Molecular Dynamics Simulation Study for Shear Viscosity of Water at High Temperatures using SPC/E Water Model

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In the past decades, many classical force fields for molecular simulations on water have been developed.[1-13] A review article in 2002 indicates that there are 46 water models,[14] which were classified as rigid, flexible, and polarizable models.[15] The most popular water models - the TIP3P (transferable intermolecular potential 3P) (original[1] and modified[2]), SPC (simple point charge) (original[3] and refined[4]), and SPC/E (extended SPC)[5] can be described as effective rigid pair potentials composed of Lennard-Jones and Coulombic terms. Recent studies[16-20] using a rigid non-polarizable water model, TIP4P/2005, reported an impressive performance for a wide variety of properties and thermodynamic conditions.

Our interest in this study concentrated on the shear viscosity η of the bulk water. The experimental value for shear viscosities of pure water have been measured to be 0.896 cP[21] at 298 K and 0.854 cP[22] at 300 K. Shear viscosities evaluated using molecular dynamics (MD) simulations have been reported: 0.31[23] and 0.321 cP[24] for TIP3P, 0.47[25] and 0.494 cP[24] for TIP4P, 0.699 cP[24] for TIP5P, 0.64,[26] 0.65,[27] 0.67,[28] 0.68,[29] 0.72,[23] and 0.729 cP[24] for SPC/E (the results for TIP3P and SPC/E correspond to temperatures slightly above 300 K except Ref. 24 for 298 K), and 0.855[24] and 0.83 cP[29] for TIP4P/2005.

Though TIP4P/2005 performs quite well, the prediction from SPC/E is somewhat acceptable at room temperatures and this water model has been widely used. However, MD results for shear viscosity at high temperatures are rarely found in the literature. In this study, we utilize the Green-Kubo (GK) formula for the calculation of shear viscosities of SPC/E water using MD simulations over the range of temperatures 300 to 550 K. The primary goal of this study is to compare shear viscosities of water with the experimental measures at high temperatures and to examine the temperature dependence of shear viscosity of SPC/E water.

Molecular Dynamics Simulation

Canonical ensemble MD simulations of N = 1024 water molecules with Ewald summation over the range of temperatures 300 to 550 K were carried out for equilibration in the cubic box of length L determined from water densities at given temperatures (see Table 1). Ewald summations were used in our simulations with the parameter for $\kappa = 2.0$ Å^{-1} and the real-space cut distance r_{cut} and K_{max} chosen as 10.0 Å

Table 1. Densities (ρ_m, kg/m^3) and lengths (L, Å) of cubic simulation box of each system at given temperatures T(K), and comparison of viscosity (cP) calculated from MD simulations with Ewald summation to experimental measures. Uncertainties (standard deviation) in the last reported digit(s) are given in the parenthesis

T(K)	ρ_m	L	η_{MD}	η_{Exp}[a]
300	996.5	31.33	0.722(5)	0.854
350	973.7	31.57	0.341(6)	0.369
400	937.5	31.97	0.251(3)	0.219
450	890.3	32.53	0.178(3)	0.153
500	831.3	33.28	0.142(2)	0.118
550	755.8	34.35	0.100(1)	0.095

[a]Ref.22

and 7, respectively. Nosé-Hoover thermostat[30,31] was used to keep the temperature constant (the Nosé-Hoover thermostat relaxation constant is given as Q = $10 f k_B$ with f as the number of degrees of freedom and k_B as the Boltzmann constant). The usual periodic boundary condition was applied in the x-, y-, and z-direction, and the minimum image convention for pair potential were applied. The equations of translational motion were solved using a velocity Verlet algorithm[32] with a time step of l0^{-15} second (1 fs) and a quaternion formulation[33,34] was employed to solve the equations of rotational motion about the center of mass of rigid SPC/E water molecules. The configurations of water molecules were stored every 10 time steps for further analysis. The systems were fully equilibrated for 500,000 time steps and the equilibrium properties are averaged over 10 blocks of 100,000 time steps (0.1 ns).

The original GK formula for viscosity η is given by

$$\eta = \frac{V}{kT} \int_0^\infty dt <P_{\alpha\beta}(0) \cdot P_{\alpha\beta}(t)>, \qquad (1)$$

where

$$P_{\alpha\beta}(t) = \frac{1}{V}[\Sigma_i m v_{i\alpha}(t) \cdot v_{i\beta}(t) + \Sigma_i \Sigma_{j \neq i} r_{ij\alpha}(t) \cdot f_{ij\beta}(t)] \quad (2)$$

is the pressure of particle i on to the wall with $\alpha\beta$ = xy, xz, yx, yz, zx, and zy.

Results and Discussion
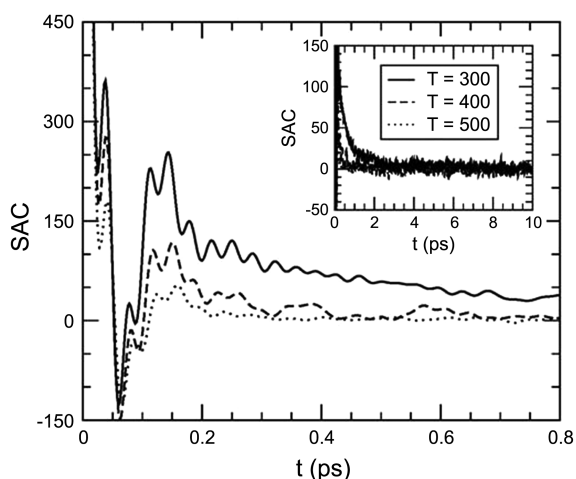
We plot the stress auto-correlation (SAC) functions, the

Figure 1. Stress auto-correlation (SAC, (kJ/mol·nm^3)^2) functions of SPC/E water at 300-500 K. The inset shows the long-time behavior of SAC functions.

integrand of Eq. (1), of SPC/E water at very short times for the temperatures of 300, 400, and 500 K in Figure 1. The SAC functions have lots of oscillations with a fast decay within 0.06 ps and an oscillatory peak at 0.13 ps. These functions are somewhat similar to the ones reported by Guo *et al.*[27] and Tazi *et al.*[29] which show much more smooth curve without lots of oscillations. The positions of the first minimum (at 0.06 ps) and the first peak (at 0.13 ps) coincide exactly. At 300 K, the SAC function does not decay to zero at 0.8 ps which reflects a large value of shear viscosity. As the temperature increases, the SAC functions lowered without changing the magnitude and the position of the first minimum.

Running integrals for η(t) of SPC/E water at 300-550 K are plotted as a function of time in Figure 2. All the running integrals for viscosity clearly show plateaus which signify that the corresponding SAC functions have decayed to zero and are fluctuating along the horizontal time axis. In general, η(t) for longer correlation will have larger statistical uncertainty because less data are available for its calculation.
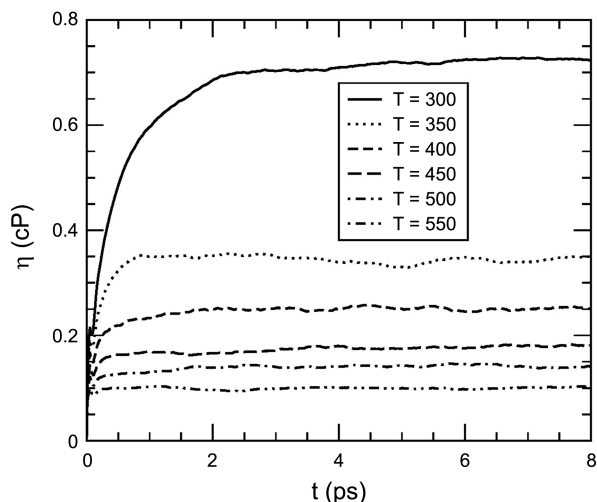
Therefore, the beginning of a plateau, which corresponds to the time when the SAC function reaches zero (not the two zero values before 0.2 ps), represents the start of the desired value of viscosity with the smallest uncertainty. As shown in the inset of Figure 1, all the SAC functions reach zero at about 4 ps and we report the shear viscosities at 300-550 K in Table 1 by averaging the running integrals for viscosity in Figure 2 for 4-8 ps.

The shear viscosities obtained by MD simulations at room temperature are discussed above. Our result for the shear viscosity using SPC/E potential at 300 K, 0.722 cP, differs from the MD results using other potentials – TIP3P, TIP4P, TIP5p, and TIP4P/2005, but agrees well with the MD results using SPC/E. It is very interesting to compare the shear viscosities evaluated using various water potentials, all the values having very similar values for each water potential.

We have compared our MD results for viscosity η with experimental data as a function of inverse temperature in Figure 3. The shear viscosity underestimates the experimental measures at low temperatures and overestimates at high temperatures; $(\eta_{MD} - \eta_{exp})/\eta_{exp}$ = −15% (300 K), −8% (350 K), 15% (400 K), 16% (450 K), 20% (500 K), and 5% (550 K). The temperature dependence of the MD result for η_{MD} and the experiment η_{Exp} over the range of temperature 300 to 550 K are suitably described by an Arrhenius plot as shown in Figure 3: $\eta = \eta_o \exp(E_\eta/RT)$ where η_o is the pre-exponential factor and E_η is the activation energy of water viscosity. The value of the activation energy is a direct measure of the temperature dependence of shear viscosity. The calculated activation energies are 2.5 and 2.9 kcal/mol for η_{MD} with Ewald summation and for η_{Exp}, respectively. The corresponding diffusion activation energies [$D = D_o \exp(-E_D/RT)$] are 3.1 and 3.7 kcal/mol for D_{MD} and for D_{Exp}, respectively.[35]

According to the Stokes-Einstein (SE) relation about a Brownian (B) particle immersed in a solvent (s), $D_B = k_BT/C\pi\eta_s r_B$, where C is the hydrodynamic boundary condition,
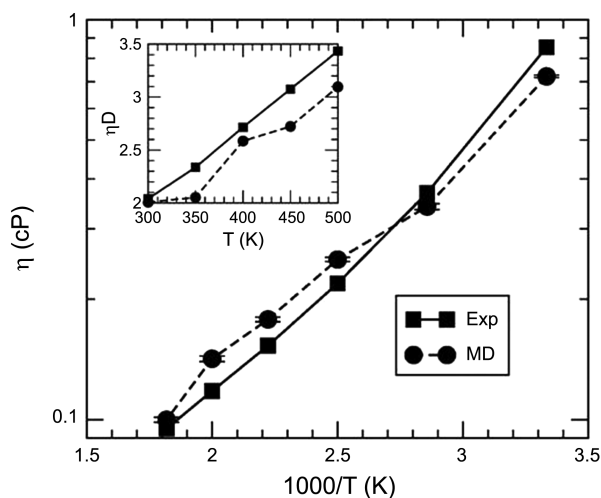

Figure 2. Running integrals for η(t) of SPC/E water at 300-550 K.

Figure 3. Comparison of viscosity η with experimental data as a function of inverse temperature. The error bar indicates standard deviation. The inset shows ηD (10^{-9} cP·m^2/s) as a function of T.

and η_s and r_B are the viscosity of solvent and the radius of the B particle. Applying the SE relation to bulk water, $\eta D \propto k_B T$. We plot ηD *vs* T in the inset of Figure 3. The behavior of ηD for the experimental data shows a linear increment with T, but that for the MD result does not, which reflects the requirement of a more refined water model for self-diffusion coefficients and shear viscosities at high temperatures. MD simulations for D and η using TIP4P/2005[16] at high temperatures are currently under investigation.

In contrast for the Green-Kubo (GK) formula to predict single-particle properties such as self-diffusion coefficient through the velocity auto-correlation (VAC) function as accurately as N (number of particle) times, the GK formula seems to have difficulty in predicting collective properties such as shear viscosity and thermal conductivity through the stress (SAC) and heat flux auto-correlation (HFAC) functions since the collective properties are the system properties which have N times less accurate statistics when compared with the single-particle properties. From this point of view, while the large deviation of our previous result for self-diffusion coefficients at 300-550 K[35] using SPC/E from the experimental data by −25~16% may come from the SPC/E model not from the GK formula, the current result for shear viscosities at the same temperatures using the same water model deviates from the experimental data by −25~20% which is rather a better agreement than those for self-diffusion coefficient since the stress is a collective property. Alternative way to overcome the poor statistical accuracy in evaluating shear viscosity and thermal conductivity through the stress (SAC) and heat flux auto-correlation (HFAC) functions is to consider the stress and heat flux as single-particle properties not as collective properties. Then the statistical accuracy is improved by N (number of particle) times large. The modified GK formula for the better statistical accuracy was applied to the Lennard-Jones systems.[36,37]

In summary, the shear viscosities of SPC/E water model over the range of temperatures 300 to 550 K were evaluated using the Green-Kubo formula by carrying out molecular dynamics (MD) simulations in the canonical NVT ensemble with Ewald summation. The MD result for the shear viscosity underestimates the experimental measures at low temperatures and overestimates at high temperatures. The temperature dependence of the MD result for η_{MD} and the experiment η_{Exp} over the range of temperature 300 to 550 K are suitably described by an Arrhenius plot. The calculated activation energies are 2.5 and 2.9 kcal/mol for η_{MD} with Ewald summation and for η_{Exp}, respectively.

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