Diffusion coefficient and shear viscosity of rigid water models

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Abstract

We report the diffusion coefficient and viscosity of popular rigid water models: two non-polarizable ones (SPC/E with three sites, and TIP4P/2005 with four sites) and a polarizable one (Dang–Chang, four sites). We exploit the dependence of the diffusion coefficient on the system size (Yeh and Hummer 2004 \textit{J. Phys. Chem. B} 108 15873) to obtain the size-independent value. This also provides an estimate of the viscosity of all water models, which we compare to the Green–Kubo result. In all cases, a good agreement is found. The TIP4P/2005 model is in better agreement with the experimental data for both diffusion and viscosity. The SPC/E and Dang–Chang models overestimate the diffusion coefficient and underestimate the viscosity.

(Some figures may appear in colour only in the online journal)

1. Introduction

The primary importance of water in biological, environmental and technical processes explains the enormous efforts devoted to its modelling on the microscopic scale. Many classical force fields for molecular simulations have been introduced to capture different aspects of its complex behaviour, including a number of ‘anomalies’. These models vary in the number of considered interaction sites, their flexibility or rigidity and their treatment or neglect of polarizability. Reviews of water models \cite{1–3} have addressed their relative merits to model the thermodynamic (e.g. phase diagram or heat capacities), structural and dynamic properties of water. The latter usually include the diffusion coefficient and the shear viscosity of the model, which are key quantities in determining the transport of water and solutions at rest or under hydrodynamic flows. In their recent review of the properties of rigid water models, Vega and Abascal underlined that dynamic properties are very sensitive to the details of the water model and that ‘the diffusion coefficient has not received the attention it should deserve as a target property’ in developing potential models \cite{3}.

The computation of diffusion coefficients from molecular dynamics simulation must be done carefully, as the result may depend on the simulation parameters (cut-off radius or method to compute electrostatic interactions), but also exhibits a systematic size-dependence arising from the screening of hydrodynamic flows under periodic boundary conditions \cite{4, 5}. When deriving the scaling of the diffusion coefficient with the system size, which involves the viscosity of the fluid, Yeh and Hummer investigated the TIP3P \cite{6} water model commonly used for biomolecular simulations. In the present work, we investigate the diffusion coefficient and viscosity of three popular rigid water models of different complexities. The SPC/E model \cite{7}, involves three interaction sites and is routinely used for the simulation of liquid water and electrolyte solutions. The TIP4P/2005 model \cite{8}, with four interaction sites, is usually the best rigid non-polarizable model for the description of the phase diagram and the physical properties of bulk solid and liquid water. The Dang–Chang model \cite{9} is a four-site polarizable model, which allows some transferability from water clusters to liquid water and the description of the water–air interface. For these three models, the system size-dependence of the diffusion coefficient allows us to determine the size-independent value and provides an estimate of the viscosity. We also estimate the latter from the Green–Kubo relation.
2. Methods

The parameters defining the geometry and force field for the three water models are summarized in Table 1. The diffusion coefficients are computed from the mean-squared displacement, using the Einstein relation:

\[ D_{\text{PBC}} = \lim_{t \to \infty} \frac{1}{6} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle. \]

The ‘PBC’ subscript emphasizes the fact that the use of periodic boundary conditions induces a box length dependence of the measured diffusion coefficient as \[4, 5\].

\[ D_{\text{PBC}} = D_0 - \frac{2.837 k_B T}{6 \pi \eta L}. \]  

where \( \eta \) is the shear viscosity of the solvent. In practice a linear fit of \( D_{\text{PBC}} \) versus \( 1/L \) provides both \( D_0 \) and an estimate of the viscosity \( \eta_{\text{PBC}} \).

A more usual determination of the viscosity uses the Green–Kubo relation:

\[ \eta_{\text{GK}} = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle \, dt, \]  

involving the auto-correlation function (ACF) of the components of the stress tensor \( \sigma_{\alpha\beta} \).

We performed molecular dynamics simulations in the \( NVT \) ensemble for \( N \) ranging from 64 to 4096 for SPC/E, 2048 for TIP4P/2005 and 512 for Dang–Chang (DC). The volume is set to ensure a density of 0.998 g cm\(^{-3}\) and a Nose–Hoover thermostat is used to maintain a temperature \( T = 300 \) K. Long-range interactions are computed using the Ewald summation technique \[10\] and a cut-off is used for short-range interactions. For the DC model, the induced polarization energy and a convergence criterion of \( 10^{-6} \) is used. Simulations of 1–10 ns are performed using a time step of 1 fs and positions are sampled every 100 fs. The equations of motion for the rigid water molecules are integrated using the SHAKE algorithm \[11\].

For simulations with the non-polarizable SPC/E and TIP4P/2005 models we use the LAMMPS \[12\] code. We also compared our results for TIP4P/2005, which contains a massless site, with those obtained using Fincham’s implicit quaternion algorithm \[13\] instead of SHAKE, and the DL_POLY code \[14\]. Since the same results were found, we only report those obtained with SHAKE.

Simulations with the polarizable Dang–Chang model were performed with FIST, the classical part of the CP2K simulation package \[15\]. The diffusion coefficients are computed from the slope of the mean-square displacement in the 100–300 ps window. Uncertainties on the diffusion coefficients for a given system size are estimated using the block averaging method \[16\]. The uncertainty on the size-independent diffusion coefficient \( D_0 \) and viscosity estimate \( \eta_{\text{PBC}} \) are obtained from the least-square fit of the size-dependent ones to equation (2). For the Green–Kubo calculations we use the systems with \( N = 256 \) molecules and collect the components of the stress tensor at every time step. The ACF is averaged over the components, and the viscosity is computed as the integral over 5 ps (see below). The uncertainty is estimated by computing the standard deviation of the values obtained for the different components.

3. Results

The results for the diffusion coefficients as a function of system size are reported in Figure 1. For the three water models, the scaling predicted by equation (2) is observed. The corresponding size-independent diffusion coefficients \( D_0 \) and viscosities \( \eta_{\text{PBC}} \) are summarized in Table 2. All the considered models overestimate the diffusion coefficient compared to the experimental results. This is consistent for SPC/E with the result of Kerisit and Liu \[17\]. To the best of our knowledge, the size-independent diffusion

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Table 1. Geometry and parameters defining the three water models: bond length \( d_{\text{OH}} \), position of the extra M site along the bisector \( d_{\text{OM}} \), angle between the OH bonds, Lennard-Jones parameters on the O atom \( \epsilon_O \) and \( \sigma_O \), charge on the H atoms \( q_O = -2q_H \) for SPC/E, \( q_M = -2q_H \) for the other models) and polarizability of the M site.

| Model       | \( d_{\text{OH}} \) (Å) | \( d_{\text{OM}} \) (Å) | Angle (deg) | \( \epsilon_O \) (kcal mol\(^{-1}\)) | \( \sigma_O \) (Å) | \( q_O \) | \( q_M \) (Å\(^3\)) |
|-------------|--------------------------|--------------------------|-------------|-------------------------------------|-------------------|--------|-------------------|
| SPC/E       | 1                        | —                        | 109.471     | 0.1554                              | 3.1656            | 0.4238 | —                 |
| TIP4P/2005  | 0.9572                   | 0.1546                   | 104.52      | 0.1852                              | 3.1589            | 0.5564 | —                 |
| Dang–Chang  | 0.9572                   | 0.215                    | 104.52      | 0.1825                              | 3.2340            | 0.5190 | 1.444             |
Table 2. Size-independent diffusion coefficient $D_0$ and viscosity ($\eta_{\text{PBC}}$ from equation (2) and $\eta_{\text{GK}}$ from equation (3)) of the three water models.

| Model       | $D_0$ (10$^{-9}$ m$^2$ s$^{-1}$) | $\eta_{\text{PBC}}$ (cP) | $\eta_{\text{GK}}$ (cP) |
|-------------|---------------------------------|---------------------------|---------------------------|
| SPC/E       | 2.97 ± 0.05                     | 0.64 ± 0.02               | 0.68 ± 0.02               |
| TIP4P/2005  | 2.49 ± 0.06                     | 0.83 ± 0.07               | 0.83 ± 0.05               |
| Dang–Chang  | 2.72 ± 0.09                     | 0.78 ± 0.06               | 0.74 ± 0.09               |

Exp. 2.3$^a$ 0.896$^b$

$^a$ Reference [18].  
$^b$ Reference [19].

The size-independent diffusion coefficient of the TIP4P/2005 and DC models had not been previously reported. This fact was noticed as a caveat in [3], where it was anticipated that extrapolating to infinite system size would bring the result for this model, which is the only rigid one to underestimate the diffusion coefficient for typical box sizes, closer to the experimental one. The extrapolated value $D_0$ turns out to be approximately 10% larger. Nevertheless, TIP4P/2005 provides the best agreement with the experimental value. This confirms the conclusion drawn, among rigid non-polarizable models, from diffusion coefficients without taking into account the system size-dependence [3]. In their paper introducing equation (2), Yeh and Hummer investigated the TIP3P water model [6] and obtained $D_0 = 6.05 \times 10^{-9}$ m$^2$ s$^{-1}$ [5], in even worse agreement with the experimental results. The polarizable DC model overestimates the diffusion coefficient by less than 20% and performs better than SPC/E (30%).

Before commenting the viscosity estimates $\eta_{\text{PBC}}$, we now turn to the Green–Kubo calculations. Chen and Smit have recently shown that the viscosity can be computed from equilibrium simulations with an accuracy comparable to that obtained with non-equilibrium methods, provided that the stress ACF is properly sampled at short times and that the integral equation (3) is estimated from times of the order of a few picoseconds [20]. Figure 2 reports the stress ACF at very short times and the time-dependent viscosity (running integral of the ACF) for the three water models. For SPC/E and TIP4P/2005, the ACF is very similar to the one reported by Gonzalez and Abascal [21], with a fast decay and oscillations within a few 100 fs which are more pronounced in the TIP4P/2005 case, followed by a slower decay which contributes significantly to the integral. The same behaviour is observed for the DC water model, for which no such study has yet been reported. As can be seen in figure 2, the choice of an upper limit of 5 ps provides a good estimate of the integral in equation (3).

The viscosities $\eta_{\text{GK}}$ obtained by the Green–Kubo formula and $\eta_{\text{PBC}}$ obtained from equation (2) are summarized in table 2. For all three models, a good agreement between the two approaches is obtained. The values for the SPC/E model are comparable to most of the previously reported values, both with equilibrium and non-equilibrium methods: 0.64 cP [22], 0.65 cP [23] and 0.67 cP [20]. A recent study of water confined in clay nanopores of width larger than 4 nm concluded from non-equilibrium molecular dynamics simulations a viscosity of SPC/E water comparable to the bulk value of 0.68–0.70 cP [24]. Slightly larger values have also been reported for bulk SPC/E: 0.72 cP [25] and 0.73 cP [21]. The value found for TIP4P/2005 is slightly smaller than the only reported values in the literature, namely 0.855 cP [21] and 0.89 cP [26]. Nevertheless, we find an excellent agreement between the two methods ($\eta_{\text{PBC}}$ and $\eta_{\text{GK}}$). Since in both references the reported values for SPC/E are also on the larger side (0.73 and 0.82 cP, respectively), it is not entirely surprising. To the best of our knowledge, no viscosity had been previously reported for the DC model. As for the size-independent diffusion coefficient, TIP4P/2005 provides the best agreement with the experimental viscosity, and the DC model performs better than SPC/E. From the scaling of the diffusion coefficient with system size, Yeh and
Hummer had found for TIP3P a value of $\eta_{\text{PRC}} = 0.31 \pm 0.01$ cP [5], in worse agreement with the experimental result, as for the diffusion coefficient.

4. Conclusion

We have determined the size-independent diffusion coefficient and shear viscosity of three popular rigid water models: SPC/E, TIP4P/2005 and Dang–Chang. A good agreement is found for each model between the viscosity determined from the slope of $D$ versus the inverse box size and from the Green–Kubo expression. The three considered models overestimate the diffusion coefficient and underestimate the viscosity. The TIP4P/2005 model is in better agreement with the experimental data for both diffusion and viscosity, followed by the Dang–Chang and SPC/E models.

This confirms the success of TIP4P/2005 in modelling not only a large variety of thermodynamic and material properties of bulk water, but also dynamic ones. While it had been shown to correctly predict the viscosity of liquid water at ambient conditions, as well as a function of temperature and pressure [3, 26], the size-independent diffusion coefficient had not been reported previously. Although the prediction of the more complex (and thus computationally more costly) Dang–Chang model are in slightly worse agreement with the experimental data, one should keep in mind that introducing polarizability should allow for a better transferability to other conditions, in particular liquid–solid interfaces and ionic solutions. The parametrization of a force field compatible with the Dang–Chang water model to such situations is currently in progress [27].

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