

## Diffusion constant of the TIP5P model of liquid water

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The diffusion constant of TIP5P [J. Chem. Phys. **112**, 8910 (2000)], the recently developed five-site rigid nonpolarizable model of liquid water that significantly improves the description of water's density anomaly, has been calculated at a range of temperatures between  $-25^{\circ}\text{C}$  and  $75^{\circ}\text{C}$  and pressures between 1 atm and 3000 atm. The diffusion constant, in units of  $10^{-5}\text{ cm}^2/\text{s}$ , for TIP5P water at  $25^{\circ}\text{C}$  and 1 atm is  $2.62 \pm 0.04$  as compared with the experimental value of 2.30. This is a significant improvement over most commonly used water models, e.g., for TIP4P and TIP3P [J. Chem. Phys. **79**, 926 (1983)] the diffusion constants are  $3.29 \pm 0.05$  and  $5.06 \pm 0.09$ , respectively, and for SPC it is  $3.85 \pm 0.09$ . The diffusion constant of TIP5P decreases dramatically with decreasing temperature, as is observed experimentally, and the change in the diffusion constant as pressure is increased is also consistent with experimental results. © 2001 American Institute of Physics. [DOI: 10.1063/1.1329346]

### I. INTRODUCTION

The TIP5P model was developed to reproduce well the experimental properties of liquid water, especially the density as a function of temperature.<sup>1</sup> Initial calculations were performed to optimize the parameters defining the model, especially the position of the negative charges along the lone-pair directions. Additional calculations demonstrated that the density maximum near  $4^{\circ}\text{C}$  at 1 atm is reproduced by the TIP5P model, while high-quality structural and thermodynamic results are maintained. All the calculations were performed with a standard Monte Carlo statistical mechanics algorithm to sample the isothermal–isobaric ensemble.<sup>1</sup> As such, dynamical information about the model was not obtained and was thus not used in the determination of the model's parameters. A key dynamical quantity of interest is the diffusion constant. The experimental value for the diffusion constant of pure liquid water at  $25^{\circ}\text{C}$  and 1 atm is  $2.30 \times 10^{-5}\text{ cm}^2/\text{s}$ .<sup>2</sup> The diffusion constant has been calculated for many models of liquid water, and for most of the commonly used models it is too large. For example, the TIP4P model of water has been reported to have a diffusion constant of  $\approx 3.3 \times 10^{-5}\text{ cm}^2/\text{s}$  at approximately standard temperature and pressure.<sup>3</sup> The three-site SPC model has been reported to have a diffusion constant of  $\approx 3.6 \times 10^{-5}\text{ cm}^2/\text{s}$  and was reparameterized to yield the SPC/E model that gives an improved value of  $\approx 2.5 \times 10^{-5}\text{ cm}^2/\text{s}$ .<sup>3,4</sup> Both of these latter calculations were at  $\approx 307\text{ K}$  and a pressure of 1 bar, leading to densities of  $0.970\text{ g/cm}^3$  and  $0.998\text{ g/cm}^3$  for SPC and SPC/E, respectively.<sup>4</sup> Diffusion constants for flexible and polarizable models have also been reported.<sup>5</sup> For example, the TIP4P-FQ model has a diffusion constant of  $1.9 \times 10^{-5}\text{ cm}^2/\text{s}$  and the Dang97 model has a diffusion constant of  $2.1 \times 10^{-5}\text{ cm}^2/\text{s}$ .<sup>5</sup> These polarizable models have

dipole moments that are larger than those of common nonpolarizable models and this is reflected in their decreased diffusion constant.

Results are reported here for the diffusion constant of TIP5P water and of other commonly used water models at standard temperature and pressure. The effects of varying temperature and pressure on the structural properties of several models of water, including TIP5P, have been presented in detail elsewhere.<sup>1,6</sup> The characterization of TIP5P water is further extended here by computation of its diffusion constant at a range of temperatures between  $-25^{\circ}\text{C}$  and  $75^{\circ}\text{C}$  and pressures between 1 atm and 3000 atm. These results are, to our knowledge, the first presentation of such a comprehensive data set for the diffusivity of a water model.

### II. METHODS AND RESULTS

In order to calculate the diffusion constant of the water models, classical molecular dynamics (MD) calculations were performed in the canonical (NVT) or isothermal–isobaric (NPT) ensemble. Code was added to the BOSS Monte Carlo program<sup>7</sup> to perform these molecular dynamics simulations for a variety of simple molecular liquids. The velocity Verlet algorithm was used for the numerical integration,<sup>8</sup> and temperature and pressure coupling were performed with the standard Berendsen method.<sup>9</sup> The dynamics part of the code was tested by reproducing thermodynamic properties of liquid argon and TIP3P and TIP4P water in the NVT and NPT ensembles, as compared with molecular dynamics results using a modified version of the TINKER program.<sup>10</sup> In addition, the MD results were also consistent with Monte Carlo results from the BOSS (Ref. 7) program for TIP3P, TIP4P, and TIP5P water.

The diffusion constant is a transport coefficient and can be expressed within linear response theory as the infinite

TABLE I. Computed diffusion constants for water models.

Ensemble		$T$ (°C)	$P$ (atm)	Density <sup>a</sup>	$D^b$
SPC	NPT	25	1		$3.85 \pm 0.09$
SPC/E	NPT	25	1		$2.49 \pm 0.05$
TIP3P	NPT	25	1		$5.19 \pm 0.08$
TIP4P	NPT	25	1		$3.31 \pm 0.08$
TIP3P	NVT	25	(1)	0.993 <sup>c</sup>	$5.06 \pm 0.09$
TIP4P	NVT	25	(1)	0.990 <sup>c</sup>	$3.29 \pm 0.05$
TIP5P	NVT	25	(1)	0.999 <sup>c</sup>	$2.62 \pm 0.04$
Expt. <sup>d</sup>		25	1	0.997	2.30

<sup>a</sup>Units are g/cm<sup>3</sup>.

<sup>b</sup>Units are 10<sup>-5</sup> cm<sup>2</sup>/s.

<sup>c</sup>Density fixed at the value that yields a pressure of 1 atm for the model.

<sup>d</sup>See Ref. 2.

time integral of an equilibrium time correlation function. In three dimensions it is given by

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle, \quad (1)$$

where the variables represent their standard quantities. It may also be calculated from the corresponding Einstein relation,

$$2tD = \frac{1}{3} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \quad (2)$$

which is valid in the limit that  $t \rightarrow \infty$ .<sup>5,11</sup> The latter expression relates the macroscopic diffusion constant to the mean-square distance that the labeled particles travel in a time  $t$  and was used to calculate the diffusion constants in the present case. The corresponding code was tested by reproducing previously computed diffusion constants for SPC, SPC/E, and TIP4P water.<sup>3,4</sup> For the NVT ensemble calculations reported here, including those on the TIP5P model, the reference temperature was set to the temperature of interest and the density was set to the average value of the density for the model, as calculated with NPT MC calculations at the temperature and pressure of interest.<sup>1</sup> The molecular dynamics time step was 1 fs, and the temperature coupling was 0.1 ps. For the NPT calculations, the pressure coupling was 0.2 ps. In all cases periodic boundary conditions were used with a box of 267 molecules and intermolecular interactions were truncated at 9 Å.

Averages and estimated errors were computed using the values calculated for the diffusion constant from 10 or 20 consecutive runs of 100 ps each. The runs followed an equilibration phase at the state point of interest and convergence diagnostics were monitored as usual.<sup>1</sup> Error estimates were obtained by the batch-means procedure and are reported at the one sigma level of significance.<sup>1,11</sup> For each run, the value calculated for the diffusion constant was obtained by calculating, every 10 or 100 fs, the average over all of the molecules of the mean-square distance that each molecule traveled since the beginning of the run, and performing a best fit of the resultant data set to a line.

The calculated and experimental<sup>2</sup> diffusion constants for several models at 25 °C and 1 atm are presented in Table I. Both the three-site SPC and TIP3P models yielded diffusion constants that are significantly too large. For the SPC/E

TABLE II. The diffusion constant for TIP5P water at state points in the NVT ensemble.

$T$ (°C)	Pressure <sup>a</sup>	Density <sup>b</sup>	$D^c$
-25.0	1	0.981	$0.14 \pm 0.02$
-12.5	1	0.998	$0.43 \pm 0.03$
0.0	1	1.007	$1.01 \pm 0.02$
12.5	1	1.005	$1.87 \pm 0.08$
25.0	1	0.999	$2.62 \pm 0.04$
37.5	1	0.989	$3.70 \pm 0.09$
50.0	1	0.978	$4.74 \pm 0.08$
62.5	1	0.967	$6.33 \pm 0.07$
75.0	1	0.951	$6.78 \pm 0.10$
25.0	500	1.026	$2.65 \pm 0.05$
25.0	1000	1.053	$2.66 \pm 0.05$
25.0	1500	1.072	$2.60 \pm 0.04$
25.0	2000	1.092	$2.63 \pm 0.05$
25.0	3000	1.128	$2.67 \pm 0.05$
75.0	500	0.985	$6.97 \pm 0.14$
75.0	1000	1.011	$6.71 \pm 0.09$
75.0	1500	1.034	$6.38 \pm 0.09$
75.0	2000	1.055	$6.33 \pm 0.12$
75.0	3000	1.091	$5.89 \pm 0.10$

<sup>a</sup>Approximate pressure in atm. See text for explanation.

<sup>b</sup>Units are g/cm<sup>3</sup>.

<sup>c</sup>Units are 10<sup>-5</sup> cm<sup>2</sup>/s.

model, the diffusion constant and the intermolecular energy are lowered relative to the values for the SPC model by increasing the magnitudes of the partial charges.<sup>4</sup> This correction is discussed in Sec. III. The TIP4P model has a diffusion constant that shows improvement over the three-site SPC and TIP3P models, but is still too large. Note that for both the TIP3P and TIP4P models, the values computed for the diffusion constant are approximately ensemble independent. For TIP5P water, the computed diffusion constant at standard temperature and pressure of  $(2.62 \pm 0.04) \times 10^{-5}$  cm<sup>2</sup>/s represents a significant improvement over the results for the popular SPC, TIP3P, and TIP4P alternatives.<sup>3,4</sup> The seminal five-site ST2 model of water<sup>12</sup> yields a diffusion constant of  $\approx 0.30 \times 10^{-5}$  cm<sup>2</sup>/s at 0 °C and 1 atm,<sup>13</sup> which is lower than the experimental value of  $1.05 \times 10^{-5}$  cm<sup>2</sup>/s, although in NVT calculations at 0 °C and 1.00 g/cm<sup>3</sup> the diffusion constant is  $\approx 1.00 \times 10^{-5}$  cm<sup>2</sup>/s.<sup>13</sup> Concern that the underestimate of the diffusion constant might be intrinsic to five-site models has been allayed by the present results for TIP5P water.

The diffusion constant for TIP5P water over a range of thermodynamic state points is presented in Table II. As a function of decreasing temperature, the dramatic decrease in the diffusion constant observed experimentally is well reproduced, as shown in Fig. 1.<sup>2</sup> In particular, the diffusion constant decreases from  $\approx 6.78 \times 10^{-5}$  cm<sup>2</sup>/s at 75 °C to  $\approx 0.14 \times 10^{-5}$  cm<sup>2</sup>/s at -25 °C.

Pressure scans at two temperatures, 25 °C and 75 °C, were also performed. The observed behavior of the diffusion constant of liquid water is unusual in that below 25 °C initial application of pressure leads to an increase in the diffusion constant.<sup>2,14</sup> Further application of pressure causes the diffusion constant to decrease, as is typical of liquid systems when subjected to high pressure. At higher temperatures, this anomalous behavior ceases to exist and the diffusion con-

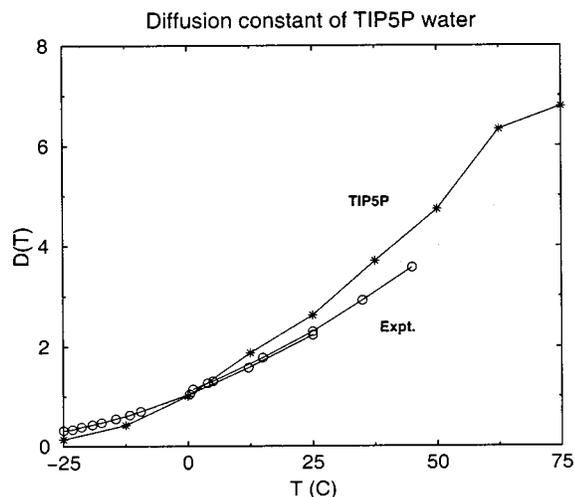


FIG. 1. The diffusion constant of TIP5P water as a function of temperature. Experimental results are from Ref. 2.

stant monotonically decreases as a function of increasing pressure. For liquid water at 25 °C, the maximum is subtle; the diffusion constant near the maximum is  $2.39 \times 10^5 \text{ cm}^2/\text{s}$ , which is only slightly higher than the value of  $2.30 \times 10^5 \text{ cm}^2/\text{s}$  at 1 atm.<sup>2</sup> This qualitative difference is at the noise level of the present calculations. Thus, reports based on much shorter calculations than the present 1 ns runs, which indicate that the diffusion constant for TIP4P passes through a maximum at  $-5^\circ\text{C}$  but not at 25 °C, may not be statistically significant.<sup>15</sup>

The results for the calculations on TIP5P water at a range of pressures are presented in Table II and Fig. 2. The results indicate that, in agreement with experiment, at 25 °C the diffusion constant is nearly constant up to 3000 atm. Interestingly, although a maximum is not clearly observed at 25 °C, an anomalous increase in the diffusion constant is seen at 75 °C upon application of pressure. However, the magnitude of this effect is near the level of the estimated error. Application of high pressure at 75 °C ultimately leads to a decreasing diffusion constant that is clearly observable

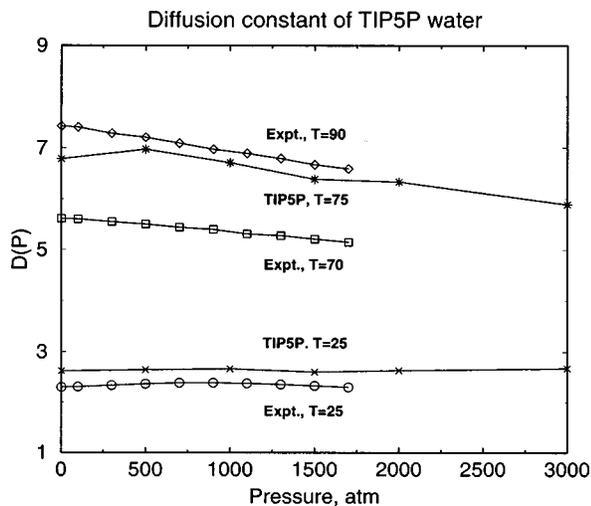


FIG. 2. The diffusion constant of TIP5P water as a function of pressure at two temperatures. Experimental results are from Ref. 2.

on the scale of Fig. 2 for both TIP5P water and experiment. This contrasts with the results at 25 °C, where both real and TIP5P water have curves that are almost flat.

### III. DISCUSSION

It is notable that at both 25 °C and 75 °C the change in the diffusion constant with increasing pressure is relatively mild when compared with its dramatic decrease with decreasing temperature. This is no doubt related to the subtle changes in the radial distribution functions as pressure is increased as opposed to the clearly increased ordering observed with decreasing temperature.<sup>1</sup> The modifications of the radial distribution functions of TIP5P water and other water models as the pressure is increased are consistent with the view that the system tends to behave structurally and dynamically more like a monatomic liquid.<sup>1,16–18</sup> On the other hand, the changes in the radial distribution functions as the temperature is decreased are consistent with a more rigidly tetrahedral arrangement in which water molecules become trapped next to one another. They also agree with experimental results that indicate that in the supercooled regime, the diffusion constant conforms to an equation that implies that the diffusion constant goes to zero as the temperature tends to  $-45^\circ\text{C}$ .<sup>2(d),19</sup>

In the SPC/E model, the magnitudes of the partial charges are increased relative to those of the SPC model. This change, which leads to improved results for some properties such as the diffusion constant, has been justified as a correction to account for the polarization self-energy required to increase the dipole moment from the gas-phase value to the solution-phase value.<sup>4</sup> Although the principle of including a polarization correction of  $\langle E_{\text{POL}} \rangle = \frac{1}{2} \sum_i \langle \mu_i^2 \rangle / \alpha_i$  to an interaction site model that has an average induced dipole moment of  $\langle \mu_i \rangle$  is no doubt correct,<sup>3,4,20</sup> its application to water models has an element of arbitrariness to it. For example, as applied to SPC/E,  $\langle \mu_i^2 \rangle$  is replaced by  $\langle \mu_i \rangle^2$  since the induced dipole moment on SPC/E does not vary in magnitude,<sup>4</sup> while others have pointed out that real water contains contributions of the form  $\langle \delta \mu_i^2 \rangle$  and thus it is not permissible to set  $\langle \delta \mu_i^2 \rangle = 0$  in  $\langle \mu_i^2 \rangle = \langle \mu_i \rangle^2 + \langle \delta \mu_i^2 \rangle$ .<sup>3</sup> In addition, the inclusion of, e.g., an  $r^{-3}$  or  $r^{-4}$  term in the Hamiltonian would lead to lower charge magnitudes since that term would absorb some of the Coulomb attraction.<sup>21</sup> This artifact of the interaction site nature of the models would lead to a smaller polarization correction since only the energy associated with the  $r^{-1}$  term would be corrected for in the standard self-polarization treatment. Further, although the correction is generally considered only for nonpolarizable models, analogous reasoning implies that it is also needed for polarizable models that have permanent dipoles greater than  $\approx 1.85 \text{ D}$ , although it has not always been included in such models.<sup>22</sup> A final example of the arbitrariness associated with the application of the correction has to do with the classical calculations which are used for the determination of the model's parameters. The use of classical rather than quantum statistical mechanics calculations may be viewed as a convenience with which is associated an implicit parameter renormalization.<sup>24</sup> Reparameterization of an

interaction site water model using path integral rather than classical statistical mechanics calculations leads to a model with a larger dipole moment in order to overcome the decreased attractiveness associated with quantum effects.<sup>23,24</sup> This would lead to an even larger polarization correction than is included in classical calculations but has not, to our knowledge, been considered.

#### IV. CONCLUSION

The recently developed TIP5P model of liquid water has a diffusion constant of  $\approx 2.62 \times 10^{-5}$  cm<sup>2</sup>/s at 25 °C and 1 atm, which compares well with the experimental value of  $2.30 \times 10^{-5}$  cm<sup>2</sup>/s. This represents a significant improvement over several commonly used alternatives. As a function of temperature and pressure, the behavior of the diffusion constant for TIP5P water is also consistent with experimental data. Coupled with the excellent results for thermodynamics, in particular the density profile,<sup>1</sup> the dielectric constant,<sup>1</sup> and liquid structure,<sup>1,25</sup> the present results support the notion that the TIP5P model provides a notably realistic representation of liquid water for temperatures below  $\approx 50$  °C. This is auspicious for its use as a basis for more accurate modeling of aqueous systems via Monte Carlo and molecular dynamics simulations.

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