# Molecular Dynamics Exercise III: Temperature Coupling

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## 1 Flying Ice Cube Phenomenon

The first exercise was the visualization of a molecule's trajectory. This was again a polymer of 20 Carbon atoms. When visualizing the trajectory using vmd ("Visual Molecular Dynamics"), one could first observe regular molecular behaviour such as changes in chain's shape. At the later stages of the simulation this behaviour stopped and the polymer stayed rigid. Furthermore, it started to rotate as indicated in figure 1.
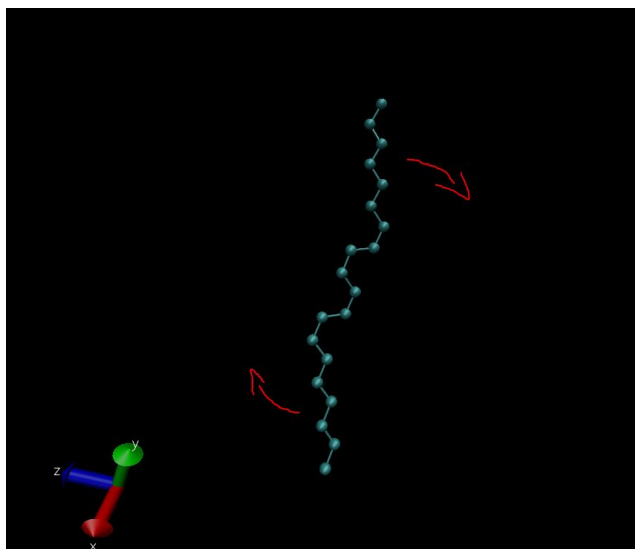


Figure 1: The rotating polymer chain.

The reason for this was found by searching for differences in the simulation in comparison to last weeks polymer simulations. The first difference is that for the given simulation the atoms were given an initial velocity as can be seen from the additional three numbers given to each atom in the .gro file. While this certainly affects the starting behaviour of the polymer, this should not lead to such unphysical behaviour. The next difference was found in the .mdp file, where a temperature coupling, namely the 'Berendsen Thermostat' had been added to the simulation. This ensures that the temperature of the simulation is maintained. However, this thermostat is also responsible for the rotations of the molecule [1]. It turns out that velocity rescaling algorithms such as the Berendsen Thermostat cause a violation of the equipartition theorem by reinforcing low frequency modes such as overall rotation or translation over higher frequency modes. Due to this the molecule remains rigid and keeps rotating.

# 2 SPC and TIP3P Water Models with different temperature coupling algorithms

## 2.1 Introduction

In this task two water models were simulated with three different temperature coupling algorithms. The models are the SPC model and the TIP3P model. Both of these are rigid three site models. They differ however in the OH bond length, HOH bond angle and the partial charge associated with each atom [2].

| Model | d(OH) [nm] | $\theta(HOH)[\circ]$ | partial charge O | partial charge H |
|-------|-----------|----------------------|------------------|------------------|
| SPC   | 10.0      | 109.47               | -0.82            | +0.41            |
| TIP3P | 95.72     | 104.52               | -0.834           | +0.417           |

As can be seen from the table, the SPC model uses slighly longer bond distance and a slighly larger angle between the bonds. Furthermore, the partial charges are smaller. Before the simulation for each of the model could be started the energy of 523 water molecules had to be minimized. Additionally, for each thermostat a equilibration of 10000 steps with a timestep of dt = 0.002 ps was carried out. Finally, the simulation with 500000 steps and the same time step was run.

The three thermostats used for simulation were: none (NVE Ensemble), Berendsen Thermostat and the Nose-Hoover-Chain Thermostat. For reference, one .mdp file, which sets the conditions for the simulation has been included in the report (figure 2 and 3).

```
title                   = small water box    ; Title

; Run parameters
integrator              = md-vv    ; Velocity Verlet Algorithm for Time Integration
nsteps                  = 500000   ; number of steps for integration
dt                      = 0.002    : time step for above integrator in ps

; Output control
nstxout                 = 500      ; Step interval between recording coordinates to output file
nstvout                 = 500      ; Step interval between recording velocities to output file
nstenergy               = 500      ; Step interval between recording energies to log file
nstlog                  = 500      ; Step interval between redording energies to energy file

; Bond parameters
continuation            = yes      ; sim does not reset shells and applies constraints at begin of simulation
constraint_algorithm    = lincs    ; Linear constraint solver
constraints             = h-bonds  ; Bonds with H atoms are used as constraints (rigid bonds?)
lincs_iter              = 1        ; steps to correct for rotational lengthening in the lincs algorithm
lincs_order             = 4        ; Order of the constraint coupling matrix

; Nonbonded settings
cutoff-scheme           = Verlet   ; Algorithm used for neighbour searching
ns_type                 = grid     ; Use of a grid to contstruct a neighbour list
nstlist                 = 10       ; Step interval in between renewing neighbour list
rcoulomb                = 1.0      ; Distance of the Coulomb Potential Cut-off
rvdw                    = 1.0      ; Distance of the Lennart-Jones Potential Cut-off
DispCorr                = EnerPres ; no long range correction for vdW forces
```

Figure 2: Part 1 of the .mdp file for the MD run of the NHC thermostat.

## 2.2 Simulation Results

The results from the simulations can be found in figures 4 and 5. In figure 4, the kinetic, potential and total energy of each simulation are plotted against the simulation time. Figure 5 on the other hand, shows the temperature of the simulations. Looking at the energies, one finds that for all configurations the energy is of roughly similar size. In general, it seems that

```
; Electrostatics
coulombtype          = PME        ; Fast Smooth Particle Ewald Electrostatics (Fast Version of classical Ewald sum)
pme_order            = 4          ; Interpolation Order for above algorithm
fourierspacing       = 0.16       ; Grid spacing for Fast Fourier Transform used in above algorithm

; Temperature coupling
tcoupl               = Nose-Hoover ; Nose-Hoover extended ensemble is used for temperature coupling
tc-grps              = system     ; I assume there is only one group coupled to the heat bath (whole system)?

tau_t                = 0.5        ; Time constant used for the coupling in ps
ref_t                = 300        ; temperture of the coupled heat bath
nh-chain-length      = 10         ; number of chained Nose-Hoover Thermostatsß

; Pressure coupling is off
pcoupl               = no         ; no pressure coupling = fixed box size

; Periodic boundary conditions
pbc                  = xyz        ; Periodic Boundary Conditions are used in all directions

; Velocity generation
gen_vel              = no         ; no generation of velocities at the start of the simulation
gen_temp             = 300        ; in case of generation velocities would come from Maxwell distribution at 300K
gen_seed             = -1         ; seed for random generation of velocities, -1 means a pseudo random seed is used
```

Figure 3: Part 2 of the .mdp file for the MD run of the NHC thermostat.

the TIP3P model has slighly higher energies for each thermostat. Furthermore, one critical property of the NVE Ensemble (no thermostat employed) can be seen from the graph: The value of the total energy does not seem to fluctuate at all. This should be the case as in this ensemble the total energy is fixed. Furthermore, it also seems that the energies in the Nose-Hoover-Chain fluctuate more. When one looks at the temperature graphs, one can see the effect of the thermostats employed. The NVE ensemble's temperature fluctuates about 227 K (SPC) and 217 K (TIP3P), which is far away from the 300 K Maxwell curve the starting velocities were drawn from. In contrast both thermostats keep the temperature at about 300 K. Again, the fluctuations of the NHC thermostat are larger than the one of the Berendsen thermostat. Finally, also the specific heat $C_V$ was calculated for each simulation. The literature value for water at this temperature is 74.5 $\frac{J}{mol\,K}$ (at 300 K and 1 bar)[3].

| Model | NVE Ensemble | Nose-Hoover-Chain Thermostat | Berendsen Thermostat |
|-------|--------------|------------------------------|----------------------|
| SPC   | 1.2770       | 76.8098                      | 16.2883              |
| TIP3P | 0.0032       | 70.1181                      | 14.4046              |

One finds that the NHC Thermostat yields by far the best values for the specific heat. Here the SPC model seems to be slighly better than the TIP3P model. The Berendsen Thermostat and the NVE Ensemble both yield values far from the literature value. In case of the NVE ensemble, the values from SPC and TIP3P even differ by 3 orders of magnitude. These results can be explained by looking at the formula for the calculation of $C_V$[3]:

$$C_V = \frac{(RMSD(E_{tot} \cdot 1000)^2 \cdot N_{mol}}{RT^2}$$

Here $N_{mol}$ is the number of molecules, R is the ideal gas constant and $RMSD(E_{tot})$ are the fluctuation of the total energy. As pointed out above the NVE ensemble has only very small fluctuations. Hence, the resulting specific heat is far too low. Also, the Berendsen Algorithm seems to partly suppress energy fluctuations, resulting in a too low specific heat. Only the NHC, which allows for fairly large energy fluctuation in the system, gives a good estimate for $C_V$.
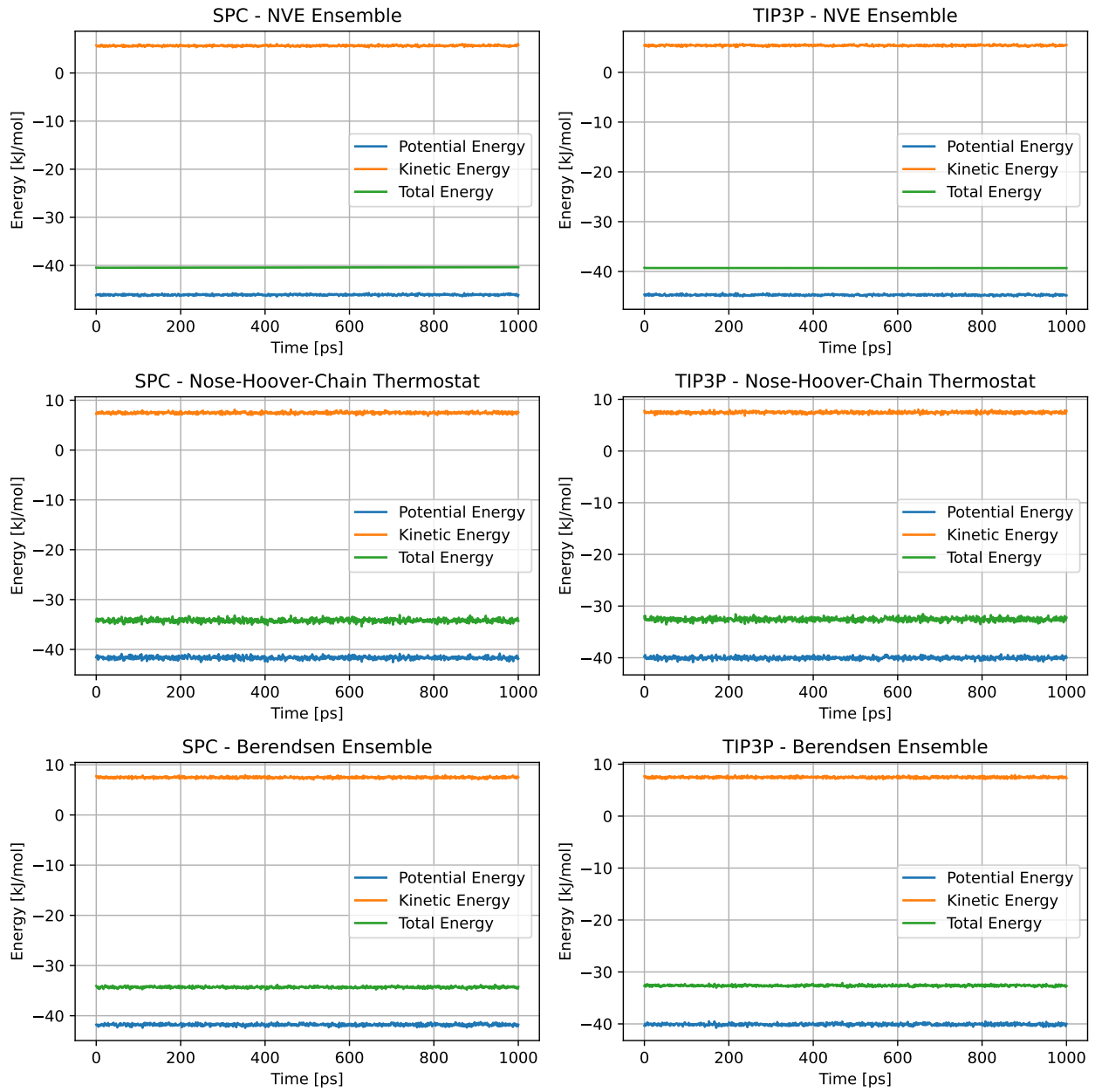
Figure 4: Kinetic, Potential and Total Energy of the water molecules plotted against the simulation time.
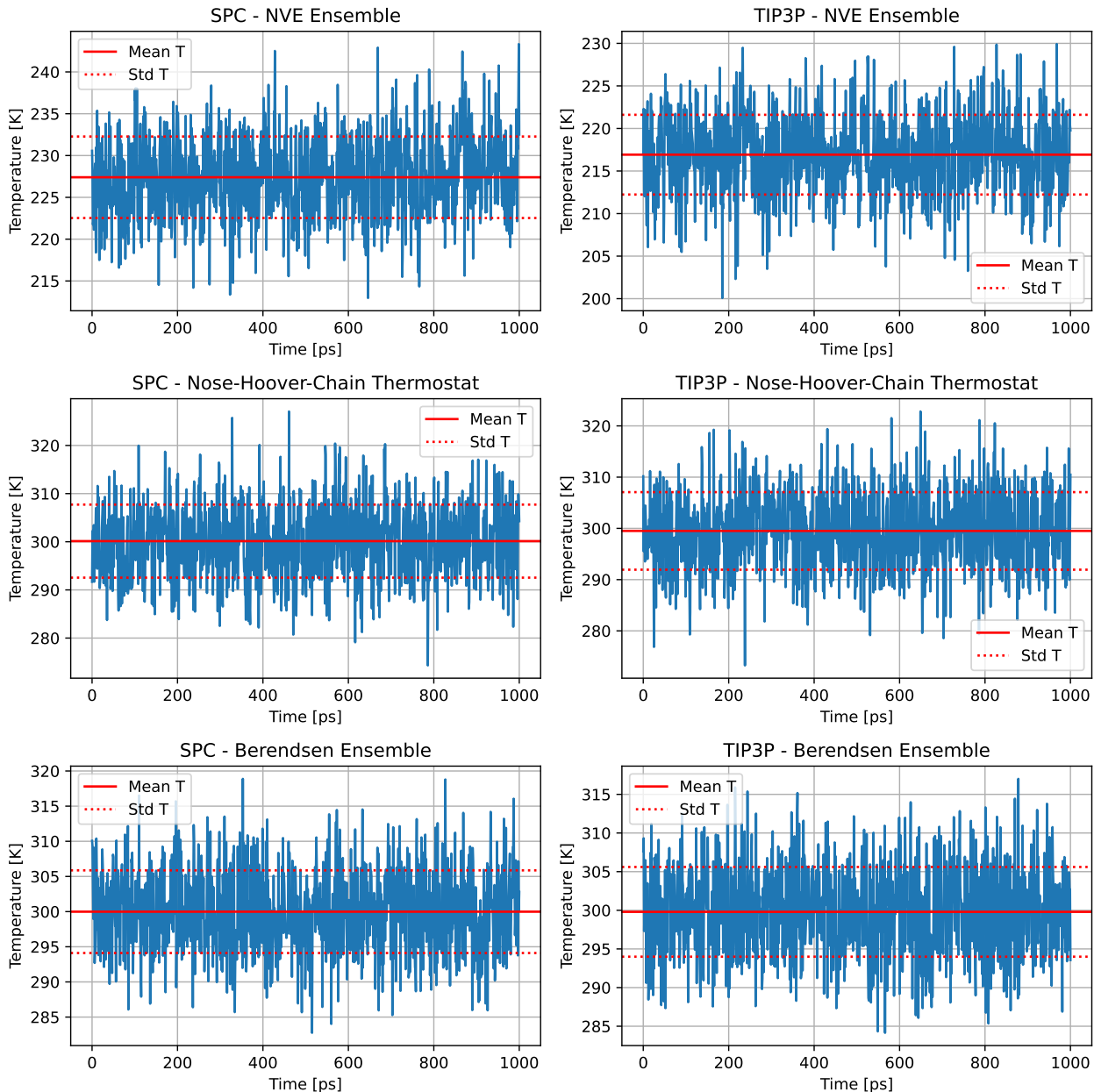
Figure 5: Temperature of the simulation plotted against simulation time.

# 3 Conclusion

In conclusion it was found that the NVE ensemble should not be used for simulations with set temperature or specific heat calculations. The Berendsen Thermostat can keep a desired temperature by construction, but leads to unphysical behaviour such as the "Flying Ice Cube" and performs poorly for specific heat calculations. Hence, out of the given 3 methods, the Nose-Hoover-Chain Thermostat stands out as the most reliable method.

# 4 Bibliography

[1] Efrem Braun, Seyed Mohamad Moosavi, and Berend Smit; Anomalous Effects of Velocity Rescaling Algorithms: The Flying Ice Cube Effect Revisited; Journal of Chemical Theory and Computation 2018 14 (10), 5262-5272 DOI: 10.1021/acs.jctc.8b00446

[2] Wikipedia Page 'Water Models': https://en.wikipedia.org/wiki/Watermodel [accessed 11.05.2023; 19:58]

[3] Vollmers, Luis; Zacharias, Martin; Reif, Maria; Molecular Dynamics: Exercise 3 - Thermodynamic Coupling; 2023