Molecular Dynamics Exercise IV: Pressure and Temperature Coupling

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1 Task I

1.1 Introduction and Procedure

For the comparison of simulation results with experimental data, it is often necessary to keep both the temperature and the pressure stable. This can be done by introducing so-called thermostats and barostats into the simulation algorithm. These additions alter the trajectory such that the required quantity remains constant. Due to the finite system size it must however be noted that fluctuations are still allowed and necessary. The two barostats which will be investigated in this report are the Berendsen barostat and the Parrinello-Rahman barostat. The Berendsen barostat works by scaling the box as well as the atom coordinates by the matrix μ_{ij}[1]:

$$\mu_{ij} = \delta_{ij} - \frac{\kappa_{Tij}\Delta t}{\tau_P}(P(t) - P_0) \tag{1}$$

Here κ_T. Δt, τ_P are the isothermal compressibility, the integration time step and the coupling constant respectively. $P(t)$ is the instantaneous pressure and P_0 the target pressure. This has the effect that P(t) is relaxed towards P_0 as follows:

$$\frac{dP}{dt} = \frac{P_0 - P(t)}{\tau_P} \tag{2}$$

For the Parrinello-Rahman barostat the box vectors are also used to control the pressure. The box vectors $\vec{b}$ follow the following equation [1]:

$$\frac{d^2\mathbf{b}}{dt^2} = V\mathbf{W}^{-1}\mathbf{b}^{-1}(\mathbf{P}(t) - \mathbf{P}_0) \tag{3}$$

V is the box volume and $\mathbf{W}^{-1}$ is the inverse mass parameter which defines the strength of the coupling. It is defined by:

$$\mathbf{W}_{ij}^{-1} = \frac{4\pi^2\kappa_{Pij}}{3\tau_P^2 L} \tag{4}$$

The parameter L is the largest box matrix element. In both barostats the parameter τ_P controls the strength of the coupling. This is why in this report the influence of different values for τ_P will be investigated.

For the simulations a box of dimensions ($2.504\,\mathrm{nm} \times 2.504\,\mathrm{nm} \times 2.504\,\mathrm{nm}$) was filled with 523 water molecules of the TIP3P model. Then an energy minimization as well as a thermalization using the Berendsen Thermostat with $\tau_t = 0.1$ and 10000 steps of 0.002 ps were conducted.

Finally, a total of 12 simulations of 1000000 with $\Delta t = 0.002$ ps were run with the following values for τ_P and either the Berendsen weak coupling barostat or the Parrinello-Rahman barostat. For these simulations the temperature was held constant using a Nose-Hover-Chain thermostat with a coupling of $\tau_T = 0.5$.

1.2 Simulation Results

The simulation results of the 12 simulations are shown below in two tables containing the isothermal compressibilities and volume variances and 3 figures showing the development of the total energy, pressure and volume versus the simulation time.

	$\tau_P[ps^{-1}]$					
Barostat	0.05	0.1	0.5	1.0	5.0	10.0
Berendsen Weak Coupling	$5.62{\cdot}10^{-5}$	$4.38{\cdot}10^{-5}$	$2.13{\cdot}10^{-5}$	$1.21{\cdot}10^{-5}$	$4.08{\cdot}10^{-6}$	$1.88{\cdot}10^{-6}$
Parrinello-Rahman	$5.35{\cdot}10^{-5}$	$5.16{\cdot}10^{-3}$	$6.98{\cdot}10^{-5}$	$6.92{\cdot}10^{-5}$	$6.51{\cdot}10^{-5}$	$6.61{\cdot}10^{-5}$
	$\kappa_T[\text{bar}^{-1}]$					

Table 1: The isothermal compressibilities κ_T obtained for different barostats and τ_T values

	$\tau_P[ps^{-1}]$					
Barostat	0.05	0.1	0.5	1.0	5.0	10.0
Berendsen Weak Coupling	0.0391	0.0290	0.0127	0.0081	0.0025	0.0013
Parrinello-Rahman	0.0371	4.0204	0.0424	0.0407	0.0408	0.0418
	σ_V^2 [nm^6]					

Table 2: Volume variances σ_V^2 obtained for different barostats and τ_T values

Looking at the total energies (figure 1), one finds that the total energies of all trajectories apart from one simulation are almost equal and have similar standard deviation. The simulation with the Parrinello-Rahman barostat and $\tau_T = 0.1\,\text{ps}^{-1}$ does deviate slighly from the value of the other simulation and also shows a larger standard deviation. The pressures of all simulations show substantial deviations from the target pressure which was $P_0 = 1.0$ bar and additionally large deviations as can be see from the stadard deviations. Again the simulation with the Parrinello-Rahman barostat and $\tau_T = 0.1\,\text{ps}^{-1}$ seems to be particularly unstable. This might hint at a error in this simulation. The volume results (figure 3) show a more clear pattern. While for the Berendsen weak coupling method one can see that an increase in τ_P causes the fluctuations in the volume to drop, the volume fluctuations of the Paronelli-Rahman barostat stay more or less constant. These variances in the volume (also shown in table 1.2) determine largerly whether the resulting isothermal compressibility claculated according to the follwoing formula is correct [2].

$$\kappa_T = \frac{MSD(V)}{k_B T \langle V \rangle} \tag{5}$$

The results for κ_T for the 12 simulations are shown in table 1.2. As a direct effect of the decreasing fluctuations of V, the values of κ_T get far too low for the Berendsen coupling. For the Parrinello-Rahman barostat, the value of κ_T changes only from $5.35 \cdot 10^{-5}\,\text{bar}^{-1}$ to $6.92 \cdot 10^{-5}\,\text{bar}^{-1}$. Here the value from the troublesome simulation was already excluded.

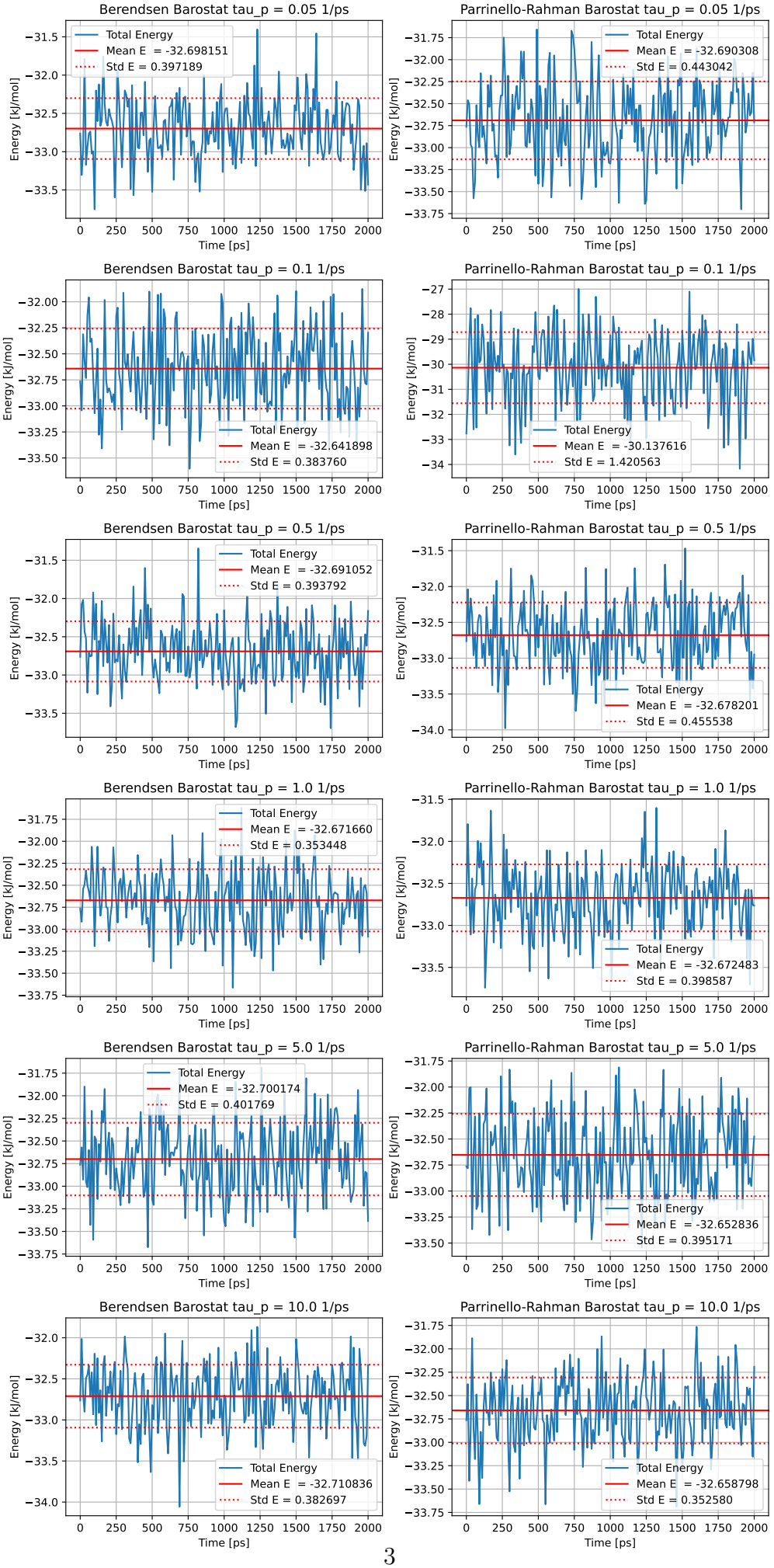

Figure 1: Total Energies of the different barostats and τ_T

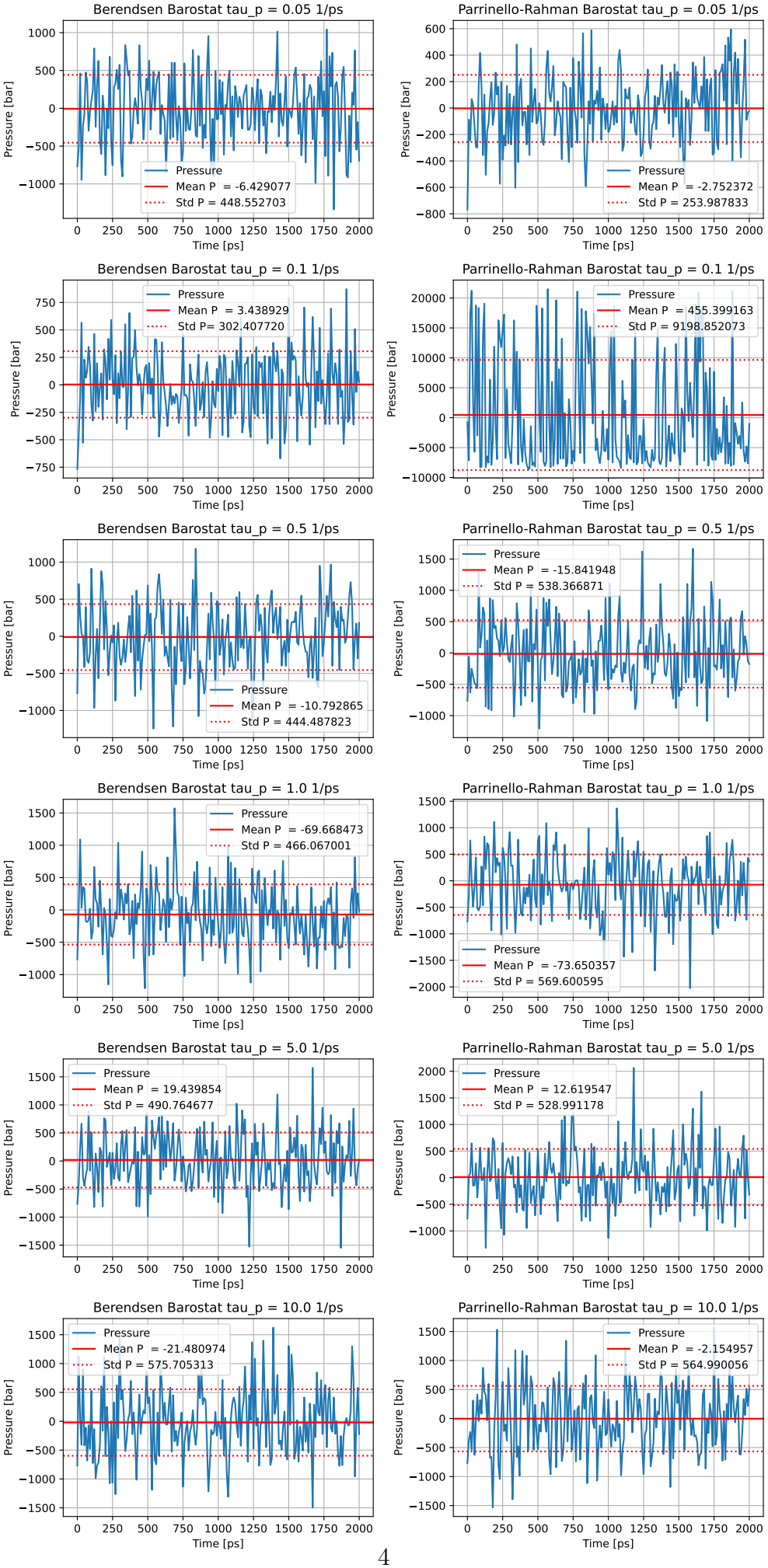

Figure 2: Pressure of the different barostats and τ_T

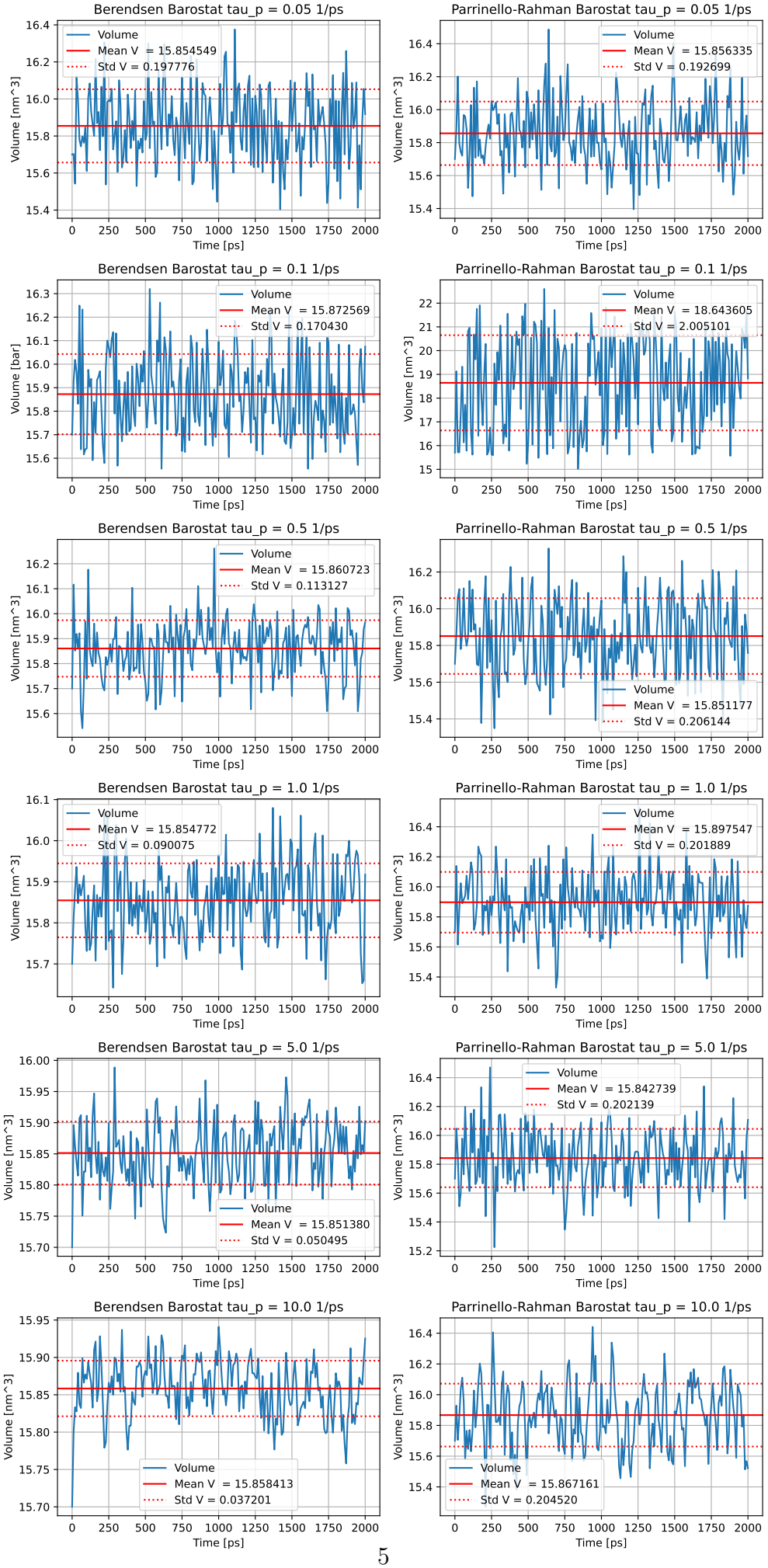

Figure 3: Volumes of the different barostats and τ_T

1.3 Discussion

From the data above it is clear that for the calculation of thermodynamic variables which depend on the physically correct treatment of volume fluctuations, one should favour the Parrinello-Rahman barostat. This result is analogous to the one from the last report. There the Berendsen weak coupling algorithm also showed weaknesses with respect to the fluctuations. In total the Parinello-Rahman barostat with a coupling of $\tau_P = 5.0\,\mathrm{ps}^{-1}$ showed the best result as it got closest to the literature value of the isothermal compressibility of TIP3P water model which is $6.3 \cdot 10^{-5}\,\mathrm{bar}^{-1}$[2].
It remains to access the the impact of τ_P in both methods. For the weak coupling scheme, one finds that the increase of τ_P leads to a decrease in the volume fluctuations. This is surprising in the sense, that the weak coupling should lead according to equation 2 to an exponential relaxation of a given volume perturbation. Hence, a smaller τ_P should correct the disturbances faster. However, it might be that this "quick" reaction causes the system to overshoot its target pressure. It could be that the slower correction using larger values for τ_P leads to less oscillations around P_0 and hence a lower variance in V.
For the Parrinello-Rahman, the variances are very similar for all values of τ_P. But one can spot a small tendency towards larger fluctuations for larger values of τ_P. This would make sense as according to equation 4, the increase in the τ_P should decrease the correction and allow for more fluctuations.

2 Influence of the Water Model on the isothermal compressibility κ_T

2.1 Introduction and Procedure

In this simulation the effect of using a different model for the water molecules was investigated. The models where the SPC/E and the TIP4P models. While the SPC/E model is a three site model, the TIP4P model is a four site model. For this a dummy atom is added close to the oxygen atom and in the middle between both OH-bonds.
Again 523 molecules of each model where placed in a box of dimensions ($2.504\,\mathrm{nm} \times 2.504\,\mathrm{nm} \times 2.504\,\mathrm{nm}$). Then an energy minimization, an thermal equilibration at 298.15 K and a pressure equlibration at 1.0 bar were run. Both the thermal and pressure equilibration used 10000 steps with $\Delta t = 0.002\,\mathrm{ps}$. The methods used were Berendsen weak coupling and no pressure coupling and Nose-Hoover-Chain thermostat and Parrinello-Rahman barostat. Lastly, the measuring run was conducted with 1000000 steps of the same time step.

2.2 Simulation Results and Discussion

The following isothermal compressibilities κ_P were obtained:

$$\kappa_T^{SPC/E} = 4.725 \cdot 10^{-5}\,\mathrm{bar}^{-1}$$

$$\kappa_T^{TIP4P} = 5.5513 \cdot 10^{-5}\,\mathrm{bar}^{-1}$$

The literature value for water at 298.15 K is $4.52 \cdot 10^{-5}\,\mathrm{bar}^{-1}$ [2]. Hence, the three site SPC/E model seems to be superior for this kind of calculation.

3 Simulation Behaviour for large τ_T values

3.1 Introduction and Procedure

The final part of this report investigates the effect of a large τ_T value on an NPT ensemble simulation. For this the same container as in the previous section was again filled with 523 water molecules of the SPC/E model and the energy minimized. As in the previous section, the system was thermally equilibrated before the data collection. For the data collection 200000 steps of $\Delta t = 0.002\,\mathrm{ps}$ were conducted with both temperature and pressure being controlled by the respective weak coupling method. For the first simulation, the values $\tau_T = 0.5\,\mathrm{ps}$ and $\tau_P = 2.0\,\mathrm{ps}^{-1}$ were taken, while for the second simulation they were changed to $\tau_T = 50.0\,\mathrm{ps}$ and $\tau_P = 0.1\,\mathrm{ps}^{-1}$.

3.2 Simulation Results

The simulation results can be found below. Looking at figure 4, one finds that the while the first simulation conserved its energy, the potential as well as the kinetic energy of the second simulation are decreasing over time. This seems to be especially the case for the potential energy. For the density, the second simulation shows stronger fluctuations, which means that also the volume variations were larger. Finally, while the first simulation just showed some fluctuation in the enthalpy H, the enthalpy of the second simulations decreases over the simulation time.

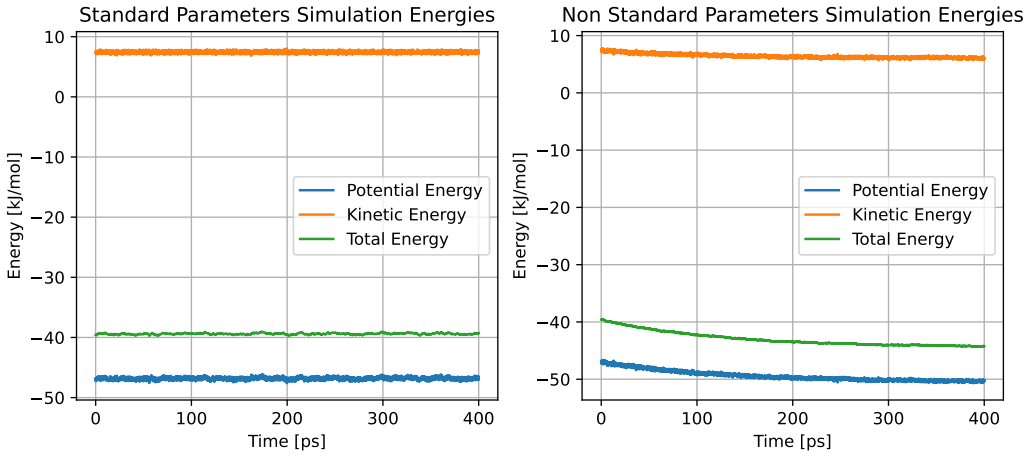

Figure 4: Energies for the first and second simulation.

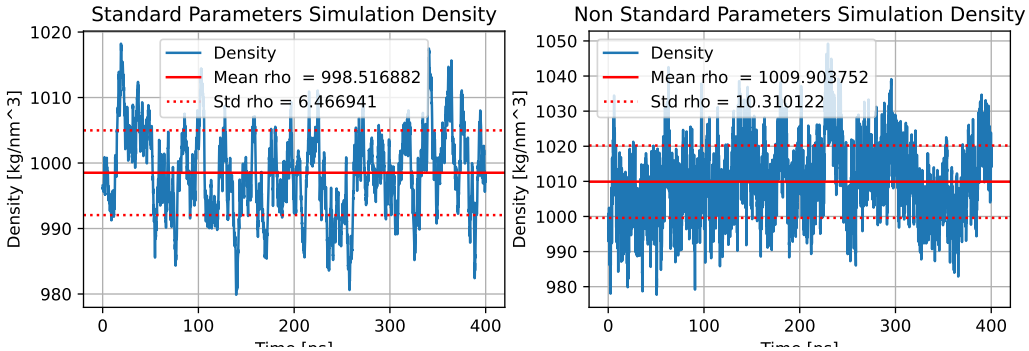

Figure 5: Density for the first and second simulation.

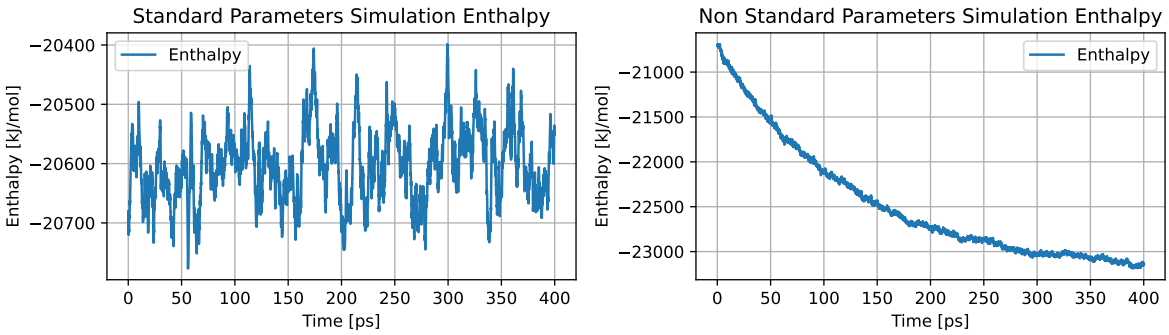

Figure 6: Enthalpy for the first and second simulation.

3.3 Discussion

The observation of the total energy as well as the enthalpy of the system decreasing is linked by the definition of the enthalpy as:

$$H = U + PV \tag{6}$$

From figure 5, one can deduce that the volume V of the system fluctuates, but stays of constant magnitude. The same is true for the pressure, which behaves similarly as the pressure from the first simulation. Hence, the decay only happens in the first term of equation 6.
With $\tau_T = 50.0\,\text{ps}$ and $\tau_P = 0.1\,\text{ps}^{-1}$ the temperature coupling is infrequent, while the pressure coupling is very strong. Also with $\tau_T = 50.0\,\text{ps}$ the scaling of the velocities due to the Berendsen thermostat are 100-times smaller than the scalings in the first simulation. Possibly, we hence simulated a NPE ensemble rather than an NPT ensemble. The shape for the curves might then just be the equlibration of the thermodynamic quantities. To test this, one could run an NPE ensemble to see which energy and enthalpy values would be obtained. If these values would be the same values as the limiting values of the second simulation this would support this hypothesis.

4 Bibliography

[1] GROMACS Reference Manual https://manual.gromacs.org/documentation/2019-rc1/reference-manual/algorithms/molecular-dynamics.html [accessed 18.05.2023; 18:31]

[2] Vollmers, Luis; Zacharias, Martin; Reif, Maria; Molecular Dynamics: Exercise 4 - Pressure and Temperature Coupling in MD Simulations; 2023