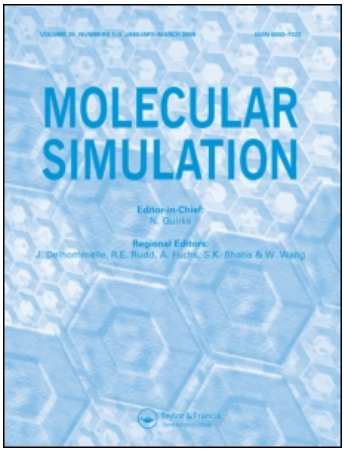

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Temperature and ion concentration effects on the viscosity of Price-Brooks' TIP3P-PME water model

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Temperature and ion concentration effects on the viscosity of Price–Brooks' TIP3P-PME water model

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The viscosity of the Price–Brooks modified TIP3P water model is investigated for different temperatures and NaCl concentrations using molecular dynamics with long-range electrostatic interactions. The viscosity has been determined from the equilibrium fluctuations of the pressure tensor by the Green–Kubo formalism. At 298 K in salt-free conditions, the resulting viscosity is higher than the value reported by other authors for TIP3P water. The viscosity is shown to decrease with temperature and increase with salt concentration, such as in real water, but with an absolute value always about half of the experimental value in analogous conditions. This difference must be attributed to the simplicity and the empirical nature of the TIP3P model, and also to the properties chosen for the original parameterisation, which did not include viscosity. At the considered levels of salinity, the effect of temperature is predominant.

Keywords: molecular dynamics; Green–Kubo; viscosity; TIP3P; water model

1. Introduction

The existence of a large number of water models implicitly underlines the difficulty to capture all water properties with only one parameterisation [1]. The usage of a model is therefore limited to the set of properties that it can reproduce within an acceptable accuracy level. Simple models, such as the three-point TIP3P and its subsequent modifications, have encountered success, because they are computationally less demanding than more sophisticated ones, such as the TIP4P or TIP5P [1]. Further interest in the TIP3P arose from the fact that the widely used CHARMM force field for biomolecular simulations was parameterised using TIP3P, and it was unclear whether the solvation properties would be preserved when using a different water model.

Only recently, a study performed by Nutt and Smith [2] using the CHARMM potential has shown that the behaviour of biomolecules in solution is fairly similar when other water models are adopted: this applies to several versions of TIP3P, TIP4P and to a lesser extent to TIP5P. Despite this, TIP3P still remains the most widely adopted water model. One of the reasons is that not all molecular dynamics (MD) packages implement the numerical optimisations that allow to compensate most of the additional computational cost of TIP4P and TIP5P [14].

Well-known limitations of the TIP3P model include its poor structure, high self-diffusion coefficient [1] and low viscosity [3]. A few years ago Price and Brooks proposed a modified set of parameters which improves the structural properties of the model and its suitability in simulations that use periodic boundary conditions (PBCs) and long-range electrostatic solvers such as Ewald summation and particle-mesh Ewald (PME) [4].

As underlined by Feller and co-workers, the viscosity of TIP3P water is greatly affected by the method used to compute electrostatic interactions. For example, with long-range electrostatics, the dynamic viscosity at 293 K was 0.35 ± 0.02 MPa, much lower than the value of 0.62 ± 0.04 MPa obtained with pairwise Coulombic potentials with a cut-off [12].

The Price–Brooks model (named TIP3P-PME) slightly modifies the charges on both oxygen and hydrogen atoms, and the Lennard-Jones (LJ) parameters for oxygen. Furthermore, it sets the LJ parameters to zero for the hydrogen atoms (introduced in the CHARMM version of TIP3P in order to improve some bulk properties such as density and heat of vaporisation), thus being closer, in this, to the original TIP3P by Price and Brooks [4] and Jorgensen et al. [13].

The choice of LJ parameters for Na^+ and Cl^- ions is more problematic. The lack of high-quality experimental data, or even any data, for the structural properties of NaCl in aqueous solution is reflected in the disagreement between the parameterisations adopted by the available force fields. A previous analysis by Patra and Karttunen [16] has shown that, in simulations of aqueous saline solutions, thermodynamic properties are in general well reproduced, whereas the structural predictions of different widely used force fields (such as AMBER, CHARMM and GROMACS) are not consistent. Therefore, the choice is still somewhat arbitrary. In this work, we have used the

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Table 1. Atomic charges q and LJ parameters ϵ and σ for TIP3P and PB TIP3P-PME water models.

Parameter	Units	TIP3P	TIP3P-PME
q_O	e	−0.8340	−0.8300
q_H	e	0.4170	0.4150
ϵ_{OO}	kcal/mol	0.1521	0.1020
σ_{OO}	Å	3.1507	3.1880
ϵ_{OH}	kcal/mol	0.0460	0.0000
σ_{OH}	Å	0.4000	0.0000
ϵ_{HH}	kcal/mol	0.0836	0.0000
σ_{HH}	Å	1.7753	0.0000

Note: Charges are expressed as a multiple of the electron charge e.

parameters of the CHARMM force field for both Na^+ and Cl^-. The parameterisation of TIP3P-PMA and ions is summarised in Tables 1 and 2, respectively.

As with most empirical models, the TIP3P-PME is parameterised for pure water at 298 K, and its behaviour under different conditions is not known a priori. In this study, we have investigated the effects of different temperatures and salt concentrations on the viscosity of the Price–Brooks variety of TIP3P (TIP3P-PME), in order to quantify the deviation from the behaviour in standard conditions. This is important for any simulation performed at non-standard temperature and ion concentrations.

2. Methods

MD [5] was used to simulate cubic domains ($60 \times 60 \times 60$ Å) filled with TIP3P-PME water, in an NPT ensemble controlled by a Nose–Hoover thermostat and barostat. PBCs were applied in all directions and a particle–particle particle-mesh (PPPM) solver was used for calculating the long-range electrostatic forces. Bonds and angles involving hydrogen atoms were constrained with the SHAKE algorithm. The target pressure was 1 atm for all simulations. Different boxes were prepared and Na^+ and Cl^- ions were added in equal amount, up to a total ion concentration (defined as the sum of the individual molar concentration of Na^+ and Cl^-) of 0, 0.1 and 1.0 M. The simulations were performed for all combinations of temperatures, 298, 323 and 348 K, and ion concentrations.

The interaction parameters for ions were taken from the widely used CHARMM27 force field [17]. Ion–water interactions in empirical force fields such as CHARMM are only of two types, namely electrostatic and van der Waals forces. These two contributions are modelled, respectively, by the Coulombic interactions (pairwise and long-range) and the LJ potential. The Coulombic interactions are easily parameterised once the atomic charges are known; therefore, no issue is expected on this side [16]. On the other hand, as mentioned in the introduction, there is currently no general agreement on

Table 2. Atomic charges q and LJ parameters ϵ and σ for Na^+ and Cl^- ions in the CHARMM force field.

Parameter	Units	Na^+	Cl^-
q	e	1	−1
ϵ	kcal/mol	0.0469	0.1500
σ	Å	2.4299	4.0447

Note: Charges are expressed as a multiple of the electron charge e.

the correct value of LJ parameters for Na^+ and Cl^- ions. Furthermore, since the interactions of heteroatomic pairs are usually not explicitly parameterised, the corresponding values for σ and ϵ are extrapolated from the homoatomic parameters, i.e. by means of the popular Lorentz–Berthelot mixing rules (also used in CHARMM):

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \tag{1}$$

and

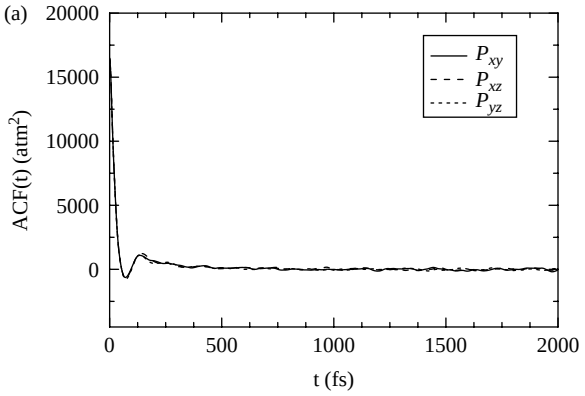
$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}, \tag{2}$$

where A and B are two arbitrary and distinct atom types. The choice of the water model, the force-field parameters for ions and the type of mixing rules clearly affect the details of the solvent–solvent and solvent–solute interactions. Therefore, the results obtained with our set of modelling assumptions cannot be assumed to be transferable to other force fields and water models. An overview of the composition of the simulated systems is presented in Table 3.

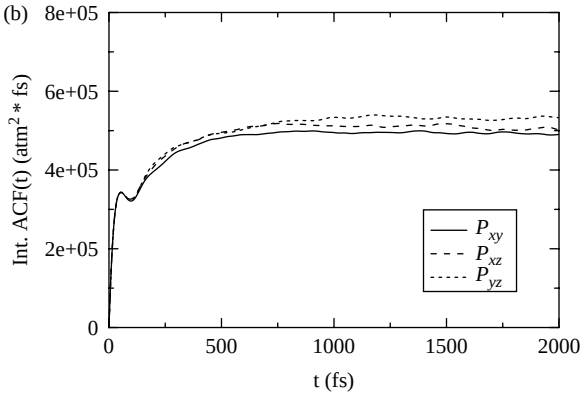
After assigning the initial positions and velocities, the potential energy of each system was minimised before equilibrating the systems to the target temperature and pressure for 1 ns with a time step of 0.5 fs. The equilibrated systems were then used for the production runs of 4 ns with a time step of 2 fs. Every combination of temperature and salt conditions was simulated in three independent runs with randomised initial conditions, in order to increase the number of samples to average over. Pressure, temperature and volume were stored at every time step. The fluid viscosity, η, was calculated using the Green–Kubo relations [6,7] from the time integral of the autocorrelation function (ACF) of the off-diagonal components of the

Table 3. Number of molecules used in the investigation for different salt concentrations.

$C(Na^+)$, (M)	$C(Cl^-)$, (M)	Total conc. (M)	H_2O	Na^+	Cl^-
0	0	0	7224	0	0
0.05	0.05	0.1	7210	7	7
0.5	0.5	1.0	7088	68	68



Plot of window-averaged autocorrelation function over a time window of 2 ps



Time integral of autocorrelation function over a time window of 2 ps

Figure 1. (a) Computed ACF and (b) corresponding time integral.

pressure tensor,

$$\eta = \frac{\langle V \rangle}{k_B \langle T \rangle} \int_0^\infty \langle P_{ij}(0) P_{ij}(t) \rangle \mathrm{d}t, \tag{3}$$

where $\langle V \rangle$ and $\langle T \rangle$ are the run averages of temperature and pressure, k_B is the Boltzmann constant and P_{ij} is one of the off-diagonal components of the pressure tensor. The ACF was computed using a window-averaging procedure analogous to that described by Nevins and Spera [8] with a time window of 2 ps and integrated numerically using the trapezoid rule with a step of 2 fs. Through the noisy tail of the ACF, the integral function reaches a plateau after about 1.5 ps, but is then subject to fluctuations. Therefore, the limit value was estimated by averaging the value over the last 0.5 ps of the time window.

An example of the pressure ACF and its integral function is given in Figures 1(a) and (b). For every simulation, the procedure was performed for the three independent pressure components P_{xy}, P_{xz} and P_{yz}. Since every condition was simulated three times, each reported value is the average of nine independent estimates.

Table 4. Results for TIP3P-PME water viscosities and comparison with experimental values.

T (K)	C_{ions}	η (MPa s)	η_{exp}(MPa s)	η/η_{exp}
298	0	0.43 ± 0.02	0.890[a]	0.48
298	0.1	0.45 ± 0.03	0.893[a,b]	0.50
298	1.0	0.48 ± 0.03	0.914[a,b]	0.53
323	0	0.31 ± 0.01	0.547[c]	0.57
323	0.1	0.31 ± 0.02	0.550[b,d]	0.56
323	1.0	0.34 ± 0.02	0.576[b,d]	0.59
348	0	0.22 ± 0.01	0.379[b,d]	0.58
348	0.1	0.24 ± 0.01	0.381[b,d]	0.63
348	1.0	0.25 ± 0.02	0.403[b,d]	0.62

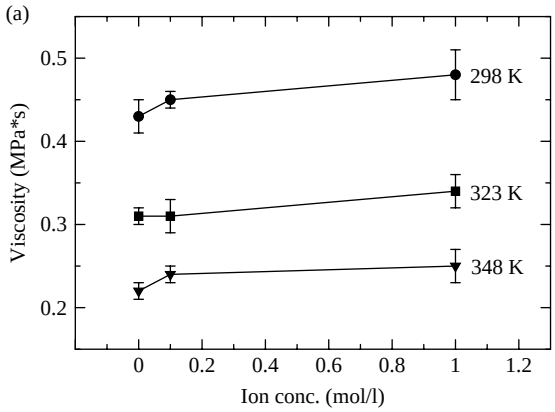
Notes: The given ion concentration must be interpreted as the sum of Na^+ and Cl^- molar concentrations. For comparison with data that use a more standard chemical notation, it must be noted that 1 mol of NaCl, in solution, produces a total ion concentration of 2.0 M (1.0 M Na^+ + 1.0 M Cl^-). [a] Experimental value, from [11]. [b] Extrapolated values. [c] Experimental value, from [10]. [d] Experimental value, from [15].

All 27 independent runs were performed using LAMMPS [9], and the results were post-processed using custom C and Octave scripts.

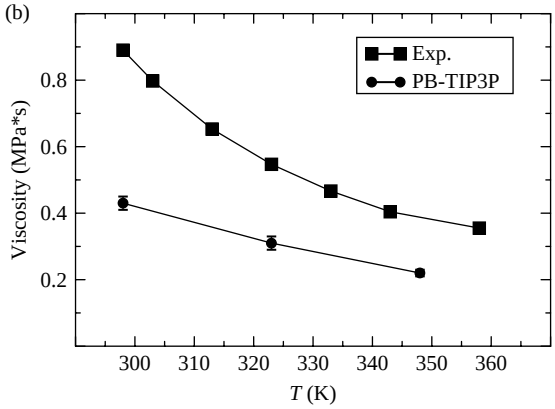
3. Results

The results obtained for water viscosity are summarised in Table 4 and compared with available experimental data for both pure water and saline mixtures. In particular, accurate measurements at 298.15 K have been produced for pure water and saline solution by Zhang [11]. For several different conditions of temperature and salt concentration, further data could be found in the papers of Kestin et al. [15]. However, for some of the simulated conditions, we were not able to locate suitable experimental values and we have relied on extrapolation. The available measurements were reported to be accurate within 1% of their absolute values [10,11,15]. As can be seen from Table 4, the viscosity of the TIP3P-PME model is consistently lower than that of real water and higher than that of the TIP3P model [3,12]. The absolute values are about half of the experimental ones. This discrepancy is partly due to the simplifications of the model. In particular, the charge distribution of the electron cloud cannot be accurately represented by three point charges whose positions are fixed relative to the atoms. Models such as TIP4P and TIP5P, while still rigid and therefore incapable of reproducing polarisation effects, add extra massless charges which mimic the charge distribution more accurately, and are (almost) always more successful in reproducing a wider range of water properties, although greater complexity is not always associated with better results [14].

In addition, the empirical and simplified nature of the model implies a poor predictive capability for those properties, such as viscosity, that were not included in the original parameterisation [13]. Nevertheless, by comparison with the experiments [11], the TIP3P-PME model is



Summary of resulting viscosity measurements at 298 K, 323 K and 348 K



Viscosity vs. temperature, for real water and TIP3P-PME, in no salt conditions. Experimental data points were taken from [10]

Figure 2. Summary of the results for TIP3P-PME viscosity at different temperatures and salt conditions.

able to reproduce at least qualitatively the trend of the viscosity increase due to ions in solution, as shown in Figure 2(a). For the simulated conditions, the effect of temperature is much more visible than that of the salt concentration.

The viscosity decreases considerably at higher temperatures: at 348 K, its absolute value is nearly half of the value measured at 298 K. For pure water, experimental data are available for a range of temperatures and a comparison is made in Figure 2(b), showing that the viscosity of the TIP3P-PME model follows the same trend as the experimentally obtained values.

The presented results can be useful in simulations that aim at the extraction of quantitative information about the diffusive properties of small molecules in aqueous saline solution: if the deviation from the behaviour of real water is known, the too low viscosity can be kept into account and the unrealistically high diffusion coefficients can be rescaled accordingly, thus recovering good estimates of the real values.

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