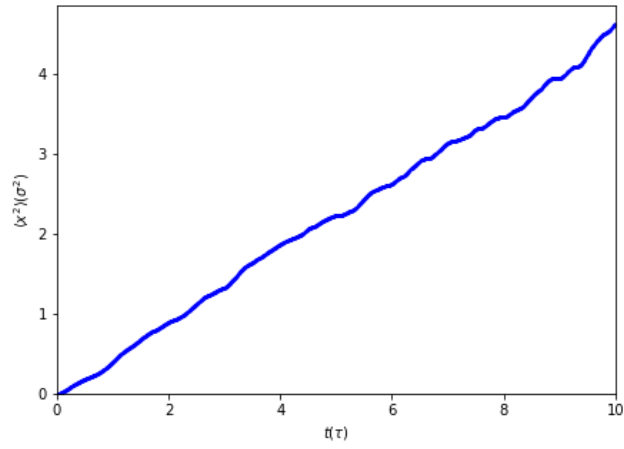


Figure 5. liquid diffusion

liquid diffusion (overbodig?)

diffusive behaviour sets in later in the gas phase than in the liquid phase. note that the msd in the gas phase levels off after some time. This is an entirely

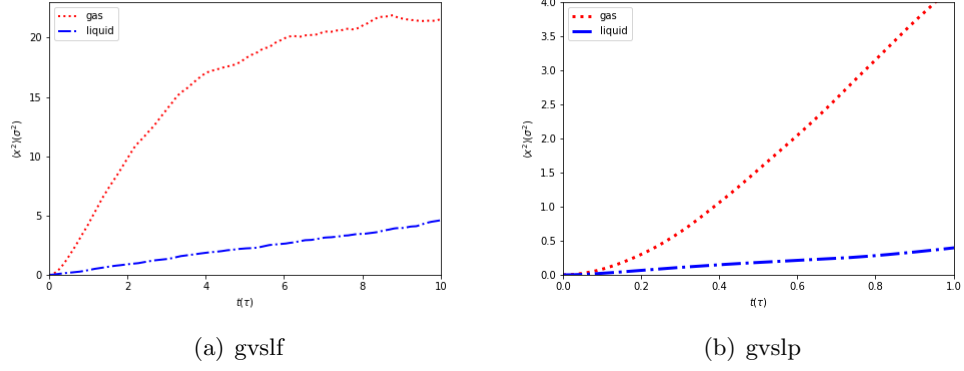


Figure 6. gas vs liq diff

unphysical effect, due to the finiteness of our system (periodic boundary conditions).



As mentioned the diffusion constant  $D$  can be obtained from the slope of the linear msd vs time relation. After selecting a suitable interval (judged by eye) as for example shown in figure 7, the slope was calculated using a standard linear regression method. For varying density and temperature the diffusion constant

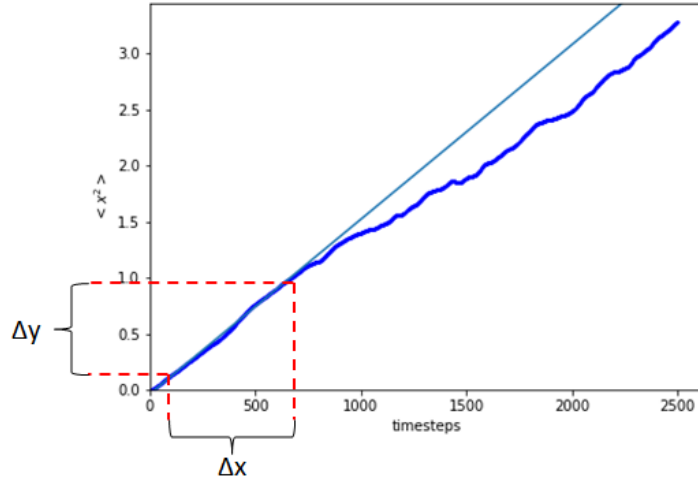


Figure 7. Example of selecting an interval from the msd vs time relation for the calculation of the diffusion constant  $D$ . Here an interval  $[100, 700]$  timesteps is selected. The slope is determined by linear regression.

was calculated, see table 2. The simulations were run with  $N = 256$  particles and a timestep of  $0.004\tau$ ; both rescaling and production time was  $10\tau$ . The obtained

Table 2. My caption

$\rho$	$T_0$	$T$	exp $D$	$D$	rel. err.
0.82	0.75	0.751	0.045	0.042	7.5%
0.78	0.83	0.824	0.066	0.066	0.021%
0.74	0.91	0.902	0.089	0.078	13%
0.69	1.0	1.019	0.11	0.11	0.39%
0.64	1.1	1.098	0.14	0.13	4.0%
0.56	1.2	1.224	0.16	0.20	25%
0.46	1.3	1.316	0.19	0.29	55%

diffusion constants compare quite well with experimental values [4], except for simulations in the gas phase ( $\rho = 0.56$ ,  $T_0 = 1.2$ ;  $\rho = 0.46$ ,  $T_0 = 1.3$ ). Perhaps this is due to the finiteness of our system, i.e. the periodic boundary conditions have too much of an effect in the gas phase and therefore we do not simulate correct diffusive behaviour. Nevertheless the correspondence of the other data shows that

diffusion of Argon in the liquid state can be simulated with reasonable accuracy.

### 3.3 Pressure

The pressure is calculated from the virial theorem:

$$\frac{\beta P}{\rho} = 1 - \frac{\beta}{3N} \left\langle \frac{1}{2} \sum_{i,j} r_{ij} \frac{\partial U}{\partial r_{ij}} \right\rangle \quad (1)$$

where  $\beta = 1/k_B T$ ,  $\rho$  is the particle density and  $N$  is the number of particles. The second term is the time average of the virial. The quantity  $\beta P/\rho$  is also known as the compressibility of the argon system. To calculate this quantity as a function of temperature, simulations were run for  $N = 256$  particles with a rescaling time and measurement time of both  $\tau = 4$  with a time step of  $\Delta\tau = 0.004\tau$ . Fig. 8 shows  $\beta P/\rho$  for some isochores at densities  $\rho = 0.6, 0.3$  and  $0.05$  in a temperature range between 130 K and 420 K. The measured compressibility, given by the dots, follows

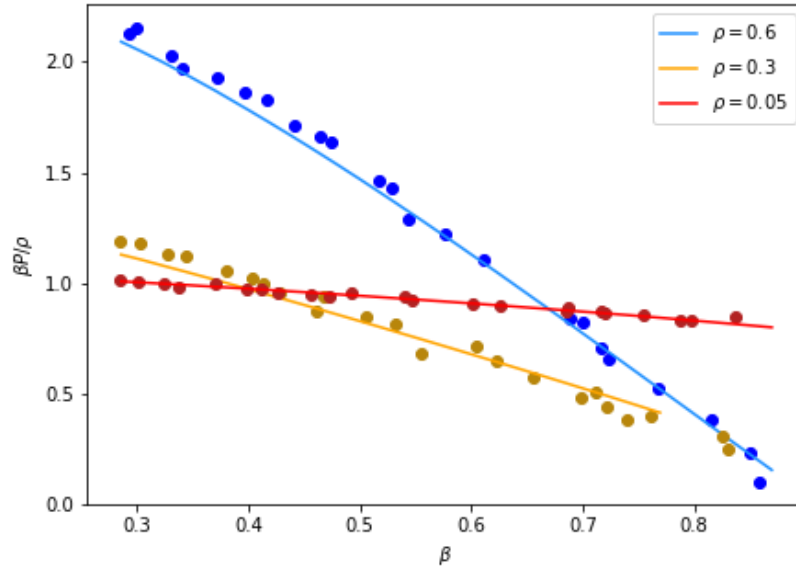


Figure 8. The measured compressibility factor  $\beta P/\rho$  as a function of  $\beta$  for the isochores  $\rho = 0.6, 0.3$  and  $0.05$  are given by the dots and compared to experimental data for argon, the solid lines.

quite nicely the experimental data [?], given by the solid lines for all isochores. It seems that the Lennard-Jones potential is a good approximation for the interaction between argon atoms.

## 4 Old Results

We present our results obtained from the production phase of our simulation of argon atoms. Note that in table 3 that the temperature extracted from the

Table 3. Canonical averages temperature  $T$ , compressibility  $Z$  and potential energy per particle  $U$  corresponding to the three phases solid, liquid and gas found from the simulation of the argon system.

phase	$\rho[1/\sigma^3]$	$T_0[1/\epsilon]$	$T[1/\epsilon]$	$Z$	$U[\epsilon]$
solid	1.2	0.5	$0.5165 \pm 5 \cdot 10^{-4}$	$0.64 \pm 6 \cdot 10^{-2}$	$-5.952 \cdot 10^{-4} \pm 6 \cdot 10^{-8}$
liquid	0.8	1	$0.969 \pm 1 \cdot 10^{-3}$	$1.04 \pm 2 \cdot 10^{-2}$	$-5.357 \pm 2 \cdot 10^{-3}$
gas	0.3	3.0	$3.045 \pm 2 \cdot 10^{-3}$	$1.01 \pm 1 \cdot 10^{-2}$	$-1.706 \pm 3 \cdot 10^{-3}$

simulation is not exactly equal to the input temperature as after rescaling it fluctuates around its equilibrium. As expected the compressibility is closest to one in the gas phase. Furthermore we observe that the potential energy is larger for the solid phase than for liquid and gas phase. This could be because the conversion of potential energy to kinetic energy occurs less as the positions of the particles are more rigid.

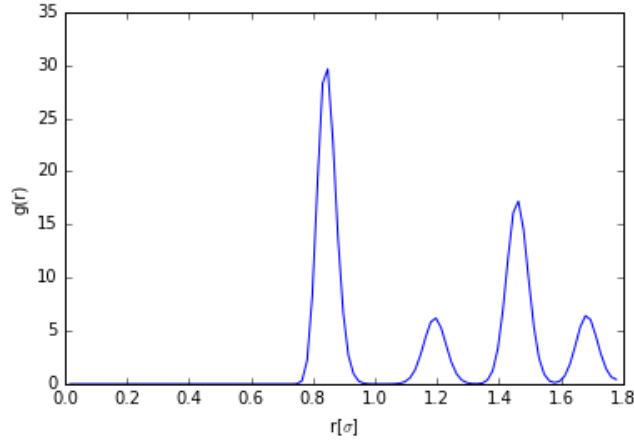


Figure 9. Pair correlation function as obtained from the simulation of the system in the solid phase.

In figure 9 we denote sharp peaks of the correlation function of the system in the solid phase. In a solid, the distances between pairs of atoms is much more uniform which corresponds to the sharp peaks. Multiple peaks show that the system easily configure into equilibrium positions, where the first peak corresponds to initial positions which is the fcc lattice.

In the gas phase, figure 11 we see only the peak corresponding to the initial positions and all larger separation distances are equally distributed which corresponds to the broad velocity distribution of the particles.

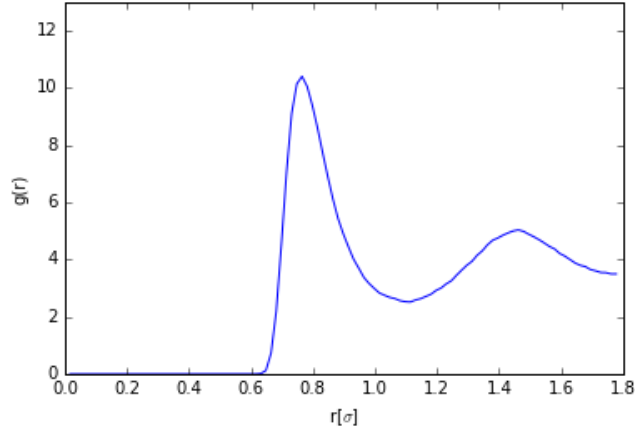


Figure 10. Pair correlation function as obtained from the simulation of the system in the liquid phase.

In figure 10 we see that the correlation function in the liquid phase is smooth, however remnants of the lattice configuration as found in the solid phase remain.

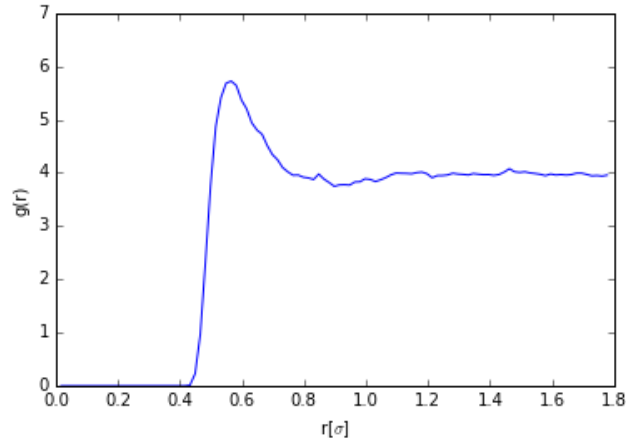


Figure 11. Pair correlation function as obtained from the simulation of the system in the gas phase.

In the gas phase, figure 11 we see only the peak corresponding to the initial po-

sitions and all larger separation distances are equally distributed which corresponds to the broad velocity distribution of the particles.

## 5 Conclusion

We have shown that we can characterize different phases of an argon system using a Molecular Dynamics (MD) simulation. Assuming the interaction is given by the Lennard-Jones potential and integrating the equations of motions via the velocity-Verlet algorithm we have obtained the pair correlation function. We found distinct behaviour of the pair correlation function for the three different phases. Furthermore we extracted some canonical averages.

## References

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