



Investigation of Water Models in GROMACS

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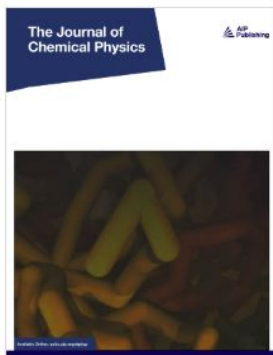
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Motivation

Our research aims to reproduce experimental data using classical molecular dynamics simulations of water molecules. Building on the widely-cited TIP4P/Ice model (Abascal et al., 2005), we investigate aqueous systems under extreme conditions. These simulations will provide crucial insights into physical-chemical phenomena that may facilitate the formation of complex organic molecules essential for life, advancing our understanding of molecular behavior in extreme environments.

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A potential model for the study of ices and amorphous water: TIP4P/Ice

J. L. F. Abascal; E. Sanz; R. García Fernández; C. Vega



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The ability of several water models to predict the properties of ices is discussed. The emphasis is put on the results for the densities and the coexistence curves between the different ice forms. It is concluded that none of the most commonly used rigid models is satisfactory. A new model specifically designed to cope with solid-phase properties is proposed. The parameters have been obtained by fitting the equation of state and selected points of the melting lines and of the



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Figure 3: Excerpt from a website featuring an article on water models.



Introduction *Standard Models(TIP3P, TIP4P,TIP4P-Ice)*

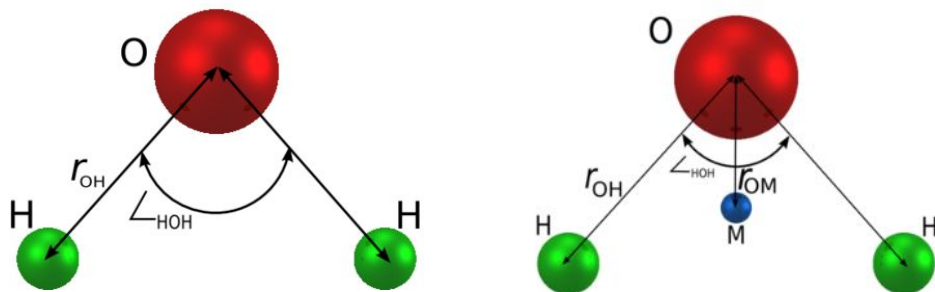


Figure 1. Water molecules representations. **Oxygen** (large red sphere), **hydrogens** (green spheres), and an additional **virtual site** (blue sphere, denoted as M in TIP4P models).

Table 1 (Right). TIP4P, TIP4P/Ice, TIP3P Water model parameters. Bond lengths(r_X), angles, partial charges($q(X)$)...

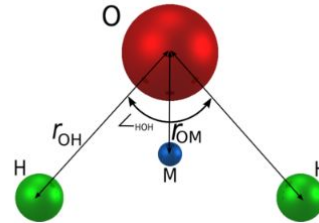
Parameter	TIP4P	TIP4P/Ice	TIP3P
$r_{OH}(\text{\AA})$	0.9572	0.9572	0.9572
$\angle HOH (^{\circ})$	104.52	104.52	104.52
$\sigma (\text{\AA})$	3.154	3.1668	3.1506
$\epsilon/k (K)$	78.0	106.1	≈ 70.5
$q(O) (e)$	0	0	-0.834
$q(H) (e)$	+0.52	+0.589	+0.417
$q(M) (e)$	-1.04	-1.1794	0 (not used)
$r_{OM} (\text{\AA})$	0.15	0.1577	0 (no M-site)

Potential Equation (TIP3P, TIP4P, TIP4P-Ice)

$$U(\vec{R}) = \underbrace{\sum_{\text{bonds}} k_i^{\text{bond}} (r_i - r_0)^2}_{U_{\text{bond}}} + \underbrace{\sum_{\text{angles}} k_i^{\text{angle}} (\theta_i - \theta_0)^2}_{U_{\text{angle}}} +$$

$$\underbrace{\sum_{\text{dihedrals}} k_i^{\text{dih}} [1 + \cos(n_i \phi_i + \delta_i)]}_{U_{\text{dihedral}}} +$$

$$\underbrace{\sum_i \sum_{j \neq i} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_i \sum_{j \neq i} \frac{q_i q_j}{\epsilon r_{ij}}}_{U_{\text{nonbond}}}$$



Equation terms:

- (1) 1. **Bond oscillations** (about equilibrium bond lengths)
2. **Angle oscillations** (between three atoms at equilibrium angles)
- (2) 3. **Dihedral (torsional) rotations** (of four atoms around a central bond)
4. **Non-bonded interactions** (Lennard-Jones and Coulombic interactions)

Introduction

Figure 2. Molecular Simulation Ensembles: **NVT (Canonical)** keeps particles, volume, and temperature fixed, while **NPT (isothermal–isobaric)** controls particles, pressure, and temperature. **Microcanonical (NVE)** maintains particles, volume, and energy constant. Selecting the right ensemble is essential for accurately studying molecular behaviors and thermodynamics.

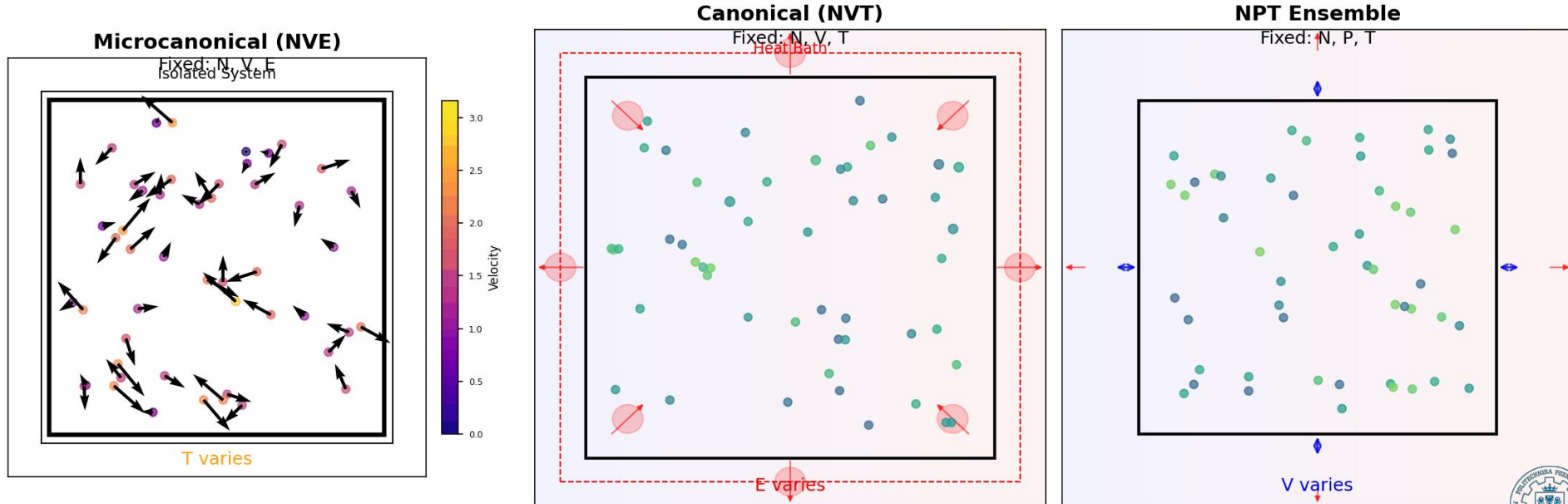


Figure 2: Visualization of Simulation Ensembles

Method

1. TIP4P and TIP4P/Ice was used as force field parameters, with rigid four-site representation and virtual charge near the oxygen to ensure accurate hydrogen-bond geometry and realistic phase behavior at cold temperatures.
2. System topology (molecules, force-field parameters, interactions) was generated using standard GROMACS tools.
3. Positioned **5500 of water** molecules in a periodic simulation cubic box of size **5.47 nm³** to create bulk-like conditions without exposed surfaces.
4. **Performed energy minimization (EM)** to relieve any initial steric clashes.
5. **Equilibrated the system** (using *NVT* and/or *NPT* ensembles) prior to production simulations in the *NVT*.
6. Simulation was run for 5 nanoseconds period.

Results *Energy plots*

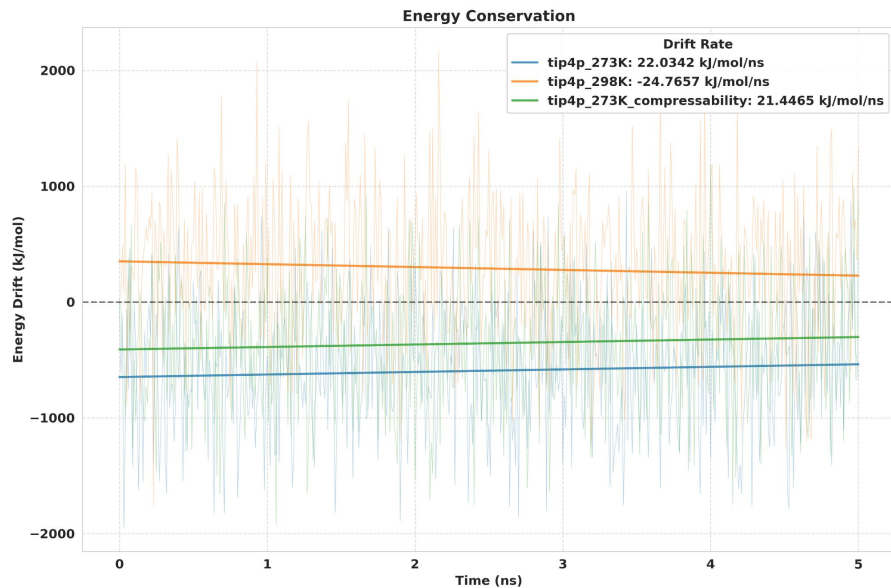


Figure 3: Energy Conservation Comparison

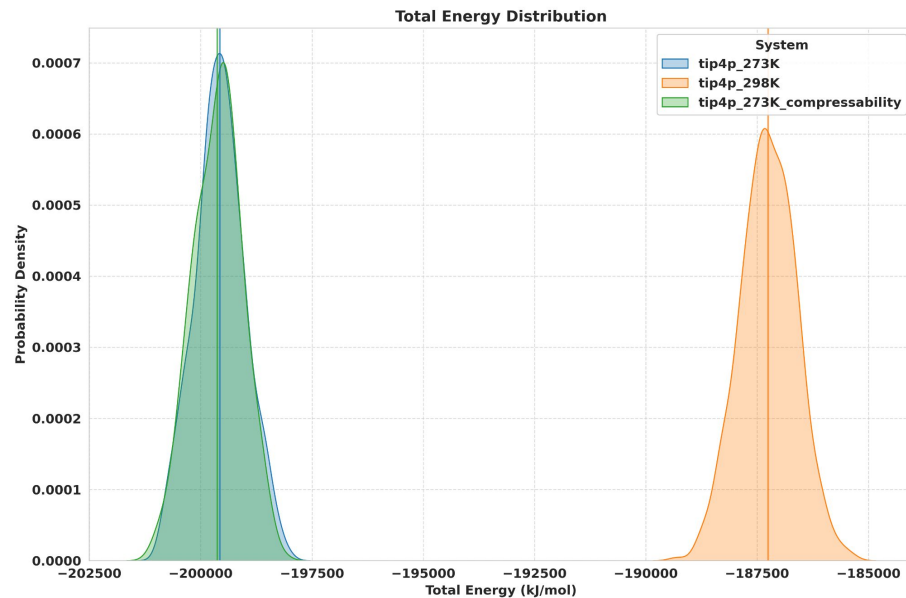


Figure 4: Total Energy Distribution Comparison

Results *Temperature/Pressure plots*

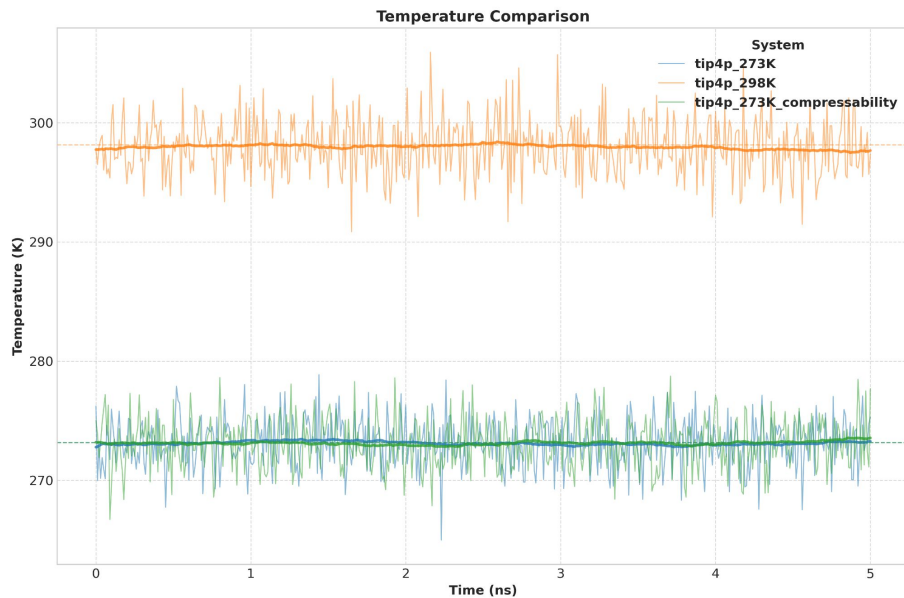


Figure 5: Temperature Comparison

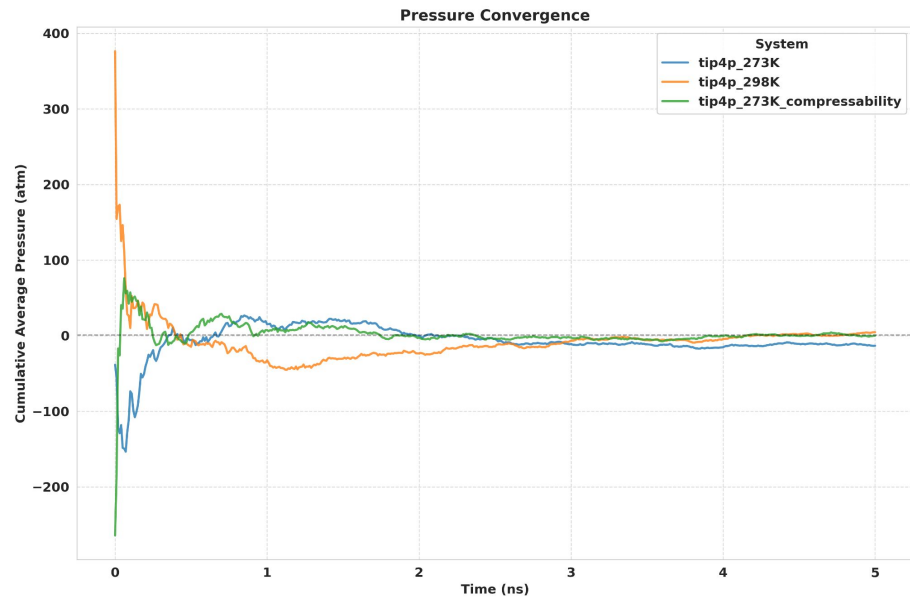


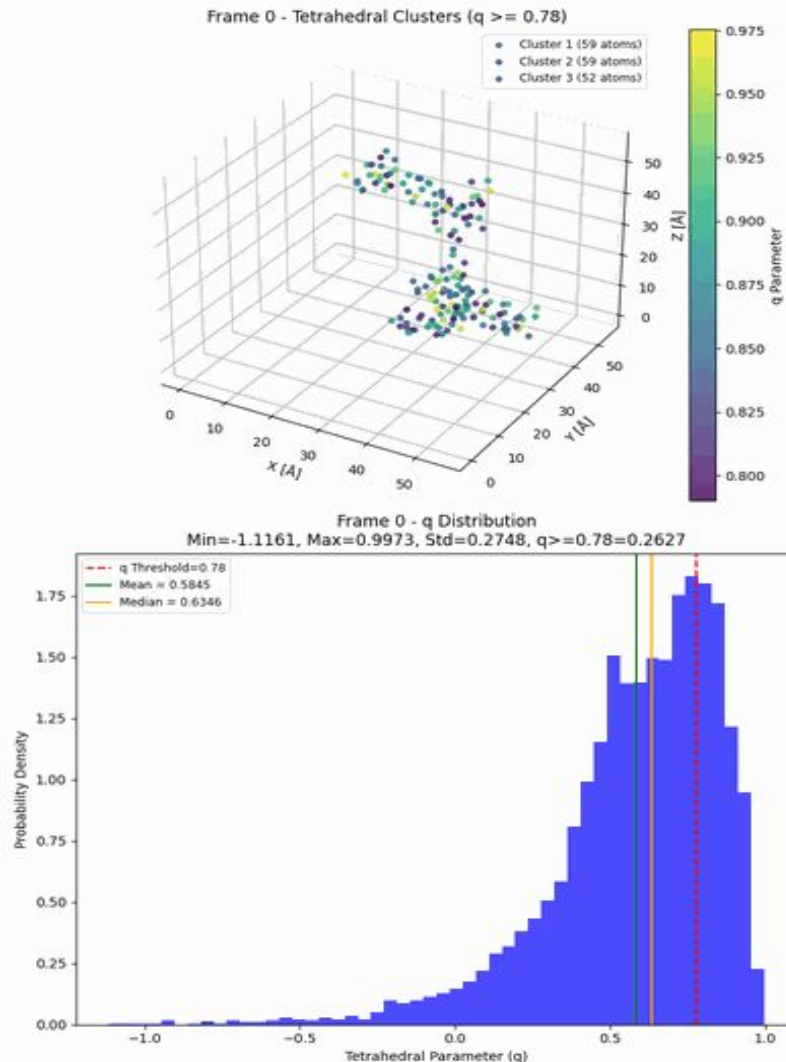
Figure 6: Pressure Convergence Comparison

Discussion

While Abscal's work tested differences in models and phase diagrams, our study focuses on existing analytical tools to evaluate key thermodynamic parameters and RMSD to assess structural changes under varying conditions.

An ad-hoc script was build, using tetrahedral parameters, RDF functions, and hydrogen bonding analysis for frame-by-frame evaluation. However, these computationally expensive methods still lack precision for identifying atomic clusters.

Figure 9: Visualization of the water clusters during frames of MD with my script.



Discussion

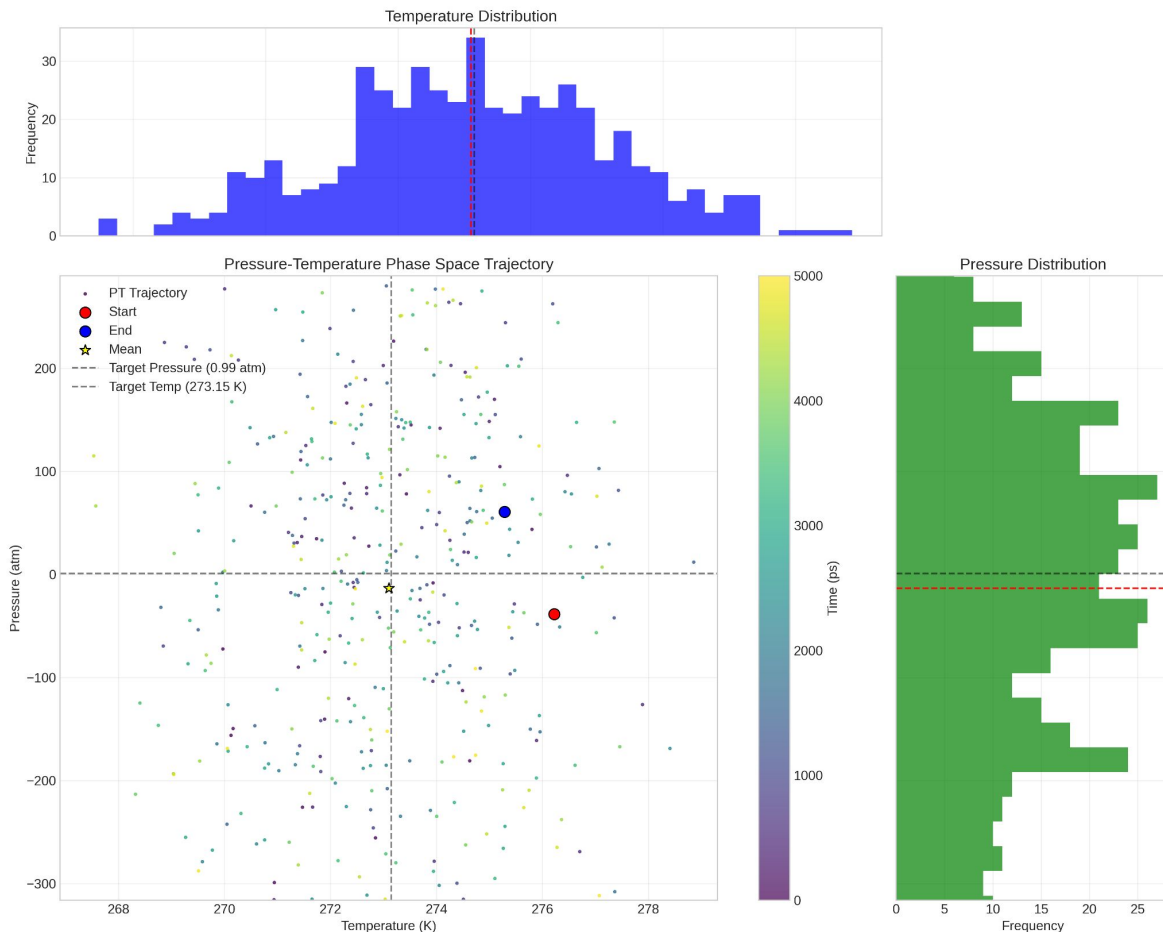


Figure 10. *Simulation Phase Space.* Topology plane of temperature and pressure as degrees of freedom are enough to determine the phase of the system. Microstates visited.

Discussion

The energy drift observed in the simulations can be attributed to inherent limitations in the numerical integration methods used in molecular dynamics. Despite simulating an isolated system where energy should theoretically remain constant, we observe gradual energy changes over time (~5-6 Kcal/mol/ns or 21-25 kJ/mol/ns in our TIP4P water models). These drifts occur because numerical integrators introduce small errors in each time step that accumulate over the course of the simulation. The moderate drift rates observed in our systems (both positive and negative) are actually within acceptable ranges for MD simulations and indicate good overall stability of the integration scheme.

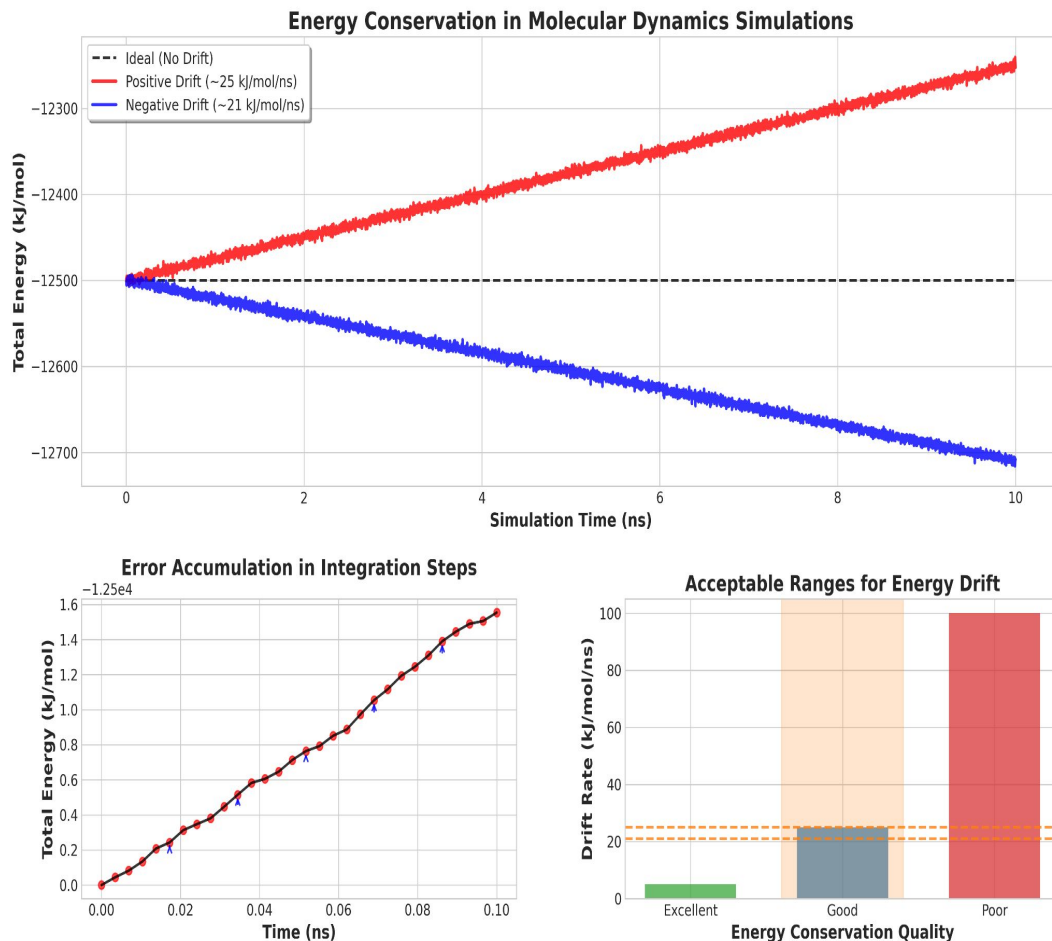


Figure 12: Energy drift in the NVT ensemble

Thank you