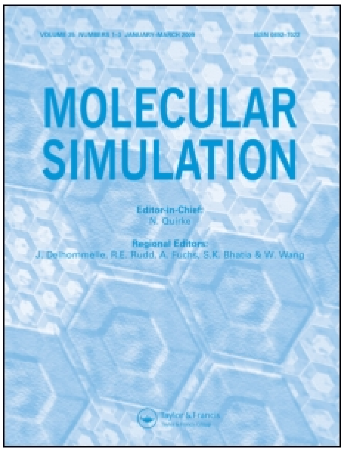

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Computer Simulation of the Dielectric Properties of Liquid Water

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COMPUTER SIMULATION OF THE DIELECTRIC PROPERTIES OF LIQUID WATER

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Monte Carlo simulations of water in the NVT ensemble using three models (SPC, TIP4P and TIPS2) are reported. The internal energy, dielectric constant, and the site-site radial distribution functions of liquid water (temperature 300 K and mass density 1 gm cc^{-1}) were calculated and compared with experiment. It was found that of the three intermolecular potential models, SPC gives the best dielectric constant. Since SPC also yields acceptable results for the energy and structure, it is judged to be the best among the three models studied.

KEY WORDS: Monte Carlo simulation, water, dielectric properties, Ewald sum

1 INTRODUCTION

Electrolyte solutions play a fundamental role in both naturally occurring systems (biological and geological) and in industrial processes. Their importance has prompted the authors to initiate the development of a statistical mechanical model for these systems. The aim of this project is to predict physical properties and phase equilibria in electrolyte systems (particularly mixed solvent systems composed of salt, water and one or more additional non-electrolytes) from a fundamentally sound basis.

The crucial role played by water in electrolyte solutions suggests that any statistical mechanical approach must begin by identifying a model for water-water interactions capable of accurately predicting experimentally measured thermodynamic, structural, and dielectric properties of water. In particular, to be useful in the context of electrolyte modeling, the potential model should produce accurate results for both thermodynamic and dielectric properties at room temperature and pressure. Among the many pair potential models for water currently available in the literature, three models (SPC, TIP4P and TIPS2) were chosen for study. Each of these models assumes that water molecules are rigid and interact through a Lennard-Jones potential between the oxygens and Coulombic potentials between positive point charges located at the hydrogens and one negatively charged site inside the molecule. The TIPS2 and TIP4P model potentials were developed by Jorgensen [1, 2] based on his transferable interaction potential (TIP) formalism, and SPC was introduced by Berendsen *et al.* [3]. Both TIPS2 and TIP4P use four interaction sites in each water molecule (three charged sites and a separate center of mass site coinciding with the oxygen center), while in SPC the negative charge is located at the center of mass thus yielding three interaction sites. Monte Carlo simulations using the Ewald sum method to correctly account for long range interactions are reported. Among the properties calculated are the internal energy, dielectric constant, and the site-site correlation functions. These are compared to experimental data to determine the "best" model for water.

Since the initiation of this comparative study, several simulations of the dielectric properties of water using these or closely related intermolecular potential models have appeared in the literature. Neumann [5] performed an equilibrium molecular dynamics simulation of water using the TIP4P potential. To account for long-ranged electrostatic interactions, Neumann used a spherical cutoff in the intermolecular potential combined with the reaction field method first introduced by Patey and co-workers [4] and refined by Neumann [6]. In addition to calculating the static dielectric constant, Neumann [5] calculated the frequency-dependent dielectric constant and compared the results with those he obtained [7] using the *ab initio* dimer potential of Matsuoka *et al.* [8]. For the TIP4P potential using 256 water molecules, Neumann found the static dielectric constant to be 53 at a temperature of 293 K and density of 1 gm cc^{-1}. Neumann suggests that the error in this result is of the order 3%-5% based on fluctuations in the Kirkwood *g*-factor over the period in which the dielectric constant is sampled (corresponding to one million time steps). Neumann did not report structural properties of TIP4P water; however, these have previously been calculated by Jorgensen *et al.* [9] using Monte Carlo simulation with simple spherical truncation of the potential. Jorgensen and co-workers [1, 9] also calculated the structural and thermodynamic properties of the SPC and TIPS2 models for water in their series of simulations; note that only the oxygen-oxygen site-site pair correlation function $g_{oo}(r)$ was compared with experimental data.

More recently, Anderson *et al.* [10] performed a molecular dynamics study of water modeled by a pair potential which is very similar to SPC. The potential used by Anderson *et al.* was introduced by Toukan and Rahman [11] and is called the flexible SPC model. It permits the water molecules to have vibrational degrees of freedom and is obtained from SPC by keeping the geometry and the charge magnitudes of the SPC intermolecular potential and introducing intramolecular potentials between the oxygen and hydrogen atoms. Anderson *et al.* performed long (approximately $4\text{–}5 \times 10^5$ time steps) of 125 water molecules at temperatures of 259, 300 and 350 K and density 1 gm cc^{-1}. The Ewald summation method was used to account for long-ranged Coulombic interactions. The diffusion constant, proton vibration spectra, dielectric constant and dielectric relaxation of the flexible SPC model were calculated. At 300 K, the static dielectric constant was calculated to be 82.5 ± 4 which compares favorably with the experimental value of 77.6 [12]. The structural and thermodynamic properties of the flexible SPC model were not reported; however, as noted above, for the usual rigid SPC model these quantities were calculated and compared with experiment in a limited way by Jorgensen *et al.* [9].

The results presented in this paper differ from these two studies as follows: neither Neumann [5] nor Anderson *et al.* [10] considered the TIPS2 potential so that the simulation results for the dielectric constant reported below for this potential are new; the Monte Carlo method is used in contrast to the molecular dynamics method employed in the Neumann and Anderson *et al.* studies for TIP4P, the use of the Ewald summation method distinguishes the present study from that of Neumann [5]; for SPC, the simulation results reported here are for the usual rigid model, rather than for the flexible model studied by Anderson *et al.* [10]. Thus, in each case, the present study complements the previous results. In the case of SPC and TIP4P, the results reported in this paper infer similar conclusions to those of Anderson *et al.* and Neumann respectively regarding the utility of these potentials in predicting dielectric properties; namely, SPC is the better of the two and is quite close to the experimental value at 300 K and 1 gm cc^{-1}. The TIPS2 model is found to give unacceptable results for the dielectric constant. However, as is clear from the results presented in Section 3 below, the present Monte Carlo simulations exhibit greater fluctuations than the molecular dynamics results, a point which is discussed in greater detail at the conclusion of the paper.

In Section 2, the details of the intermolecular potentials and the simulation methodology are briefly described. Further details are given in the Appendix. The simulation results are presented and discussed in Section 3. Section 4 contains the conclusions that follow from the present study.

2 MONTE CARLO SIMULATION OF LIQUID WATER

The three models considered in this paper, SPC, TIPS2 and TIP4P, are site-site models for the water intermolecular potential with three (SPC) and for (TIPS2 and TIP4P) sites. A site-site model approximates the energy of interaction between two molecules as the sum of spherically symmetric interactions between sites (usually associated with the centers of atoms) located in the molecules [13]. For molecules composed of m sites, the site-site model for the intermolecular potential can be written as

$$u(\mathbf{r}_{12}, \omega_1, \omega_2) = \sum_{a=1}^{m} \sum_{b=1}^{m} u_{ab}(r_{12}^{ab}) \qquad (1)$$

where $u(\mathbf{r}_{12}, \omega_1, \omega_2)$ is the intermolecular potential between molecule 1 (located at position $\mathbf{r}_1$ in orientation ω_1) and molecule 2 (located at position $\mathbf{r}_2$ in orientation ω_2), $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ is the vector joining the centers of mass of the two molecules, and $\mathbf{r}_{12}^{ab} = |\mathbf{r}_1^a - \mathbf{r}_2^b|$ is the distance and u_{ab} the pair potential between site a on molecule 1 and site b on molecule 2. Notice the convention introduced here that defines $\mathbf{r}_i^a$ as the position of site a in molecule i.

The original TIPS3 site-site model [14] has three sites with positive charges on the hydrogens and a negative charge on the oxygen such that $q_O = -2q_H$. Berendsen *et al.* [3] modified TIPS3 deriving the SPC model which gives better energy for liquid water and a smaller peak in the oxygen-oxygen site-site distribution function, $g_{oo}(r)$ at the cost of poorer agreement between the first peak and experimental data. (The site-site distribution, $g_{ab}(r)$, is defined to be proportional to the probability density of finding site a on one molecule a distance r away from site b on another molecule [13].) The TIPS3 three site model was modified by Jorgensen [9] to improve the energy and density calculated for liquid water. This new version of TIPS3 is called TIP3P. However, the second peak of $g_{oo}(r)$ tends to vanish as the accuracy of the density improves so that the improved agreement with experimentally measured thermodynamic properties comes at the expense of diminished accuracy in structural properties.

The perceived shortcomings of three site models for simultaneously predicting thermodynamic and structural properties accurately led to the development of four site models. In general, four site models are found to be better than three site models at predicting the structure and density of liquid water at room temperature and pressure. In the four site models, the negative charge is moved off the oxygen towards the hydrogens to a point (M) on the bisector of the HOH angle. This idea was first suggested by Bernal and Fowler [15] in the 1930's. Jorgensen [1, 2] developed the four site model TIPS2 as an improvement over the three site models TIPS3; he also developed an alternative parametrization of TIPS2 called TIP4P [9].

Each of these potentials (SPC, TIPS2 and TIP4P) has a Lennard-Jones interaction between the oxygens. The 3- and 4-site models have 9 other site-site interactions making a total of 10 site-site interactions. The potential $u(\mathbf{r}_{12}, \omega_1, \omega_2)$ between two water molecules is calculated from Coulombic interactions (site-site point charge interactions) and a Lennard-Jones term between the centers of the molecules. It is given by

$$u(\mathbf{r}_{12}, \omega_1, \omega_2) = \sum_{a=1}^{s} \sum_{b=1}^{s} \frac{q_1^a q_2^b e^2}{r_{12}^{ab}} + \frac{A_{LJ}}{r_{00}^{12}} - \frac{C_{LJ}}{r_{00}^{6}} \tag{2}$$

where e is the electrostatic charge, q_i^a is the charge on site a of molecule i in units of e, s is the number of charged sites, r_{00} is the distance between the centers of the oxygen atoms in the two molecules and A_{LJ} and C_{LJ} are the Lennard-Jones parameters. The parameters characterizing SPC, TIPS2 and TIP4P are given in Table 1 in which the angle $\angle HOH$ is the angle between the two lines made by joining the hydrogen sites to the oxygen site. The distances r_{OH} and r_{OM} are the distances from the oxygen site to the hydrogen site and to the center of mass M respectively. The point charges for the molecule are q_O for oxygen, q_H for hydrogen and q_M for the center of mass as illustrated in Figure 1.

The Monte Carlo simulations were carried out with the three potential models (SPC, TIPS2, and TIP4P) in the NVT ensemble at temperature $300\,K$ and density $1.00\,\text{gm cc}^{-1}$ using 108 molecules in a cubic simulation cell with periodic boundary conditions and an acceptance rate of about 40%. For an infinitely replicated simulation system with overall spherical symmetry surrounded by a dielectric continuum of dielectric constant ε', the energy H of the central cubic simulation cell containing N molecules is given by [16, 17, 19]

$$\begin{aligned} \mathrm{H}(\varepsilon') = {} & \frac{1}{L} \sum_{1 \leq i < j \leq N} \left[\sum_{a=1}^{m} \sum_{b=1}^{m} q_i^a q_j^b \frac{\operatorname{erfc}(\alpha |r_{ij}^{ab}|/L)}{|r_{ij}^{ab}|/L} + \frac{A_{LJ}}{r_{OO}^{12}} - \frac{C_{LJ}}{r_{OO}^{6}} \right] \\ & + \frac{1}{2L} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{a=1}^{m} \sum_{b=1}^{m} q_i^a q_j^b \sum_{\mathbf{n} \neq 0}^{\infty} \frac{1}{\pi |\mathbf{n}|^2} e^{\pi^2 |\mathbf{n}|^2/\alpha^2} e^{2\pi i \mathbf{n} \cdot \mathbf{r}_{ij}^{ab}/L} \\ & + \frac{1}{2L} \sum_{i=1}^{N} \underbrace{\sum_{a=1}^{m} \sum_{b=1}^{m}}_{a \neq b} q_i^a q_i^b \left[\frac{\operatorname{erfc}(\alpha |\mathbf{r}_{ii}^{ab}|/L)}{|\mathbf{r}_{ii}^{ab}|/L} - \frac{1}{|\mathbf{r}_{ii}^{ab}|/L} \right] \\ & + \frac{6\pi}{3L^3(2\varepsilon' + 1)} \left[\left| \sum_{i=1}^{N} \boldsymbol{\mu}_i \right|^2 \right] - \frac{\alpha}{L\sqrt{\pi}} \sum_{i=1}^{N} \sum_{a=1}^{m} (q_i^a)^2 \\ & - \frac{4\pi(1 - \varepsilon')}{3L^3(2\varepsilon' + 1)} N\mu^2 \end{aligned} \tag{3}$$

In equation 3, L is the length of the side of the simulation cell, μ_i is the dipole moment of molecule i and $\mu = |\mu_i|$. The adjustable parameter α is introduced in the Ewald resummation of the electrostatic interactions; its value is made large enough so that the complementary error function summation in the first term can be neglected beyond the minimum image. The constitutive relation yielding the dielectric constant

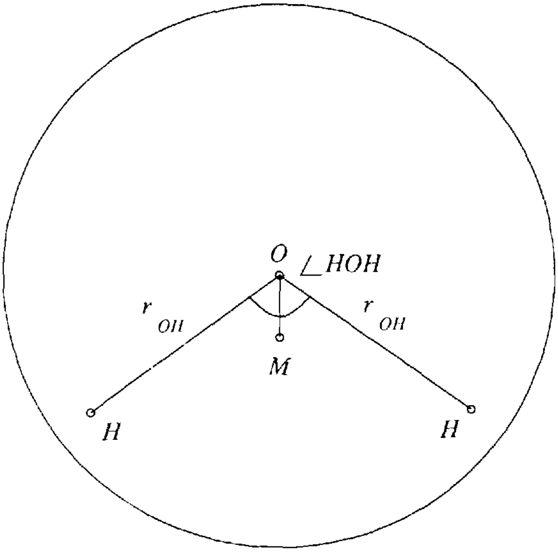

Figure 1 The geometry of the water molecule employed in the SPC, TIPS2 and TIP4P intermolecular pair potential models.

Table 1 Parameters in the SPC, TIPS2 and TIP4P models for the intermolecular potential of water.

Property	*SPC*	*TIPS2*	*TIP4P*
r_{OH} (Å)	1.0	0.9572	0.9572
$\angle HOH$ (deg)	109.47	104.52	104.52
$A \times 10^{-3}$ (kcal Å^{12}/mol)	629.4	695.0	600.0
C (kcal Å^{6}/mol)	625.5	600.0	610.0
q_O	−0.82	0.0	0.0
q_H	0.41	0.535	0.52
q_M	0.0	−1.07	−1.04
r_{OM} (Å)	0.0	0.15	0.15

ε of the simulated system can be derived using classical electrostatics and is given by [16, 17]

$$\frac{(\varepsilon - 1)(2\varepsilon' + 1)}{3(2\varepsilon' + \varepsilon)} = y g(\varepsilon') \tag{4}$$

where the Kirkwood g-factor, $g(\varepsilon')$, is given by

$$g(\varepsilon') = \frac{\langle M^2 \rangle}{N\mu^2} \tag{5}$$

and $y = 4\pi\varrho\mu^2/9k_BT$ is the dimensionless dipolar strength. In Equation 5, $\langle M^2 \rangle$ is the ensemble average of the square of the total dipole moment **M** of the simulation cell,

$$\mathbf{M} = \sum_{i=1}^{N} \mu_i.$$

Notice that the energy (and therefore the g-factor) and the constitutive relation both depend on ε'. According to de Leeuw *et al.* [17], consistent use of the ε'-dependent energy and constitutive relation yields a dielectric constant that is independent of ε'. [Strictly speaking, perturbation theory calculations [17] show that the difference between ε calculated with differing ε' is $(1/N)$.] In view of the energy formulation 3, *all* properties calculated in the simulation have some dependence on ε'; in practice, for most thermodynamic and structural properties, this dependence is negligible.

Although the results for ε are, in principle, independent of ε', in practice, de Leeuw *et al.* [18] have shown that the dielectric constant converges most rapidly if $\varepsilon' \to \infty$. Therefore, the simulations reported in this paper employed $\varepsilon' \to \infty$, corresponding to the value for a conductor (the so-called tin-foil boundary conditions). Neumann [6] has pointed out that the constitutive relation (4) is not quite correct in simulated systems since the true symmetry of the simulation is toroidal rather than spherical. However, for tin-foil boundary conditions the corrections to Equation 4 are reportedly negligible [6].

3 RESULTS

Details of the simulations, including initial conditions and equilibration, are given in the Appendix. The simulations were run for about $3 - 6 \times 10^6$ configurations after the initial equilibration in varying sized blocks yielding calculations of the energy, U, dielectric constant, ε, the three radial distribution functions, $g_{HH}(r)$, $g_{OH}(r)$, $g_{oo}(r)$ and the orientational correlation functions $g_D(r)$ and $g_\Delta(r)$ defined by

$$g_D(r) = (64\pi^4)^{-1} \int\int g(12) D(\omega_1 \omega_2 \omega) d\omega_1 d\omega_2 \tag{6}$$

$$g_\Delta(r) = (64\pi^4)^{-1} \int\int g(12) \Delta(\omega_1 \omega_2) d\omega_1 d\omega_2 \tag{7}$$

In these equations, ω is the direction of $\mathbf{r}_{12}$ and the quantities D and Δ are defined by

$$\Delta(\omega_1 \omega_2 \omega) = \mathbf{n}_1 \cdot \mathbf{n}_2 \tag{8}$$

$$D(\omega_1 \omega_2 \omega) = 3(\mathbf{n}_1 \cdot \mathbf{n})(\mathbf{n}_2 \cdot \mathbf{n}) - \mathbf{n}_1 \cdot \mathbf{n}_2 \tag{9}$$

where $\mathbf{n}_i$ is the unit vector along ω_i and $\mathbf{n} = \mathbf{r}_{12}/r_{12}$, the unit vector along $\mathbf{r}_{12}$. The thermodynamic and dielectric constant results are shown in Table 2 along with the dimensionless density $\varrho^* = \varrho\sigma^3$ (where σ is determined from the Lennard-Jones parameters A_{LJ} and C_{LJ}) and the dimensionless polar strength y. All simulations were performed at density $\varrho = 1$ gm cc^{-1} and temperature $T = 300\,K$.

The structure of a fluid is described via the site-site distribution function, $g_{ab}(r)$, which is measured experimentally in scattering experiments [13]. As one measure of the quality of a given pair potential model for water, one can compare experimental results for the structure with those obtained from simulation of the model potential. This comparison can be ambiguous since the published experimental [21, 22, 23, 24] data are themselves inconsistent. In a very thorough review of Monte Carlo simulations of water devoted to assessing the accuracy of the structural and thermodynamic

Table 2 Results obtained from Monte Carlo simulation of the TIPS2, TIP4P, and SPC potential models for water.

Model	*Configs* $\times 10^6$	y	$\rho\sigma^3$	U *kcal/mole*	U_{tot} *kcal/mole*	ε
TIPS2	3.100	5.656	1.139	−9.25	−7.47	36 ± 11
TIP4P	5.175	5.343	1.049	−9.71	−7.92	29 ± 13
SPC	6.150	5.631	1.061	−9.23	−7.44	63 ± 31
	Experiment [3, 12]			−9.92	−8.13	77.6

predictions of pair potential models (including the SPC and TIPS2 potentials), Beveridge *et al.* [25] conclude that among the experimental data available at that time (1983) only the oxygen-oxygen correlation function, $g_{oo}(r)$, could be regarded as having been determined experimentally with acceptable accuracy. Consequently, Beveridge *et al.* compared the structural predictions of several models for water pair potential models with a composite $g_{oo}(r)$ obtained from several experimental studies. They concluded that the MCY potential predicts $g_{oo}(r)$ most accurately; however, they also found that SPC and TIPS2 yield acceptable results for this quantity.

Recently, experimental results for the site-site distribution functions of liquid water at 25° have been obtained by Soper and Phillips [24]. There is evidence that these data are reliable for $g_{OH}(r)$ as well as for $g_{oo}(r)$. Lie [26] evaluated several sets of experimental data [22, 23, 24] on water site-site distribution functions by checking the site-site correlation functions for self-consistency: in essence, the integral over the site-site correlation should be independent of site label and related to the isothermal compressibility. The experimental data of Soper and Phillips was found to be the most self-consistent by this analysis. Consequently, in comparing the site-site correlation functions obtained from Monte Carlo simulation of the SPC, TIPS2 and TIP4P potentials with experiment, the data of Soper and Phillips will be used.

In Figure 2 the oxygen-oxygen site-site distribution functions calculated via simulation are compared with experimental data. The first peak is in the correct position for all potential models (SPC, TIPS2 and TIP4P); all three models underestimate the first peak, with SPC having the lowest peak. Beyond the first peak, SPC has very little structure with very shallow peaks and wells. TIP4P and TIPS2 both have peaks and wells that are more pronounced than those of SPC but are less pronounced than those of the experimental data. These results for the models simulated are reasonably consistent with those of Jorgensen's [9]. Based on this comparison between the simulated $g_{oo}(r)$ and experiment, TIP4P appears to be the best potential in view of the relative accuracy of the predicted secondary peaks in $g_{oo}(r)$.

Figure 3 compares the oxygen-hydrogen site-site distribution function calculated by simulation with the experimental data. The magnitude of the first peak for each of the potentials (SPC, TIPS2 and TIP4P) is slightly underestimated and the position of the peak is correct for all potentials. The position and magnitude of the first well for SPC is correct while both TIPS2 and TIP4P predict a shallower well with the position shifted to a slightly larger distance. All the potentials represent the second peak with respect to position but underestimate its magnitude. There are some small scale oscillations evident in the experimental data not found in the simulation. There is a small third peak in the experimental data which is difficult to see in the figure. Both TIPS2 and TIP4P show some evidence of this structure (although both tend to have a plateau rather than a peak) while SPC shows no evidence of this feature. Overall,

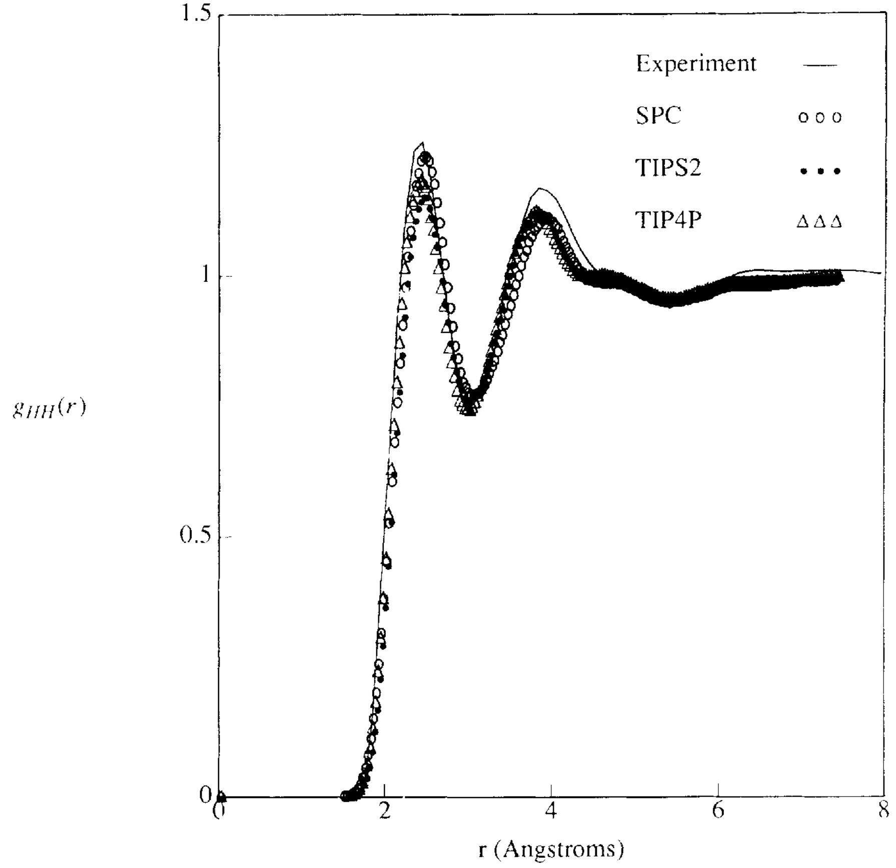

Figure 2 The oxygen-oxygen site-site radial distribution function, $g_{oo}(r)$. The solid line shows the experimental data of Soper and Phillips [24]. The symbols denote the Monte Carlo simulation results obtained in the present study: SPC(○), TIPS2 (●) and TIP4P (△).

it is apparent that TIPS2 and TIP4P have a slight edge over SPC in predicting $g_{OH}(r)$.

In Figure 4 the hydrogen-hydrogen distribution functions computed by simulation and obtained experimentally are compared. It is evident that all three potentials have the position of the first peak predicted correctly. The SPC potential predicts the peak height most accurately, while TIPS2 and TIP4P provide slight underestimates. All three potentials predict the first well correctly in both position and magnitude. All three potentials underestimate the magnitude of the second peak but are all rather close in position. Beyond the second peak, the three potentials give equivalent results which all follow the experimental data quite well. It is clear that SPC is slightly more accurate than TIPS2 and TIP4P in predicting $g_{HH}(r)$.

From the comparsion of the structural predictions of the models with experiment, it is clear that none of the three potentials emerges as a clearly superior potential. Rather, it is evident that there is little substantive disagreement between the three potential models. Certainly, as pointed out by Beveridge *et al.* [25], the discrepancy

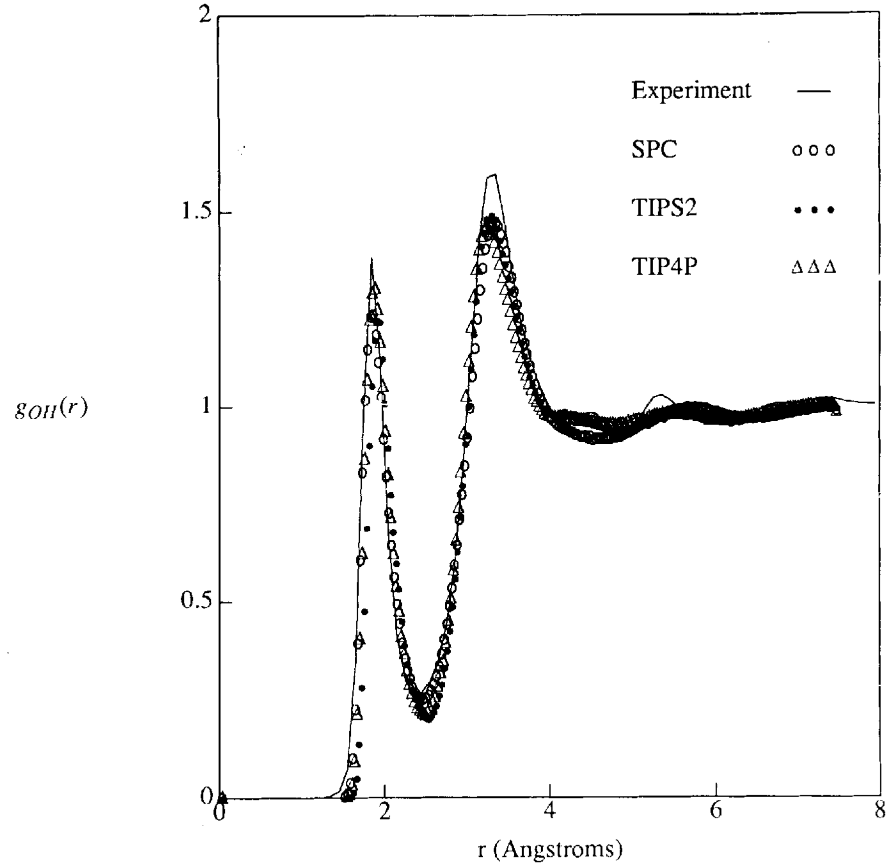

Figure 3 The oxygen-hydrogen site-site radial distribution function, $g_{OH}(r)$. The significance of the curve and symbols is given in Figure 2.

between the theoretical predictions for the site-site distribution of water is much less than that between the experimental measurements.

In Figure 5, the angular correlation functions $g_D(r)$ and $g_\Delta(r)$ are shown. Since these quantities are not accessible experimentally, no comparison can be made with experiment. However, it is evident that the TIPS2 and TIP4P exhibit less angular structure than SPC, which is reflected in the higher dielectric constant of the latter.

In addition to the structural properties, the model pair potentials can be evaluated by comparing predictions for thermodynamic and dielectric properties with the corresponding experimental data given in Table 2. The energy calculated for each of the potentials is close to experiment with TIP4P being the closest (within 2%) followed by SPC and TIPS2 which have very similar results (within 7% of experiment). These results are in general agreement with those of Jorgensen *et al.* [9]; however, Jorgensen *et al.* find that TIPS2 has the best agreement with experiment (within 04%), TIP4P is the next best (1.5%) and SPC is worst (2.6%). The source of the discrepancy between the present results and those of Jorgensen *et al.* is likely to

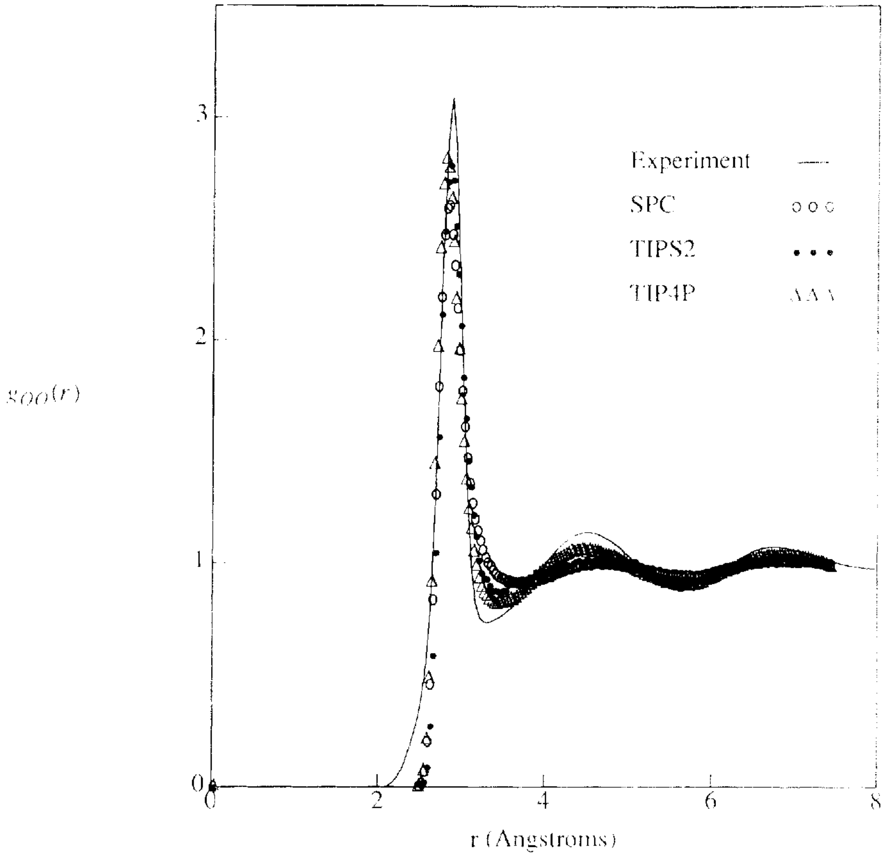

Figure 4 The oxygen-hydrogen site-site radial distribution function, $g_{OH}(r)$. The significance of the curve and symbols is given in Figure 2.

be the difference in the method of evaluating the energy: Jorgensen *et al.* use a simple spherical truncation while the present study uses the Ewald summation with minimum image in the short range part of the interaction.

Internal energy is a reasonable indicator of the accuracy of pair potential models but it is mostly dependent on the center of mass correlation with the contribution due to orientational correlation being relatively short-ranged. A more sensitive indicator is the dielectric constant since it depends on the orientational and spatial correlations at both short and long ranges. The closest dielectric constant to the experimental value of 77.6 is SPC with a value of 63 ± 31. [The method for estimating the error in the dielectric constant is described in the Appendix.] The dielectric constant for SPC oscillated around a value of approximately 65 over several million configurations and then took a steep drop to minimum of six before returning to this equilibrium value. This is part of the reason for the large estimated error in the reported value. For both TIP4P and TIPS2, the dielectric constant oscillated around its final value for several simulation blocks before the simulation was ended. Clearly, both TIPS2 and

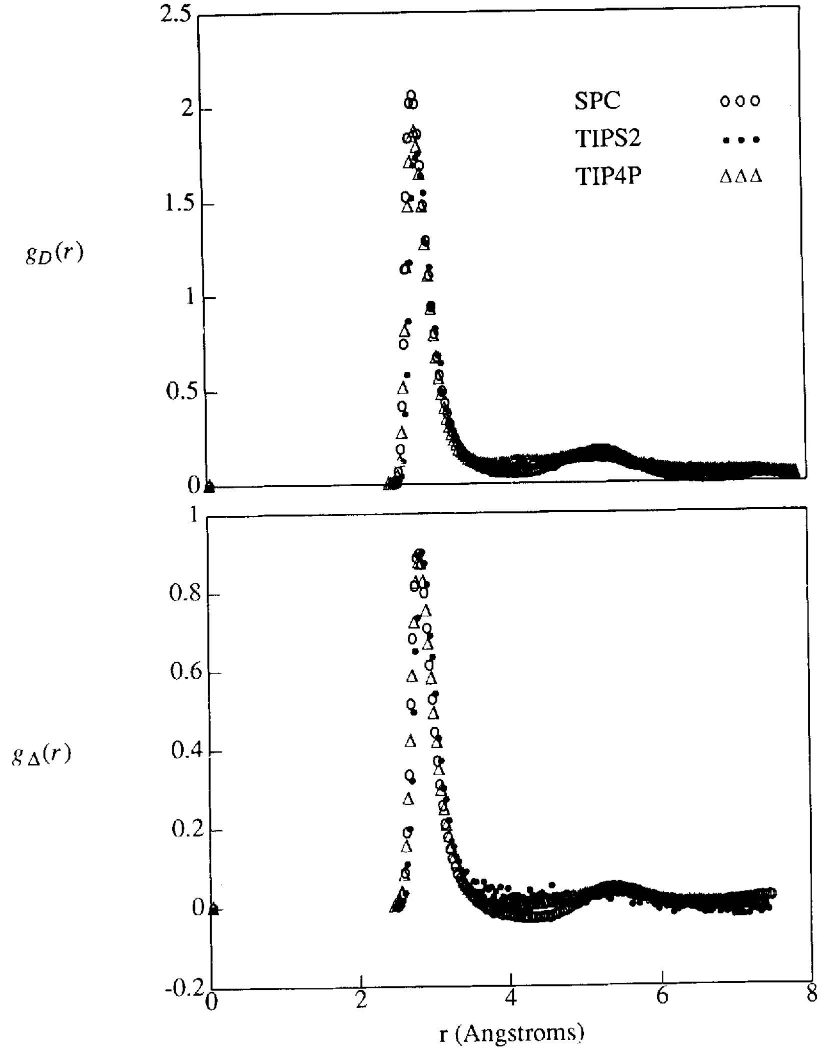

Figure 5 The angular correlation functions $g_D(r)$ and $g_\Delta(r)$ obtained by Monte Carlo simulation for the SPC (○), TIPS2 (●) and TIP4P (△) pair potentials.

TIP4P yield dielectric constants that are very low compared to the experimental result. It is worth noting that TIPS2 and TIP4P yield quite similar results which, in retrospect, is perhaps not surprising given the similarity between the two models.

For TIP4P, the dielectric constant of 29 ± 13 obtained in the present study differs significantly from the values of 53 at 293 K and 43 at 373 K found by Neumann [5] using spherical cutoff with reaction field. The source of the discrepancy is not clear and will require further simulations to be elucidated. Simulation length is one possible source of discrepancy: Neumann's simulations were performed using molecular dynamics on systems of 256 molecules for up to one million time steps. These correspond to Monte Carlo simulations that are much longer than those reported here; on the other hand, there is little evidence in the present study that running the TIP4P simulation longer would significantly raise the value of the dielectric constant. Other possible sources of discrepancy are the system size and energy evaluation methods. With the computational resources presently available to the authors, resolution of the discrepancy is beyond the scope of the present paper. In spite of the difference between the results presented here and those of Neumann, the conclusion is the same in both cases: TIP4P yields an unacceptably low dielectric constant.

In the case of rigid SPC model considered here, no other simulations have been reported which yield the dielectric constant and so direct comparison with other work is not possible. However, the result of 82.5 ± 4 reported by Anderson *et al.* [10] for flexible SPC lends credibility to the present result as it lies within the estimated error bounds. The low error bounds in the Anderson *et al.* calculation are attributable to very long molecular dynamics simulation runs (up to half a million time steps). Since Anderson *et al.* use the Ewald method on a similar sized system (125 molecules) to that employed here (108 molecules), one expects that for the same potential comparable results should be obtained for the dielectric constant. As far as can be judged (given the differences between flexible and rigid SPC), the present calculations are consistent with those of Anderson *et al.* [10].

4 CONCLUSIONS

From the results presented above, one can conclude that all three potentials (SPC, TIPS2 and TIP4P) yield accurate predictions for thermodynamic properties and reasonably accurate predictions for structural properties for liquid water at room temperature and density. The most significant difference between the three models is the predicted dielectric constant, and it is clear that TIPS2 and TIP4P are unacceptable in this regard while SPC yields a result which is reasonably close to the experimental value. Overall, then, SPC emerges as the most promising pair potential for use in modeling electrolyte solutions since in these systems the dielectric behavior of the solvent makes a direct and substantial contribution to solution properties.

Acknowledgments

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APPENDIX: SIMULATION METHODOLOGY

In this appendix, details of the simulation methodology are provided.

Hamiltonian

The energy is calculated using the Ewald summation [16, 17, 19] for the electrostatic interactions with tin-foil boundary conditions (i.e., the dielectric continuum surrounding the simulated system is a conductor-see Section 2 of text). Thus, the configurational energy H is

$$\begin{aligned} H = {} & \frac{1}{L} \sum_{1 \leqslant i<j \leqslant N} \left[\sum_{a=1}^{m} \sum_{b=1}^{m} q_i^a q_j^q \frac{\operatorname{erfc}(\alpha |\mathbf{r}_{ij}^{ab}|/L)}{|\mathbf{r}_{ij}^{ab}|/L} + \frac{A_{LJ}}{r_{OO}^{12}} - \frac{C_{Lj}}{r_{OO}^{6}} \right] \\ & + \frac{1}{2L} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{a=1}^{m} \sum_{b=1}^{m} q_i^a q_j^b \sum_{\mathbf{n} \neq 0}^{\infty} \frac{1}{\pi |\mathbf{n}|^2} e^{-\pi^2 |\mathbf{n}|^2/\alpha^2} e^{2\pi i \mathbf{n} \cdot \mathbf{r}_{ij}^{ab}/L} \\ & + \frac{1}{2L} \sum_{i=1}^{N} \underbrace{\sum_{a=1}^{m} \sum_{b=1}^{m}}_{a \neq b} q_i^a q_i^b \left[\frac{\operatorname{erfc}(\alpha |\mathbf{r}_{ii}^{ab}|/L)}{|\mathbf{r}_{ii}^{ab}|/L} - \frac{1}{|\mathbf{r}_{ii}^{ab}|/L} \right] \\ & - \frac{\alpha}{L\sqrt{\pi}} \sum_{i=1}^{N} \sum_{a=1}^{m} (q_i^a)^2 + \frac{2\pi N \mu^2}{3L^3} \end{aligned} \tag{10}$$

The error function summation over molecule pairs in the first term is restricted to minimum image pairs by choosing α large enough. Based on previous experience [19] with simulation samples of this size, α was chosen to be 5. This requires that the summation over lattice vectors in the second term in the energy include 256 simple cubic lattice vectors $\mathbf{n}$ enclosed in the sphere $|\mathbf{n}| \leqslant 4$. The Lennard-Jones interaction is truncated at the minimum image distance.

Algorithm

A standard Metropolis algorithm [28] for molecular fluids was employed in which attempted moves alternated between molecule center translations and rotations about the center of mass. At the outset of each simulation, the molecules are placed in a face-centered cubic (fcc) structure with zero net dipole moment. During the early stages of the simulation, the translational and orientational order parameters described by Freasier *et al.* [20] are monitored to ensure that the initial fcc structure is lost and orientational order is absent before thermodynamic, structural and dielectric properties are accumulated for averaging. The acceptance rates for translational and rotational moves are calculated separately and the maximum translational and rotational movement parameters are adjusted so that each acceptance rate is approximately 40%.

Properties calculated

After equilibration, the major properties accumulated for averaging are the histograms required for calculating site-site correlation functions $g_{ab}(r)$ between sites a and b on distinct molecules, the angular correlation functions $g_D(r)$ and $g_\Delta(r)$, the squared dipole moment of the simulation cell $\mathbf{M}^2$ and the configurational energy H. These latter two quantities are accumulated every configuration, the distribution functions every 200 configurations. In the case of the squared dipole moment and the configurational energy, this yields $k = 1, \ldots, N_s$ sampled values of each quantity ($\mathbf{M}_k^2$, H_k and h_k^{ab}) over the course of the simulation. The mean squared dipole moment ($\mathbf{M}^2$) and the average configurational internal energy$U$ are then calculated by

$$\langle \mathbf{M}^2 \rangle = \frac{1}{N_s} \sum_{k=1}^{N_s} \mathbf{M}_k^2 \tag{11}$$

$$\langle U \rangle = \frac{1}{N_s} \sum_{k=1}^{N_s} H_k \tag{12}$$

The mean squared dipole moment is used to calculate the Kirkwood g-factor using Equation 5 above which in turn yields the dielectric constant in a tin-foil simulation using

$$\varepsilon = 1 + 3yg(\infty) \tag{13}$$

The experimentally measurable structural properties of the water simulation are conveniently represented by the site-site radial distribution functions $g_{oo}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$. These were determined by calculating a histogram, $h_{ab}(n)$, containing the number of a-b site pairs with separations in the annulus $\Delta r(n\text{-}1/2) < r < \Delta r(n + 1/2)$ where $\Delta r = 0.01\sigma$ is the width of the annulus to which each histogram element corresponds. Each value in this histogram is then divided by the number of a-b site pairs which would be found in the annulus if the molecules and their sites were uniformly distributed yielding the site-site radial distribution function, $g_{ab}(r)$. The angular correlation functions, $g_D(r)$, and $g_\Delta(r)$, are obtained by accumulating the values of D and Δ for molecules with center-to-center separations in the annulus $\Delta r(n\text{-}1/2) < r < \Delta r(n + 1/2)$ into histograms $h_D(n)$ and $h_\Delta(n)$.

Validation of program

The program is a generalization of programs written previously by one of the authors [19, 27] to perform Monte Carlo simulations of systems with strong electrostatic interactions. Comparisons with previously published results on water are given in Section 3 and 4 of the text and the results of the present simulation are in reasonable agreement with the earlier simulations. The error in the internal energy is estimated to be about 1% based on fluctuations during the course of the simulation. The error in the dielectric constant is obtained by taking block averages of ε over varying sized blocks of about 150,000 configurations over all but the initial configurations during which the starting fcc structure is broken up; the errors in ε quoted in Table 2 represent the standard deviations derived from this analysis. This leads to quite large values for the errors which the authors believe overestimate the true errors in the simulation. For example, averaging over 10^6 configurations in the equilibrated regime yields dielectric constants of 42 ± 8, 34 ± 7 and 67 ± 11 for TIPS2, TIP4P and SPC respectively.

Other details

The simulations were performed on 108-molecule systems for lengths varying from three to six million configurations (see Table 2 above). The configurations generated during equilibration from the initial face centered structure are discarded as described above. The simulations were performed on a CSPI 6420 64-bit word array processor hosted by a Prime 850 minicomputer in the Center for Computer-Aided Engineering at the University of Virginia. For the three and four site water models, the array processor generates about 8,000 configurations per hour.

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