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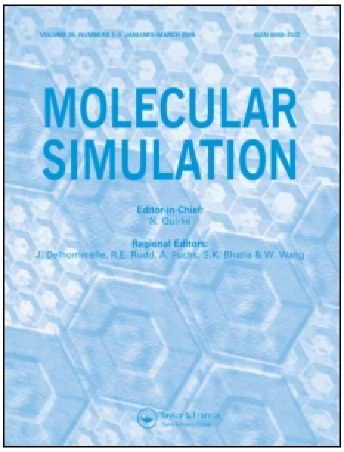

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The Dielectric Constant of the TIP4P and SPC Point Charge Models for Water at Ordinary and High Temperatures

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THE DIELECTRIC CONSTANT OF THE TIP4P AND SPC POINT CHARGE MODELS FOR WATER AT ORDINARY AND HIGH TEMPERATURES

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We report results for the dielectric constant of TIP4P and SPC water from Monte Carlo simulations at elevated temperatures. The dielectric constants from these simulations, which are much less time-consuming than those carried out at room temperature, can nevertheless be reliably extrapolated to room temperature. We find that the temperature-dependence of the Kirkwood g-factor, g_k, of the TIP4P model is qualitatively the same as that of real water.

KEY WORDS: Dielectric constant, high temperature, water, point charge models, Monte Carlo simulation

INTRODUCTION

Chemists like point-charge models for water [1–6]. This is because they are well-suited for simulations and they more accurately represent the structural, dynamic, and thermodynamic properties of real water than do the older point-multipole models such as the Stockmayer [7] and generalized Stockmayer [8] models. For example, the ST2 [3, 9], TIP4P [5, 9] and SPC [6, 9] models all predict roughly the correct number of nearest neighbours (4–6) while the Stockmayer-like models behave much like non-polar liquids in this regard; they predict ~9–12 nearest neighbours in the liquid at ordinary conditions [10].

The application of point-charge models to electrolyte systems frequently requires a knowledge of their static dielectric constant, ε. For example, the lack of a correct value for ε for the SPC model led to an overly compact picture of a micelle in a fairly recent study [11, 12]. Again, the discovery that ε for the original MCY water model was only 35 at 19°C [13] led (among those who were aware of this result) to its abandonment as a model for the aqueous environment of electrolytes. Our interest in ε values for these models derives from our work on polyelectrolytes. We are in the process of obtaining counterion distribution functions near high charge-density polyelectrolytes where the ions are dissolved in SPC water. We will compare our results to what arises from a continuum model for this solvent; the continuum solvent is manifest only through its coulombic screening, the extent of which is controlled by its value of ε.

A long-standing impediment to determining ε for strongly polar fluids by simulations stems from the significant effect of distant particles on the fluctuations in the dipole moment of the central simulation cell, and hence on ε (equation (1) below).

Two approximations designed to include long-range effects are the Reaction Field (RF) [14] and the Ewald Sum (EW) methods [15, 16]. Briefly, the RF approach replaces distant particles, i.e. those beyond a cutoff distance R_c, by a dielectric continuum. The presence of this continuum at distances beyond R_c, is explicitly brought into the potential energy through classical electrostatics. In the EW method, the central simulation cell is surrounded by an infinite number of identical cells. Then lattice vector sums are taken sequentially over spherical shells of an infinite spherical lattice surrounded by a continuum of infinite dielectric constant ε'. This choice of ε' for the external environment is (colloquially) referred to as "tin foil boundary conditions."

Until recently, it was believed that the RF and EW approximations gave different values for ε. Therefore, this field owes much to Neumann and Steinhauser [16, 17] who showed conclusively that for large systems, RF and EW yield the same value of ε.

At present there remain two problems, one fundamental and the other practical, in applying the existing methodology to obtain values of ε for point-charge water models. The fundamental issue stems from a calculation by Neumann [13, 18] on both MCY and TIP4P water that seemed to indicate that for these models the infinite system Kirkwood g-factor, g_k (equation 4 below) increased with increasing temperature, as opposed to the decrease in g_K with increasing temperature that occurs with real water. Neumann raised the possibility that this unrealistic behaviour may be due to an inadequacy in the MCY and TIP4P models. If this were so, it would compromise the usefulness of these models, at least in applications to electrolytes. The practical problem is the *huge* amount of computer time needed to generate reliable estimates of ε for these models at liquid densities and room temperature.

In this paper, we do three things. First we show, by working over a large temperature range, that the TIP4P model does in fact display the correct temperature-dependence of the Kirkwood g-factor. Second, we show that the SPC and TIP4P models yield reasonably accurate ε values much more quickly when studied at elevated temperatures (i.e. 500 K–1000 K) than they do at ~ 300 K. We also demonstrate that the dependence of ε on the "dipolar strength" function y (defined by equation 2) in the range ~ 300 K–1000 K is nearly linear for these models, so that ε values at ~ 300 K can be obtained both reliably and (relatively) efficiently by a linear extrapolation from the moderately high-temperature regime. Third, we provide working equations that can be used to generate values of ε for TIP4P and SPC water over a wide range of temperatures and densities.

THEORY

For a sample of N particles, each with permanent dipole moment μ, the finite system G-factor, G_K, is defined as:

$$G_K = \frac{\langle M^2\rangle - \langle M\rangle^2}{N|\mu|^2} \tag{1}$$

Here $\boldsymbol{M}$ is the total dipole moment of the sample, in a particular configuration ($\boldsymbol{M} \equiv \Sigma_{i=1}^{N} \mu_i$). The angular brackets denote the ensemble average. For an infinitely long simulation, in the absence of external fields, the mean net dipole $\langle \boldsymbol{M}\rangle$ will be zero. Thus G_K is a unitless function that measures the size of the fluctuations of $\boldsymbol{M}$ in an equilibrated polar sample.

Neumann has shown that the correct fluctuation formula, in the RF approximation is [19]:

$$\frac{\varepsilon - 1}{\varepsilon + 2}\left[1 - \frac{\varepsilon - 1}{\varepsilon + 2}\frac{2(\varepsilon' - 1)}{2\varepsilon' + 1}\right]^{-1} = yG_K \tag{2}$$

where

$$y = \frac{4\pi\varrho|\boldsymbol{\mu}|^2}{9K_BT}$$

Here ε' is the (arbitrary) dielectric constant of the surrounding continuum, K_B is the Boltzmann constant, T is the absolute temperature, and ϱ is the particle number density. The most convenient choice of ε' in equation (2) is ∞ which defines tin foil boundary conditions. With this choice we get:

$$\frac{\varepsilon - 1}{3} = yG_K \tag{3}$$

as our working fluctuation equation for ε. Neumann has shown that equation (3) is also the appropriate fluctuation equation for the EW approximation with tin foil boundary conditions [16, 17]. Thus, we used equation (3) as our working fluctuation equation in both our RF and EW calculations.

The finite system G_K is, in general, different from the infinite system Kirkwood g-factor, g_k. However, the latter can be obtained from the former via equation (3) and the following equation [20]:

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = yg_k \tag{4}$$

Both the TIP4P and SPC models have three distributed point charges rigidly imbedded inside Lennard-Jones cores. For both models and for both the RF and EW approximations, the total potential energy, U, is given by:

$$U = \sum_{\substack{i<j \\ (r_{ij}<R_c)}}^{N} 4\varepsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}}\right)^{6}\right] + U^{EL} \tag{5}$$

Here ε_{LJ} and σ_{LJ} are the Lennard-Jones parameters that characterize the soft cores, the first term gives the Lennard-Jones contribution to U, U^{EL} is the electrostatic contribution to U, and r_{ij} is the center-to-center distance between particles "i" and "j". The inequality in parenthesis under the sum in equation (5) means that for both the RF and EW approximations, the Lennard-Jones interactions were set to zero for distances beyond a cutoff distance R_c; i.e. we used spherical cutoff for the non-coulombic part of the potential. R_c was always taken to be $\frac{1}{2}$ the cubic cell length. The expressions for U^{EL} are long and so are given in the Appendix; the values of the parameters that characterize the TIP4P and SPC potentials are given in Table A1.

CALCULATIONS

Values of G_K, and hence ε and g_k, were generated by Monte Carlo simulations applied to a canonical ensemble, using single-particle moves, periodic boundary conditions,

Table 1 Simulation Details and Results for TIP4P and SPC water at 1.0 $\mathrm{g\,cm^{-3}}$

Simulation Geometry	*Total no. of configurations*	*T(K)*	$\langle U\rangle/NK_BT^{(2)}$	*y*	$G_K^{(3)}$	$\varepsilon^{(4)}$	$g_k^{(5)}$	*approximate*$^{(6)}$ *error in* ε	*Reference*
TIP4P $\varrho^* = \varrho\sigma^3 = 1.0557$									
MC-RF	1×10^6	3000	−0.17	0.5380	1.46	3.4	1.12	±0.5	(7)
MC-RF	2×10^6	873	−3.44	1.849	2.06	12.4	1.43	±2	(7)
MC-RF	2×10^6	673	−5.14	2.398	1.98	15.3	1.37	±5	(7)
MC-RF	4×10^6	573	−6.53	2.817	2.80	24.7	1.91	±5	(7)
MC-RF	2×10^6	500	−7.98	3.228	2.99	29.9	2.02	±5	(7)
MC-EWALD	2×10^6	500	−7.94	3.228	2.29	23.2	1.56	±5	(7)
MD-RF	0.5×10^6 MD time steps	373	−12.1	4.33		43	2.20	±2	(18)
MD-RF	1.0×10^6 MD time steps	293	−16.7	5.50		53	2.11	±2	(18)
SPC $\varrho^* = \varrho\sigma^3 = 1.0608$									
MC-RF	2.5×10^6	773	−4.26	2.261	2.93	20.9	2.00	±5	(7)
MC-RF	2.0×10^6	673	−5.27	2.597	2.64	21.5	1.79	±5	(7)
MC-RF	2.0×10^6	573	−6.69	3.050	2.43	23.2	1.65	±5	(7)
MC-RF	4.0×10^6	473	−8.81	3.695	3.25	37.1	2.20	±5	(7)

(1) All the simulations in this work were force and torque-biased Monte Carlo; MD-RF means Molecular Dynamics – Reaction Field Approximation. N = 216 for this work. N = 256 for MD-RF [18]

(2) The entries for this work are for no cut-off other than that for the Lennard-Jones contribution (text). The entries for ref [18] include this Lennard-Jones cut-off correction and omit the "self-energy" term (the last term in equation (A1)).

(3) Calculated with equation (1).

(4) Calculated from G_K and equation (3).

(5) Calculated from ε and equation (4).

(6) See text for a discussion of these error estimates

(7) This work.

and force and torque biasing [21, 22]. The potential energy of the system at each step was obtained by equations (5) and (A1) in the RF calculations, and (5) and (A2) in the EW calculations.

The forces and torques used in the biasing part of the algorithm were those obtained solely from interactions within the central simulation cell. The RF or EW contribution to the force and torque on the central particle were both relatively small, so that we did not include them in the bias. The biasing parameter, λ, for both forces and torques was taken to be 0.5, i.e. the biasing was only partially turned on [23]. The maximum move sizes were adjusted so that our acceptance rates were ~ 0.5.

Our calculations for both the TIP4P and SPC models were done with 216 particles at a density of $1.0\,\mathrm{g cm^{-3}}$ at a series of temperatures between 473 K and 3000 K. The RF approximation turned out to be considerably more efficient than EW, and so it was used for all except one of our runs. The EW approximation was run as an internal check on one of our TIP4P calculations (Table 1).

For all the runs, we selected the initial configuration from a final configuration of a prior run carried out on the same model, at the same density, but at a different temperature. This configuration was used to start a 5×10^5 trial step pre-equilibration run. The run length of 5×10^5 was selected on the basis of energy equilibration – we found that this number of trial steps was, in every case, more than enough to ensure that the internal energy oscillated without drift around an equilibrium value. Our data collection was then started and continued for between 1×10^6 and 4×10^6 trial steps. Specific details are given in Table 1.

Our calculations were done on the Guelph FPS-164 Array Processor, the $(\mathrm{GWC})^2$ SUN 3/280 and the Guelph IBM 4381. In every case, we used double precision arithmetic.

RESULTS AND DISCUSSION

Our results are given in Table 1 and in Figures 1–4. From Figure 1, it is seen that, provided a sufficiently large temperature range is considered, g_k for TIP4P water does decrease as T increases. Evidently, g_k is very difficult to obtain accurately by simulation. Therefore, comparisons of g_k values over increments of even several hundred Kelvin can be misleading. Clearly the uncertainty in g_k can exceed the influence of T for temperature increments of several hundred Kelvin. By considering a temperature increment of several thousand Kelvin we avoided this problem. Despite the large error bars, Figure 1 shows that TIP4P water does give the qualitatively correct dependence of g_k on T.

We also mention that the uncertainties in ε, that we report in Table 1, are not true standard deviations, but merely our best "guestimates" of the uncertainty. They were arrived at from a consideration of both the closeness of $\langle M \rangle$ to zero, and from the size of the fluctuations in ε over the last half of the collection part of each run.

Our results on the dependence of ε on y are displayed in Figures 2 and 3 for the TIP4P and SPC models respectively. We also include with these plots, Neumann's points [18] at 293 K and 373 K (Figure 2) and the point of Watanabe *et al.* [12] for the SPC model at 300 K (Figure 3).

As has been reported elsewhere [13, 18, 24], we have confirmed through preliminary trial calculations, that the function G_K (and so ε or g_k) converges *very* slowly for point charge models at liquid densities and temperatures at or below 373 K. Specifically,

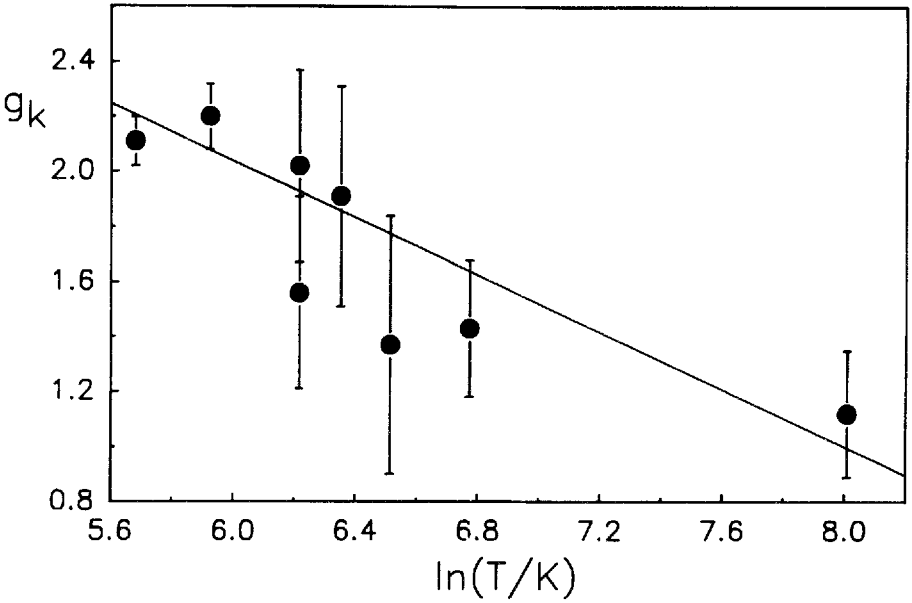

Figure 1 The temperature dependence of g_k for TIP4P water. The error bars were estimated from error estimates for ε (Table 1) and equation 4. The straight line has no theoretical significance – it was drawn to show that, when the uncertainties are included, g_k decreases smoothly with T.

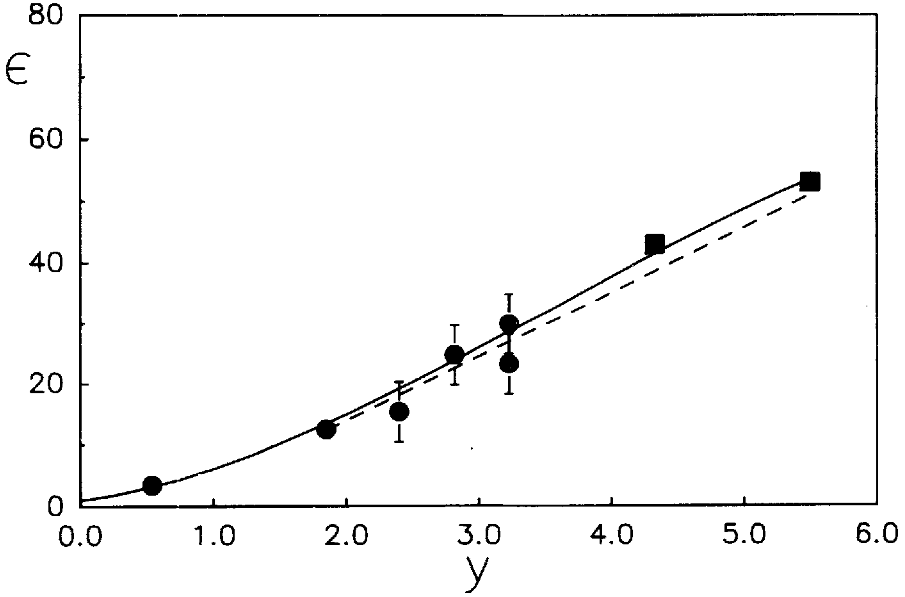

Figure 2 ε vs y for TIP4P water. (●) This work; (■) ref 18; (———) eq. (8); (– – – –) eq. (6). Error estimates are from Table 1.

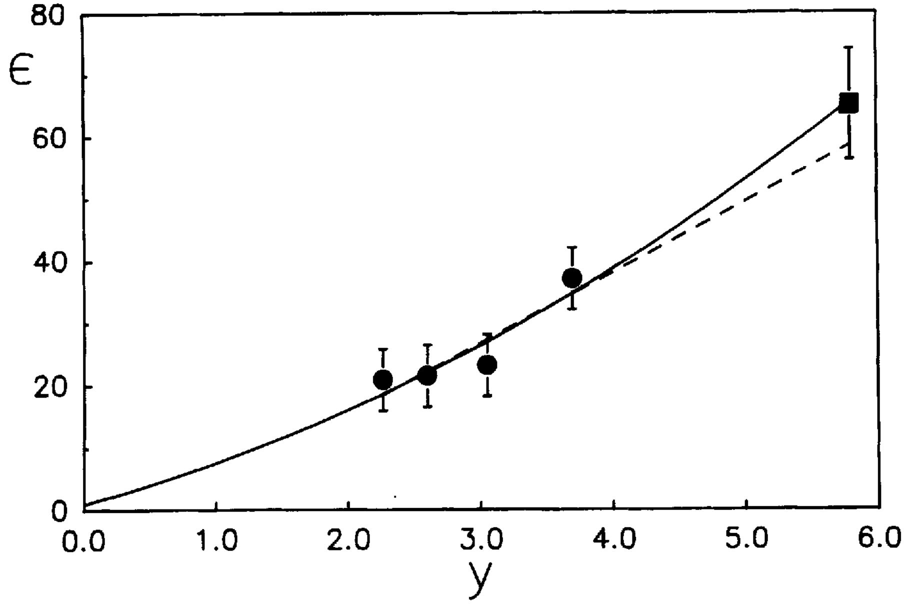

Figure 3 ε vs y for SPC water (●) This work; (■) ref 12; (———) eq. (10); (– – –) eq. (9).

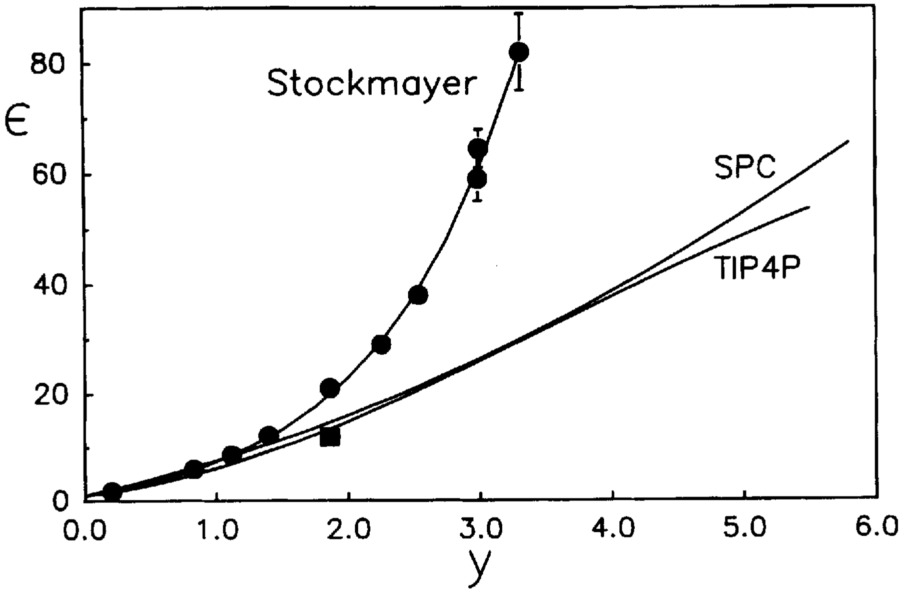

Figure 4 ε vs y for a Stockmayer potential, generalized Stockmayer potential, TIP4P and SPC water. (●) refs. 17, 19, 25–27; (——) eq. 11. To avoid clutter, some of the points used for eq. (11) are omitted from this Figure. (■) generalized Stockmayer potential (Lennard-Jones + dipole + quadrupole) taken from ref. 30. The curves for TIP4P and SPC water are from equations 8 and 10 respectively.

molecular dynamics simulations seem to require run lengths of $5 \times 10^5 - 1 \times 10^6$ time steps in order to obtain reliable estimates for ε when ε is large [13, 18, 24]. Assuming a conversion factor determined elsewhere [21], this is equivalent to $5 \times 10^7 - 1 \times 10^8$ single-particle Monte Carlo trial steps for systems of the size used here. For this reason, direct simulations for ε with water-like models, at or around room temperature, are beyond the reach of most of us.

However, an examination of Figures 2 and 3 reveals that unlike the Stockmayer potential (Figure 4), these point charge models display only a mild non-linearity in their ε versus y dependencies. Since y is a slowly varying function of T (equation 2) this slow variation of ε suggests an efficient way to obtain ε for these models at room temperature: a smooth extrapolation from results at moderately high temperatures ($\sim$ 500 K to $\sim$ 1000 K) where convergence is much more rapid. Note that the ten runs we report, collectively required $\sim\frac{1}{3}$ the CPU time that would be required for one simulation at room temperature.

We demonstrate in Figures 2 and 3 that this procedure works. The dashed lines in each case are weighted, linear least-squares fits through our 500 K–873 K points for TIP4P water and through our 473 K–773 K points for SPC water. We used the reciprocal of the square of the uncertainty in each ε (Table 1) as a weight function. In two out of three cases (TIP4P at 293 K and SPC at 300 K), a linear extrapolation gives the same value of ε, within the noise as Neumann and Watanabe *et al.* have obtained directly but with much greater computer time expenditures. In the third case (TIP4P at 373 K), the agreement with the value of Neumann is qualitatively good. We have therefore achieved a five to ten-fold improvement in efficiency by this simple procedure.

The efficiency gain comes from the much faster convergence rates at elevated temperatures and the slow onset of curvature in the ε versus y plots for these models. In Figure 4 we compare the ε versus y behaviour for TIP4P water, SPC water, the Stockmayer potential, and a generalized Stockmayer potential.

The fact that the generalized Stockmayer point falls on or close to our fits suggests that the slow onset of curvature and the depressed values of ε given y with the distributed charge models, are due to the disruptive influence of higher multipoles on dipole–dipole correlations.

We see no reason why this procedure should not be applicable to other distributed point charge models such flexible SPC water [24], ST2 water, or others. The key requirement seems to be the existence of significant higher multipole moments. These are implicit in distributed charge models.

Our fits can be used to generate values of ε over a wide range of T and/or ϱ so they are given below. As with the linear fits, the least-squares polynomial fits involved the use of a weight function taken to be the square of the reciprocal of the estimated uncertainty at each point. The polynomial fits were constrained to give $\varepsilon = 1$ at $y = 0$.

TIP4P (our work): $\varepsilon = -7.3 + 10.6y;\ 1.849 \leqq y \leqq 3.228$ (6)

TIP4P (our work and ref [18]): $\varepsilon = -8.7 + 11.4y;\ 1.849 \leqq y \leqq 5.50$ (7)

TIP4P (our work and ref [18]): $\varepsilon = 1 + 2.80y + 2.577y^2 - .2454y^3;$ (8)

$$0 \leqq y \leqq 5.50$$

SPC (our work): $\varepsilon = -7.1 + 11.3y;\ 2.261 \leqq y \leqq 3.695$ (9)

SPC (our work and ref [12]): $\varepsilon = 1 + 5.67y + .938y^2; \quad 0 \leqq y \leqq 5.8$ (10)

Stockmayer Potential [17, 19, 25–27]: $\varepsilon = 1 + 2.932y + 4.210y^2 - 1.323y^3 + .6115y^4; \; 0 \leqq y \leqq 3.31$ (11)

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APPENDIX

For the RF approximation, the electrostatic contribution to U for both the TIP4P and SPC model is given by [18]:

$$U^{EL} = \sum_{i<j}^{N} \sum_{\gamma=1}^{3} \sum_{\beta=1}^{3} \frac{q_i^\gamma q_j^\beta}{r_{ij}^{\gamma\beta}} \left\{1 + \frac{(\varepsilon'_{RF} - 1)}{2(\varepsilon'_{RF} + \frac{1}{2})} \left(\frac{r_{ij}^{\gamma\beta}}{R_c} \right)^3 \right\} - \frac{N}{2} \frac{(\varepsilon'_{RF} - 1)}{(\varepsilon'_{RF} + \frac{1}{2})} \frac{|\mu|^2}{R_c^3} \qquad \text{(A1)}$$

In equation (A1) $r_{ij}^{\gamma\beta}$ is the distance between charges "γ" of molecule "*i*" and "β" of molecule "*j*". All interactions between molecules "*i*" and "*j*" are set to zero if the center-to-center distance r_{ij} exceeds the cutoff radius R_c. As mentioned in the text, we used tin foil boundary conditions so that $\varepsilon'_{RF} = \infty$ and the term $(\varepsilon'_{RF} - 1)(\varepsilon'_{RF} + \frac{1}{2}) = 1$ in equation A1.

In the EW approximation, the electrostatic contribution to U, for both the TIP4P and SPC models, is given by [15, 28, 29].

$$\begin{aligned} U^{EL} = {} & \frac{1}{L} \sum_{i<j}^{N} \sum_{\gamma=1}^{3} \sum_{\beta=1}^{3} q_i^\gamma q_j^\beta \sum_{\mathbf{n}} \frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ij}^{\gamma\beta}/L + \mathbf{n}|)}{|\mathbf{r}_{ij}^{\gamma\beta}/L + \mathbf{n}|} + \qquad \text{(A2)} \\ & \frac{1}{2\pi L} \sum_{\mathbf{n}}^{*} \frac{\exp\{-\pi^2|\mathbf{n}|^2/\alpha^2\}}{|\mathbf{n}|^2} \times \left\{ \left[\sum_{i=1}^{N} \sum_{\gamma=1}^{3} q_i^\gamma \cos(2\pi\mathbf{n}\cdot\mathbf{r}_i^\gamma/L) \right]^2 + \right. \\ & \left. \left[\sum_{i=1}^{N} \sum_{\gamma=1}^{3} q_i^\gamma \sin(2\pi\mathbf{n}\cdot\mathbf{r}_i^\gamma/L) \right]^2 \right\} + \\ & \frac{1}{L} \sum_{i=1}^{N} \sum_{\gamma<\beta}^{3} q_i^\gamma q_i^\beta \left\{ \sum_{\mathbf{n}}^{*} \frac{\operatorname{erfc}(\alpha|\mathbf{r}_{ii}^{\gamma\beta}/L + \mathbf{n}|)}{|\mathbf{r}_{ii}^{\gamma\beta}/L + \mathbf{n}|} - \frac{\operatorname{erf}(\alpha|\mathbf{r}_{ii}^{\gamma\beta}/L|)}{|\mathbf{r}_{ii}^{\gamma\beta}/L|} \right\} + \\ & \frac{1}{2L} \sum_{i=1}^{N} \sum_{\gamma=1}^{3} (q_i^\gamma)^2 \left\{ \sum_{\mathbf{n}}^{*} \frac{\operatorname{erfc}(\alpha|\mathbf{n}|)}{|\mathbf{n}|} - \frac{2\alpha}{\pi^{1/2}} \right\} \end{aligned}$$

Here **n** is the lattice vector (n_x, n_y, n_z) which specifies the position of an image cell relative to the central cell. The vector between charges "γ" on molecule "i" and "β" on molecule "j", for "i" and "j" in different cells is $\mathbf{r}_{ij}^{\gamma\beta} + \mathbf{n}L$. In equation A2, $\sum\limits_{\mathbf{n}}^{*}$ means

Table A1 Parameters and geometries that define the TIP4P and SPC potentials

	TIP4P [5]	*SPC [6]*
$\varepsilon_{LJ}/K_B(K)$	78.03	78.23
$\sigma_{LJ}(\text{Å})$	3.1536	3.166
$r_{OH}(\text{Å})$	0.9572	1.0
$r_{OM}(\text{Å})^{(a)}$	0.15	-
$< HOH$	104.52°	109.47°
$q_H^{(c)}$	0.52e	0.41e
$q_O^{(c)}$	–	$-0.82e$
$q_M^{(c)}$	1.04e	–
$\lvert\boldsymbol{\mu}^*\rvert^{2(b)}$	14.03	15.09

(a) M, denotes the location of the negative charge for TIP4P water. It lies on the bisector of $< HOH$

(b) $|\boldsymbol{\mu}^*|^2 = |\mu|^2/(\varepsilon_{LJ}\sigma_{LJ}^3)$

(c) e is the electronic charge (1.602×10^{-19} coulombs)

that when $|\mathbf{n}| = 0$, i.e. when we are summing inside the central cell, the divergent term with $\gamma = \beta$ is omitted. The lattice vector sums are done sequentially over spherical shells of an infinite spherical lattice surrounded by a continuum of infinite dielectric constant. α is an arbitrary constant whose value is chosen to speed convergence. It is chosen so that only the $|\mathbf{n}| = 0$ term is significance in the erfc summation in the first multiple sum involving $\sum_{i<j}$ Specifically, α is chosen on the basis of how much error "δ", is to be tolerated by using this approximation. The remainder of the infinite lattice sum is set to zero when the error in dropping a subsequent term is less than δ. That is, only lattice vectors having $|\mathbf{n}| \leq |\mathbf{n}|_{max}$ are included. As α increases, the error in incorporating only $|\mathbf{n}| = 0$ in the first term decreases, but the required value of $|\mathbf{n}|_{max}$ increases. We chose a value of $\alpha = 6$ and $|\mathbf{n}|_{max} = 6$, so that a total of 462 lattice points were included. With this choice the error was a few parts in 10^5 in the total energy per particle for 216 TIP4P particles at T = 500 K.

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