

## The shear viscosity of rigid water models

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In this work, the shear viscosity at ambient conditions of several water models (SPC/E, TIP4P, TIP5P, and TIP4P/2005) is evaluated using the Green–Kubo formalism. The performance of TIP4P/2005 is excellent, that of SPC/E and TIP5P is more or less acceptable, whereas TIP4P and especially TIP3P give a poor agreement with experiment. Further calculations have been carried out for TIP4P/2005 to provide a wider assessment of its performance. In accordance with experimental data, TIP4P/2005 predicts a minimum in the shear viscosity for the 273 K isotherm, a shift in the minimum toward lower pressures at 298 K, and its disappearance at 373 K.

Computer simulation is a useful tool which can be employed to validate models of physical systems by comparing the simulation results with experimental data. Obviously, the quality of a model should be established by its ability to predict other properties different from those used to fit the model parameters. Given the importance of water, there have been a large number of computer simulation studies.<sup>1</sup> Among the successful water models, we may cite SPC/E (Ref. 2) and TIP4P (Ref. 3) proposed more than 20 yr ago. Despite their simplicity (both models are rigid and nonpolarizable) and the work devoted to refine the water force field, until recently there has been no clear improvement. In the 2000s, Mahoney and Jorgensen<sup>4</sup> proposed a new promising water model, TIP5P. More recently, the study of the phase diagram of water<sup>5</sup> has triggered several reparametrizations of TIP4P.<sup>6,7</sup> One of these, TIP4P/2005, has an impressive performance for a wide variety of properties and thermodynamic conditions.<sup>7–11</sup> In fact, for condensed phases, the predictions of TIP4P/2005 are better than those of TIP4P for *all the properties* investigated up to now. But it is important to note that this model has not been thoroughly checked for dynamical properties. The shear viscosity of water is particularly interesting because it shows an “anomalous” behavior: its dependence with pressure exhibits a minimum below 306 K.<sup>12</sup>

An accurate calculation of the shear viscosity requires significant computer resources. There are some reports of simulations of this property for SPC/E,<sup>13–17</sup> TIP4P,<sup>18</sup> and TIP3P.<sup>16</sup> To the best of our knowledge, the viscosities of TIP5P and TIP4P/2005 have not yet been reported. Thus, in this work, we have undertaken the task of calculating the viscosity of SPC/E, TIP3P, TIP4P, TIP5P, and TIP4P/2005 at ambient conditions. As we will see below, it turns out that the models providing a better account of the water viscosity at 298 K are SPC/E and especially TIP4P/2005. A deeper investigation of the performance will be done only for these models.

The Green–Kubo formula relates the shear viscosity to the autocorrelation function (ACF) of the off-diagonal components of the stress tensor  $P_{\alpha\beta}$ , namely,

$$\eta = \frac{V}{kT} \int_0^\infty \langle P_{\alpha\beta}(t_0) P_{\alpha\beta}(t_0 + t) \rangle_{t_0} dt. \quad (1)$$

The main contribution comes from the short time ACF, but an accurate computation of the shear viscosity also requires a precise calculation of the ACF tail (for this reason, alternative methods have been proposed to compute the shear viscosity; see Ref. 15 and references therein). A careful analysis for the case of SPC/E water made by Guo and Zhang<sup>14</sup> has shown that the Green–Kubo relation leads to reliable results using an upper limit of the order of 3 ps in the above integral. In order to obtain good statistics for the ACF at such correlation times, simulations of about 4 ns were required. In this work, we follow the same methodology as in the paper by Guo and Zhang,<sup>14</sup> but we have extended the simulation length to improve the statistics of the ACF tail and, thus, the accuracy of the calculations. As the system is isotropic, the off-diagonal elements of the pressure tensor,  $P_{xy}$ ,  $P_{xz}$ , and  $P_{zy}$ , are equivalent. Besides, due to the rotational invariance of the molecule, the terms  $(P_{xx} - P_{yy})/2$  and  $(P_{yy} - P_{zz})/2$  are also equivalent.<sup>14,19</sup> In this way, in our calculations, the accuracy of the resulting ACF is enhanced by averaging over five pressure components.

For the simulations, we have used the GROMACS package.<sup>20</sup> The simulations have been performed in the canonical ( $NVT$ ) ensemble using the Nosé–Hoover thermostat<sup>21,22</sup> for a sample size of 500 water molecules. The box size was fixed from the knowledge of the density of the model at the desired pressure. As a result, the final pressures were slightly different from the target ones—typically by less than 1 MPa—but this has a negligible effect on the reported viscosities.

Long range electrostatic interactions have been calculated with the Ewald summation method using Particle Mesh Ewald for the reciprocal part.<sup>23</sup> The simulated time was between 20 and 60 ns using a timestep of 1 fs. The ACF has been calculated from the stress components saved on disk

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TABLE I. Shear viscosities (in mPa s) of several rigid water models at 298 K and 1 bar.

TIP3P	TIP4P	TIP5P	SPC/E	TIP4P/2005	Expt. <sup>a</sup>
0.321	0.494	0.699	0.729	0.855	0.896

<sup>a</sup>Reference 26.

every 2 fs. All the configurations were used as a time origin. The upper limits in the integral were between 3 and 10 ps depending on the system.<sup>24</sup> Other details of the simulations as well as the ACF functions and the numerical values of the viscosity are given in Ref. 24.

The shear viscosities at ambient conditions for the water models considered in this paper are shown in Table I. It is interesting to note that our results are close to those recently reported by other authors at about the same temperature: 0.31 mPa s for TIP3P,<sup>16</sup> 0.47 mPa s for TIP4P,<sup>18</sup> and 0.64,<sup>15</sup> 0.65,<sup>14</sup> 0.67,<sup>17</sup> and 0.72 mPa s (Ref. 16) for SPC/E (the results for TIP3P and SPC/E correspond to temperatures slightly above 300 K, which may explain the small departures from our values). The predictions of TIP3P and TIP4P are quite poor. The estimates from TIP5P and SPC/E are somewhat better but still far from the experimental value (around a 20% departure). On the contrary, TIP4P/2005 performs quite well since the deviation from the experiment is slightly less than 5%. This is in accordance with the excellent predictions of TIP4P/2005 at normal pressure shown in Ref. 25.

Figure 1 shows the viscosities of SPC/E and TIP4P/2005

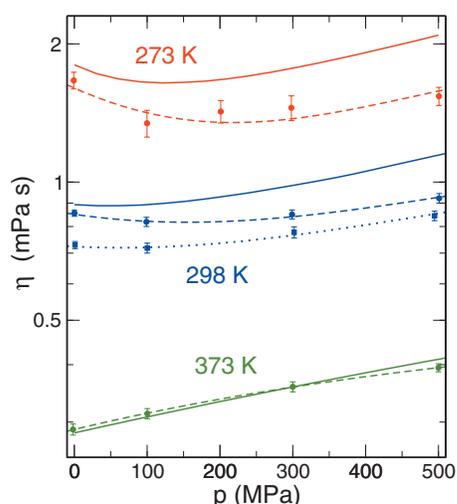


FIG. 1. Shear viscosities, in logarithmic scale, of TIP4P/2005 (circles, dashed lines) and SPC/E (squares, dotted line). Full lines are the experimental results.

for several temperatures. Although both models systematically underestimate the viscosity at 298 K, the results for TIP4P/2005 are closer to the experimental data. Besides, the latter model predicts a minimum whereas SPC/E does not show it (or, if it exists, it is a very shallow one). The minimum shifts toward lower pressures at increasing temperatures so it does not appear at 373 K. Thus, the overall behavior of TIP4P/2005 closely follows the experimental trends.<sup>12,26</sup> The results shown in this work together with those previously reported for the self-diffusion coefficient<sup>11</sup> indicate that TIP4P/2005 also gives an impressive performance for the dynamical properties. We may conclude that the model is able to account for the “anomalies” in the dynamical properties of water as well as for the static ones.<sup>10</sup>

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<sup>1</sup>B. Guillot, *J. Mol. Liq.* **101**, 219 (2002).<sup>2</sup>H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).<sup>3</sup>W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).<sup>4</sup>M. W. Mahoney and W. L. Jorgensen, *J. Chem. Phys.* **112**, 8910 (2000).<sup>5</sup>E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, *Phys. Rev. Lett.* **92**, 255701 (2004).<sup>6</sup>J. L. F. Abascal, E. Sanz, R. García Fernández, and C. Vega, *J. Chem. Phys.* **122**, 234511 (2005).<sup>7</sup>J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005).<sup>8</sup>C. Vega, J. L. F. Abascal, and I. Nezbeda, *J. Chem. Phys.* **125**, 034503 (2006).<sup>9</sup>C. Vega and E. de Miguel, *J. Chem. Phys.* **126**, 154707 (2007).<sup>10</sup>H. L. Pi, J. L. Aragonés, C. Vega, E. G. Noya, J. L. F. Abascal, M. A. González, and C. McBride, *Mol. Phys.* **107**, 365 (2009).<sup>11</sup>C. Vega, J. L. F. Abascal, M. M. Conde, and J. L. Aragonés, *Faraday Discuss.* **141**, 251 (2009).<sup>12</sup>K. E. Bett and J. B. Cappi, *Nature (London)* **207**, 620 (1965).<sup>13</sup>S. Balasubramanian, C. J. Mundy, and M. L. Klein, *J. Chem. Phys.* **105**, 11190 (1996).<sup>14</sup>G.-J. Guo and Y.-G. Zhang, *Mol. Phys.* **99**, 283 (2001).<sup>15</sup>B. Hess, *J. Chem. Phys.* **116**, 209 (2002).<sup>16</sup>Y. J. Wu, H. L. Tepper, and G. A. Voth, *J. Chem. Phys.* **124**, 024503 (2006).<sup>17</sup>T. Chen, B. Smit, and A. T. Bell, *J. Chem. Phys.* **131**, 246101 (2009).<sup>18</sup>E. Wensink, A. Hoffmann, P. van Maaren, and D. van der Spoel, *J. Chem. Phys.* **119**, 7308 (2003).<sup>19</sup>D. Alfè and M. J. Gillan, *Phys. Rev. Lett.* **81**, 5161 (1998).<sup>20</sup>D. van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. C. Berendsen, *J. Comput. Chem.* **26**, 1701 (2005).<sup>21</sup>S. Nosé, *Mol. Phys.* **52**, 255 (1984).<sup>22</sup>W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).<sup>23</sup>U. Essmann, L. Perera, M. L. Berkowitz, T. A. Darden, H. Lee, and L. Pedersen, *J. Chem. Phys.* **103**, 8577 (1995).<sup>24</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3330544> for other simulation details and numerical values of the viscosity.<sup>25</sup>J. Vrabc, personal communication.<sup>26</sup>K. R. Harris and L. A. Woolf, *J. Chem. Eng. Data* **49**, 1064 (2004).