

Molecular Dynamics Exercise III: Temperature Coupling

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1 Abstract

In this exercise the native molecular dynamics ensemble, being the microcanonical ensemble, is changed to the canonical ensemble by the insertion of a thermostat. With a constant temperature, the observations of the simulations are closer to the experiment as a microcanonical ensemble is often not of interest. To highlight the importance of choosing a good thermostatting algorithm, a common issue with the weak-coupling algorithm known as "flying ice cube" phenomenon is shown for a polymer chain. Furthermore, the heat capacity of a system of water molecules, being an observable dependant on the correct modelling of the temperature fluctuations is calculated for no thermostat, the weak-coupling thermostat and the Nose-Hoover thermostat. These simulations are conducted for the two three site water model TIP3P and SPC. All simulations were conducted using the MD software GROMACS.

2 Flying Ice Cube Phenomenon

The first exercise asked to visualize a given trajectory of a polymer of 20 Carbon atoms. This was conveniently done using the vmd software ("Visual Molecular Dynamics") and for the first part of the trajectory one could 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 more rigid. Additionally, the polymer started to rotate as indicated in figure 1. The reason

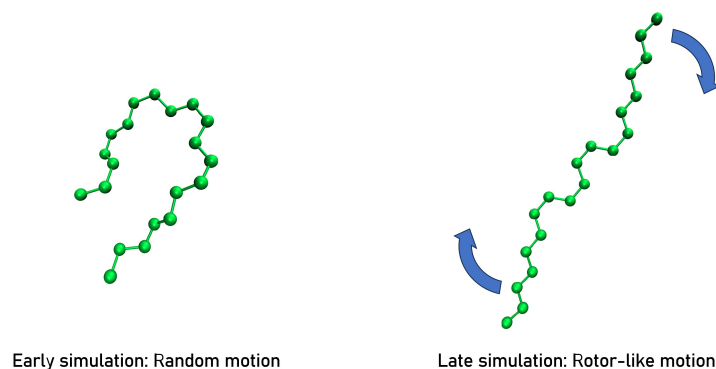


Figure 1: The rotating polymer chain.

for this clearly unphysical behaviour was found by searching for differences in the provided simulation files in comparison to the previous exercise's polymer simulations. A first difference

ca be found in the .gro-file, which contains additional three numbers for each atom. These are the initial velocities which are provided. While this certainly affects the initial motion of the polymer, this should not lead to any unphysical behaviour. The next difference was found in the simulation’s .mdp-file. Here a temperature coupling, namely the ‘Berendsen Thermostat’, had been added to the simulation parameters. This thermostat ensures that the temperature of the simulation is maintained. However, as can be found by literature review, 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 becomes rigid and starts rotating.

3 SPC and TIP3P Water Models with different temperature coupling algorithms

3.1 Simulation Setup

In the simulations of the water system, two models are used, the SPC model and the TIP3P model. Both of these are rigid three site models. The models differ in their representation of the quantum mechanical reality to classical parameters. Hence, they differ in the O-H bond length, H-O-H bond angle and the partial charge associated with each atom [2]. The relevant parameters are summarized in the table below.

Model	d(OH) [nm]	$\theta(\text{HOH}) [^\circ]$	q^O	q^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 slightly longer bond distance and a slightly larger angle between the bonds. Furthermore, the partial charges are smaller. Before the simulation for each of the model was started, the energy of the 523 water molecules was minimized. Additionally, for each thermostat an equilibration run with 10000 steps with a time step of $\Delta t = 0.002$ ps was carried out. Finally, the actual simulation with 500000 steps and the same time step was conducted.

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

3.2 Simulation Results

The results from the simulations can be found in figures 4 and 5. In figure 4, the kinetic, potential and total energies 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. Overall, it seems that the TIP3P model has slightly higher energies for each thermostat. Furthermore, one inherent 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 is not surprising as in this ensemble the total energy is fixed. Furthermore, one observes 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

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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

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

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; 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 Thermostatsβ

; 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

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Figure 3: Part 2 of the .mdp file for the MD run of the Nose-Hoover-Chain thermostat.

(SPC) and 217 K (TIP3P), which is far away from the 300 K Maxwell-Boltzmann distribution 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 ones of the Berendsen thermostat. Finally, also the specific heat C_V was calculated for each simulation. The literature value for water at 300 K and 1 bar is $74.5 \frac{\text{J}}{\text{mol K}}$ [3].

Model	NVE Ensemble	NHC Thermostat	WC Thermostat
SPC	1.2770	76.8098	16.2883
TIP3P	0.0032	70.1181	14.4046

Looking at the results, one finds that the NHC Thermostat yields by far the best values for the specific heat. Additionally, the SPC model seems to be perform slightly 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 calculated with the 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]:

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

Here N_{mol} is the number of molecules, R is the ideal gas constant and $\text{RMSD}(E_{tot})$ are the fluctuation of the total energy. As pointed out above the NVE ensemble has only very small fluctuations. Hence, the resulting specific heat values are 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 estimates for C_V .

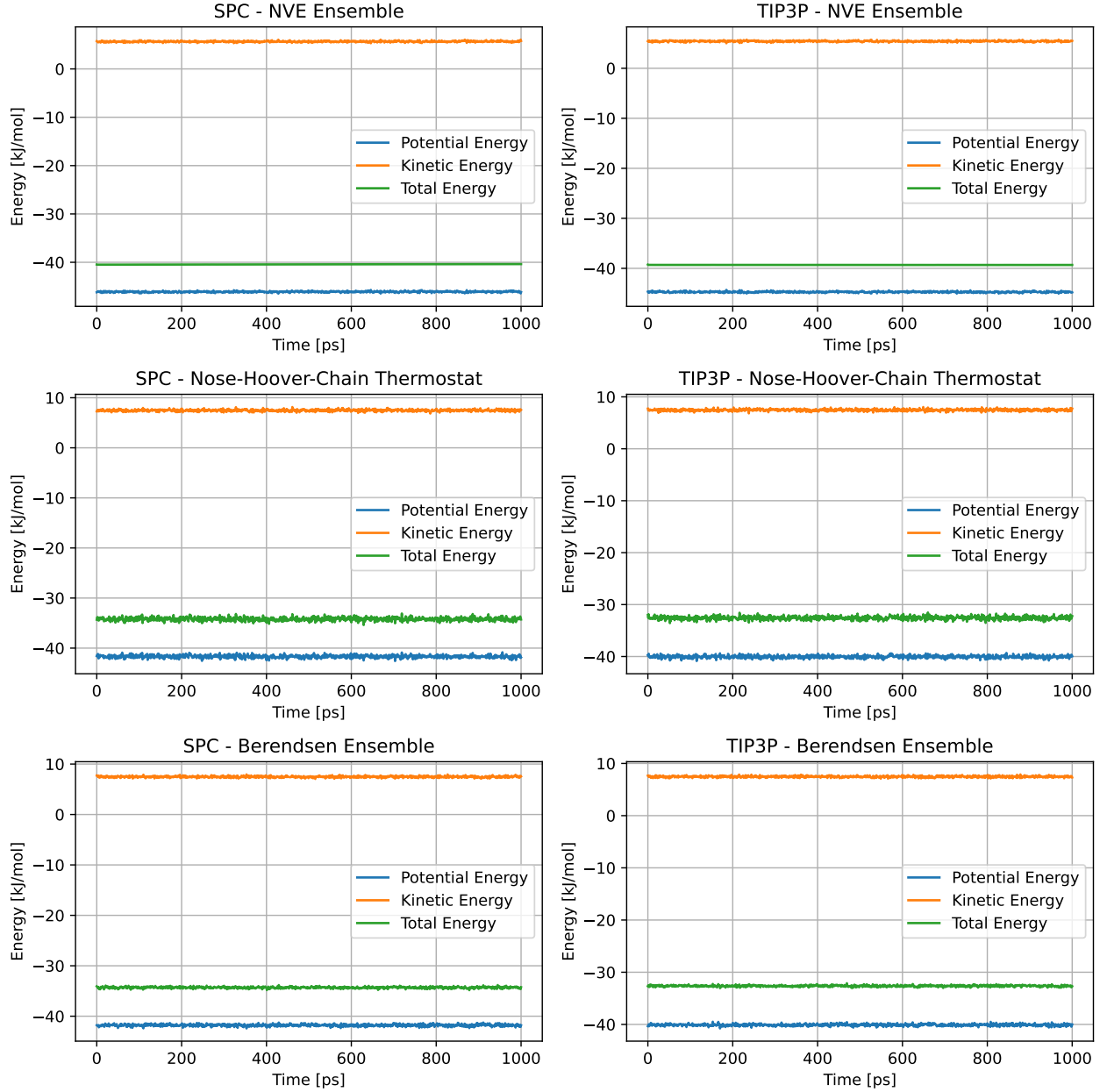


Figure 4: Kinetic, potential and total energy of the water molecules plotted against the simulation time. Each row presents the results from one thermostat.

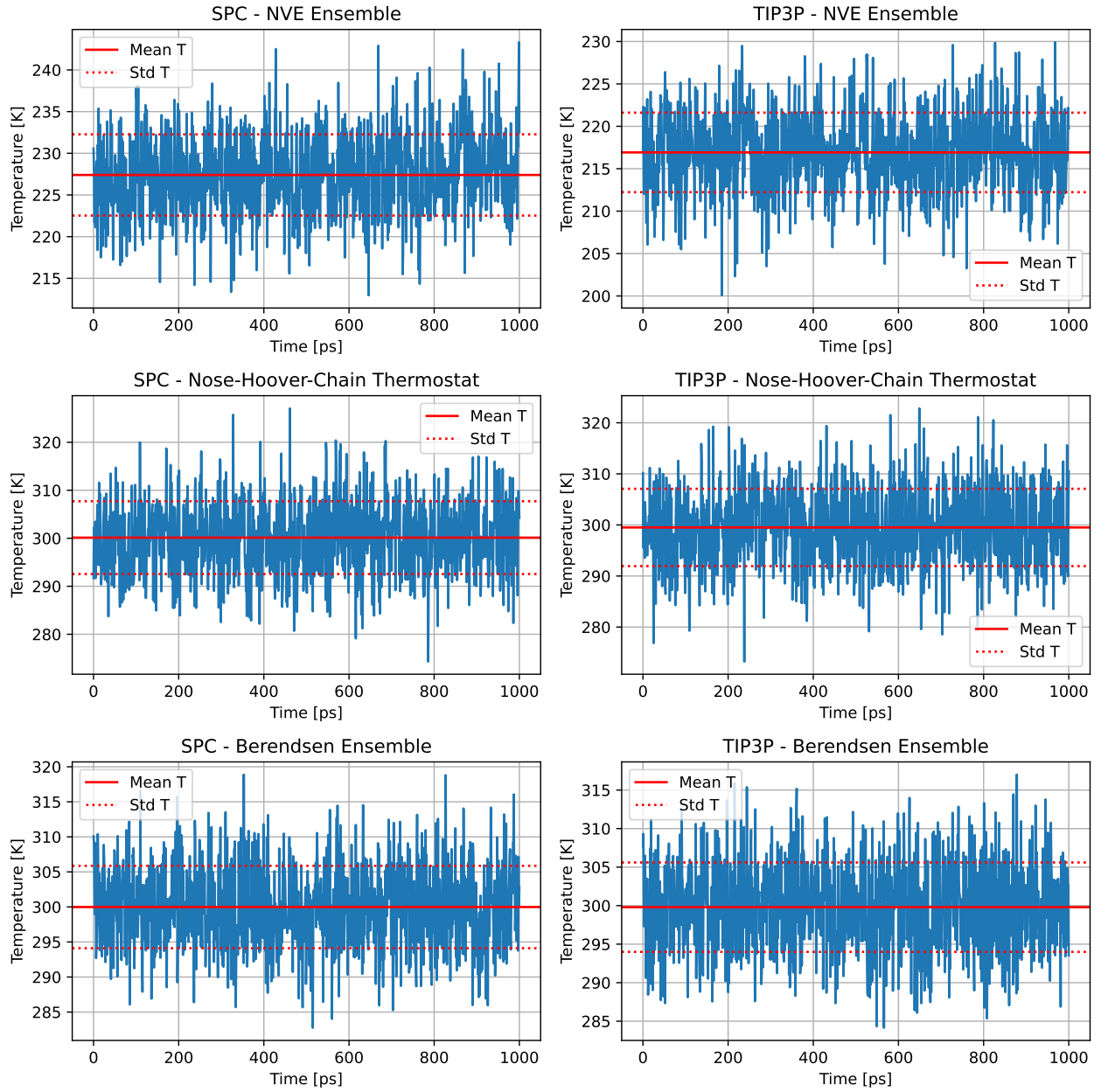


Figure 5: Temperature of the simulation plotted against simulation time.

4 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. This is due to an incorrect modelling of the heat fluctuations which do not agree with the fluctuations in a canonical ensemble. Hence, out of the given 3 methods, the Nose-Hoover-Chain Thermostat stands out as the most reliable method. A simulation controlled by the Nose-Hoover thermostat can be shown to reproduce a canonical ensemble in the limit of a large particle number.

5 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] [2] Wikipedia Page 'Water Models': <https://en.wikipedia.org/wiki/Watermodel> [accessed 11.05.2023; 19:58]
- [3] [3] Vollmers, Luis; Zacharias, Martin; Reif, Maria; Molecular Dynamics: Exercise 3 - Thermodynamic Coupling; 2023