Project 1, Fys4460, spring 2013

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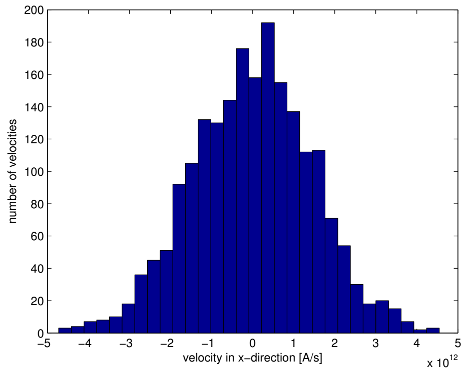

Figure 1: Histogram of velocities in x-direction.

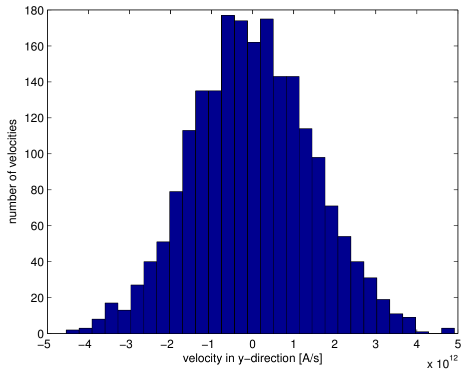

Figure 2: Histogram of velocities in y-direction.

(a) A face-centered cubic lattice consisting of 2048 Argon atoms was generated.

(b) The Argon atoms were given initial velocities from a normal distribution with a standard deviation of $\sqrt{k_B T/m}$. The distribution of the velocities can be seen in the plots in figures 1 - 4. The plots show a normal distribution of velocities.

(c) The system was brought forward in time by integrating Newton's second law (from the project description):

$$\mathbf{v}_i(t + \Delta t/2) = \mathbf{v}_i(t) + \frac{\mathbf{F}_i(t)}{2m}\Delta t \tag{1}$$

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \Delta t/2) \cdot \Delta t \tag{2}$$

$$\mathbf{F}_i(t + \Delta t) = -\nabla_i U_i(\mathbf{r}(t + \Delta t)) \tag{3}$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t + \Delta t/2) + \frac{\mathbf{F}_i(t + \Delta t)}{2m} \cdot \Delta t \tag{4}$$

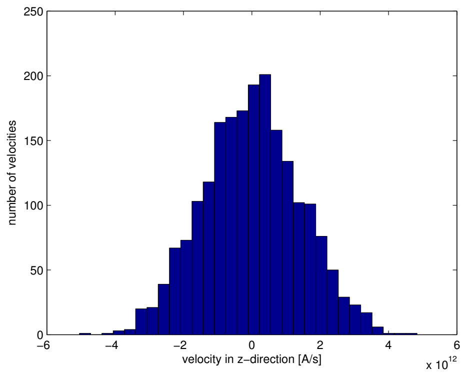

Figure 3: Histogram of velocities in z-direction.

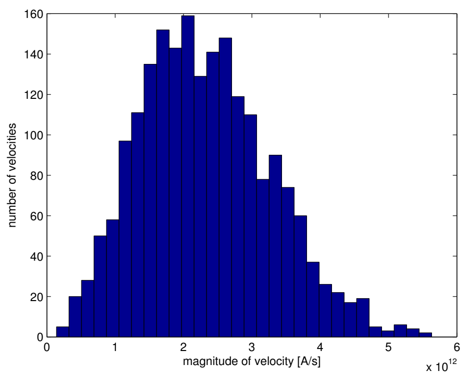

Figure 4: Histogram of the magnitude of the velocities.

No forces were acting on the system in this instance, and the system behaved linearly. As time passed, most of the atoms disappeared outside the original lattice.

(d) Periodic boundary conditions were implemented. Every time an atom moved outside the lattice, it came back on the other side of the "box". It was assumed that the box was part of a much larger system of identical boxes.

(e) The Lennard-Jones potential (from the project description):

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{5}$$

describes interactions between the atoms.

The force on the atoms was found to be

$$F_x = -\frac{\partial U}{\partial r}\frac{\partial r}{\partial x} \tag{6}$$

$$F_x = -\frac{\partial U}{\partial r} \cdot \frac{1}{2} \cdot \frac{1}{r} \cdot 2x \tag{7}$$

$$F_x = -4\epsilon \left[\frac{-12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] \frac{x}{r} \tag{8}$$

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

In order to find the equilibrium interatomic distance, this expression has to be zero, $F_x = 0$.

$$2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} = 0 \tag{10}$$

$$2\left(\frac{\sigma}{r}\right)^{12} = \left(\frac{\sigma}{r}\right)^{6} \tag{11}$$

$$2\left(\frac{\sigma}{r}\right)^{6} = 1 \tag{12}$$

$$r^6 = 2\sigma^6 \tag{13}$$

$$r = 2^{1/6}\sigma \tag{14}$$

The equilibrium interatomic distance is 3.82 Å.

(f) The equations needed to be rewritten with dimensionless units, for instance $r' = r/\sigma$. The new equations of motion were:

$$\mathbf{v}_i'(t' + \Delta t'/2) = \mathbf{v}_i'(t') + \frac{\mathbf{F}_i'(t')}{2}\Delta t' \tag{15}$$

$$\mathbf{r}_i'(t' + \Delta t') = \mathbf{r}_i'(t') + \mathbf{v}_i'(t' + \Delta t'/2)\Delta t' \tag{16}$$

$$\mathbf{F}_i'(t' + \Delta t') = 24 \left[\frac{2}{(r'(t' + \Delta t'))^{12}} - \frac{1}{(r'(t' + \Delta t'))^{6}} \right] \frac{x'(t + \Delta t')}{(r'(t' + \Delta t'))^{2}} \tag{17}$$

$$\mathbf{v}_i'(t' + \Delta t') = \mathbf{v}_i'(t' + \Delta t'/2) + \frac{\mathbf{F}_i'(t' + \Delta t')}{2}\Delta t' \tag{18}$$

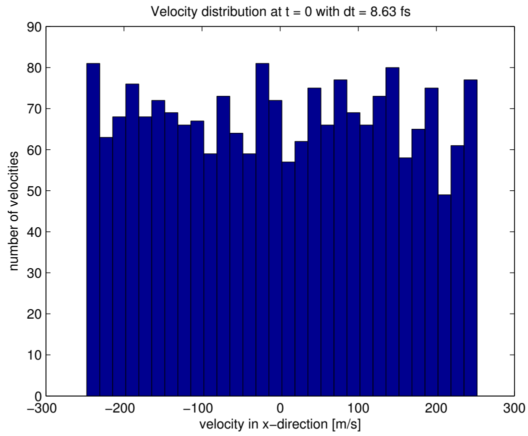

Figure 5: Velocity distribution at t = 0.

(g) The Lennard-Jones force was implemented in the program, and the minimum image convention was used to handle the periodic boundary conditions. This was to make sure that the distance that was used to calculate the forces was the minimum distance, as the system was assumed to continue in all directions in identical boxes. The minimum distance is $\mathbf{min}_\delta(x_i - x_j + \delta L)$ where $\delta \in (-1, 0, 1)$ and L is the length of the "box".

(h) The system was divided into cells of approximately 3σ in size, in order to limit the force calculations on each atom to atoms in the same cell and the 26 neighboring cells. The force between atoms further apart is very small in comparison.

(i) The initial velocities were set to come from a uniform distribution instead of a normal distribution. Over time the distribution became a normal distribution, as predicted by the central limit theorem. In figure 5 the distribution is uniform, in figure 6 the distribution has started to change, and in figure 7 it looks like a normal distribution.

(j) The internal energy consists of the kinetic and the potential energy. The kinetic energy is given by $1/2 \cdot v'^2$ in dimensionless variables and the potential energy is given by the Lennard-Jones potential.

Figure 8 shows the energy fluctuations without a thermostat in the system. Figure 9 and 10 shows the energy with a thermostat in the system. The energy is smaller in the system without a thermostat than in the systems with thermostat. The thermostat was removed after 200 time steps, and the plots show 300 time steps. The two plots have different time steps. The fluctuations seem to be slightly larger for the larger time step, but they seem to be fluctuating around the same value.

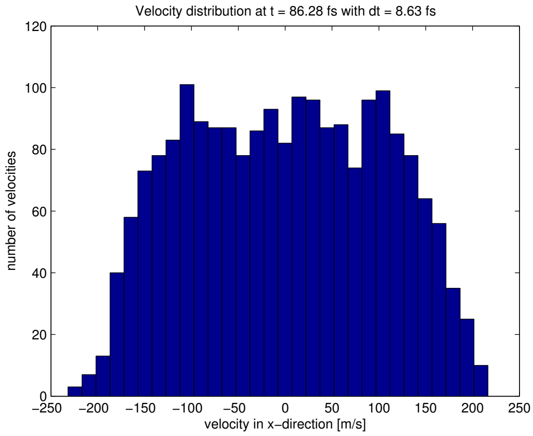

Figure 6: Velocity distribution at t = 86.3 fs.

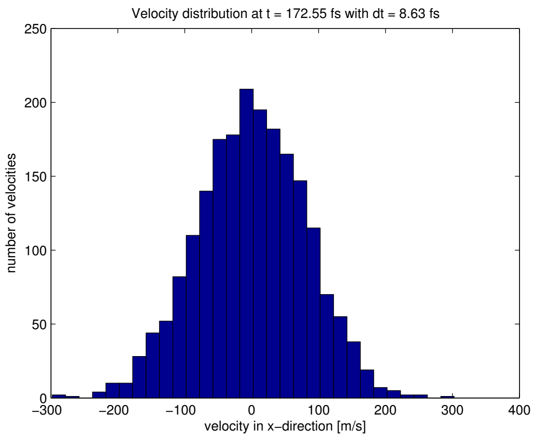

Figure 7: Velocity distribution at t = 172.5 fs.

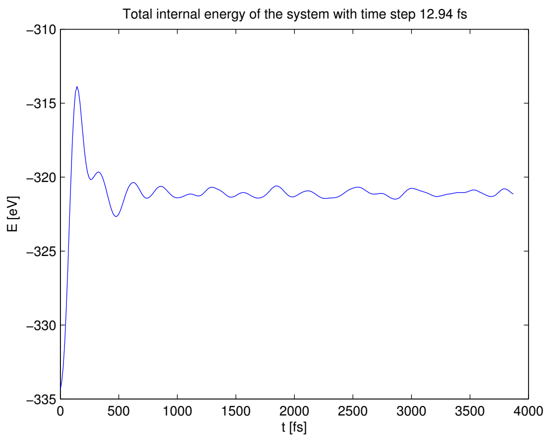

Figure 8: Total internal energy in a system without thermostat.

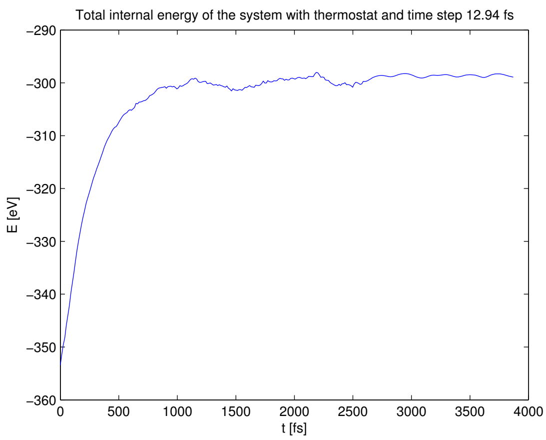

Figure 9: Total internal energy in a system with thermostat. The time step is 12.94 fs.

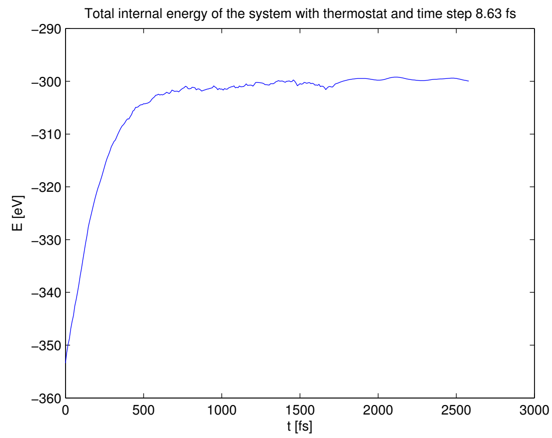

Figure 10: Total internal energy in a system with thermostat. The time step is 8.63 fs.

(k) The temperature of the system can be found from the equation:

$$T' = \frac{2 < E'_k >}{3N} \tag{19}$$

The average of the kinetic energy is actually a time average, but here the kinetic energy of all the atoms for only one time step has been used as an approximation.

Figure 11 and 12 shows the temperature without a thermostat, for two different system sizes, the first with 2048 atoms, and the second with 10000 atoms. The fluctuations seem to be slightly larger for the smaller system. Both the systems equilibrate at approximately the same temperature, which is a smaller temperature than the initial temperature.

In figure 13 the system includes a thermostat. The initial temperature was set as 85 K, and it seems to fluctuate around this value. When the thermostat is turned off, after two thirds of the time steps, the temperature drops slightly below the initial value, and the fluctuations become more even.

(l) The pressure can be found from the equation

$$P' = \rho' T' + \frac{1}{3V'} \sum_{i<j} F'_{ij} \cdot r'_{ij} \tag{20}$$

in dimensionless units. In figure 14 the pressure is plotted as a function of temperature. These values were found after the system had reached equilibrium with different initial temperatures. The liquid phase of Argon is supposed to be found around 80-90 K, but this plot shows no signs of a phase transition here. It is possible that a transition can be found around 300 K instead, but additional measurements in this area would be needed to be certain of this.

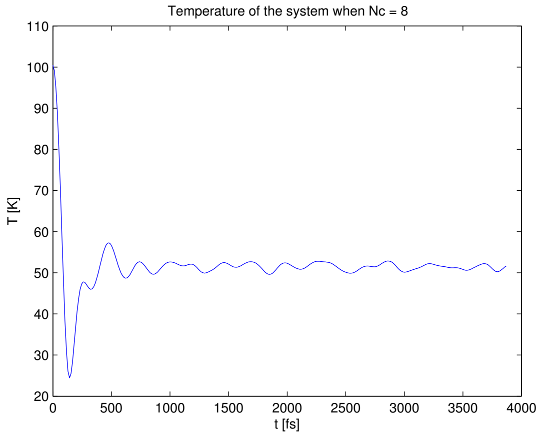

Figure 11: Temperature of a system without thermostat.

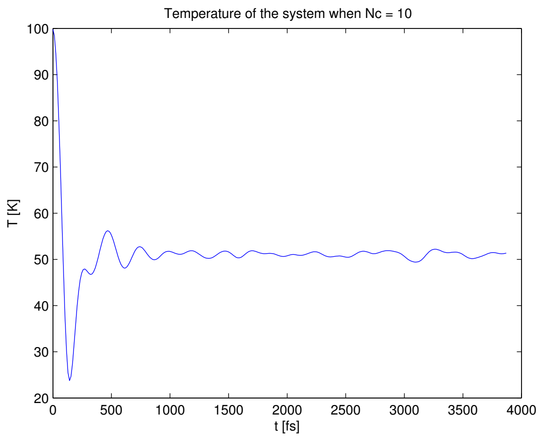

Figure 12: Temperature of a larger system without thermostat.

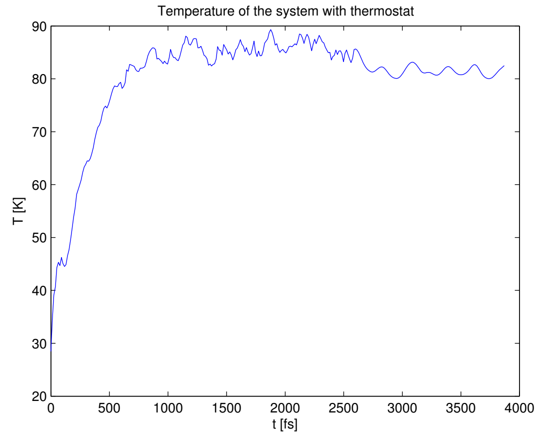

Figure 13: Temperature of a system with thermostat.

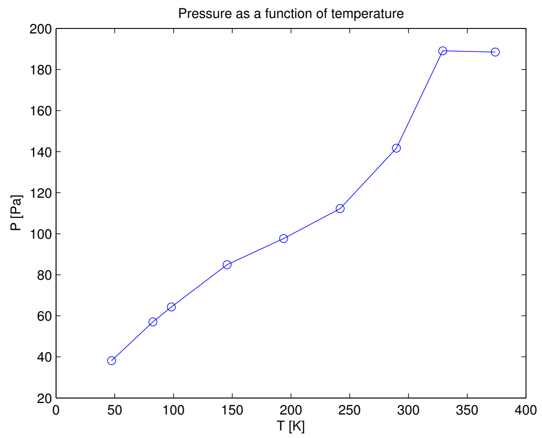

Figure 14: Pressure as a function of T.

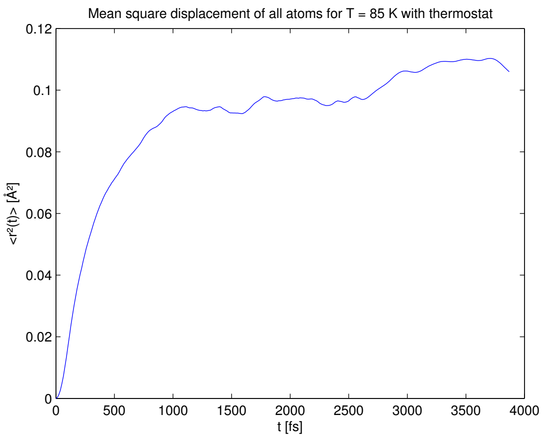

Figure 15: Mean square displacement at T = 85 K, with thermostat.

(n) The mean square displacement can be found with this equation

$$< r'^2(t') >= \frac{1}{N}\sum_{i=1}^{N}(\vec{r'}(t') - \vec{r'}_{initial})^2 \tag{21}$$

A plot of the mean square displacement can be found in figure 15. The displacement is not large, and it seems to be constant after the first time steps. This plot was made from a system with T = 85 K, and the atoms seemed to oscillate around a fixed point for this temperature, as in a solid.

The diffusion constant D is related to the mean square displacement like this

$$< r'^2(t') >= 6Dt' \tag{22}$$

when $t' \to \infty$. A plot of the diffusion constant can be seen in figure 16. It goes toward zero as the mean square displacement in figure 15 becomes almost constant, so there is very little movement of the atoms at this temperature. It is possible that a larger temperature would have generated more diffusion in the system.

(o) The radial distribution function $g(r)$ gives the radial probability of finding another atom a distance r from another atom. The function was calculated by dividing the distance $r \in (0, L/2)$ into 50 interval bins, counting the number of atoms that was found in each bin, and dividing this number by the volume of each interval.

In figure 17 the radial distribution function of the initial crystal structure can be seen. A few clear peaks can be observed. In figure 18 $g(r)$ can be seen after some time has passed in a system with a temperature of 85 K. The measurements were made after the thermostat had been switched off. The same peaks can be observed, but now they are not as sharp as in the previous plot. There are some areas with very little probability of findig other atoms.

In figure 19 the radial distribution function was found on a system with a temperature of 300 K. Now the function is almost continuous after the initial

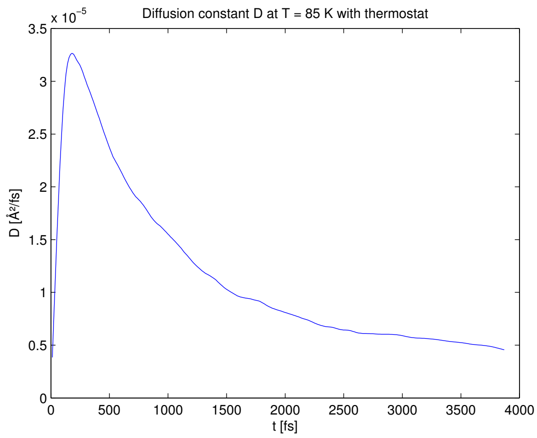

Figure 16: Diffusion constant at T = 85 K, with thermostat.

peak, indicating that the crystal structure is no longer as strong. But there is still no probability of finding two atoms very close together.

(p) One of the thermostats that were implemented in the code was the Berendsen thermostat. For each time step, the velocities were rescaled by multiplying them with a factor

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau}(\frac{T_{bath}}{T} - 1)} \tag{23}$$

τ was set to be $10\Delta t$. T is the actual temperature of the system, and T_{bath} is the desired temperature of the system.

(q) The Andersen thermostat works by simulating collisions between the atoms in the system and in the surrounding heat bath by generating a random number in the interval [0,1]. If the number is less than $\Delta t/\tau$, the atom gets a random new velocity from a normal distribution with a standard deviaton of $\sqrt{k_B T_{bath}/m}$ or $\sqrt{T/T_0}$ in dimensionless units.

In figure 20 the Berendsen thermostat has been used on the system, and in figure 21 the Andersen thermostat has been used. In both cases the temperature has been measured. The wanted temperature was 85 K in both cases. The Andersen thermostat seems to be giving sharper fluctuations than the Berendsen thermostat, but both of them fluctuate around 85 K. The thermostat that was used to obtain the previous measurements was the Andersen thermostat.

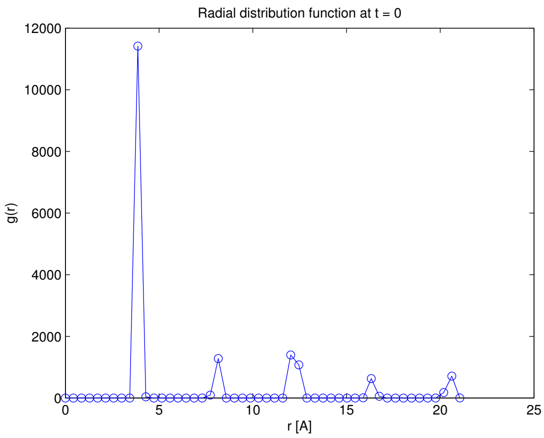

Figure 17: g(r) when t = 0.

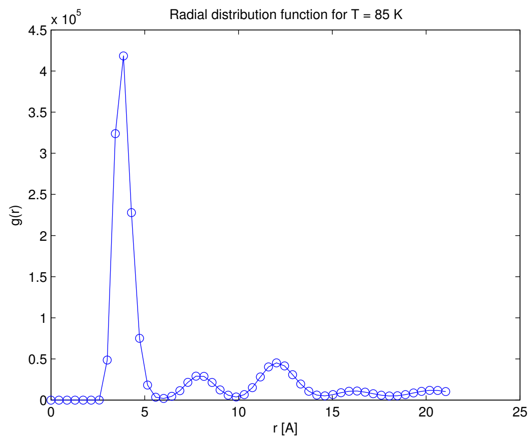

Figure 18: g(r) at T = 85 K, with thermostat.

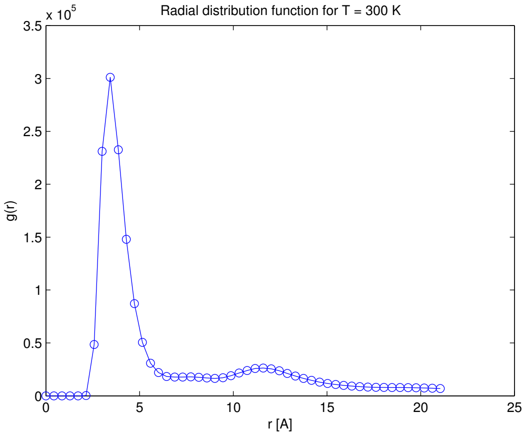

Figure 19: g(r) at T = 85 K, with thermostat.

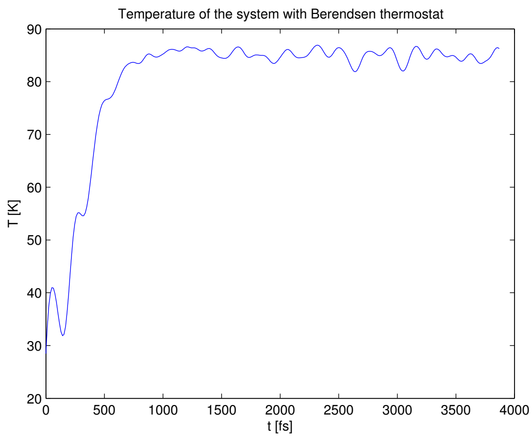

Figure 20: Temperature of the system with the Berendsen thermostat.

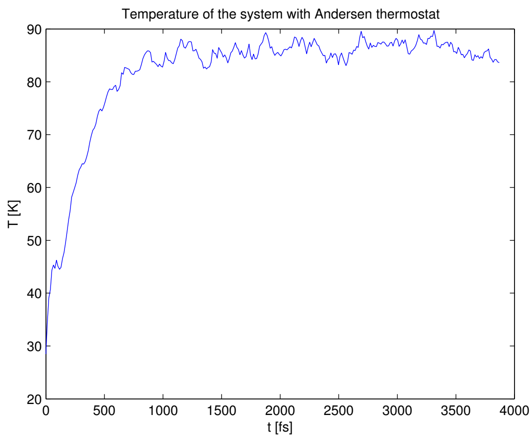

Figure 21: Temperature of the system with the Andersen thermostat.