Exercise_4 Molecular Dynamics Simulation

Andrea Scaioli

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1 Introduction

This exercise involves simulating a system in which P and T are coupled. Both T and P are controlled in these simulations via a thermostat and a barostat to generate the NPT ensemble.
There are two main barostats for controlling pressure: the Berendsen and the Parrinello-Rahman.

1. The Berendsen barostat is a pressure coupling algorithm used in molecular dynamics to weakly couple the system to an external pressure bath. It adjusts the simulation box volume to bring the system pressure closer to a target pressure — but does so in a way that does not reproduce the correct pressure fluctuations of the NPT ensemble.
   At each MD step, the Berendsen barostat rescales the simulation box and the atomic coordinates to reduce the difference between the instantaneous pressure P and the reference pressure P_{ref}. The rescaling follows this differential equation:

$$\frac{dV}{dt} = \frac{1}{\tau_P} \left(P_{ref} - P \right) V$$

   Although this is easy to implement and suitable for equilibration, fluctuations are suppressed and the NPT ensemble is not generated.

2. The Parrinello-Rahman barostat is a widely used method for pressure coupling in molecular dynamics simulations, especially when accurate sampling of the NPT ensemble is required.
   It extends the Berendsen method by not only adjusting the system volume, but also treating the simulation box as a dynamical variable, subject to equations of motion. This allows the system to exhibit realistic volume and pressure fluctuations, making it appropriate for production runs. Parrinello-Rahman adds fictitious dynamics to the simulation cell vectors, allowing the shape and size of the box to evolve according to the pressure tensor:

$$\frac{d^2 h}{dt^2} \propto \left(P - P_{ref} \right) h$$

   The evolution is governed by a "mass-like" parameter, indirectly controlled via the relaxation time τ_P, which sets how fast the box adapts to pressure differences.

2 Methods

In this exercise 12 simulations have been performed to measure σ_V^2, k_T, E_{tot}, V and P as time series. First of all a water box has been created. To do so we have defined a box volume, added the particle and the potential interaction between them.
Obtained the desired `.top` file, before running the simulation is necessary to perform a energy minimization and an NVT, NPT equilibration.
For each simulations, that differs for the T_P parameter and for the water model used, we have computed σ_V^2 and k_τ. The times series obtained are plotted in Fig. 1.
σ_V^2 is the standard deviation o the volume while $k_\tau = \frac{\sigma_V^2}{K_B \langle T \rangle \langle V \rangle}$. For each of the two 3-point water models,

SPC and TIP3P, has been computed 6 different simulation where $\tau_P = 0.05, 0.1, 0.5, 1, 5, 10$.
From the results of the previous simulation is possible to do a further step in order to obtain a more realistic simulation. To do so other water models are introduced: the SPCE and the TIP4P.

- The SPC/E water model ("Simple Point Charge Extended") is a commonly used rigid 3-site model for simulating water molecules in molecular dynamics. It is a refinement of the original SPC model, designed to better reproduce experimental thermodynamic and structural properties.

- Unlike 3-point models (like SPC or TIP3P), TIP4P adds a fourth site (M) to represent the location of the negative charge (electron cloud). This site is not on the oxygen atom, but slightly shifted along the bisector of the H–O–H angle.

From the previous simulation the best values for k_T are 0.05, 0.1, 0.5. From this starting point we have run other three simulation for each water model and compared the results obtained from the literature values. In the end two different parametrization of τ_P and τ_T has been studied. From two similar `.mdp` files is obtained a standard and a non standard simulation. With the `vimdiff` commands is clear that the differences between the two files is that in the standard one $\tau_P = 2.00$ and $\tau_T = 0.5$ while in the other non standard one $\tau_P = 0.1$ and $\tau_T = 50$.

3 Results

From the first twelve simulations, as shown in table 1, the best τ_P's values, in order to obtain the correct Isothermal compessibility $k_T = 6.3 \times 10^{-5} [bar^{-1}]$, are $\tau_P = 0.05, 0.1, 0.5$.
As can be noticed from the Figure 1, the Berendsen thermostat reveals two different problems:

- there is no energy fluctuation, so the quantities are not sampled accordingly to the ensemble.

- for $\tau_P = 0.05$ the algorithm fails to simulate the system properly, in fact, the k_τ is too small.

Model	$\mathbf{T_p}$	σ_V	k_T
Berendsen	0.05	0.0002	3.6761e-11
PR	0.05	0.1954	5.8619e-05
Berendsen	0.10	0.1618	4.0017e-05
PR	0.10	0.1622	4.0403e-05
Berendsen	0.50	0.1121	1.9195e-05
PR	0.50	0.2378	8.6415e-05
Berendsen	1.00	0.0887	1.2062e-05
PR	1.00	0.2528	9.7506e-05
Berendsen	5.00	0.5000	3.8155e-04
PR	5.00	0.5000	3.8155e-04
Berendsen	10.0	0.0333	1.6954e-06
PR	10.0	0.5552	4.7131e-04

Table 1: Comparison of σ_V and k_T for Berendsen and Parrinello-Rahman barostats at various pressure coupling times T_p.
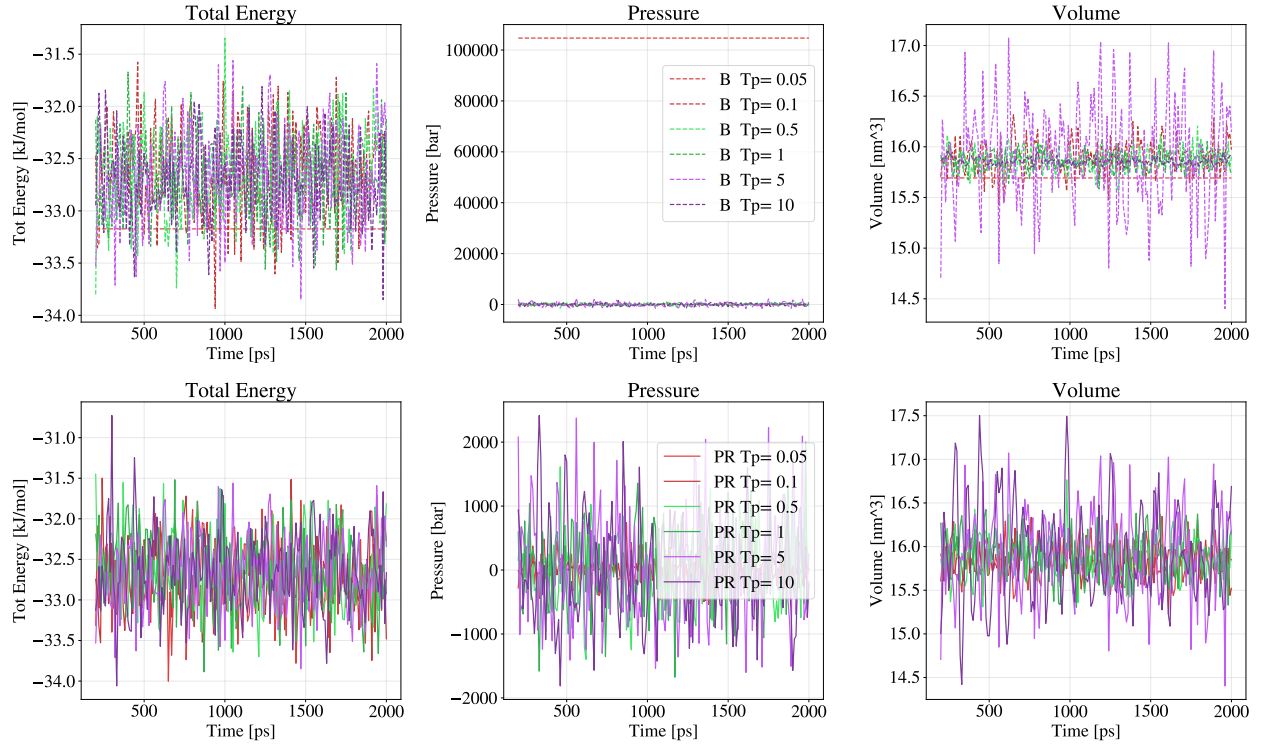
Figure 1: In this figure are shown Total Energy, Pressure and Volume time series. All the quantities show fluctuations excepts for the Berendsen with the smaller τ_P value that present a too big pressure too. For the other values the time series are similar.

The Isothermal compressibility k_T and standard deviation of the volume σ_V^2 obtained from the simulations with the more sophisticated water models, SPC/E and TIP4P , are shown in table 2. The best values is obtained for $T_P = 0.1$ with the TIP4P water models that is very close to the literature value $k_T = 4.52 \times 10^-5$.

Model	$\mathbf{T_p}$	$\boldsymbol{\sigma_V}$	$\boldsymbol{k_T}$
SPC/E	0.05	0.1826	5.1954e-05
TIP4P	0.05	0.1829	5.1764e-05
SPC/E	0.10	0.1449	3.2648e-05
TIP4P	0.10	0.1598	3.9396e-05
SPC/E	0.50	0.1818	5.1323e-05
TIP4P	0.50	0.2165	7.2148e-05
SPC/E	1.00	0.2234	7.7478e-05
TIP4P	1.00	0.2595	1.0407e-04
SPC/E	2.00	0.2873	1.2832e-04
TIP4P	2.00	0.3209	1.5729e-04

Table 2: Comparison of σ_V and k_T for SPC/E and TIP4P water models at various pressure coupling times T_p.
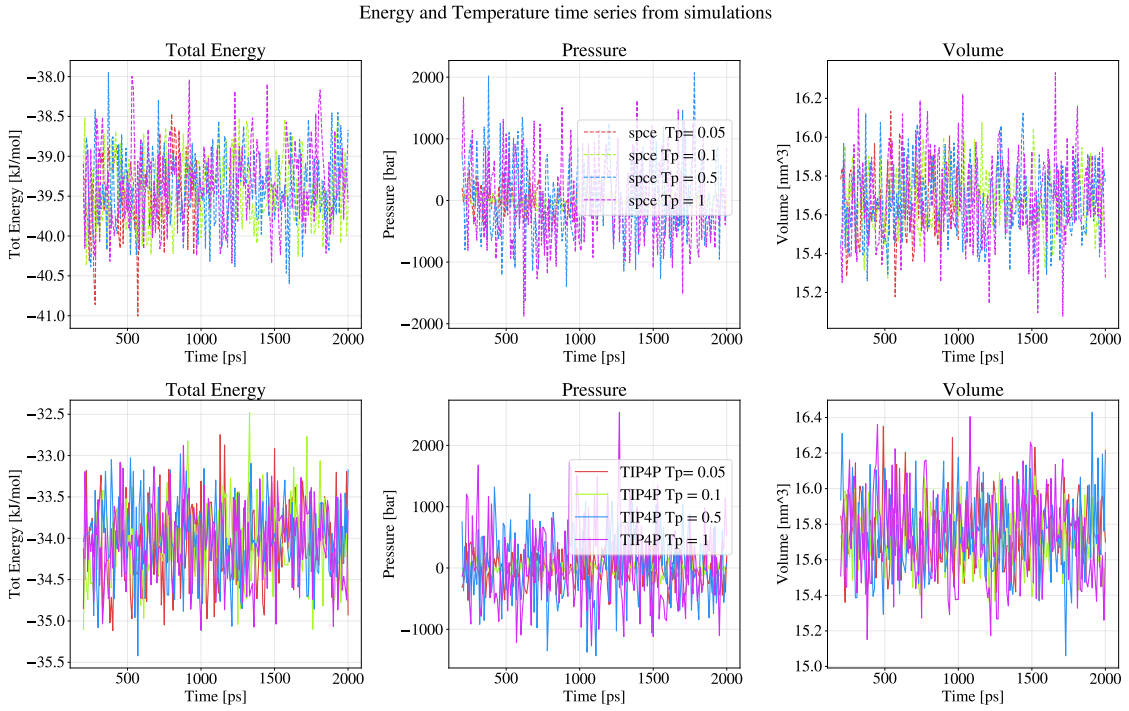

Figure 2: both the water models simulated with Nose-Hoover and Parrinello-Rahman thermostat and barostat perform good simulations.

For the comparison of the standard and non standard `.mdp` file it's clear that the convergence of the energy with the non standard file is very slow compared with the standard one. To verify how τ_T and τ_P affect the convergence we have modified the standard file changing only one between τ_T and τ_P for each test and observing wich quantities varied.

As shown in figure 3 an high value of τ_P causes a slow convergence of the density while an high value of τ_T causes a slow convergence of the energies and of the Enthalpy.
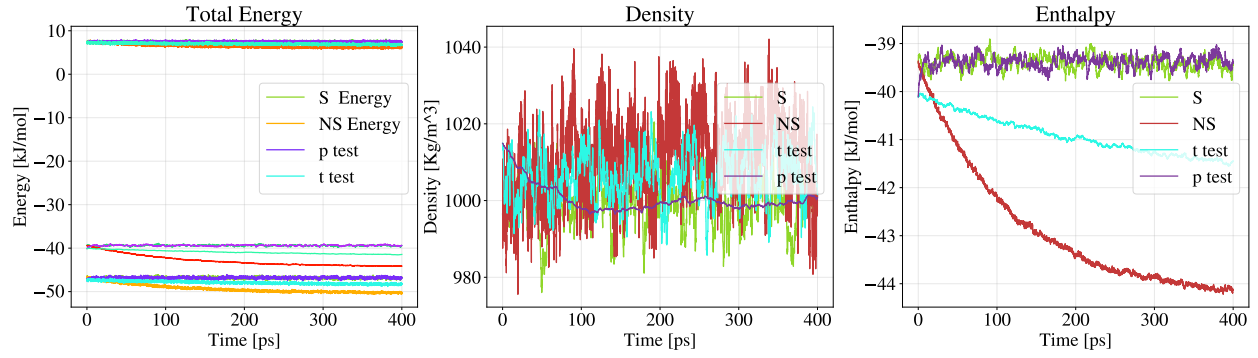
Figure 3: in this plot is shown how standard and non standard values of τ_P and τ_T affects the quantities convergence. In the p test $\tau_p = 100$, while in the t test $\tau_T = 50$