FYS4460 - Project 1

Henrik Sveinsson

March 26, 2013

Abstract

1 The Lennard Jones Potential

A commonly used potential for simple MD-simulations is the Lennard Jones potential. It has the following form:

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

Where ϵ is the strength of the potential, in units of energy, and σ is a characteristic length for the potential. These parameters are set according to the system the potential is applied to.
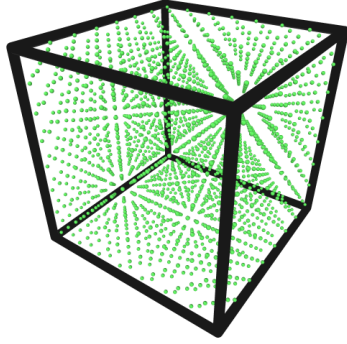
Figure 1: An FCC lattice with $8 \times 8 \times 8$ unit cubes.

2   System

The system considered in this project is argon atoms in a face centered cubic lattice (FCC).

2.1   Setting parameters

Optimal values of the parameters in the Lennard Jones potential for argon are;

$$\frac{\epsilon}{k_B} = 119.8K, \quad \sigma = 4.405\text{Å} \tag{2}$$

3 Dimensionless equations and MD-units

All results presented in this report are in MD-units, unless stated explicitly, or SI-units are trailing a number.

3.1 Removing dimensionality from EOM for the Lennard Jones potential

Defining dimensionless parameters x' and r':

$$x' = \frac{x}{\sigma}, \quad r' = \frac{r}{\sigma}, \quad t' = \frac{t}{\tau} \tag{3}$$

Using spherical coordinates, we have $r = \sqrt{x^2 + y^2 + z^2}$, which means $\frac{\partial r}{\partial x} = \frac{x}{r}$.

The equation of motion for the Lennard Jones potential in x-direction:

$$m\frac{d^2 x}{dt^2} = -\nabla_x u \tag{4}$$

From the dimensionless parameter definitions, we immidiately get:

$$m\frac{d^2 x}{dt^2} = m\frac{d^2(\sigma x')}{d(\tau t')^2} = \frac{m\sigma}{\tau^2}\frac{d^2 x'}{dt'^2} \tag{5}$$

For the potential in the x coordinate direction, we get

$$-\nabla_x u = -\frac{\partial u}{\partial r}\frac{\partial r}{\partial x} = -\epsilon\left[-12\frac{\sigma^{12}}{r^{13}} + 6\frac{\sigma^6}{r^7}\right]\frac{x}{r} \tag{6}$$

$$= 24\epsilon\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]\frac{x}{r^2} \tag{7}$$

$$= 24\frac{\sigma\epsilon}{\sigma^2}\left[2\left(\frac{1}{r'}\right)^{12} - \left(\frac{1}{r'}\right)^6\right]\frac{x'}{(r')^2} \tag{8}$$

$$-\nabla_x u = 24\frac{\epsilon}{\sigma}\left[2\left(\frac{1}{r'}\right)^{12} - \left(\frac{1}{r'}\right)^6\right]\frac{x'}{(r')^2} \tag{9}$$

From equations 9 and 5 combined with the equation of motion in the x-direction (4), we get:

$$\frac{d^2 x'}{dt'^2} = \frac{\tau^2\epsilon}{m\sigma^2}24\left[2\left(\frac{1}{r'}\right)^{12} - \left(\frac{1}{r'}\right)^6\right]\frac{x'}{(r')^2} \tag{10}$$

We fix the timescale of the equation by requiring $\frac{\tau^2\epsilon}{m\sigma^2} = 1$, thus

$$\tau^2 = \frac{m\sigma^2}{\epsilon} \tag{11}$$

This means that when interpreting the simulation results, time will be in units of $\sqrt{\frac{m\sigma^2}{\epsilon}}$. Energies will be in units of ϵ, lengths in units of σ.

The equation to go into the integrator for each particle i is then:

$$\ddot{\mathbf{r}}_i = \sum_{j\neq i} 24\left[2\frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^6}\right]\frac{\mathbf{r}_{ij}}{r_{ij}^2} \tag{12}$$

Where the primes are dropped for convenience.

3.2 Dimensionless temperature

The dimensionless temperature is defined to be:

$$T' = \frac{T}{T_0} \tag{13}$$

That means the dimensionless standard deviation in the normal distributed velocities in each coordinate direction is:

$$\sigma'_v = \sqrt{T'} \tag{14}$$

4 Implementation

4.1 Neighbor lists and cells

The simulation domain is divided into $N_x N_y N_z$ cells with $l_i > r_{crit}$, and as small as possible with an integer number of cells. The forces acting on an atom are the contributions from neighbor cells.

4.2 States

A state is defined by the position and velocity for all particles. They are saved as an xyz-file for use with VMD or similar visualization tool. The program can reload states, and run simulations with that state as the initial state.

4.3 Periodic boundary

Given a position (x, y, z) of a particle i, its cell indices are calculated as the integer values of $(\frac{x}{N_x}, \frac{y}{N_y}, \frac{z}{N_z})$. Before this calculation, the particle has to be checked for being outside the boundarary of the system in any coordinate direction. If outside, L is added to or subtracted from its position in that particular direction.

5 Thermostats

5.1 Berendsen thermostat

The Berendsen thermostat rescales the particle velocities according to the following formula:

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T_{bath}}{T} - 1 \right)} \tag{15}$$

It is hardly possible to see the effect of the Berendsen thermostat on the dynamics of the system. Over time, one can see that the particles speed up or down, but over shorter time ranges, the system appear unaffected. However, it is possible to see that the thermostat introduces something artificial. If the system is brought down in temperature, and the thermostat is turned off too soon, the temperature slightly rises again. This means that while the thermostat is on, the equipartition theorem is not valid.
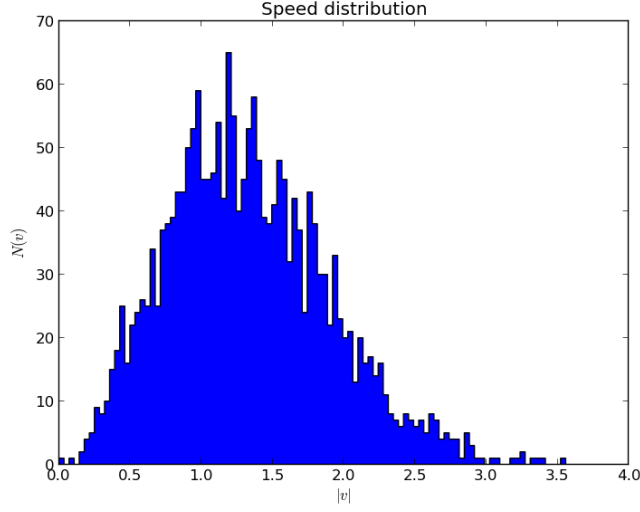
5.2 Andersen thermostat

Figure 2: Distribution of absolute values of velocities. Qualitatively, this looks like a Maxwell-Boltzmann distribution.

6 Macroscopic observables

6.1 The Maxwell-Boltzmann distribution

The distribution of particle velocities evolves sponateously into a Maxwell-Boltzmann distribution. Velocity magnitude and velocity component distributions are shown in figures 2 and **??**. These are taken from a simulation initially started with a uniform distribution for each velocity component.

6.2 Pressure vs temperature

The pressure as a function of temperature is measured in each timestep, creating a path in PV-space through a simulation. The included figure is taken for a simulation with consecutive thermostat actions in steps from $T = 5$ to $T = 0.01$. It shows that when the thermostat is on, strange things can happen in the PV-diagram, so physics should not be measured with the thermostat on.

6.3 Internal energy

The kinetic energy is measued as:

$$E_K = \sum_{i=1}^{N} \frac{1}{2} v_i^2 \tag{16}$$

And the potential energy:

$$E_P = \sum_{i<j} 4 \left[\frac{1}{r_{ij}^{12}} - \frac{1}{r_{ij}^{6}} \right] \tag{17}$$
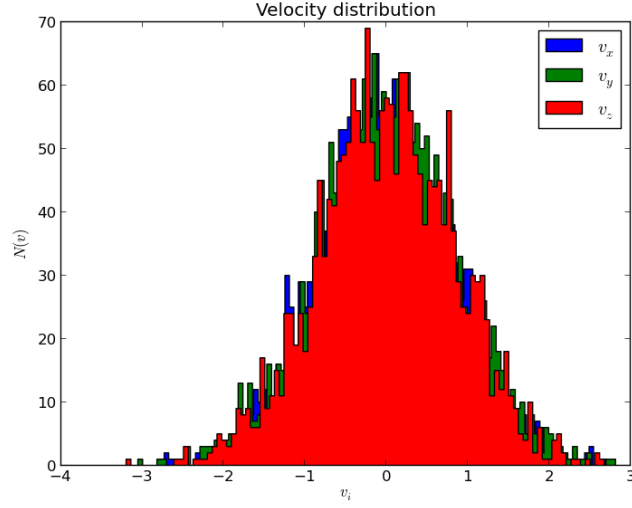
8

Figure 3: Distribution of component values of velocity. The distributions look gaussian, so the absolute values should be distributed according to the Maxwell-Boltzmann distribution.
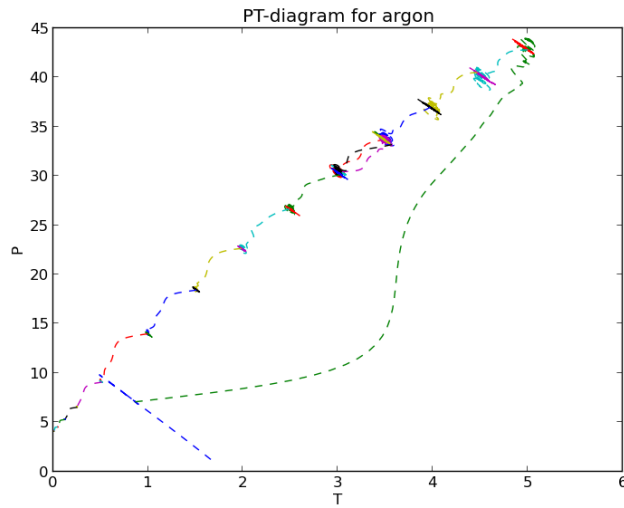

Figure 4: PT-diagram for argon at constant volume stepping down in temperature with the Berendsen thermostat. States without thermostat are shown as clusters in the diagram, and the mean values of these should give a better estimate of the actual pressure.
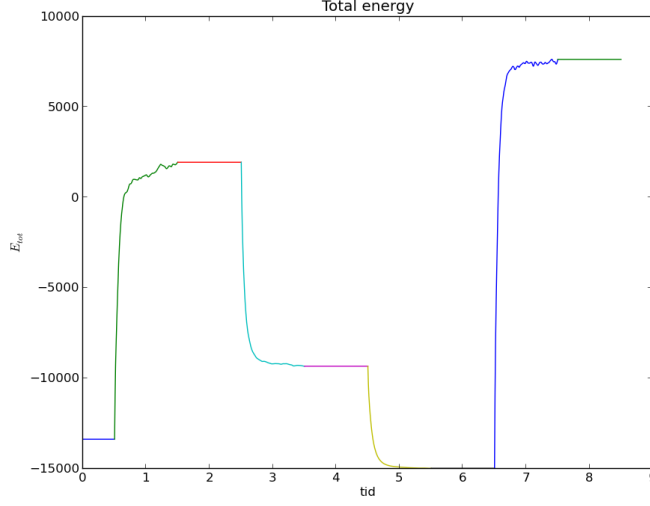
9

Figure 5: Total energy in system of 2048 argon atoms. Changes in total energy are due to thermostat action. The thermostat time is too short for the first temperature drop.

When plotting the total energy, fluctuations are neglilible compared to the changes when turning the thermostat on. The total energy plot is useful to check roughly whether the thermostat has been on long enough. The total energy of a run with several changes in temperature, and following thermalizations is shown in figure 5.

6.4   Temperature

Temperature is estimated assuming that the translational and potential degrees of freedom are in equilibrium, then:

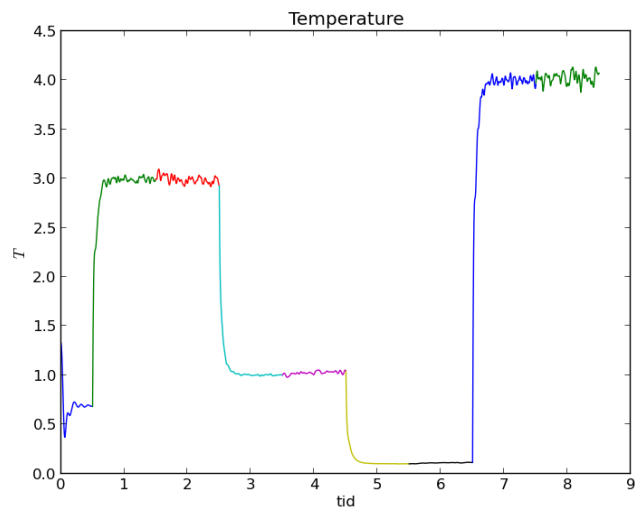$$\langle E_k \rangle = \frac{3}{2} N k_b T \tag{18}$$

Figure 6: Estimated temperature corresponding to figure 5. In units of T_0
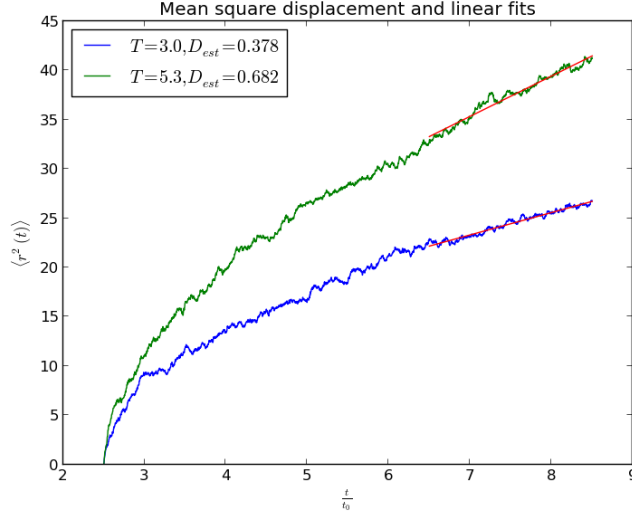
Figure 7: Mean square displacement for 2048 argon particles at two different temperatures. The simulation time is probably slightly low for good results.

7   The diffusion constant

The diffusion constant is measured through the mean self-diffusion af the atoms:

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}(t) - \mathbf{r}(t_0))^2 \tag{19}$$

From the project description, this can be related to the diffusion constant through:

$$\langle r^2(t) \rangle = 6Dt \text{ when } t \to \infty \tag{20}$$

In practice, this means that if the mean square displacement as a function of time becomes linear after some time, the diffusion constant can be estimated as:

$$D = \frac{a}{6} \tag{21}$$

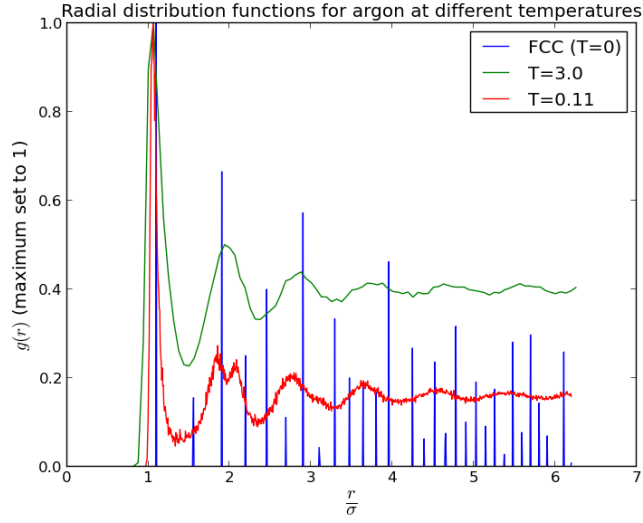where a is the slope of the best linear fit for $\langle r^2(t) \rangle$.

Figure 8: Radial distribution functions for Argon at different temperatures

8   Radial distribution functions

The radial distribution function is inspected for different temperatures. The initial FCC-lattice ha a characteristic radial distribution function.