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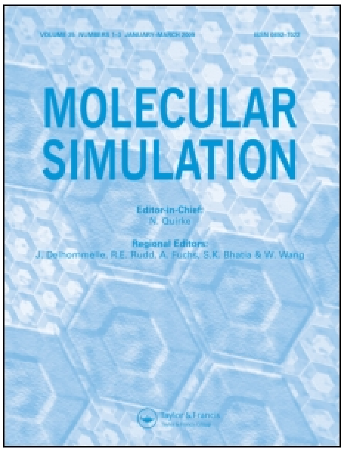

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The shear viscosities of common water models by non-equilibrium molecular dynamics simulations

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We have performed non-equilibrium molecular dynamics simulations to simulate the shear viscosity of five commonly used water models, SPC, SPC/E, TIP3P, TIP4P and TIP5P, using the periodic perturbation method. By comparing the computed viscosities of the water models, we find that the viscosities of SPC/E and TIP5P are in better agreement with the experimental value than the others. Furthermore, we have systematically investigated the effects of system size, acceleration amplitude, electrostatic treatment and cut-off length on the viscosities of the SPC/E and TIP5P models. Finally, by simulating the viscosity of water as a function of temperature, our work suggests that the SPC/E and TIP5P models reasonably reproduce the water viscosity vs. temperature experimental profile from 283 to 373 K at 1 bar, although SPC/E gives a better viscosity at high temperatures and TIP5P reproduces closer viscosity values at low temperatures.

Keywords: shear viscosity; water models; non-equilibrium molecular dynamics simulation

1. Introduction

The shear viscosity is a key kinetic property of water. Other than practical significance, in computational modelling, the viscosity not only is an important parameter for evaluating the accuracy of water models but also affects the dynamics of the substance dissolved or dispersed in the water. Unfortunately, it is a difficult property to be quantified by molecular dynamics (MD) simulations and has received less attention than other physical properties. Several methods have been available for determining the viscosities of liquids using equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) [1] simulations. From the EMD simulations, the viscosity can be calculated by pressure fluctuations [2] or momentum fluctuations [3]. However, the pressure fluctuation method was found to converge slowly because of the large fluctuations in pressure in the simulation box. In addition, it is very sensitive to the type of electrostatic treatment [4]. In contrast, methods based on the NEMD simulations are performed by applying a force to the system to create a shear flow, which usually converges much faster than the EMD methods.

The SLLOD algorithm [5,6] and periodic perturbation method [7] are two most common methods used in NEMD simulations. In the SLLOD algorithm, viscosity is obtained by imposing a linear velocity profile to the simulation system. Recently, Petravic and Delhommelle [8] obtained accurate viscosity of ethanol by the SLLOD method, and the extrapolation at zero-shear rate is in excellent agreement with EMD results. The periodic perturbation method is similar to the momentum fluctuation method. However, instead of measuring internal fluctuations, an external periodic force is applied to the simulation box, and the viscosity is calculated by measuring the response of the system to the applied force. One can choose a sufficiently small shear rate to avoid disturbing the structure and dynamics of the liquid and a large elongated simulation box to produce better statistics. Recently, Hess [4] compared the above four methods in MD simulations and found that the periodic perturbation method is the best choice for calculating the viscosity of simple liquids in terms of both accuracy and computational efficiency. However, the periodic perturbation method has only been applied to a few systems. By applying this method, Vasquez et al. [9] reported a good quality viscosity data of Lennard-Jones liquids for wide ranges of temperature and density with fast speed calculations. Wensink et al. [10] adopted the periodic perturbation method to calculate the viscosities of alcohol–water mixtures. In this work, the periodic perturbation method is used to compute the viscosity of liquid water.

Over the past 30 years, many different water models have been developed, for example the popular three-site SPC [11], SPC/E [12], TIP3P [13], four-site TIP4P [14] and five-site TIP5P [15]. They provide opportunities to study water structure and reproduce the physical properties such as density, diffusion constant, viscosity and compressibility. A key element before performing simulations involving water molecules is the choice of a

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water model. Every water model has its own strength, and models can be selected based on specific objectives, systems and force fields. For example, although the radical distribution functions of SPC and SPC/E models at room temperature are very similar, the dielectric constant and diffusion constant of SPC/E show great improvements over the SPC model [12,16]. By investigating the absolute entropy and hydrogen bonds of water models, the SPC and TIP4P models are found to best describe the structural property of water [17]. In terms of temperature dependence of properties of liquid water, the four-site TIP4P model produces more consistent results with experimental thermodynamic and structural data than the three-site models [18]. The five-site, fixed-charge TIP5P water model, developed by Mahoney and Jorgensen [15] in 2000, reproduces the density and energy profile of liquid water as a function of temperature within an averaged error of 1%, including the position of the temperature of maximum density. Although many efforts have been undertaken to evaluate various properties of different water models, very rare information has been reported on the viscosities of commonly used water models, which motivates the initiation of this work.

In this report, we present the viscosities of five commonly used water models, SPC, SPC/E, TIP3P, TIP4P and TIP5P, under ambient conditions and compare the simulation results with experimental data. This work provides a comprehensive study and fundamental basis for choosing the best water model in terms of viscosity. We systematically investigate the effects of system size, electrostatic treatment, cut-off length and acceleration amplitude on the viscosity values of the SPC/E and TIP5P models. Furthermore, we calculate the temperature dependence of the viscosity values of these two water models. These results here are, to the best of our knowledge, the first systematic study for the viscosities of commonly used water models using periodic perturbation methods from MD simulations.

2. Methods and simulation details

In the periodic perturbation method, which originates from Gosling et al.'s work [7] and is well explained by Hess [4], the viscosity can be calculated by applying an external force to the system with details described below. At each time step during the simulation, a periodic external force in the x-direction, which is a function of z only, can be imposed on each molecule. Consequently, a velocity field $\mathbf{u}$ can be created according to Navier–Stokes equation [1]:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \rho \mathbf{a} - \nabla p + \eta \nabla^2 \mathbf{u}. \tag{1}$$

Since u_y and u_z are equal to zero and there is no pressure gradient in the x-direction of the simulation box, Equation (1) then becomes:

$$\rho \frac{\partial u_x(z)}{\partial t} = \rho a_x(z) + \eta \frac{\partial^2 u_x(z)}{\partial z^2}. \tag{2}$$

For steady state, the solution becomes:

$$a_x(z) + \frac{\eta}{\rho} \frac{\partial^2 u_x(z)}{\partial z^2} = 0. \tag{3}$$

The magnitude of the external force depends on the molecule's z-coordinate as:

$$F_{i,x} = m_i a_x(z) = m_i A \cos(kz), \tag{4}$$

where m_i is the mass of the molecule, A is the applied acceleration and k is the wave-index number, which is defined as:

$$k = \frac{2\pi}{l_z}, \tag{5}$$

where l_z is the height of the simulation box. The steady-state velocity profile generated by the external acceleration (force) is given as:

$$u_x(z) = \nu(1 - \mathrm{e}^{-t/\tau_\mathrm{r}}) \cos(kz), \tag{6}$$

$$\nu = A \frac{\rho}{\eta k^2}, \tag{7}$$

where τ_r is the macroscopic relaxation time of the liquid, which is given by

$$\tau_\mathrm{r} = \frac{\rho}{\eta k^2}. \tag{8}$$

The viscosity of the liquid can be calculated by measuring the averaged ν during an MD simulation based on Equation (7).

In this work, all MD simulations have been performed using GROMACS 3.3.3 package [19,20]. The leap-frog algorithm was used for integrating Newton's equation of motion. All simulations were carried out under NPT (constant number of molecules, constant pressure and constant temperature) ensemble. Temperature and pressure were controlled by the Berendsen thermostat method. Periodic boundary conditions (PBCs) were applied to all three directions of the simulated boxes. The electrostatic interactions were treated by the particle-mesh Ewald (PME) method with a cut-off of 1.2 nm (except for Section 3.4).

In most cases (except for Section 3.1), we first set up a cubic box with a length 5 nm and then stack three of these boxes in the z-direction in order to eliminate the wavelength dependence effects. All the NEMD simulations start from equilibrated configurations by EMD. In all cases, the EMD simulations reach equilibrium within

0.5 ns according to the monitoring of the potential energy and density, although we run the EMD simulation for 2 ns. In order to calculate the viscosity of water, we run NEMD simulations for 2 ns. The first 400 ps were dropped from the analysis and the viscosity was analysed over 400 ps to 2 ns. The errors of the calculated viscosity are estimated based on the block averaging method [21].

3. Results and discussion

3.1 Comparison of viscosities of the five commonly used water models

The experimental value for the viscosity of pure liquid water at 300 K and 1 bar is $0.854 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ [22]. The comparisons of the simulated viscosities of the five commonly used water models, SPC, SPC/E, TIP3P, TIP4P and TIP5P, are presented in Table 1. In order to understand the wavelength dependence, we simulate two system sizes for each water model, with one and three cubic boxes stacked in the z-direction of the simulation boxes. The small and large systems give compatible viscosity results, which indicate that systems consisting of approximately 4000 molecules can produce good statistics with negligible wavelength effects.

First, it is notable that under the investigated simulation protocols, the calculated viscosities for all five water models in Table 1 are less than the experimental value at 300 K and 1 bar. Clearly, SPC/E and TIP5P are better choices for simulating liquid water from the perspective of shear viscosity, although TIP3P, TIP4P and SPC have been the most commonly used water models since 1983 [23]. At 300 K and 1 bar, the calculated viscosities of SPC/E and TIP5P are $(0.722 \pm 0.006) \times 10^{-3}$ and $(0.708 \pm 0.005) \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively, which are about 15 and 17% less than the experimental value of $0.854 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$.

For the two single-point charge models SPC and SPC/E, the only minor difference is that the charge for the oxygen molecule in the latter is $-0.8476e$ instead of $-0.8200e$ in the former, and for each hydrogen molecule, the charge is $+0.4238e$ instead of $+0.4100e$. Interestingly, this small difference results in a great improvement of the viscosity of $0.722 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ for SPC/E over the viscosity of $0.475 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ for SPC. It has been reported that this difference also leads to the improvements of many other properties such as density, radical distribution function and diffusion constant of SPC/E compared to SPC. For example, SPC/E has been found to be able to give the closest agreement with the experimental data for bulk water property [24,25]. The self-diffusion constants from the SPC/E model are between 2.5×10^{-9} and $3.3 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, which are in good agreement with the experimental value of $2.30 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, whereas those from the SPC model are between 4.1×10^{-9} and $5.0 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ [25]. Berendsen et al. [12] ascribed all these improvements as the correction of the polarisation self-energy for the effective pair potentials of the SPC/E model. The simulated viscosities here are slightly smaller comparing to the values reported by Smith and Van Gunsteren [26]. They reported that the viscosity of SPC and SPC/E is 0.54×10^{-3} and $0.82 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively, by simulating 512 water molecules using a pressure fluctuation method. The difference here is likely due to the different calculation methods, simulation methodology and system sizes.

Among the TIPnP models, TIP5P performs much better than TIP3P and TIP4P in reproducing the viscosity of liquid water, especially in comparison to TIP3P, which has a viscosity of $0.316 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, 63% less than the experimental value. In addition, TIP5P yields a significant improvement in many other areas over other fixed-charge water models. For example, it provides

Table 1. Comparison of viscosities of the five liquid water models.

Simulation box size (nm^3)	No. of water molecules	T (K)	P (bar)	Density (kg m^{-3})	η (10^{-3} kg m^{-1} s^{-1})
SPC					
5.336 × 5.316 × 10.357	8284	299.998	1.008	971.88	0.467 ± 0.008
5.180 × 5.176 × 20.265	16,568	300.005	1.006	971.90	0.475 ± 0.006
SPC/E					
5.016 × 5.015 × 5.017	4142	299.998	1.001	993.88	0.727 ± 0.005
5.172 × 5.122 × 15.194	12,426	299.998	1.008	993.71	0.722 ± 0.006
TIP3P					
5.162 × 5.149 × 5.146	4142	299.990	1.017	979.83	0.333 ± 0.009
5.201 × 5.185 × 15.028	12,426	300.008	1.014	979.86	0.316 ± 0.007
TIP4P					
5.140 × 5.122 × 5.122	4125	299.994	1.001	988.28	0.505 ± 0.008
5.151 × 5.143 × 15.154	12,375	300.007	1.005	988.22	0.506 ± 0.007
TIP5P					
5.004 × 5.004 × 5.004	4096	299.973	0.999	977.93	0.714 ± 0.006
5.139 × 5.149 × 15.163	12,288	299.983	1.006	978.09	0.708 ± 0.005
Experiment		300	1	997	0.854

Notes: For all the simulations, the electrostatics was treated by the PME method with a cut-off of 1.2 nm. The acceleration amplitude is 0.005 nm ps^{-2}.

relatively accurate results on the temperature effect of density over the temperature range from −37.5 to 62.5°C at 1 atm [15]. The self-diffusion constant of TIP5P at 25°C and 1 atm is $2.62 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, which is closer to the experimental value than the TIP3P, TIP4P and SPC alternatives [27]. Based on the viscosity data in Table 1, we focus the rest of the discussions on the systematic study of the viscosities of the TIP5P and SPC/E models.

3.2 *Effects of system size*

System-size effects, caused by the usage of PBCs, may lead to significant artefacts in MD simulations. Long-range interactions such as Coulombic or hydrodynamic interactions might be distorted by the PBC in a small system. Dünweg and Kremer [28,29] observed significant system-size effects for the diffusion coefficients of polymer chains in solution even if the polymer chain fits nicely into the simulation box, and they attributed the influences to the long-range nature of the hydrodynamic interaction. For small molecules such as water, the diffusion constants under ambient conditions increase significantly as the system size increases, and the diffusion constant can be underestimated by 10% for a system including approximately 2000 water molecules [30].

In order to investigate the dependence of viscosity of TIP5P and SPC/E on system size, we calculate the shear viscosities of the TIP5P and SPC/E water models as a function of the number of water molecules *N* under ambient condition (300 K, 1 bar), as shown in Figure 1. The results show that there is no strong system-size dependence for the calculated viscosities of the TIP5P and SPC/E water models as long as the number of the water molecules in the system is above 1024 (in a $2.5 \times 2.5 \times 5.0\,\mathrm{nm^3}$ box). Similar results were also reported by Hess [4] for the viscosity calculation of SPC. However, the system-size effect becomes an issue when the water molecules are below 1000, in which the calculated viscosity has a strong dependence on system size. For the system with 256 water molecules, the viscosities of TIP5P and SPC/E are 0.66×10^{-3} and $0.68 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, respectively, which are both 7% smaller than the values for ~4000 molecule systems. Balasubramanian et al. [31] also found strong system-size effects for the viscosity calculations of the SPC/E model over two small systems using the SLLOD algorithm. In their study, the viscosity of the SPC/E water model at 303.15 K for the 512 molecule system is $(0.66 \pm 0.8) \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, whereas for the 216 molecule system, it is only $(0.55 \pm 0.3) \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$.

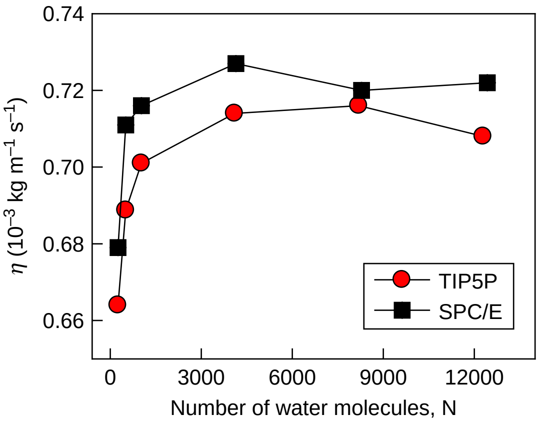

Figure 1. Shear viscosity η of the SPC/E and TIP5P water models as a function of the number of simulated water molecules *N*. The electrostatic interaction was treated by the PME method with a cut-off length of 1.2 nm for systems with water molecules over 512. The cut-off length for a system with 216 water molecules is 0.9 nm.

3.3 *Effects of acceleration amplitude*

One of the most important criteria for using the periodic perturbation method is to choose an optimised shear rate. Theoretically, shear rate should be sufficiently low so that the external shear flow does not disturb the structure and dynamics of the liquid. The maximum shear rate occurs when the generated velocity approaches the maximum in the z-direction [3],

$$S_{\max} = \max\left|\frac{\partial v_x(z)}{\partial z}\right| = A\,\frac{\rho}{\eta k}. \tag{9}$$

Unreasonably large shear rate applied to the simulation system will cause the simulated viscosity to be too low. For example, using the periodic perturbation method, the simulated viscosities of liquid argon and ethanol were found to decrease linearly with increasing the acceleration amplitudes [32]. On the other hand, one would not choose the shear rate to be too small since it leads to a low signal-to-noise ratio.

The simulated viscosities of the TIP5P and SPC/E models as a function of acceleration amplitude are presented in Table 2 and Figure 2. For both TIP5P and SPC/E, the simulation results show a large dependence of viscosity on the acceleration amplitude. For a $5 \times 5 \times 15\,\mathrm{nm^3}$ system, the acceleration should not be higher than $0.01\,\mathrm{nm\,ps^{-2}}$, corresponding to a maximum shear rate of $0.03\,\mathrm{ps^{-1}}$; above this value, the viscosity starts to decrease rapidly and the temperature of the system starts to increase. For comparison, Hess [4] obtained the maximum shear rate of $0.1\,\mathrm{ps^{-1}}$ in a 648 water molecule system in order to correctly simulate the viscosity of the SPC water model. For both water models here, stable plateaus were observed when the acceleration amplitude was below $0.005\,\mathrm{nm\,ps^{-2}}$. We expect that the calculated viscosities will not change significantly with further decreasing of the acceleration amplitude, although

Table 2. The calculated viscosities of theTIP5P and SPC/E water models with various acceleration amplitudes.

Acceleration (nm ps^{-2})	$S_{\max}$ (ps^{-1})	T (K)	P (bar)	Density (kg m^{-3})	η (10^{-3} kg m^{-1} s^{-1})
TIP5P					
0.05	0.416	301.835	1.005	958.62	0.275 ± 0.010
0.04	0.223	300.756	1.002	975.01	0.417 ± 0.012
0.025	0.119	300.191	1.007	978.05	0.589 ± 0.008
0.01	0.034	300.005	0.999	978.08	0.680 ± 0.009
0.005	0.016	299.983	1.006	977.97	0.708 ± 0.005
0.0025	0.008	299.977	0.993	977.93	0.710 ± 0.006
SPC/E					
0.05	0.260	301.132	1.011	992.49	0.455 ± 0.011
0.04	0.174	300.599	1.007	993.81	0.546 ± 0.009
0.025	0.091	300.190	1.003	993.97	0.652 ± 0.006
0.01	0.033	300.021	1.005	993.89	0.711 ± 0.004
0.005	0.016	299.998	1.008	993.71	0.722 ± 0.006
0.0025	0.008	299.993	1.015	993.86	0.718 ± 0.004

Note: The maximum shear rate $S_{\max}$ was calculated based on Equation (9).

we were not able to calculate the zero-shear rate viscosity due to the limit of the small shear rate applied in this method. It is worth pointing out here that recent studies [33,34] have shown that the application of the transient time correlation function formalism, originally developed by Evans and Morriss [6,35], in NEMD simulations can greatly reduce the small shear rate limit without reducing the signal-to-noise ratio, although it is beyond the scope of this report. Based on this result, the acceleration amplitude was chosen as 0.005 nm ps^{-2} for the rest of this study.

3.4 Effects of electrostatic treatments and cut-off length

Another important factor that may affect the viscosity calculations is the treatment of long-range electrostatic interactions. Although the interactions become smaller with increasing distance between two molecules, the long-range force cannot be negligible. Therefore, the estimation of long-range electrostatic interactions in the MD simulation is always a difficult task. Up to now, various treatment methods for Coulombic interactions have been applied in MD simulations, with the most prominent one being the PME method [36,37] and others are plain cut-off, reaction field [38–42] and shift function [43]. Different treatment methods are chosen according to the specific purposes or systems of simulations. Furthermore, finding an optimised cut-off length is an important step in the MD simulation. Many MD simulation studies have suggested that increasing the cut-off length does not necessarily improve the simulation results. It has been shown that using a large cut-off of 1.8 nm can lead to a huge artificial phase transition in the simulation of water [44]. Inappropriate simulation parameters can cause some water models to form layers and change density abruptly [43].

Table 3 compares the viscosity of the TIP5P and SPC/E water models and some other important observables from the simulations under various electrostatic treatments and cut-off lengths. In all cases, the size of the simulation box is $5 \times 5 \times 15\,\text{nm}^3$ and the acceleration amplitude is 0.005 nm ps^{-2}. First, it is notable that treating the electrostatics with a cut-off and reaction field of 0.9 nm in the simulation usually heats up the system and causes the temperature of the system to raise one to two degrees higher than the coupling temperature. The viscosities of both TIP5P and SPC/E show a slight dependence on the electrostatic treatment methods. Under the same cut-off length, the plain cut-off and reaction field simulations produce larger viscosity values than the PME and shift function. With the commonly used cut-off length

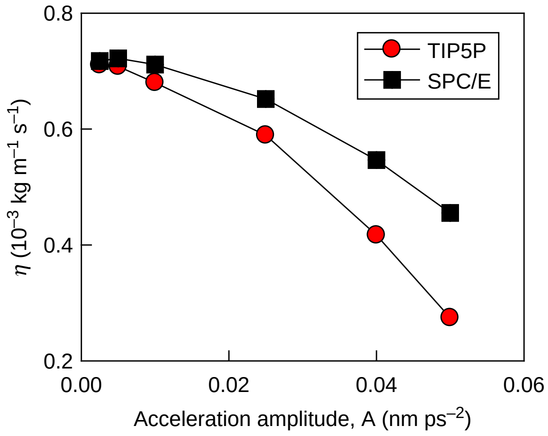

Figure 2. Shear viscosity η of the SPC/E and TIP5P water models as a function of acceleration amplitude. The electrostatic interaction was treated by the PME method with a cut-off length of 1.2 nm.

Table 3. Effects of electrostatic treatments on the viscosities of TIP5P and SPC/E.

Electrostatic treatment	Cut-off	T (K)	P (bar)	Density (kg m^{-3})	η (10^{-3} kg m^{-1} s^{-1})
TIP5P					
Cut-off	0.9	301.547	1.042	961.36	0.748 ± 0.008
	1.2	300.557	1.002	999.46	0.805 ± 0.010
	1.5	300.273	1.009	1006.26	0.793 ± 0.011
PME	0.9	299.983	1.016	969.11	0.704 ± 0.006
	1.2	299.983	1.006	978.09	0.708 ± 0.005
	1.5	299.998	1.002	981.08	0.706 ± 0.006
Reaction field	0.9	301.558	1.022	966.95	0.760 ± 0.006
	1.2	300.558	1.016	999.52	0.802 ± 0.008
	1.5	300.273	1.013	1006.23	0.807 ± 0.005
Shift	0.9	300.013	0.998	975.78	0.714 ± 0.008
	1.2	300.054	1.006	980.94	0.707 ± 0.007
	1.5	300.027	1.008	982.55	0.718 ± 0.010
SPC/E					
Cut-off	0.9	302.091	1.007	1003.37	0.781 ± 0.011
	1.2	300.711	1.010	1009.30	0.831 ± 0.009
	1.5	300.332	1.001	1012.72	0.836 ± 0.010
PME	0.9	299.952	1.009	986.59	0.727 ± 0.008
	1.2	299.998	1.008	993.71	0.722 ± 0.006
	1.5	300.006	1.010	996.36	0.716 ± 0.010
Reaction field	0.9	302.093	1.001	1003.37	0.780 ± 0.010
	1.2	300.710	1.005	1009.25	0.832 ± 0.008
	1.5	300.332	1.001	1012.70	0.835 ± 0.011
Shift	0.9	300.851	1.007	992.46	0.735 ± 0.008
	1.2	300.645	1.030	995.90	0.729 ± 0.006
	1.5	300.407	1.009	998.52	0.711 ± 0.009

of 1.2 nm, the viscosity of TIP5P for cut-off simulations is 14% higher than the PME simulations. Interestingly, we also note that, for both TIP5P and SPC/E, comparable viscosity results were obtained for PME and shift simulations and for cut-off and reaction field simulations, respectively.

In MD simulations, the cut-off length is defined as the radius beyond which all interactions are set to zero. In Table 3, we observe a trend that the density increases slightly with increasing the cut-off length. This is likely due to the underestimates of the long-range van der Waals contributions to the energy and pressure using the small cut-off lengths in the simulations. For the cut-off and reaction field simulations, the viscosity results are sensitive to the cut-off length. For example, under the cut-off simulations, the viscosity of TIP5P with a cut-off length of 1.2 nm is 8% higher than the cut-off length of 0.9 nm. In contrast, in the PME and shift simulations, different cut-off lengths reproduce very consistent viscosity results for both TIP5P and SPC/E. For example, under the PME simulations, the maximum deviation of the viscosity using the different cut-off lengths of 0.9–1.5 nm is only 0.6 and 1.5% for TIP5P and SPC/E, respectively.

3.5 *Temperature dependence*

The simulated viscosities as a function of temperature for the TIP5P and SPC/E models are presented in Figure 3, along with the experimental data from reference [22]. Over the temperature range from 283 to 373 K, both the TIP5P and SPC/E models yield comparable viscosity with

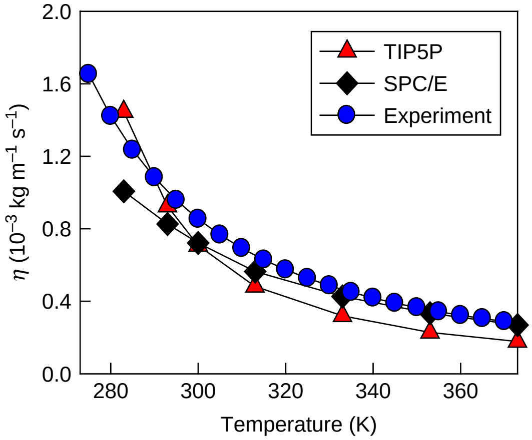

Figure 3. Comparison of simulated viscosities of the TIP5P and SPC/E water models and experimental viscosity of liquid water as a function of temperature at a pressure of 1 bar.

the experimental value, although all the simulated viscosity values are below the experimental value at temperatures higher than 290 K. It is noticeable that, in the low-temperature range (283–300 K), TIP5P reproduces a better steep decrease as a function of temperature than that of SPC/E, compared to the experimental observation. The viscosity of TIP5P decreases from $1.45 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ at 283 K to $0.708 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$ at 300 K. In contrast, the viscosity of SPC/E in this low-temperature range shows larger deviation from the experimental data, and the deviation increases with decreasing temperature. In particular, the largest deviation occurs at 283 K, where the viscosity of SPC/E is only $1.01 \times 10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$, which is about 30% smaller than the experimental viscosity of water. On the other hand, SPC/E fits the experimental results much better than TIP5P at high-temperature range (300–373 K). For example, SPC/E can reproduce the viscosity of water at 373 K with the error of only 3%. Based on these results, we suggest that the viscosity of water vs. temperature profile can be well reproduced by both TIP5P and SPC/E models. The SPC/E model gives an excellent viscosity result at higher temperatures (above 300 K), whereas the TIP5P model reproduces much closer viscosity value at lower temperatures (below 300 K), although we cannot offer any convincing interpretations.

4. Conclusion

In this work, we have systematically simulated the shear viscosities of the five commonly used water models, SPC, SPC/E, TIP3P, TIP4P and TIP5P, by applying the periodic perturbation method in NEMD simulations. Although the calculated viscosities for all five water models are found to be less than the experimental value, the work suggests that the SPC/E and TIP5P models are better choices in reproducing the viscosity of liquid water. The effects of system size, electrostatic treatment, cut-off length and acceleration amplitude on the viscosity for the TIP5P and SPC/E models were also investigated. The PME simulations, with a cut-off of 1.2 nm, suggest that the system-size effect becomes a significant issue in the viscosity calculations if the number of water molecules in the system is below approximately 1000. We found that inappropriate acceleration amplitude applied in the NEMD simulation causes significant errors. For example, in a system with 15 nm in the z-direction, the shear rate cannot be higher than $0.03\,\mathrm{ps^{-1}}$; above this value, the viscosities for both TIP5P and SPC/E decrease rapidly with increasing the shear rate. Under the same cut-off length and other simulation parameters, the plain cut-off and reaction-field simulations produce larger viscosity values than the simulations using PME and shift function. The PME and shift simulations give very comparable viscosity values for both TIP5P and SPC/E models with negligible dependence on cut-off lengths which varied from 0.9 to 1.5 nm. Finally, the simulations suggest that both TIP5P and SPC/E models reasonably reproduce the water viscosity vs. temperature experimental profile from 283 to 373 K at 1 bar; SPC/E gives a better viscosity at high temperatures above 300 K, and TIP5P reproduces a closer viscosity value at low temperatures below 300 K.

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