# Chapter 1

# Three-dimensional atomistic system

For the determination of the lattice constant and lattice type, 3 different configurations are considered:

1. Face-centered cubic (FCC)
2. Body-centered cubic (BCC)
3. Primitive cubic (PC)

The system will take those configuration, which shows the least total energy per atom. Since interactions happen not only with the closes neighbors, but also with other atoms, an simulation has to be performed to get the exact energys. However, a good first approximation can be made analytically by considering the following observations: All atoms within a lattice type are equal, meaning that an atom that appears as a center atom in BCC can also be viewed as a corner atom just by shifting the connections. Secondly, if one denoted the length of the cube as lattice constant $a$, one can easily determine the distances between all atom by simple geometric means.
By looking only at the closest neighbours, one can derive the following expression for the energy per atom in all 3 grids:

$$E_{FCC} = 6U(a_{FCC}) + 12U(a_{FCC}/\sqrt{2}) \tag{1.1}$$
$$E_{BCC} = 6U(a_{BCC}) + 8U(a_{BCC}\sqrt{3}/2) \tag{1.2}$$
$$E_{PC} = 6U(a_{PC}) \tag{1.3}$$

By solving for local minima, the following lattice constants are obtained

$$a_{FCC,min} = 5.7432\mathring{A} \tag{1.4}$$
$$a_{BCC,min} = 4.6143\mathring{A} \tag{1.5}$$
$$a_{PC,min} = 4.097\mathring{A} \tag{1.6}$$
$$\tag{1.7}$$

Susbstitutin this back in to the equation for the energies per atom, one can see, that the FCC configuration with an approximate lattice constant of $5.7432\mathring{A}$ gives the smalles total energy and is therfore the configuration obtained.

Scripts used for this question: lattice_constant_approximation.m
Of course, the lattice constant can also be obtained by simulations. This has been done with the input script in.latticeconstant. To run the simulations just call run_latticeconstant.sh.
The lattice-constant obtained after minimization is $5.64\mathring{A}$. The minimization process is visualized in Figure 1.1.

## 1.1 Constant temperature and molecular dynamics

Through several simulations, a timestep of $10fs$ has been determined as stable. The inputfiles for all simulations are in.NVT_template for the Noose-Hover thermostat and in.NVEBer_template for the "weak-coupling" Berendsen thermostat.

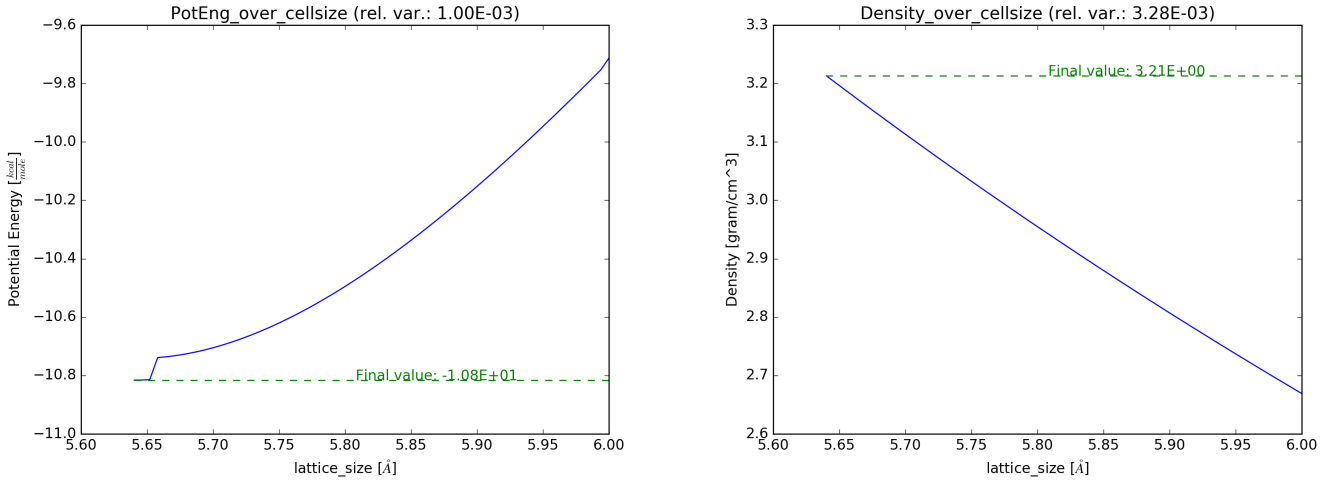


Figure 1.1: Convergence of Potential energy on the left, Final density value on the right. The final lattice-constant determined by the simulation is **5.640** $\AA$.

### 1.1.1 Equilibriation

For the equilibriation phase, the lattice constant of $5.90\AA$, as states on the instruction, has been used. The results are plotted in Figure 1.2. All relative variances have been calculated after the system has reached equilibrium. The plots show, that the weakly coupled Berendsen thermostat capable of delivering the exact temperature value. However, while damping helps to reduce the fluctuation in Potential energy, it increases the variance of the temperature values. For the NVT thermostat on the other hand, damping can help to reduce fluctuations in all quantities of interest. Overall, the weakly-coupled Berendsen thermostat clearly performs superior compared to Nose-Hoover.

### 1.1.2 Stability comparison between Noose-Hoover and Berendsen

A comparison between the Nose-Hoover thermostat and the weakly-coupled Berendsed thermostat is provided in Figure 1.3. Overall, one can say that the weakly-coupled Berendsen delivers more accurate and stable results. Also, it does not benefit from damping, on the contrary, the relative variance increases with an increasing damping parameter.

### 1.1.3 Dependece on the system-size

To determine the dependence of the Nose-Hoover thermostat's convergence on the system size, simulations with a boxsize of 5, 6, 7, 8, 9, 10, 11 and 12 have been carried out, which correlates to a total number of atoms of 500, 864, 1372, 2048, 2916, 4000, 5324 and 6912. The results are visualized in Figure 1.4. It can be observed, that the relative variance decays with the system size as $\frac{<T^2>-<T>^2}{<T>^2} \sim \frac{1}{N}$.

### 1.1.4 MCMC

## 1.2 Constant pressure/temperature molecular dynamics

### 1.2.1 Finding the equilibrium box sizes

To determine the equilbrium box sizes, a regular simulation has been conducted and the final, equilbrium average has been used as a mean value. This is viualized in Figure 1.5. By dividing the final boxlength by the original, one can obtain a scaling factor that is applied to the following simulations via the "change_box" command(in.NPT_boxmod_template). As a verification, the box-size is again plotted over time in the right hand side of Figure 1.5.

In Figure 1.6, the pressure distribution of the scaled simulation is plotted for different box sizes. We can clearly see a normal-like distribution centered around the target value of 1.0 atm and a shrinking variance with increasing

system size.
The dependency of the relative variance on the number of atoms is also plotted in the bottom two figures. Clearly, the relative variance decays invers proportional with the system size.

From the LAMMPS manual, we can see that the pressure is computes via the formula

$$P = \frac{Nk_BT}{N} + \frac{\sum_i^{N'} r_i \cdot f_i}{dV} \tag{1.8}$$

where $N$ is the number of atoms $k_B$ is the Boltzmann constant, $T$ is the Temperature and $V$ is the control volume. The second term contains all interactions where $r_i$ and $f_i$ are the position vector if atom $i$ and dV is the change rate of the control volume. Since we are in equilibrium, the control volume remains constant, the second term can thus be neglected. Also, in the first term, $\frac{N}{V}$ is related to the density and also constant. We can therfore expect the convergence to be of the same rate as the convergence of $T$ which has already been shown in the first part to be of first order.

### 1.2.2 Evaluation of CV

#### EQuilibriation

First, the system has been equilibriated under NPT enselmble as required in the instructions. The plots, confirming that equilibrium has been reached are shown in Figure 1.8.
The inputfile for this task was in.CV_equi.

#### Estimation of box length

The equilibrium box-length estimation under NPT ensemble in visualized in Figure 1.9. The equilibrium box length value calculates to 601 $\mathring{A}$. The inputfile for this task was in.CV_equi.

#### Equilibriation under NVT-ensemble

From the previous simulations we obtain a lattice size of 54.64 $\mathring{A}$, which corresponds to a scaling factor of 9.26 w.r.t the original box length of 5.9 $\mathring{A}$.
This scaling factor has been used in the input file for the following simulations The inputfile for this task was in.CV_NVT.

#### Estimation of specific heat capacity

The specific heat capacity $C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N}$ can, according to the instruction be written as a function of the total energy variance: $C_v = \frac{<E^2>-<E>^2}{k_B * T^2}$. I, however had problems with this formula. Even a short dimension analysis doesnt't fit: $\frac{(kJ)^2}{(\frac{kJ}{K})(K)^2} \neq \frac{kJ}{kgK}$. However, one can also get a good approximation of $C_V$ by using a finite difference approach. I did a central difference around 300.15 $K$ with a stencil width of 1 $K$ and opbtained a value of 0.1516 $\frac{kJ}{kgK}$, which coincides perfectly with the literature. The inputfiles for this task were in.CV_NVT_plus, postprocessing was done via postprocess_NVT.sh and the finite difference approximation was cariied out via calc_CV.py.

## 1.3 Phase transition of Krypton

For the phase transition anlaysis, simualtions between 25 $K$ and 230 $K$ have been cvaried out with a temperature-step of 1 $K$. Each time the final configuration is written to a file and read by the subsequent simulation as a initial configuration.
The inputfiles are in.phasetrans for the first simulation and in.phasetrans_template for all following.
The results are postprocessed via postprocess_phasetrans.py and plotted via plot_phasetrans.py.
For the non-dimensionalization, the equilibrium box length is read from the logfile for each temperature.

**Prove of equilibrium**

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**Stability of tghe two algorithms**

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### 1.3.1 Nose-Hoover dependency on system size

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### 1.3.2 MCMC

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## 1.4 Constant pressure/temperature thermostats

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### 1.4.1 Equilibrium box size with NPT esemble

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**Noose-Hoover barostat**

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**Relative pressure variance**

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**Density calculation**

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### 1.4.2 CValculation of specific heat capacity

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**Equilibrium calculation**

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**Estimation of equilibrium box length**

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**Equilibroium in NVT esmeble**

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**Specific heat capacity for constatn volume**

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## 1.5 Phase transition of Krypton

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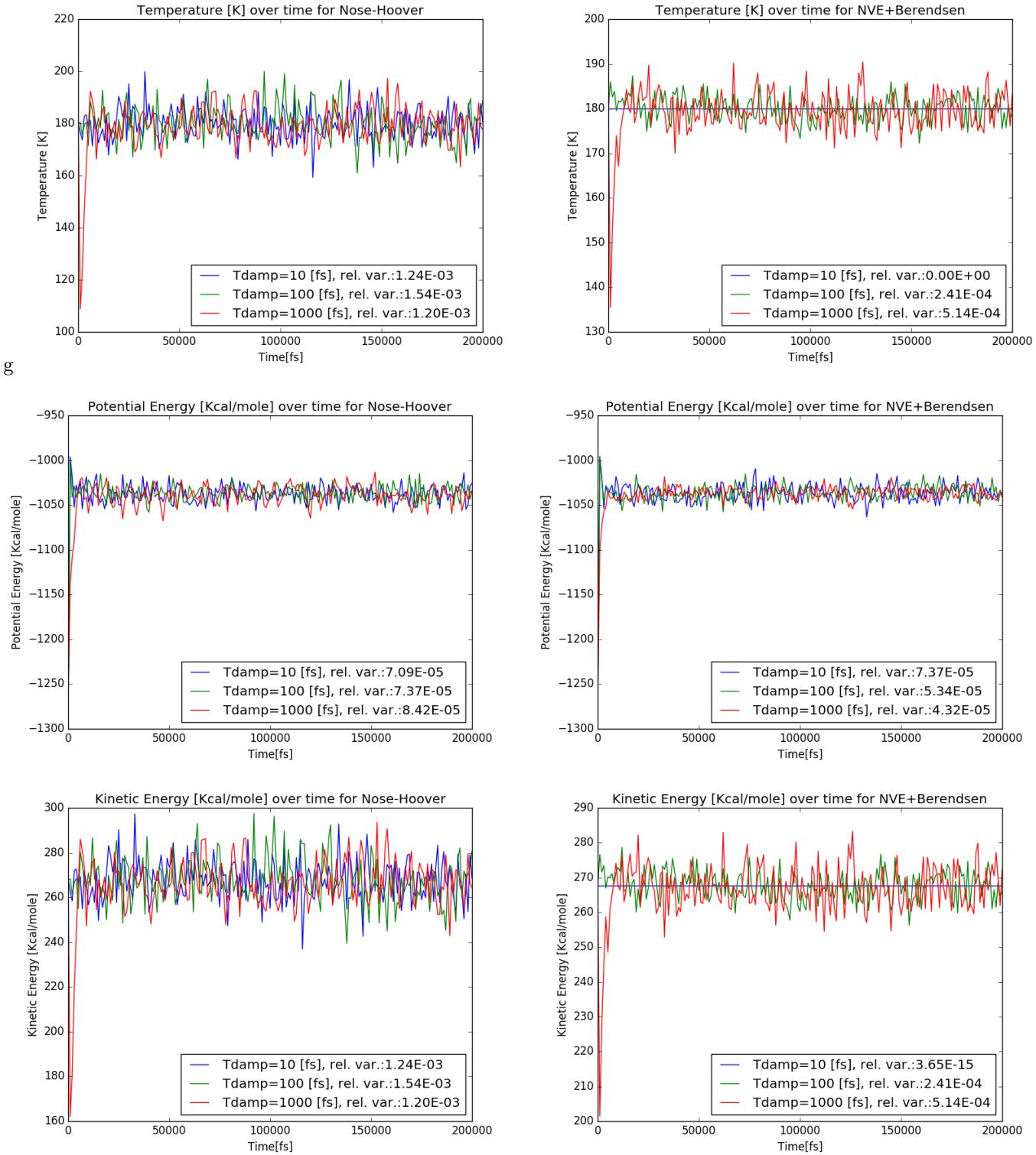


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Figure 1.2: Equiulibriation of Temperature(top), Potential Energy(middle) and Kinetic Energy(bottom) for the Nose-Hoover thermostat(left) and the "weak-coupling" thermostat(right). The equilibriation is plotted for different damping parameters and the relative variance of the equilibriated part is provided.

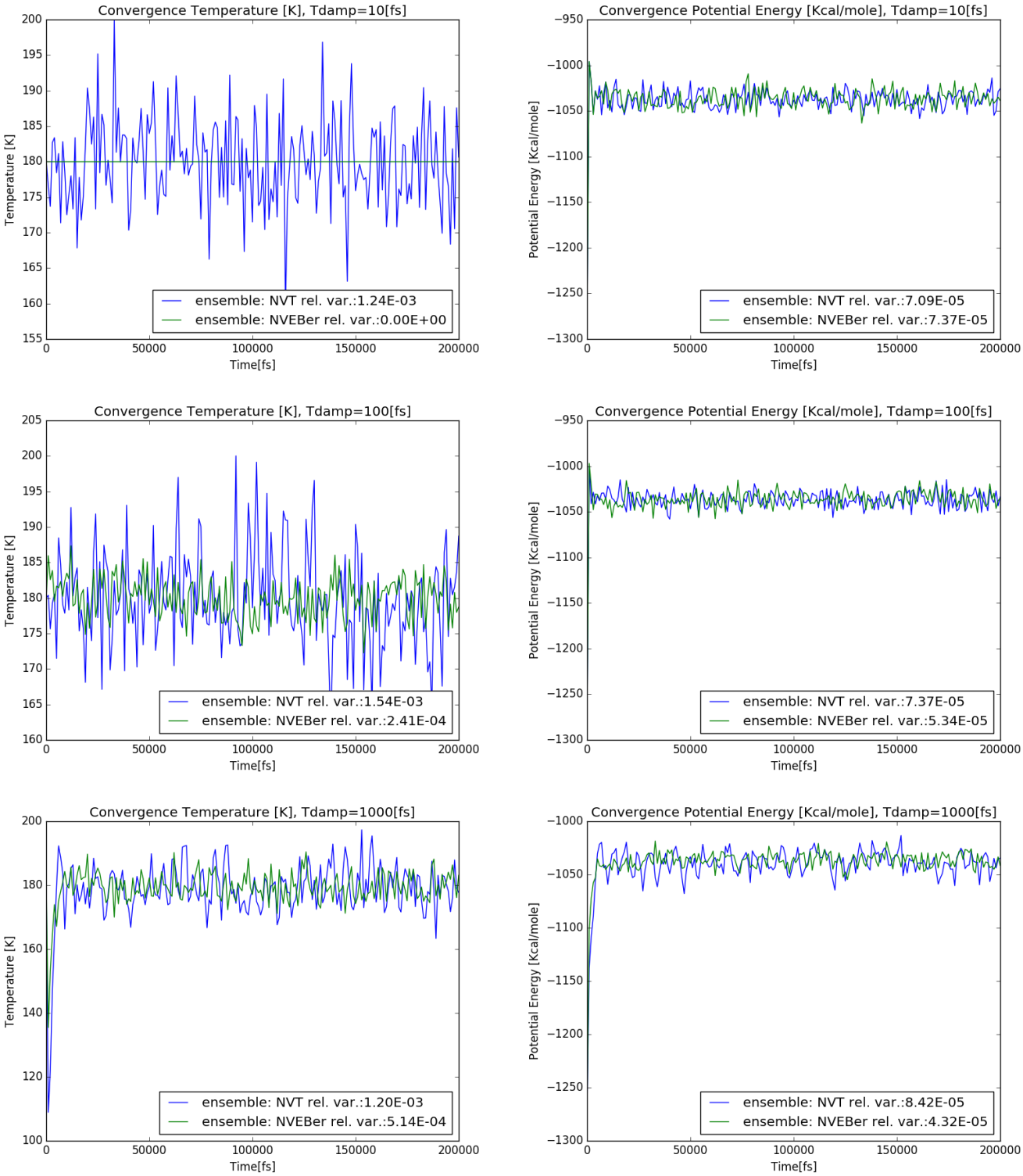



Figure 1.3: Comparions between Nose-Hoover thermostat(blue) and weakly-coupled Berendsen(green) for temperature (left) and Potential Energy(right). The 3 rows show the convergence for 3 different damping parameters.

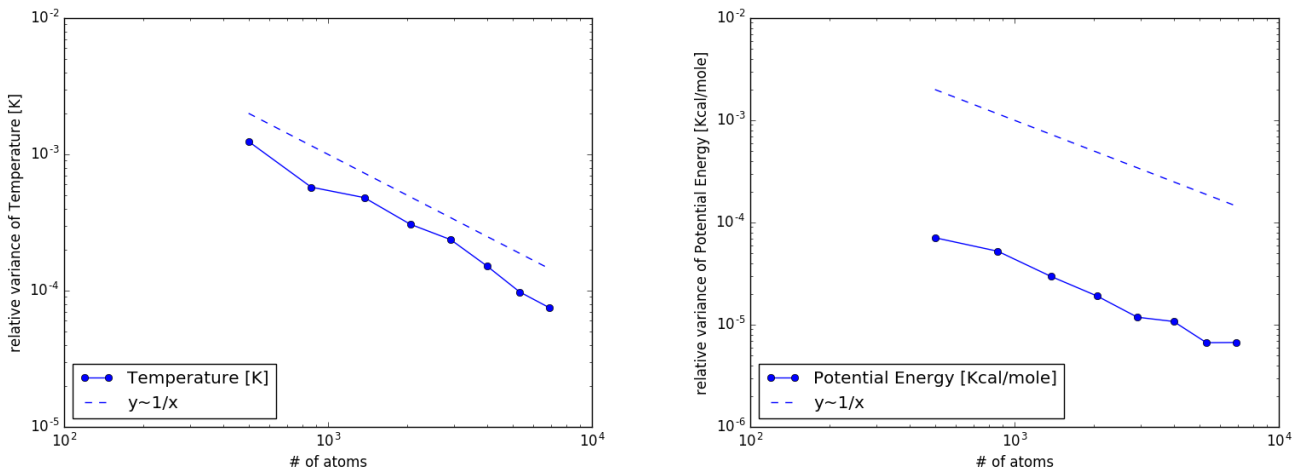



Figure 1.4: Relative variance of Temperature(left) and Potential Energy(right) with respect to the number of atoms in the simulation. As the dashed line shows, the relative variance decays with the system size as $\frac{<T^2>-<T>^2}{<T>^2} \sim \frac{1}{N}$.

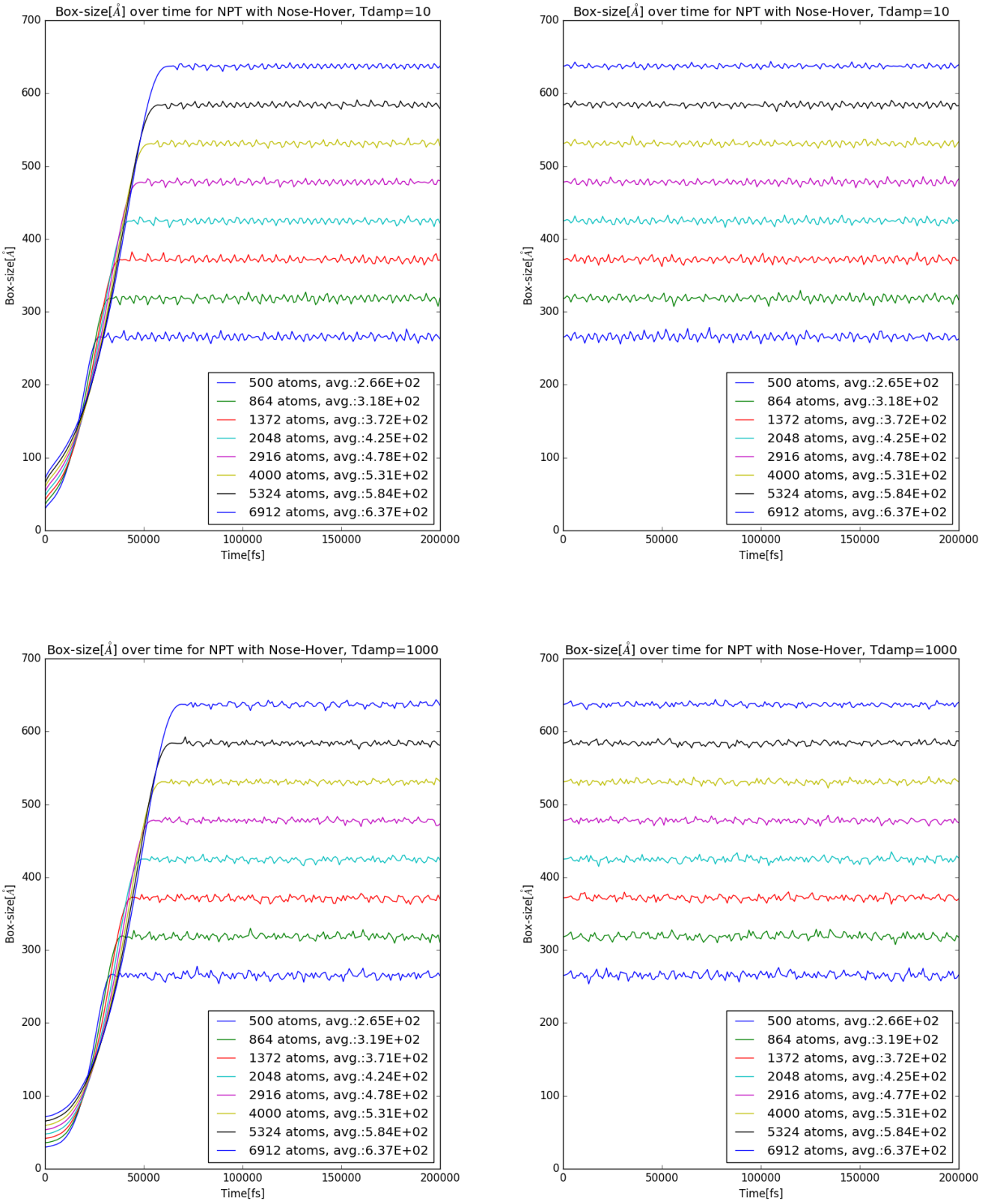



Figure 1.5: Determination of the boxsize by equilibriation(left) and Time convergence after box-size modification (right).

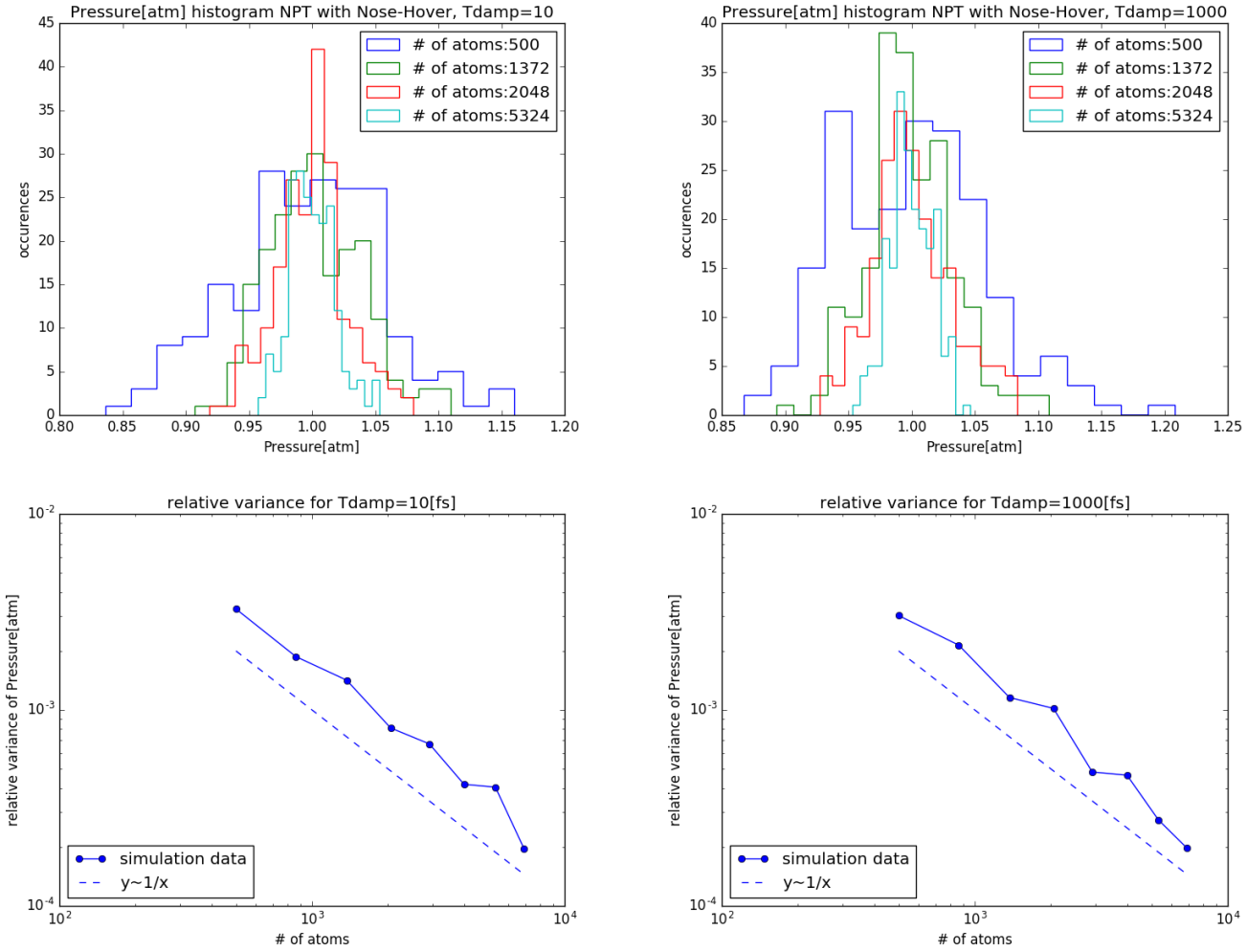



Figure 1.6: Influence of the system size on the simulation. The top two figures show histograms of the obtained pressure values, the bottom two figures show the dependencey of the relative variance on the system size. The left two figures have been calculated with a dampin value of $10fs$ the right two with $1000fs$.

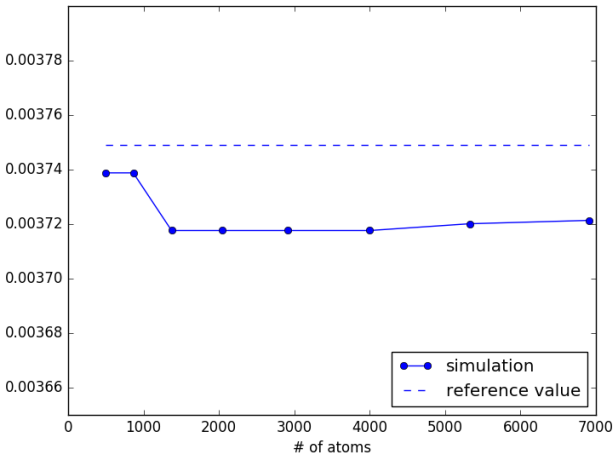



Figure 1.7: Density results as a function of the simulation box size. Clearly, the reference density is very well approximated. On should also take into account, that the 275.15 $K$ that the instruction requires is slightly higher than the $C$ that the provided reference value is based upon.

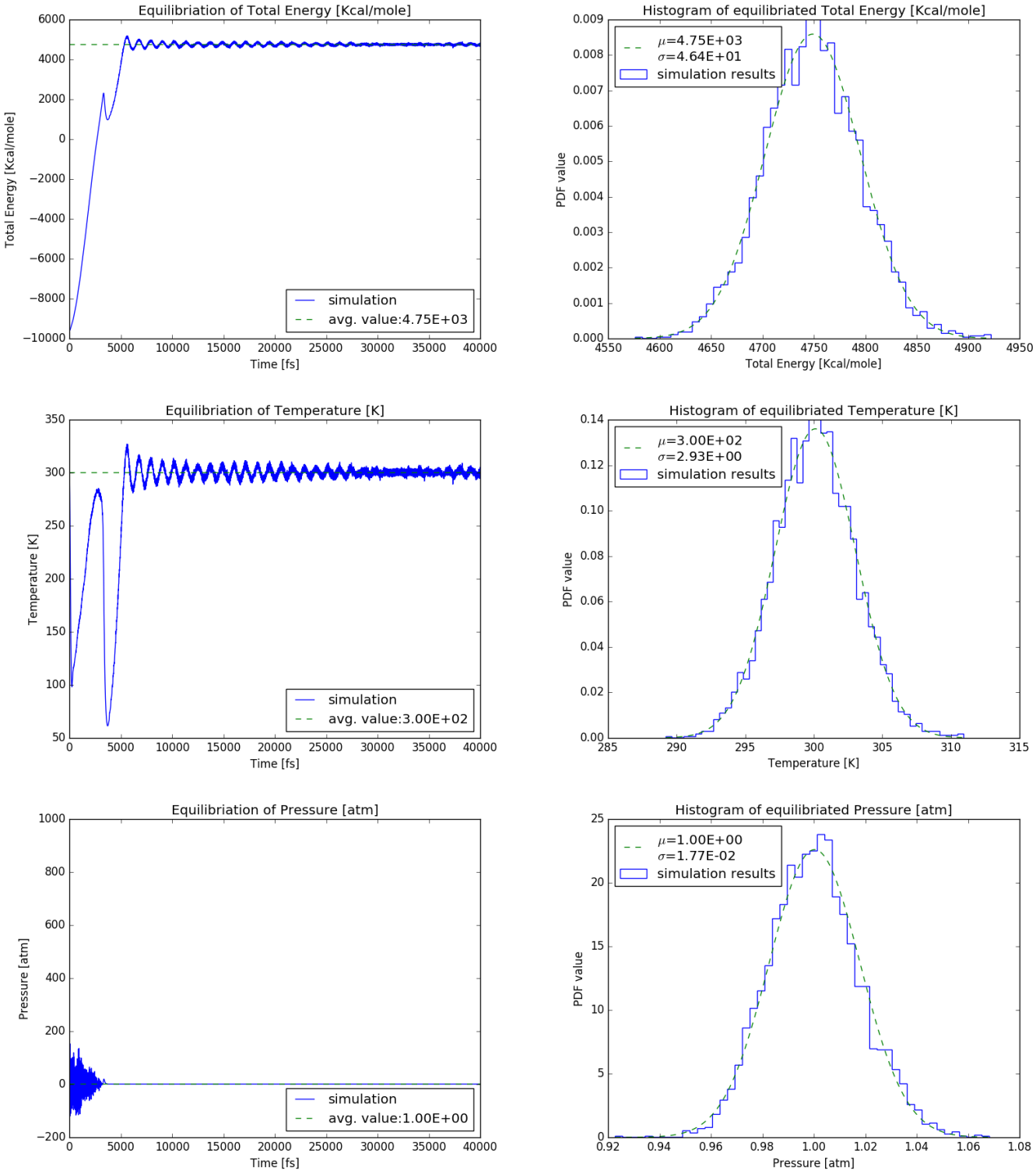



Figure 1.8: Equilibriation of the system under NPT-Ensemble. The left part shows the development of themerodynamic quantities over time, the right figures show the distribution of those quantities after euqilibriation has been reached. Both the target Temperature and target Pressure have been reached with an acceptable standard deviation.

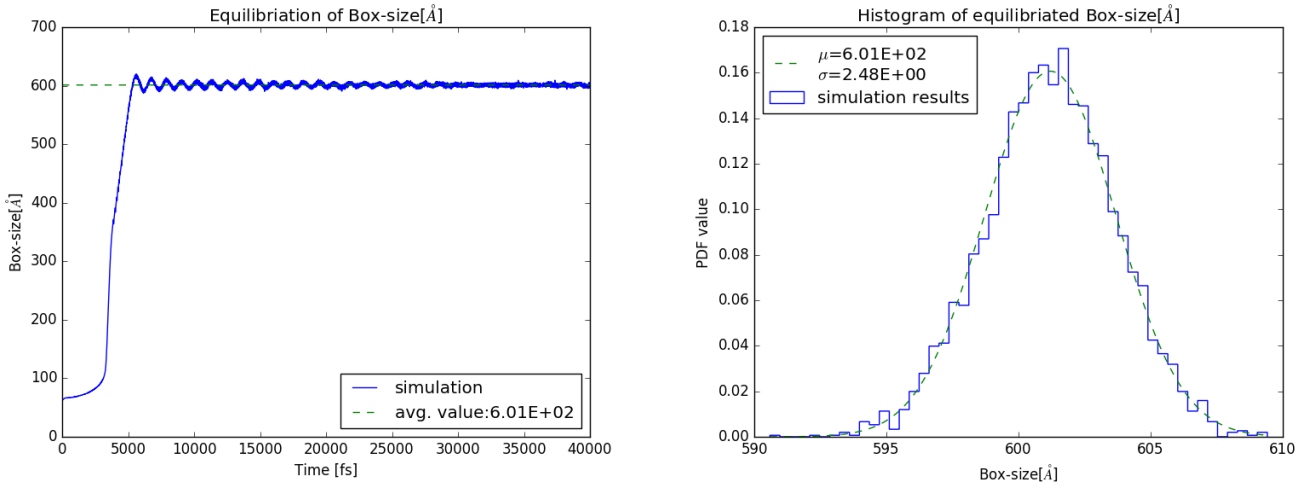
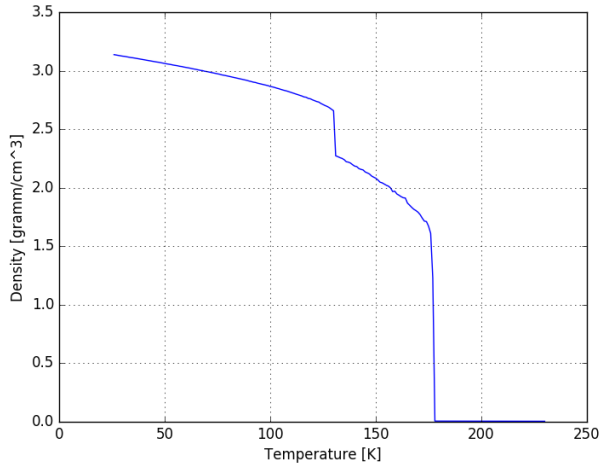
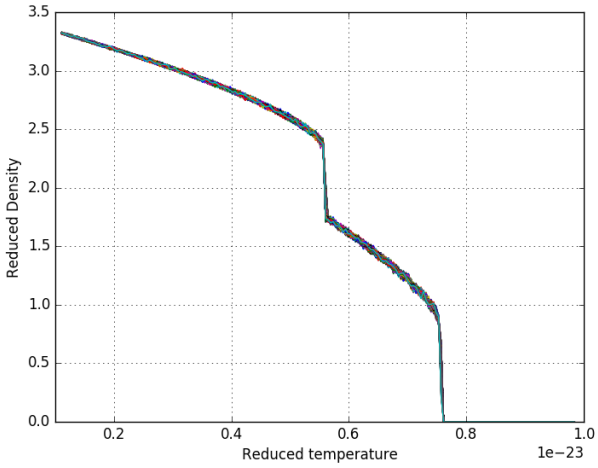
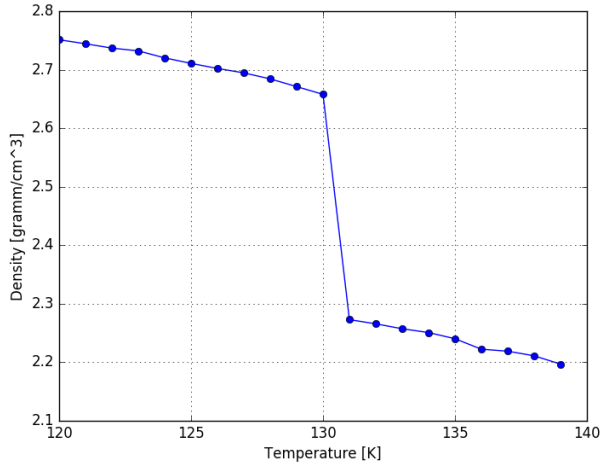
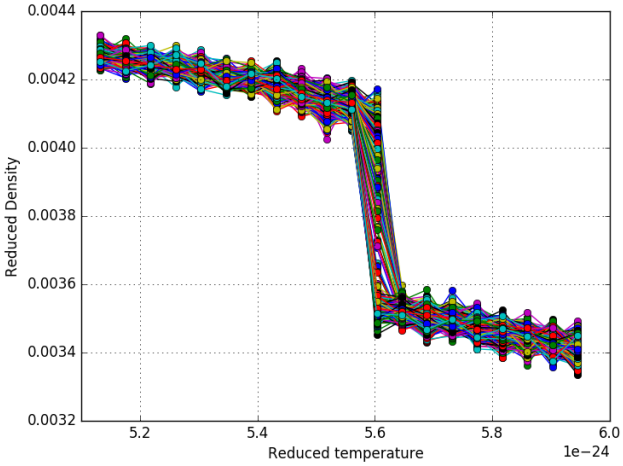


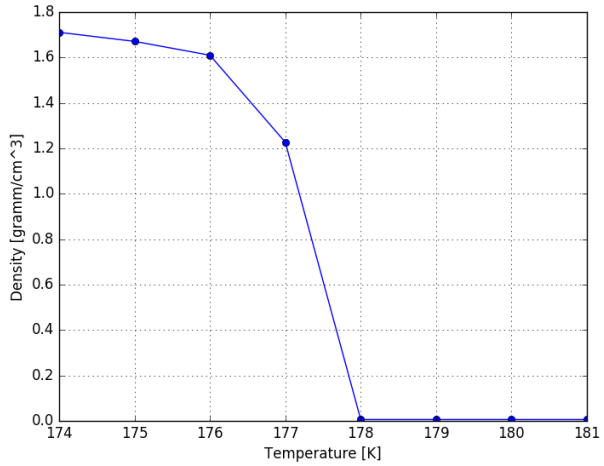

Figure 1.9: Estimation of the equilibrium Box length under the NPT emsemble. An equilibriated value of 601 $\mathring{A}$ is obtained with a standard deviation of 2.48$\mathring{A}$.



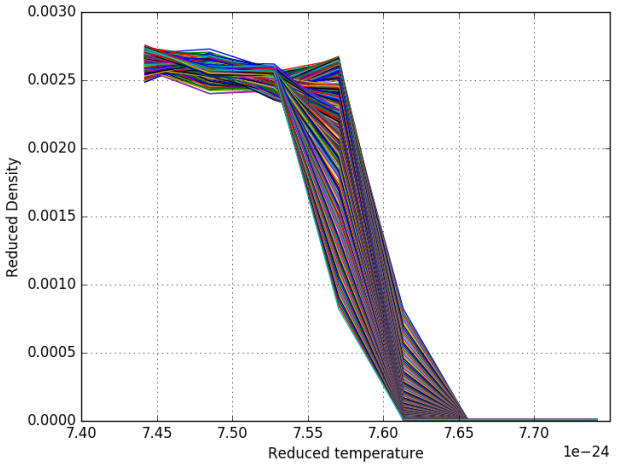




Figure 1.10: aa

# Chapter 2

# Two-dimensional tensile test

## 2.1 Equilibriation

### 2.1.1 2.1.1

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### 2.1.2 2.1.2

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## 2.2 Tensile test

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