



Simulating argon

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Abstract

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Chapter 1

Introduction

Chapter 2

Theory

Four questions have to be answered in order to simulate argon, these are:

1. What is the interaction between the argon atoms?
2. How do the argon atoms move around?
3. What are the boundary conditions?
4. What are the initial conditions?

These will be answered in the following sections.

2.1 Lennard-Jones potential

In this section the question “What is the interaction between the argon atoms?” will be answered.

A simple model that simulates interaction between argon atoms is the Lennard-Jones potential:

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.1)$$

The r^{-12} term describes repulsion when the distance between the atoms is too small, which causes electrons to overlap and the r^{-6} describes attraction, due to the van der Waals force. The corresponding Lennard-Jones force is:

$$\mathbf{F}_{LJ} = -\frac{d}{dr}V_{LJ}\hat{\mathbf{r}} = 4\frac{\epsilon}{\sigma} \left[12 \left(\frac{\sigma}{r} \right)^{13} - 6 \left(\frac{\sigma}{r} \right)^7 \right] \hat{\mathbf{r}}. \quad (2.2)$$

This force will be used to calculate the acceleration which will be discussed in the next section.

2.2 Velocity Verlet

In this section the question “How do the argon atoms move around?” will be answered.

Newton’s equation of motion can be used to describe the motion of argon:

$$\mathbf{a}(t) \equiv \frac{d\mathbf{v}(t)}{dt} = \frac{d^2\mathbf{r}(t)}{dt^2} = \frac{\mathbf{F}(t)}{m}. \quad (2.3)$$

The Verlet algorithm was used to solve this ODE and in particular the velocity Verlet algorithm. There are two reasons for using this algorithm. Firstly it has a high order of accuracy $\mathcal{O}(h^3)$ and secondly it is very stable. The derivation for the velocity Verlet algorithm is as follows:

The Taylor expansions for the position:

$$\mathbf{r}(t+h) = \mathbf{r}(t) + h\frac{d\mathbf{r}(t)}{dt} + \frac{h^2}{2}\frac{d^2\mathbf{r}(t)}{dt^2} + \mathcal{O}(h^3). \quad (2.4)$$

Equation (2.4) can be expressed in terms of velocity and force:

$$\mathbf{r}(t+h) = \mathbf{r}(t) + h\mathbf{v}(t) + h^2\frac{\mathbf{F}(t)}{2m} + \mathcal{O}(h^3). \quad (2.5)$$

The Taylor expansion for velocity can be expressed as:

$$\mathbf{v}(t+h) = \mathbf{v}(t) + h\frac{d\mathbf{v}(t)}{dt} + \frac{h^2}{2}\frac{d^2\mathbf{v}(t)}{dt^2} + \mathcal{O}(h^3). \quad (2.6)$$

A second way to express the velocity in a Taylor expansion is:

$$\mathbf{v}(t) = \mathbf{v}(t+h) - h\frac{d\mathbf{v}(t+h)}{dt} + \frac{h^2}{2}\frac{d^2\mathbf{v}(t+h)}{dt^2} + \mathcal{O}(h^3). \quad (2.7)$$

Subtracting Equation (2.7) from Equation (2.6) can be expressed as:

$$2\mathbf{v}(t+h) - 2\mathbf{v}(t) = h\frac{d\mathbf{v}(t+h) + d\mathbf{v}(t)}{dt} + \frac{h^2}{2}\frac{d^2\mathbf{v}(t) - d^2\mathbf{v}(t+h)}{dt^2} + \mathcal{O}(h^3). \quad (2.8)$$

If the Taylor expansion is taken for $\mathbf{v}(t+h) = \mathbf{v}(t) + \mathcal{O}(h)$ then the term $\frac{d^2\mathbf{v}(t) - d^2\mathbf{v}(t+h)}{dt^2}$ from Equation (2.8) reduces to $\mathcal{O}(h)$ and Equation (2.8) can be expressed as:

$$\mathbf{v}(t+h) = \mathbf{v}(t) + \frac{h}{2}\frac{d\mathbf{v}(t+h) + d\mathbf{v}(t)}{dt} + \mathcal{O}(h^3). \quad (2.9)$$

So Equation(2.9) can then be expressed in terms of force:

$$\mathbf{v}(t+h) = \mathbf{v}(t) + \frac{h}{2m}(\mathbf{F}(t+h) + \mathbf{F}(t)) + \mathcal{O}(h^3). \quad (2.10)$$

The standard implementation of this scheme is:

1. $\tilde{\mathbf{v}} = \mathbf{v}(t) + h\mathbf{F}(t)/2$,
2. $\mathbf{r}(t+h) = \mathbf{r}(t) + h\tilde{\mathbf{v}}$,
3. Calculate the acceleration using Equation (2.2),
4. $\mathbf{v}(t+h) = \tilde{\mathbf{v}} + h\mathbf{F}(t+h)/2$.

2.3 Boundary conditions

In this section the question “What are the boundary conditions?” will be answered.

There are two types of boundary conditions that can be used these are the:

1. Hard wall boundary conditions.
2. Periodic boundary conditions.

The hard wall boundary conditions will make the argon atoms bounce of the wall. The periodic boundary conditions will make the argon atoms appear on the other side of the volume, this approximates a large (infinite) system.

For the simulation of interacting argon atoms, it is best to have periodic boundary conditions. The problem with hard walls is the interaction between the walls and the argon atoms. This simulation has to simulate the interaction between the argon atoms and this is best done by using periodic boundary conditions.

2.4 Initial conditions

In this section the question “What are the initial conditions?” will be answered.

There are two variables that have to be initialized, these are the ‘position’ and the ‘velocity’. The best way to initialize the position is to arrange the argon atoms in a face-centered cubic lattice, this minimizes the potential energy. Note that arranging the atoms randomly is not a good idea since there is chance that two atoms will have the same initial position, this should not be possible due to the repulsion term in the Lennard-Jones potential.

The atoms will be given a random velocity using the Maxwell-Boltzmann distribution. This will give the atoms a random velocity according to the desired temperature.

2.5 Pressure

The calculation of the pressure can be rigourously done by calculating the force of each particles exerted on the walls of the system. But since we are using periodic boundary conditions to minimize the effects of a system of finite size our system doesnt actually have walls. Thus the virial theorem is used to calculate the pressure. The following shows shortly how the virial theorem can be used to calculate the pressure. The pressure is calculated using the virial theorem and the equation is given in equation 2.11.

$$\frac{p}{\rho k_b T} = 1 - \frac{1}{3Nk_b T} \left\langle \sum_i \sum_{j>i} r_{ij} \frac{\partial U(r)}{\partial r_{ij}} \right\rangle - \frac{2\pi N}{3k_b T V} \int_{r_{cut}}^{\infty} r^3 \frac{U(r)}{\partial r} g(r) dr \quad (2.11)$$

Whereby the second term on the R.H.S. is the virial term and the third term is a correction term for the cutting off the potential tail.

2.6 Constant volume heat capacity

Since our measurements have been performed in the microcanonical ensemble (NVE) we cannot use fluctuations of the total energy to determine the heat capacity. But fortunately Lebowitz[2] has derived a formula where we can use the fluctuation of the kinetic energy to determine the heat capacity, this wouldbe equation 2.12

$$\frac{\langle \partial K^2 \rangle}{\langle K \rangle^2} = \frac{2}{3N} \left(1 - \frac{3N}{2C_v} \right) \quad (2.12)$$

Whereby:

$\langle \partial K^2 \rangle$: variance of kinetic energy of the particles over an amount of timesteps
 $\langle K \rangle^2$: The average of the kinetic energy of the particles over an amount of timesteps

2.7 Thermostat

In our simulation, the particles are initialized in with a initial velocity drawn from the Maxwell velocity distribution, which is a function of the temperature of the system. At this moment, the mean velocity is so that the temperature of the system is at the desired value, as 'measured' using equation 2.13.

$$T = \frac{2}{3} \overline{E_k} \quad (2.13)$$

After the initialization, the mean velocity can change as because of transfer of potential energy to kinetic energy or vice versa. If this happens, the temperature of the system will no longer have the desired value. To correct this, we use a *thermostat*, meaning we will scale the velocity of all particles with a factor λ , so the mean velocity will have the correct value corresponding to the desired temperature of the system. We use the scaling factor λ given in equation 2.14. Note that this thermostat will change the kinetic, but not the potential energy of the system. Thus the total energy of the system will also change.

$$\lambda = \sqrt{\frac{\overline{E_{k,\text{desired}}}}{\overline{E_{k,\text{actual}}}}} = \sqrt{\frac{3}{2} \frac{T_{\text{desired}}}{\overline{E_k}}} \quad (2.14)$$

This step can be repeated until the temperature is approximately stable, after which the total energy will stay constant (microcanonical ensemble). The thermostat can also be applied at every iteration. In that case, the kinetic energy will be constant at each step, but the total energy will fluctuate (canonical ensemble).

2.8 Pair correlation

The pair correlation function $g(\Delta r)$ shows the local structure of the particles in the system. It shows the average number of particles located at distance Δr from a particle. This function can be useful to see in which state a system is. The correlation function of a crystal lattice can be easily recognized as it will have distinct peaks at the spacing of the lattice, and is clearly different from a gas, which will be mostly smooth.

The correlation function $g(\Delta r)$ is computed by counting the atoms in a spherical shell centered on a particle, with radius r and thickness Δr , using equation 2.15.

$$g(\Delta r) = \frac{V}{N(N-1)} \left(\int d^3r' \sum_{i \neq j}^N \delta(r' - r_i) \delta(r' + \Delta r - r_j) \right) \quad (2.15)$$

Chapter 3

Results

To control the correctness of the MD program we have simulated at values that have been achieved by others [1] in their table 8.1. The results that has been achieved with our simulation which are given in table 3.1 are in accordance with results from others. Thus we can hereby assume that the parameters of the simulation are correct.

Table 3.1: Simulation results

ρ	T	D	$\frac{\beta p}{\rho} \pm \sigma$	$C_v \pm \sigma$	U_{pot}
0.7	1	<i>unknown</i>	0.14 ± 0.14	2.33 ± 0.15	-4.77 ± 0.01
0.8	1	<i>unknown</i>	1.44 ± 0.18	2.71 ± 0.31	-5.39 ± 0.005
0.88	1	<i>unknown</i>	2.97 ± 0.19	-3.5 ± 26.8	-5.84 ± 0.014

Further some simulations were made to study argon in the the gas, liquid and solid phase. From the correlation function it can be easily seen in which phase the argon is in. Thus in the following sections we will show results that has been achieved for the gas, liquid and solid phase.

3.1 Microcanonical ensemble

To control that we had a microcanonical ensemble we controlled the total energy of the system which should be constant after the equilibration, and this is indeed seen in figure 3.1.

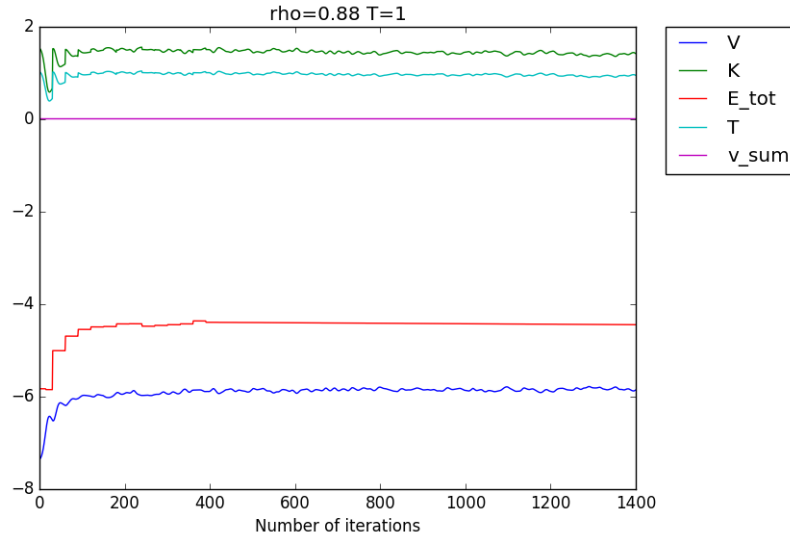


Figure 3.1: The potential energy(blue) and kinetic energy(green) fluctuates but the total energy is constant(red)

The results for the gas phase are showed in figure 3.2, from this figure it is evident that system is in the gas phase because the system doesnt exhibit structure that a liquid would exhibit which is shown in figure 3.3. But a solid on the other hand has

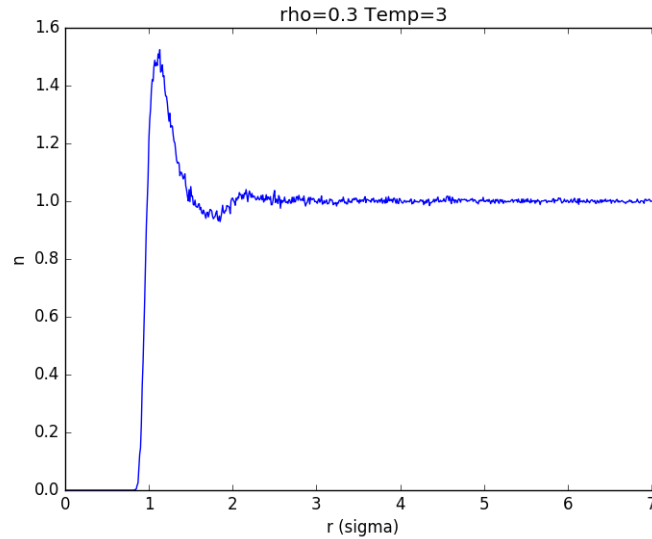


Figure 3.2: Spatial correlation function for $\rho = 0.3$ and $T=3$ thus system is in the gas phase

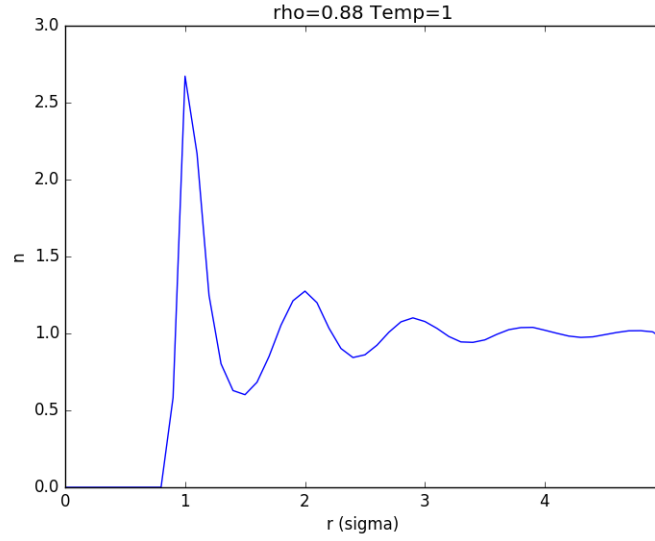


Figure 3.3: Spatial correlation function for $\rho = 0.88$ and $T=1$ thus system is in the liquid phase

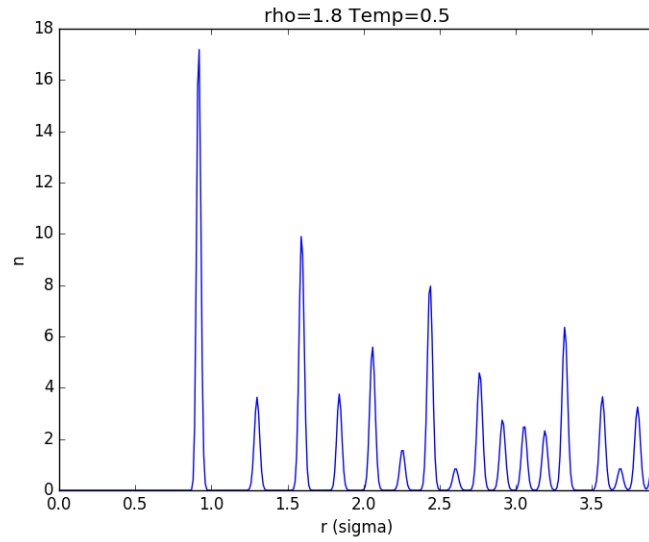


Figure 3.4: Spatial correlation function for $\rho = 1.8$ and $T=0.5$ and the structure shows that this is a solid

Bibliography

- [1] J.M. Thijssen. *Computational Physics*. Cambridge University Press, 2007.
- [2] J. L. Lebowitz, J. K. Percus, and L. Verlet. Ensemble dependence of fluctuations with application to machine computations. *Phys. Rev.*, 153:250–254, Jan 1967.