

FYS4460: Project 1

Molecular Dynamics Modeling

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Abstract

The molecular dynamics of the Argon atom systems are studied by developing a computer program. Using a Lennard-Jones potential the motion of the atoms are simulated, and statistical properties, such as the internal energy, the temperature and the pressure of the system are measured and characterized.

Keywords: Molecular dynamics, Argon, Lennard-Jones potential, Internal energy, Temperature, Pressure, Diffusion constant, Radial distribution function, Berendsen and Andersen thermostats

Crystal structure

Some of the theoretical material in this text is based on the book *Concepts in Thermal Physics*, Blundell (2010).

We start the project by making a program that generates the crystalline structure of Argon. Argon atoms are placed on a $N_c \times N_c \times N_c$ face-centered cubic lattice where the position of every cell is given by

$$\vec{R}_{i,j,k} = i\hat{u}_1 + j\hat{u}_2 + k\hat{u}_3. \quad (1)$$

Here $i, j, k \in \{1, 2, \dots, N_c\}$, and $\hat{u}_n = b\hat{e}_n$ is the set of base vectors with b being defined as the length of the unit cell and $\hat{e}_n = \{\hat{e}_1, \hat{e}_2, \hat{e}_3\}$ are the cartesian unit vectors. The position of atoms in each cell is given relative to

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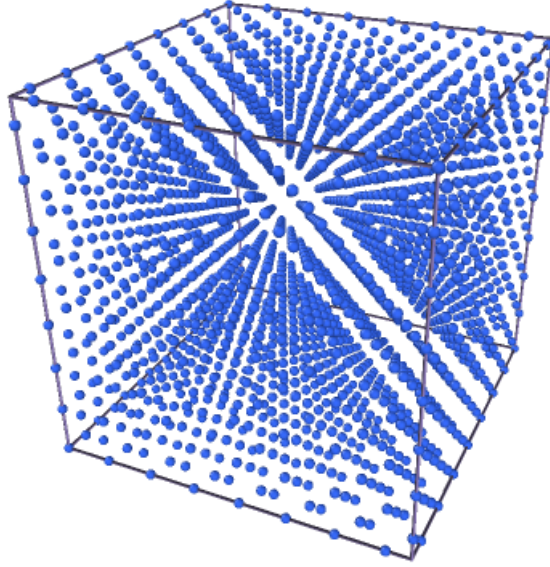


Figure 1: Lattice with $L_c = 8$.

the origin of the cell by

$$\vec{r}_1 = 0\hat{e}_1 + 0\hat{e}_2 + 0\hat{e}_3, \quad (2)$$

$$\vec{r}_2 = \frac{b}{2}\hat{e}_1 + \frac{b}{2}\hat{e}_2 + 0\hat{e}_3, \quad (3)$$

$$\vec{r}_3 = 0\hat{e}_1 + \frac{b}{2}\hat{e}_2 + \frac{b}{2}\hat{e}_3, \quad (4)$$

$$\vec{r}_4 = \frac{b}{2}\hat{e}_1 + 0\hat{e}_2 + \frac{b}{2}\hat{e}_3, \quad (5)$$

We start the program with solid Argon and therefore choose the lattice constant to be $b = 5.260 \text{ \AA}$. The visualization of the lattice for $N_c = 8$ is given in Fig. 1.

Now that we have generated the lattice, the next step is to generate the velocities for all the atoms. We make use of the fact that the velocity distribution function is defined as the fraction of particles with velocities

in, for example x -direction, between v_x and $v_x + dv_x$, as $f(v_x)dv_x$, and it is proportional to a Boltzmann factor which is e to the power of the energy, in this case $\frac{1}{2}mv_x^2$, divided by $k_B T$. Hence

$$f(v_x) \propto e^{-mv_x^2/2k_B T}. \quad (6)$$

Normalizing this function we get

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_B T}, \quad (7)$$

which is a Gaussian distribution with average zero and standard deviation $\sqrt{\frac{k_B T}{m}}$.

The velocity vector is given by $\mathbf{v} = (v_x, v_y, v_z)$, which lives in a 3D velocity space. The magnitude of the velocity or the speed is given by $v = |\mathbf{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2}$. The speed distribution function is defined as the fraction of particles with speeds between v and $v + dv$, which is a spherical shell in the velocity space of radius v and thickness dv , as $g(v)dv$. The volume of this spherical shell is $4\pi v^2 dv$, therefore, the speed distribution is given by

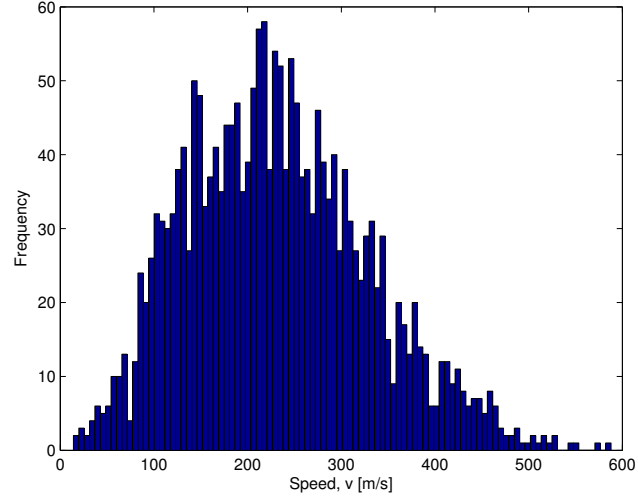
$$g(v) \propto 4\pi v^2 e^{-mv^2/2k_B T}. \quad (8)$$

Normalizing this function we get the Maxwell-Boltzmann distribution

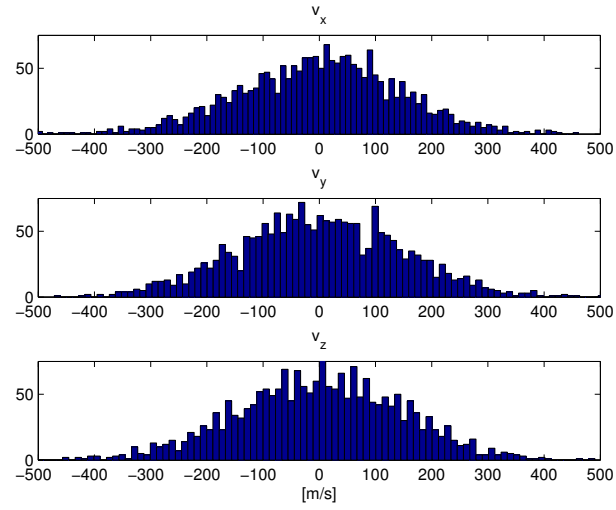
$$g(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}. \quad (9)$$

We know that for a given temperature T in thermal equilibrium the velocities of the atoms are given by the Boltzmann distribution. Therefore, the components of the velocities are normally distributed with average zero and standard deviation $\sqrt{\frac{k_B T}{m}}$.

In Fig. 2 we have plotted the distribution of the components of all velocities as well as the distribution of the speeds for all the atoms. The average and the standard deviation for the velocity components are given in table 1. From this table we see that the averages close to zero, and, the standard deviations are close to $\sqrt{\frac{k_B T}{m}} \approx 144.3$. From Fig. 2(a) we see that the magnitude of velocities are given by Boltzmann distribution.



(a) v .



(b) v_x, v_y and v_z .

Figure 2: The speed distribution, which is a Maxwell-Boltzmann distribution, is given in Fig 2(a). The distribution functions of the components of velocities are given in Fig. 2(b).

Velocity	Average	Standard deviation
v_x	-5.8109×10^{-6}	142.9844
v_y	1.5940×10^{-6}	146.3595
v_z	8.2624×10^{-6}	146.1341

Table 1: The average and standard deviation for the components of the velocities.

Motion

In order to obtain the time development of the motions of the particles we use the *Verlet* algorithm to integrate the dynamical equations, which are given by

$$\mathbf{v}_i(t + \Delta t/2) = \mathbf{v}_i(t) + \frac{\mathbf{F}_i(t)}{2m} \Delta t, \quad (10)$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \Delta t/2) \Delta t, \quad (11)$$

$$\mathbf{F}_i(t + \Delta t) = -\nabla_i U_i(\mathbf{r}_i(t + \Delta t)), \quad (12)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t + \Delta t/2) + \frac{\mathbf{F}_i(t + \Delta t)}{2m} \Delta t. \quad (13)$$

With $U_i = 0$ we get a linear motion for all atoms. This is what we expected because with no potential there is no force (hence no acceleration), and therefore, particles move with constant velocity in their original directions.

Boundary conditions

Since we have a finite number of Argon atoms, because of their motions, they will eventually spread out into space. We, therefore, implement periodic boundary conditions so that if a particle goes out the boundaries we rescale its position by the length of the box, which we set equal to $L = bN_c$.

Forces

The potential scalar field that use to describe the interatomic interactions is the Lennard-Jones potential, which is given by

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (14)$$

We know that the force is defined as the negative of the gradient of the potential, i.e.

$$\mathbf{F} = -\nabla U(r), \quad (15)$$

which has the following form for the Lennard-Jones potential

$$\mathbf{F} = -\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) U(r), \quad (16)$$

$$= -\left(\frac{\partial r}{\partial x}, \frac{\partial r}{\partial y}, \frac{\partial r}{\partial z}\right) \frac{\partial}{\partial r} U(r), \quad (17)$$

$$= -\frac{(x, y, z)}{r} \frac{\partial}{\partial r} U(r), \quad (18)$$

$$= -\frac{\mathbf{r}}{r} \frac{\partial}{\partial r} U(r), \quad (19)$$

$$= 24\epsilon \left[2 \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \frac{\mathbf{r}}{r^2}. \quad (20)$$

The equilibrium interatomic distance is

$$0 = \mathbf{F}, \quad (21)$$

$$= 24\epsilon \left[2 \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \frac{\mathbf{r}}{r^2}, \quad (22)$$

$$= 2 \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6, \quad (23)$$

$$\Downarrow \quad (24)$$

$$2 \left(\frac{\sigma}{r}\right)^{12} = \left(\frac{\sigma}{r}\right)^6, \quad (25)$$

$$2\sigma^6 = r^6, \quad (26)$$

$$\Downarrow \quad (27)$$

$$r = \underline{\sqrt[6]{2}\sigma}. \quad (28)$$

In our program we use MD units that are given in table 2. We assume that all particles are identical so that they have the same mass. Using the MD units we do a dimensional analysis and rewrite our equations without units. For a given quantity A in our equations we rewrite it as $A = \bar{A}A_0$, where \bar{A} is just the numerical value and A_0 is given by the corresponding

Quantity	Conversion factor	Value
Length	$L_0 = \sigma$	3.405 Å
Time	$t_0 = \tau = \sigma \sqrt{m/\epsilon}$	2.1569×10^3 fs
Force	$F_0 = m\sigma/\tau^2 = \epsilon/\sigma$	3.0303×10^{-1} eV/Å
Energy	$E_0 = \epsilon$	1.0318×10^{-2} eV
Temperature	$T_0 = \epsilon/k_B$	119.74 K

Table 2: MD units.

MD units. So, for position and time we have $r = \bar{r}\sigma$ and $t = \bar{t}\tau$. Using this we can rewrite the velocity and the force as

$$v = \bar{v} \frac{\sigma}{\tau}. \quad (29)$$

$$F = m \frac{d^2 r}{dt^2} = m \frac{\sigma}{\tau^2} \frac{d^2 \bar{r}}{d\bar{t}^2}. \quad (30)$$

For energy we have $E = \bar{E}\epsilon$. Using these transformations we can now rewrite Eqs. (14) and (20) as

$$\bar{U}(\bar{r}) = 4 \left[\left(\frac{1}{\bar{r}} \right)^{12} - \left(\frac{1}{\bar{r}} \right)^6 \right], \quad (31)$$

$$\frac{d^2 \bar{\mathbf{r}}}{d\bar{t}^2} = 24 \left[2 \left(\frac{1}{\bar{r}} \right)^{12} - \left(\frac{1}{\bar{r}} \right)^6 \right] \frac{\bar{\mathbf{r}}}{\bar{r}^2}. \quad (32)$$

From these two equations we see that they only include numerical values. Now, dropping the bars, we rewrite the dynamical equations in Eqs. (10)-(13) as

$$\mathbf{v}_i(t + \Delta t/2) = \mathbf{v}_i(t) + \frac{1}{2} \frac{d^2 \mathbf{r}}{dt^2} \Delta t, \quad (33)$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \Delta t/2) \Delta t, \quad (34)$$

$$\mathbf{F}_i(t + \Delta t) = -\nabla_i U_i(\mathbf{r}_i(t + \Delta t)), \quad (35)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t + \Delta t/2) + \frac{1}{2} \frac{d^2 \mathbf{r}}{dt^2} \Delta t. \quad (36)$$

The next step is to implement Eqs. (31)-(36) in our program to model the behavior of Argon, and use the minimum image convention to handle periodic

boundary conditions (MIC). The MIC works as follows: when calculating the distance between two atoms, say atoms i and j , in the x direction we use $\min_{\delta}(x_i - x_j + \delta L)$, where $\delta \in \{-1, 0, 1\}$ and $L = bN_c$ is the length of box in x direction. With the MIC implemented into the program the range of interaction reduces to half the system size, which is more than enough for Lennard-Jones potential.

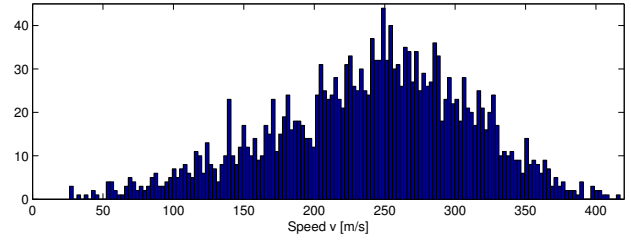
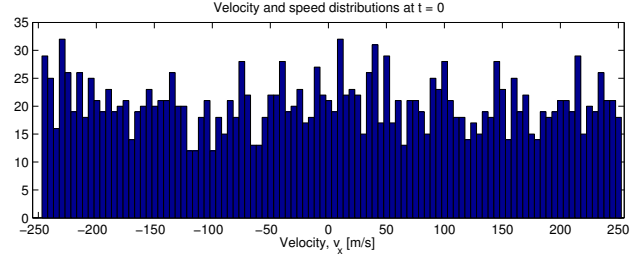
Neighbor lists

For the Lennard-Jones potential the interatomic interactions are short ranged and can be neglected for distances over $r_{cut} \approx 3\sigma$. With the Verlet algorithm we are calculating $\frac{1}{2}N(N-1)$ force terms for each time step. By implementing neighbor lists we improve our program by neglecting force terms for particles with distances greater than r_{cut} . What we are doing is to divide the space into cells of size r_{cut} . And every atom in each cell will only interact with atoms in same cell and in the 26 neighboring cells.

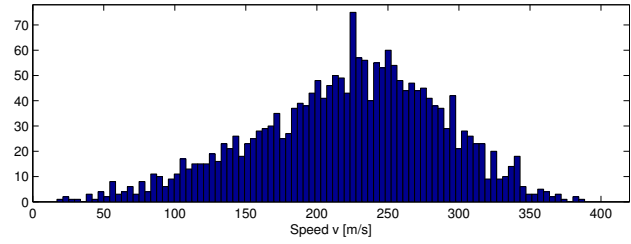
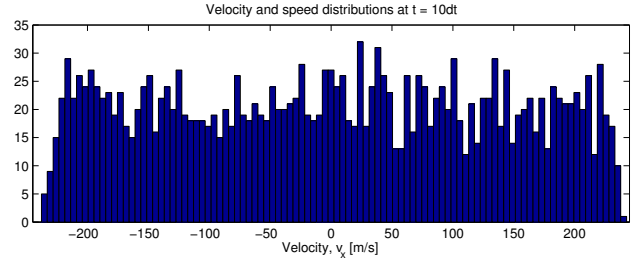
Macroscopic obseables

Evolution of the speed distribution

In this part of the program we are testing the central limit theorem, which states that the sum of many independent random variables tends to a Gaussian, whatever the original distribution might have looked like. That is, the Gaussian distribution is the fixed-point function for large sums. When summing many random numbers, the details of the distributions of the individual random variables becomes unimportant; simple behavior emerges. Since the components of the velocities tend to a Gaussian, the speed distribution of particles will eventually evolve into a Maxwell-Boltzmann distribution independent of initial conditions. We started our simulations with velocities that were uniformly distributed random numbers in the interval $[-v, v]$. The results are given in Figs. 3 and 4. From these histograms we see that after 35 to 40 time steps the velocity distribution tends to a Gaussian distribution.

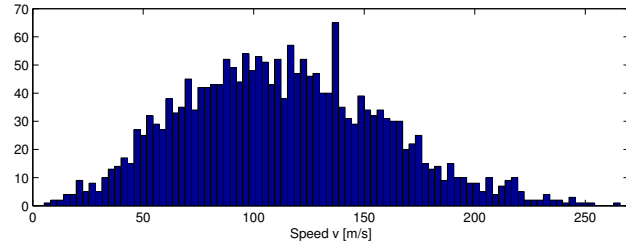
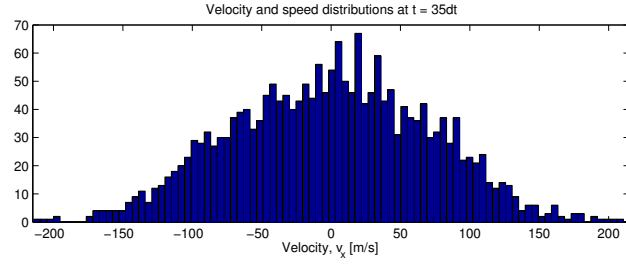


(a) v_x and v .

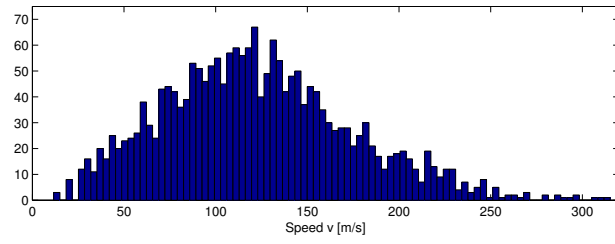
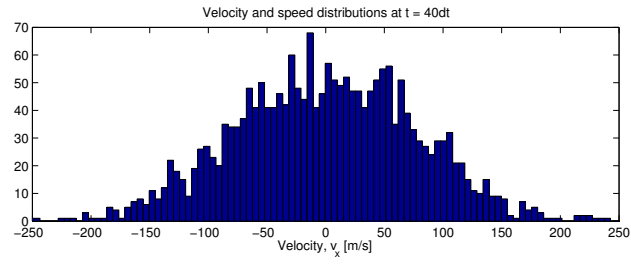


(b) v_x and v .

Figure 3: The distributions for the speeds and the x -component of the velocities at $t = 0$ and after 10 time steps are given in Fig. 3(a) and Fig. 3(b), respectively.



(a) v_x and v .



(b) v_x and v .

Figure 4: The distributions for the speeds and the x -component of the velocities after 35 and 40 time steps are given in Fig. 4(a) and Fig. 4(b), respectively.

Internal energy

The total internal energy of the system is given by

$$E_{total} = E_{kinetic} + E_{potential}, \quad (37)$$

$$= \sum_{i=1}^N \frac{1}{2} m v_i^2 + 2 \sum_{i < j} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]. \quad (38)$$

The internal energy is plotted for two different time-steps in Fig. 5. From these figures we see that the total energy is negative, which means that the potential energy contributes most to the total energy. Furthermore, we see that as t increases the total energy goes toward a finite value with small fluctuations. In figure 6 we have plotted the fluctuations for four different time-steps. What we can conclude from this plot is that as Δt increases the fluctuations also increase, and in this interval the fluctuations are linearly dependent on the time-steps.

Temperature

The temperature is found by using the equipartition principle, which states that the average total kinetic energy is related to the temperature by

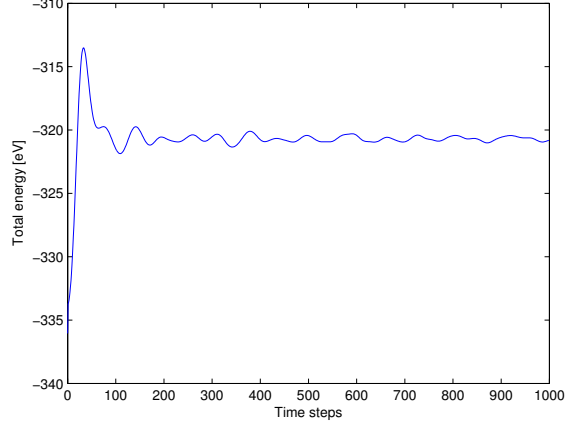
$$\langle E_{kinetic} \rangle = \frac{3}{2} N k_B T, \quad (39)$$

where N is the total number of atoms in the box. In Fig. 7(a) we have plotted the temperature as a function of time. This figure shows that at the beginning of the time evolution, the temperature drops drastically, and the reason for this is that the potential energy is close to zero at the beginning. But, as t increases the temperature stabilizes around $50K$ with small fluctuations. The fluctuations in the temperature as a function of number of atoms is plotted in Fig. 7(b). From this figure we see that the fluctuations decrease with the number of atoms in the system.

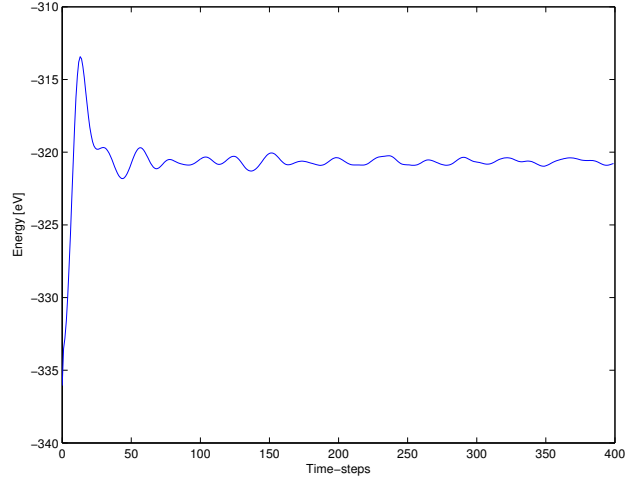
Pressure

For the micro-canonical ensemble the pressure of the system is given by the average of the *virial*

$$W := \sum_{i < j} \vec{F}_{ij} \cdot \vec{r}_{ij}. \quad (40)$$



(a) $E(t)$.



(b) $E(t)$.

Figure 5: The total energy as a function of time with time-steps $\Delta t = 0.002$ and $\Delta t = 0.005$ given in Fig. 5(a) and Fig. 5(b), respectively.

The average pressure is given by

$$P = \rho k_B T + \frac{\langle W \rangle}{3V}, \quad (41)$$

where V is the volume of the system and ρ is the particle density. The pressure as a function of temperature is plotted in Fig. 8. Fig. 8(a) shows the pressure as a function of temperature for several systems. From this

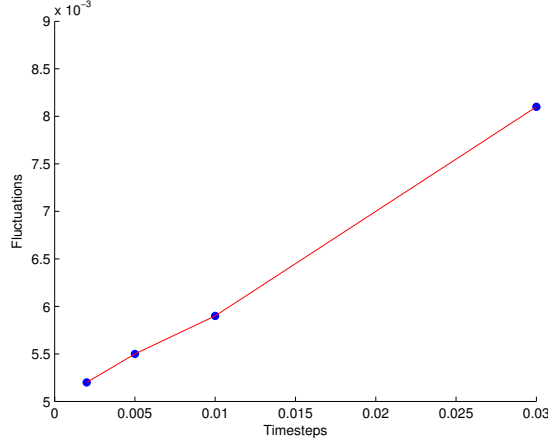


Figure 6: Fluctuations.

figure we can see that at $T \approx 310K$, the pressure jump to higher values, which could indicate a phase transition.

The diffusion constant

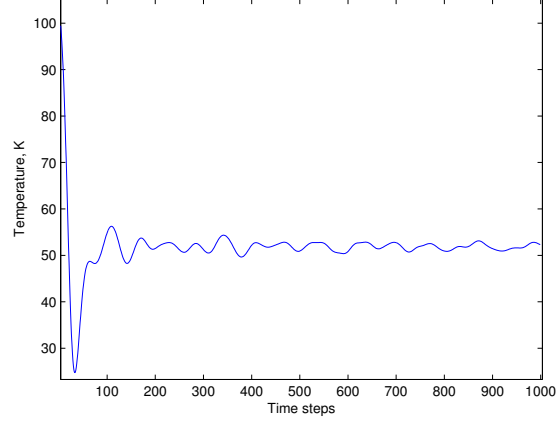
The mean square displacement (MSD) of all atoms is given by

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N (\vec{r}(t) - \vec{r}_{initial})^2. \quad (42)$$

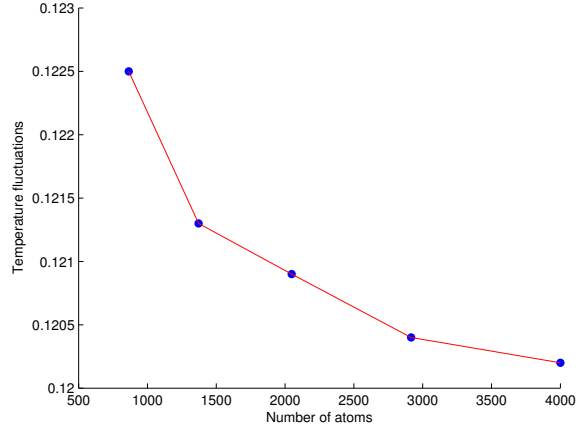
The MSD is proportional to the observation time in the limit that the observation time goes to infinity. The proportionality constant that relates the MSD to the observation time is called the diffusion constant, i.e.

$$D := \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle r^2(t) \rangle}{t}, \quad (43)$$

where $d = 3$ is the dimension of the system, which in this case is equal to the number of dimensions in the physical space. In Fig. 9 we have plotted the MSD for two different temperatures to see the effect of the temperature on the diffusion constant. Based on linear fitting we found $D_{450K} = 5.54 \times 10^{-4}$ and $D_{87K} = 6.15 \times 10^{-5}$ (both without units). We see clearly that higher temperature corresponds to bigger diffusion constant. This is what we expected because higher temperature means higher particle velocities, which in turn means that the particles move longer distances.



(a) $T(t)$.

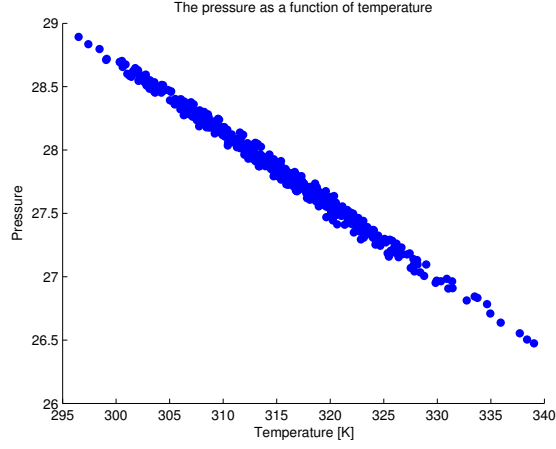


(b) *Temperature fluctuations.*

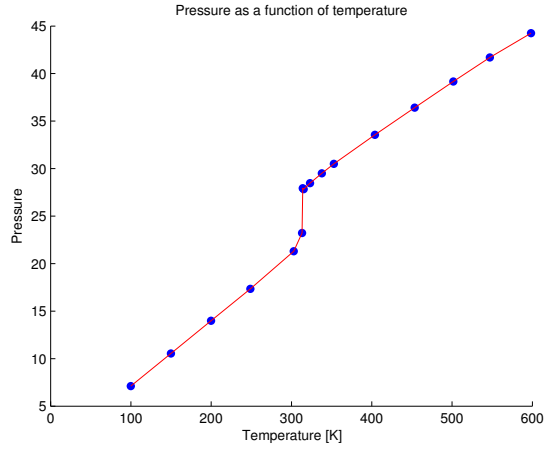
Figure 7: Temperature as a function of time in Fig. 7(a). Temperature fluctuations as a function of number of atoms in the system in Fig. 7(b).

Radial distribution functions

In order to characterize the microscopic structure of a fluid we measure the particle density at different distances, r , from a given particle. This is equivalent to find the particle density in a spherical shell of radius r around



(a) $P(T)$ for a single system.



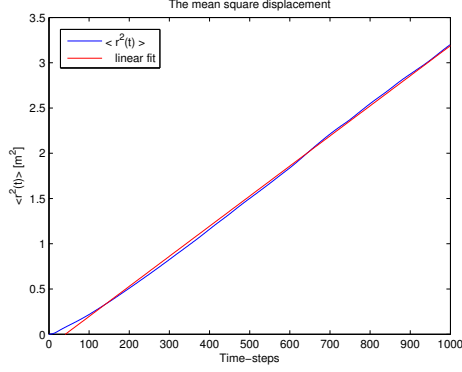
(b) $P(T)$ for several systems.

Figure 8: The pressure as a function of temperature for a single system in Fig. 8(a). The pressure as a function of temperature for several systems with a phase transition at $T \approx 310K$ in Fig. 8(b).

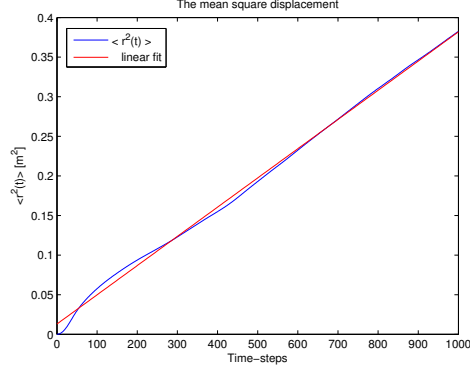
a particle. We define the radial distribution function $g(r)$ as

$$g(r) = \frac{\rho(r)}{\rho}, \quad (44)$$

where ρ is the average particle density, and $\rho(r)$ is the average density at a distance r of a given particle. So, the radial distribution function can be



(a) The mean square displacement for $T = 450K$.



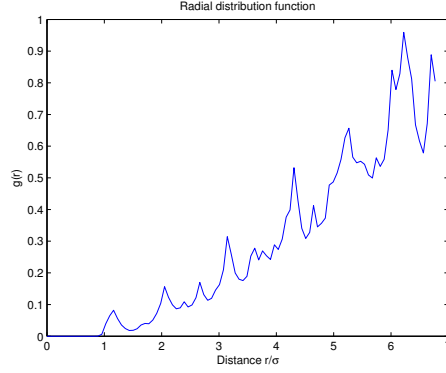
(b) The mean square displacement for $T = 87K$.

Figure 9: The MSD as a function of time for $T = 450K$ and $T = 87K$ in Fig. 9(a) and Fig. 9(b), respectively.

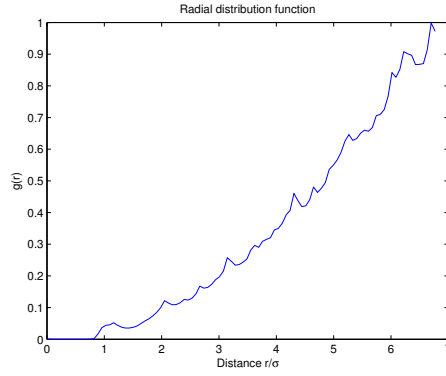
interpreted as the probability of finding another atom a distance r from an arbitrary atom. From this definition we see that $\lim_{r \rightarrow \infty} g(r) = 1$.

In Fig. 10 we have plotted $g(r)$ for two different phases. From these figures we see that for low temperatures (solid phase) there are distances that correspond to high peaks, and between all peaks there are troughs, which means that the probability of finding another particle at some distances is bigger than others. As the temperature increases, $g(r)$ gets smoother and we will have less peaks and troughs, which means that the system is more continuous.

We know that crystals are well spaced and the system is not continuous, thus, from what we see we can conclude that for a perfect crystal $g(r)$ will have peaks and troughs equally spaced, i.e., the probability of finding a particle at some specific distances is very high, and in between these distances the probability is very low.



(a) The radial distribution function for $T \approx 50K$.



(b) The radial distribution function for $T \approx 450K$.

Figure 10: The radial distribution function for equilibrate temperatures $T \approx 50K$ and $T \approx 450K$ in Fig. 10(a) and Fig. 10(b), respectively.

Thermosats

The canonical ensemble governs the equilibrium behavior of a system at fixed temperature. If we want to simulate the canonical ensemble we need to

have interactions with an external heat bath. This is done by implementing a thermostat into our program. In this project we use the Berendsen and the Andersen thermostats.

Berendsen thermostat

With the Berendsen thermostat we rescale the velocities of all atoms by multiplying them with the factor, γ , given by

$$\gamma = \sqrt{1 + \frac{\Delta}{\tau} \left(\frac{T_{bath}}{T} - 1 \right)}, \quad (45)$$

where τ is the relaxation time. In the simulations we used $\tau = 15\Delta t$. The time evolution of the temperature with the Berendsen thermostat is plotted in Fig. 11. From this figure we see that in the beginning the temperature decreases somewhat, but soon it will increase and stabilize around the temperature of the thermostat with small fluctuations.

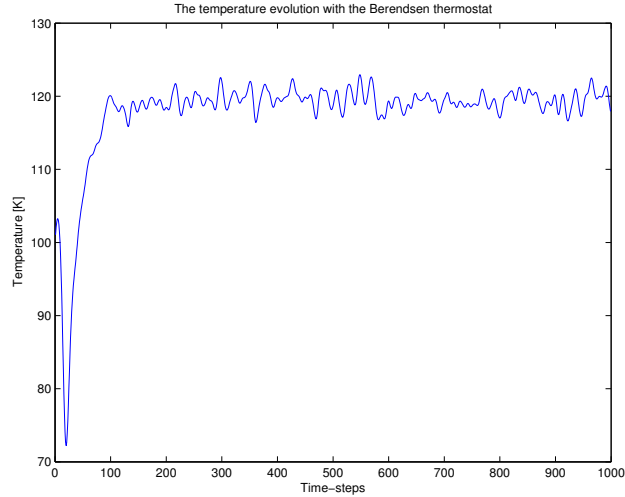


Figure 11: The time evolution of the temperature with the Berendsen thermostat.

Andersen thermostat

With the Andersen thermostat we generate a random uniformly distributed number in the interval $[0, 1]$ for all the atoms. If the number is less than $\frac{\Delta t}{\tau}$, the atom is assigned a new velocity which is normally distributed with standard deviation $\sqrt{k_B T_{bath}/m}$. In this case, τ is treated as a

collision time, and in the simulations it had the same value as in the Berendsen thermostat, namely $\tau = 15\Delta t$. The time evolution of the temperature with the Andersen thermostat is plotted in Fig. 12. From this figure we see, as in the case with the Berendsen thermostat, that in the beginning the temperature decreases somewhat, but soon it will increase and stabilize around the temperature of the thermostat. The main observable difference in the temperature evolution between these two thermostats is that in the case of the Andersen thermostat the fluctuations are somewhat bigger.

From the visualization of the motions of the atoms in VMD (or OVITO), we also see some behavior differences in the atomic motions. With the Berendsen thermostat all the atoms in the system have a smooth motion (because the velocities of all atoms are multiplied by the same factor, namely γ), but, with the Andersen thermostat we can see some sudden movements from some of the atoms (because, some of the atoms that are chosen randomly get new normally distributed velocities), which can explain why the fluctuations in the temperature are higher in the case with the Andersen thermostat.

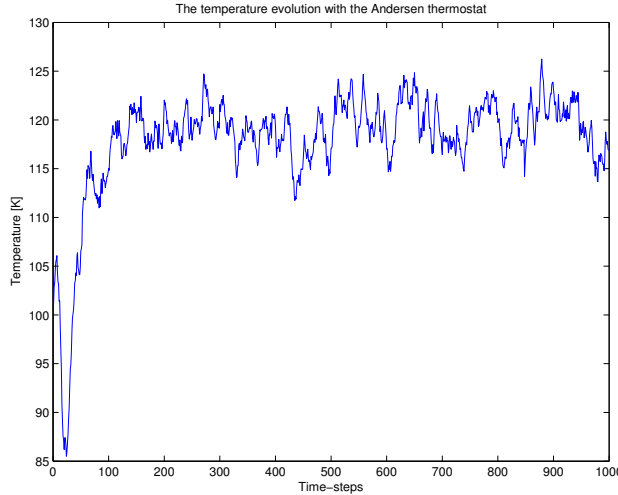


Figure 12: The time evolution of the temperature with the Andersen thermostat.

References

Stephen J. Blundell and Katherine M. Blundell. *Concepts in Thermal Physics*. 2nd ed. New York: Oxford University Press Inc., 2010.