

CHAPTER 5

A Review of the TIP4P, TIP4P-Ew, TIP5P, and TIP5P-E Water Models

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Recent advances in simulation techniques have prompted the re-parameterization of earlier water models, which were originally parameterized using older simulation methods. Many of these newly developed water models focused on reproducing specific properties, or a number of properties in a particular phase; other models have been designed to save on computational costs while some others take advantage of faster computational resources by treating various interactions more effectively. In this review, we examine the TIP4P and TIP5P water models and the recent re-parameterizations to include current Ewald summation techniques to treat long-range electrostatics, which has been shown to be superior to that of previous truncation cut-off techniques. The empirical differences between the models along with the change in observed properties will be reviewed, as well as the applications of these models in the literature.

1. INTRODUCTION

Molecular simulations have been used for the past 40 years to observe properties of bio-molecules, organic, and inorganic compounds in their natural environment

on a time scale that is not feasible with current experimental techniques [1,2]. Data from molecular simulations has been used to save huge amount of resources in the scientific community, but still are only as reliable as the work that was put into simulation and its preparation [3]. In order for a molecular model to be as accurate as possible, one must consider all influences in that particular system and the contribution that each makes to the overall stability of the observed molecules. Thus, it is reasonable to assume that the solvent would be one of the most important choices in preparing a molecular simulation, as solvents tend to make up most of the bulk of a bio-molecular simulation. The bulk of bio-molecules, proteins, and ions are found naturally occurring in an aqueous solution, so the natural environment for most molecular simulations is in water or some type of aqueous solution. Prior to computational molecular simulations, there have been many proposed models to try and explain all the unique properties of water [4–7]. The models of water have unique forms and properties that are associated with them and influence molecular simulations accordingly.

As there is no one water model that can provide all the properties of water within experimental uncertainty, there have been numerous water models proposed throughout the literature, each with its advantages and weaknesses [8,9]. In choosing a water model for use in a molecular simulation, the desired properties of interest must be planned, as it will determine which water model would be optimal for the simulation. Efforts have been taken in parameterizing certain empirical water models to make them suitable for simulations under specific conditions [10–12]. An important feature of water molecules is the transferability of the force fields in different simulation programs. In some cases, transferability of the model may not be possible, as some programs use different functional forms for their potential energy. The functional form is also a computational consideration, since more descriptors of the water molecule may lead to better calculated properties, at the cost of the speed and resources needed for the simulation [1,2,13]. These considerations have been dealt with in many of the water molecules, and certain water molecules have emerged from the literature as the more popular water molecules in these types of simulations.

Among some of the most widely used water molecules are the 4-site and 5-site transferable intermolecular potential water molecules, TIP4P and TIP5P, respectively, developed by Jorgensen and coworkers [12,14]. These water molecules were parameterized to be used in a wide range of simulations and reproduce many experimental water properties, with reasonable computational cost. The TIP4P and TIP5P water molecules were originally parameterized using truncated cut-off methods for long-range electrostatics to save on computational costs [12,14]. As computational resources have increased in recent years, the treatment of the long-range electrostatics has become a priority in the simulation community, as the truncated portion can now be treated more precisely and more reasonably from a resource standpoint [15–21]. Re-parameterization of these

water molecules has been done in order for Ewald summation techniques to be used in the long-range electrostatic summation, which has been shown to be superior to its predecessor cut-off method. These new models, the TIP4P-Ew and TIP5P-E, have shown improved properties of water over their base models, even without the use of flexibility or polarizability, which has been previously done in the literature [3,22].

With each developed water molecule, there come a number of simulations that show the simulated properties of the water molecule, along with the limits of the molecule for use in bio-molecular and phase transitional simulations. This review will encompass the simulations completed with the previously mentioned water models, the TIP4P, TIP4P-Ew, TIP5P, and TIP5P-E. An examination of the parameters and properties that were used in the parameterization will be presented, along with the literature use of these water models. Comparisons of the water molecules simulated structural, kinetic, and thermodynamic properties will be shown along with their comparisons to water's experimental values.

2. METHODS

All the water models in this review are empirical water models that use a force field equation that involves only non-bonded terms, as the water molecules themselves are rigid. The interaction for any of the water molecules with themselves or external influences can be calculated as:

$$U(r)_{\text{non-bonded}} = \sum (\epsilon_{ij} [\{(\sigma_{ij}/r_{ij}) \times 12\} - \{(\sigma_{ij}/r_{ij}) \times 6\}] + (q_i q_j) / (\epsilon_D r_{ij})) \quad (1)$$

where the $U(r)$ is the potential energy of the system that is summed over all the non-bonded atoms of the system, ϵ_{ij} the well depth calculated from the individual atoms, σ_{ij} the collision diameter, q the charges on the atoms, ϵ_D the dielectric constant, and r_{ij} the distance between atoms i and j . The well depth and collision diameter for the pairs are calculated from the standard mixing rules that can be shown as [23]:

$$\sigma_{AB} = [(\sigma_{AA} + \sigma_{BB})/2] \quad (2)$$

and

$$\epsilon_{AB} = [(\epsilon_{AA}\epsilon_{BB}) \times \frac{1}{2}] \quad (3)$$

where the AA and BB terms are the interaction of two like atoms and the AB terms are the mixed terms.

For the potential energy of the system to be calculated, the Lennard-Jones (LJ) and the Coulombic interactions are calculated separately. The LJ interactions are calculated between a pair and are based on a cut-off distance with both a smoothing function and a correction term applied for the energy lost after the cut-off. The electrostatic interaction can be calculated in several ways, including the truncated cut-off method and the Ewald summation method.

The Ewald summation technique has been shown to be superior to that of the truncated cut-off method used in previous simulations. It has been shown that the cut-off technique underestimates the energy of the system due to the interactions that were disposed of after the cut-off boundary. Although the energies after the cut-off might seem negligible at first to the contribution to the overall energy, the conservation of energy in the simulation is affected enough to make an impact on the outcome of the simulation.

Problems arise when treating long-range electrostatics due to the summation of the electrostatic interaction converging quite slowly, which makes the electrostatics quite costly. Methods were used that would save computational costs in the area of the expensive electrostatic contribution summations. Truncated cut-off methods looked at the overall contribution of the electrostatic summation and found a defining radius where indispensable electrostatic contribution was defined, where the interaction beyond this point could be deemed negligible and were excluded from the overall electrostatic contribution. This cut-off distance depended on the type of simulation being done, the types of molecules in the system, the solvent choice, and, as it seems in some cases, the discretion of the user, although explicit spherical cut-offs were set in the original parameterizations.

The Ewald summation technique is effective in treating the long-range electrostatics by splitting the summation into two separate series and then treating the two summations with a self-correction factor. The advantage of splitting the summation into two series is that each of the series converges much more rapidly than the original summation. With the series in the Ewald summation converging much more rapidly than that of the traditional calculation of the long-range electrostatics, it is possible to treat all electrostatic interactions using Ewald summation techniques. For a more thorough discussion on how to calculate or implement the Ewald summation techniques, refer to articles by De Leeuw *et al.* [24–26] and sections in referenced books [23,27].

3. 4-SITE WATER MODELS

3.1. TIP4P

The 4-site transferable intermolecular potential (TIP4P) model was developed by Jorgensen *et al.* to reproduce experimental structural and thermodynamic

properties of water at 1 atm pressure [12]. At the time of its development, TIP4P was a balance between computational cost and reliability, with a rigid 4-site model. This is computationally less expensive than earlier 5-site models, and reproduces liquid structure and density at 298 K and 1 atm better than some previous 3-site models, including the CF1, TIP3P, and SPC water models [10,12,28].

The orientation of the TIP4P water model can be seen in Fig. 1. It is an adaptation of a 3-site model with the charge of the oxygen moved down to a fictitious site, M. This site M is located in the bisecting plane of the HOH angle and at a distance of 0.15 Å from the oxygen atom. For the geometry of the water model, the experimental gas-phase geometry was chosen, where the distance from the oxygen to the hydrogen, d , is set at 0.9572 Å, with an HOH angle of 104.52°. The charge of the midpoint was set to $-1.040e$, with a 0.520e charge placed on each of the hydrogen atoms; this yields an overall dipole moment of 2.177 D. This dipole moment is significantly improved over the rigid 3-site models in the literature. For the LJ interactions, the σ was set at 3.15365 Å, with a well depth, ϵ , of 0.1550 kcal/mol. A summary of the empirical parameters for the TIP4P water model can be seen in Table 1.

Since its development, numerous Monte Carlo (MC) and molecular dynamic (MD) simulation have been performed using the TIP4P water model [29–37]. From these simulations, many property values have been computed with reasonable statistical uncertainty. Densities of liquid water have been calculated over a temperature range for the TIP4P model, and it has been found that the density maximum occurs at ~ 260 K, with a value of 1.001 ± 0.001 g/cm³ at STP (298 K and 1 atm) [32,38–41]. The $\Delta_{\text{vap}}H$ at STP is shown to be 10.65 ± 0.01 kcal/mol showing $< 1\%$ deviation from the experimental value of 10.51 kcal/mol. Other calculated thermodynamic and kinetic values for TIP4P, such as C_p , κ , α , and ϵ , are within reasonable agreement with the experimental values at STP. TIP4P yields a C_p value of 20.4 ± 0.7 cal/mol K, a $\kappa \times 10^6$ value of 60 ± 5 atm⁻¹, an $\alpha \times 10^5$ value of 44 ± 8 deg⁻¹, and ϵ values of 53, 61, and 72 [38,42–44]. The corresponding experimental values for C_p , κ , and α are, respectively, 18.0 cal/mol K, 45.8×10^6 atm⁻¹, 25.7×10^5 deg⁻¹, and ϵ is found to be 78 [12,41,45–47]. While these values are close to values reported from

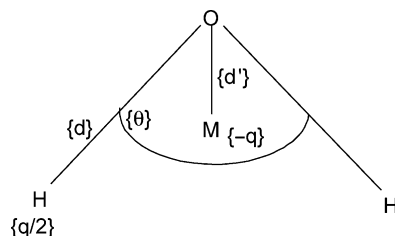


Fig. 1. Structure of TIP4P and TIP4P-Ew water models.

Table 1. Force field parameters for TIP4P and TIP4P-Ew

	TIP4P	TIP4P-Ew
σ (Å)	3.15365	3.16435
ε (kcal/mol)	0.155	0.16275
d (Å)	0.9572	0.9572
θ (°)	104.52	104.52
d' (Å)	0.15	0.125
q (e ⁻)	1.04	1.04844
Dipole moment, μ (D)	2.177	2.321

TIP3P and SPC water, the radial distribution functions (RDFs) for TIP4P are much closer to experiment, with an OO RDF showing well-defined second and third peaks, without sacrificing the OH and HH RDFs [38].

3.2. TIP4P-Ew

More recently, there has been a move to treat electrostatic interactions more accurately than previous truncated cut-off methods as computational resources have increased and algorithms are more refined. The truncated energy in the original TIP4P water model has been found to play a significant part in the overall energy of the molecular system, and the use of the Ewald summation technique for long-range electrostatics with the original TIP4P water model shows significant deviation from the properties that it was originally parameterized to reproduce [3]. A re-parameterization of the TIP4P water model was undertaken to account for the changes in structural, thermodynamic, and electrostatic properties of liquid water, with the use of the Ewald summation and long-range Lennard-Jones interactions, as it has been shown to lower energies of the order of $\sim 2\%$ [48,49]. This new model has been dubbed the TIP4P-Ew water model, as it is meant for use with electrostatic contributions calculated with Ewald summation techniques and more precise long-range Lennard-Jones interactions.

Precise experimental thermodynamic and structural properties were used to re-parameterize the new water model for use with Ewald. Of these precise experimental quantities, the enthalpy of vaporization, $\Delta_{\text{vap}}H(T)$, and the density, $\rho(T)$, were used to parameterize the new model, without sacrificing any of the previous model properties. This was done by minimizing the error of both $\Delta_{\text{vap}}H(T)$ and $\rho(T)$, over a desired temperature range, with the new inclusion of the more precise energies. The temperature range selected for the parameter error reduction was from 235.5 to 400 K, the entire liquid range for simulated water; these were all done at 1 atm pressure. The authors of the TIP4P-Ew model also note the precise calculation of the structural and thermodynamic properties of the system with statistical uncertainties weighted appropriately for the analysis.

The TIP4P-Ew water model retains the gas-phase geometry of its predecessor, TIP4P, with changes being done with the other parameters of the water model. The re-parameterization included changing the charge, q , on site M from 1.040e in the original TIP4P model to 1.04844 and subsequently changing the charge on the hydrogens. This change improves the overall dipole moment (μ) of the water molecule to a value of 2.321 D, which is a significant improvement over the TIP4P μ , which is 2.177 D. TIP4P's ϵ was changed to a value of 0.162750 with a σ value set at 3.16435 Å. Although changes to these values appear only miniscule, they have drastically changed the structural, thermodynamic, and kinetic properties of the simulated bulk water.

The desired properties of the re-parameterization were improved significantly over the original model. Since the TIP4P-Ew model has only recently been released, the calculated properties are reported by Horn *et al.* [3] The bulk density curve moved its maximum to the experimental value of 277 K at 1 atm. This density curve also more closely follows the experimental density curve than TIP4P and even more closely than that of the polarizable TIP4P-pol [50], at lower temperatures, and the 5-site TIP5P, although the shape of the TIP5P models more closely matches the experimental slope. The overall absolute average density error is found to be 0.0056 g/cm³ for the TIP4P-Ew model. The $\Delta_{\text{vap}}H(T)$ over the simulated temperature range for the TIP4P-Ew model closely follows the experimental values and slope, with a maximum error of +1.7% at 235.5 K; this yields heat capacities, $C_p(T)$, that are slightly high [3].

4. 5-SITE WATER MODELS

4.1. TIP5P

The TIP5P water model was developed by Jorgensen and Mahoney to reproduce known experimental values of water better than its 4-site and 5-site predecessors, including the TIP4P and ST2 models [12,14,51]. The 5-site transferable intermolecular potential (TIP5P) is similar to previous 5-site models, where the sites are located on the atoms of the water molecule and on two lone pair sites, as can be seen in Fig. 2. The geometry of water in the TIP5P model is the same as the TIP4P model, where the experimental gas-phase geometry was adopted. The distance from the oxygen to the lone pairs, r_{OL} , is 0.70 Å, while the θ_{LOL} angle is set to 109.46°. Charges for the water molecule reside on the two hydrogens and the two lone pairs, with LJ terms only residing on the oxygen. The charge for the lone pairs is each 0.241e, with corresponding charge residing on each hydrogen atom; this charge separation yields a dipole moment, μ , of 2.29 D for the molecule. The LJ terms were set as 3.120 Å for σ and 0.160 kcal/mol for ϵ . All the empirical parameters for the TIP5P model can be seen in Table 2.

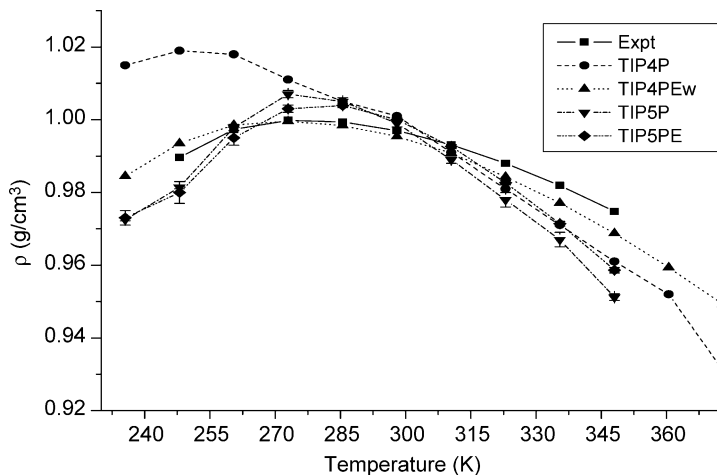


Fig. 2. Temperature dependence of bulk water density for TIP4P, TIP4P-Ew, TIP5P, and TIP5P-E.

TIP5P water reproduces the experimental density curve from 235.5 to 335.5 K remarkably well with an average error in density of only 0.006 g/cm³ [14]. The maximum density of TIP5P reproduces the experimental maximum at 277 K, with better agreement below 323 K. Trends for C_p , κ , and α are similar to that of TIP4P water, with only slight error from experimental value. However, the error reported from TIP4P is from only STP, while the TIP5P model follows the temperature range from 235.5 to 348 K considerably well, with slight deviation at the extremes [14]. The dielectric constant from 273 to 373 K is reproduced well when compared to experiment, and the slope is similar only translated higher by $\sim 6\%$, although this would be assumed as the dielectric constant would improve with a better description of the quadrupole moment, as seen in the literature [42,52].

Structural properties of the TIP5P model show similar results to the TIP4P model, which offered significant improvements over 3-site models. The TIP5P

Table 2. Force field parameters for TIP5P and TIP5P-E

	TIP5P	TIP5P-E
σ (Å)	3.12	3.097
ε (kcal/mol)	0.16	0.16275
d_{OH} (Å)	0.9572	0.9572
d'_{OL} (Å)	0.7	0.7
θ_{HOH} (°)	104.52	104.52
θ'_{LOL} (°)	109.47	109.47
q_H (e ⁻)	0.241	0.241
Dipole moment, μ (D)	2.29	2.29

model reproduces the experimental g_{00} as well as the TIP4P model, with even better improvements in the shape of the second peak, with some H–H RDF being somewhat high [14]. Hydrogen bonding over the simulated temperature scales seems to be in agreement with the TIP4P model, with more tetrahedral-like geometries being sampled at higher temperatures [14]. Kinetically, TIP5P water reproduces the D_{self} over a wide range of temperatures (235.5–348 K) reasonably well, following the trend with a maximum deviation from experiment occurring at higher temperatures [22,53]. There has been considerable work done on the pressure dependence of the D_{self} of TIP5P at high pressures; it is noted that there is good correlation between experimental values and TIP5P from 1 to ~ 1700 atm for temperatures between 298 and 363 K [53]. Similar results reported by Rick are with $\sim 2\%$ error [22].

4.2. TIP5P-E

Recently released is the re-parameterization of the TIP5P model to include Ewald summations, dubbed the TIP5P-E model [22]. Similar to that of the 4-site models, the use of Ewald summations lowers the energies and changes the properties of the original water model, to a certain degree, as previously discussed. The TIP5P-E model reproduces many of the experimental properties of water and is as quantitative in reproducing the accuracy that has been associated with the TIP5P model.

The TIP5P re-parameterization, TIP5P-E, has made changes to the LJ terms of the TIP5P model, as can be seen in Table 2. Structural geometries and electrostatic potentials remain the same as the original model, but the LJ potentials were modified for use with the Ewald summations by lowering the short-range repulsion forces by $\sim 2\%$ and raising the long-range attractive forces by $\sim 6\%$ from their original TIP5P values. The well depth was set at 0.162750 kcal/mol and the collision diameter was set to 3.097 Å. Since the charge was not changed in this model, the dipole moment remains the same as the original TIP5P model.

The results reported here for the structural, thermodynamic, and kinetic properties are values reported by Rick [22]. TIP5P-E reproduces the density curve of water over a wide range of temperatures, with an average error in the density of only 0.004 g/cm^3 and a maximum density occurring at 277 K. The enthalpy of vaporization, $\Delta_{\text{vap}}H(T)$, maintains a similar slope to that of TIP5P, which is in reasonable agreement over the simulated temperature range of 235.5–348 K. The TIP5P-E $\Delta_{\text{vap}}H$ results at 298 K are 10.377 kcal/mol for 512 water molecules, which is $< 1\%$ higher than that of TIP5P water at 298 K. $\Delta_{\text{vap}}H(T)$, over the temperature range mentioned above, for TIP5P and TIP5P-E shows that the Ewald model reproduces the experimental enthalpy better at lower temperatures, while TIP5P does slightly better at higher temperatures. The temperature

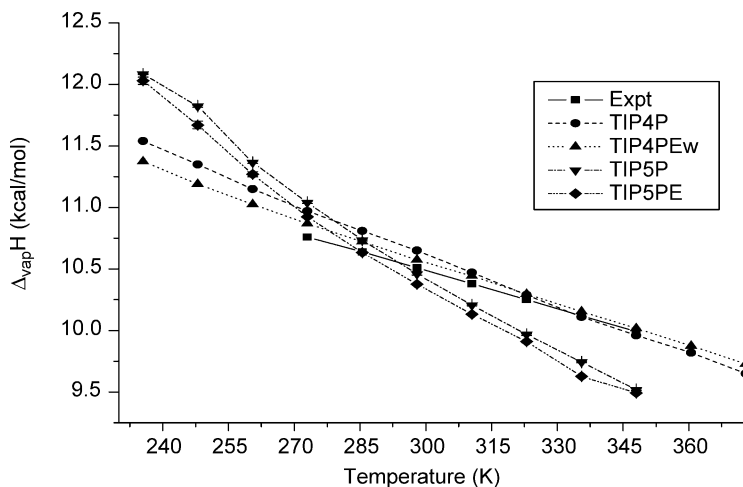


Fig. 3. Temperature dependence of enthalpy of vaporization for TIP4P, TIP4P-Ew, TIP5P, and TIP5P-E.

dependence for TIP5P and TIP5P-E can be seen in Figs 2 and 3, of the density and enthalpy of vaporization, respectively.

Calculated properties of the TIP5P-E model show similar results to that of the TIP5P model. TIP5P reproduces the C_p , κ , and α over the temperature range of 235.5–348 K reasonably well. Results seen in Table 3 show that agreement is seen between the 5-site models presented here and with experimental values. The C_p and α values are closer to the experimental values than TIP5P, for values < 260 K; the TIP5P and TIP5P-E results deviate differently here, as the TIP5P-E seems to make a drastic change. TIP5P-E reproduces the κ better than TIP5P for temperatures lower than 298 K, but results are similar between the two models above 298 K. The static dielectric constant is reproduced better with the TIP5P model, but is within the error of the TIP5P-E model over the specified temperature (Fig. 4).

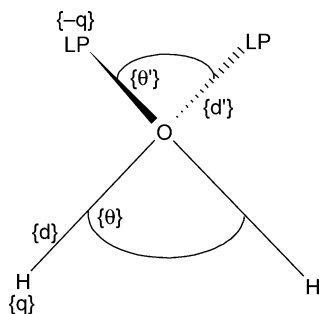


Fig. 4. Structure of TIP5P and TIP5P-E water models.

Table 3. Calculated properties of TIP4P, TIP4P-Ew, TIP5P, and TIP5P-E

Property	Model	235.5 K	248 K	260.5 K	273 K	285.5 K	298 K
ρ (g/cm ³)	TIP4P [38]	1.015	1.019	1.018	1.011	1.005	1.001
	TIP4P-Ew [3]	0.9845 (4)	0.9935 (4)	0.9986 (3)	0.9996 (3)	0.9984 (3)	0.9954 (3)
	TIP5P [53]	0.9725 (3)	0.9814 (4)	0.9979 (8)	1.007 (1)	1.005 (1)	0.999 (1)
	TIP5P-E [22]	0.973 (2)	0.980 (3)	0.995 (2)	1.003 (1)	1.0039 (6)	1.0000 (5)
	Expt [58,59]	0.9688	0.98924	0.99714	0.99981	0.99953	0.99716
$\Delta_{\text{vap}}H$ (kcal/mol)	TIP4P [38]	11.54	11.35	11.15	10.97	10.81	10.65
	TIP4P-Ew [3]	11.373 (4)	11.191 (4)	11.025 (4)	10.869 (4)	10.723 (4)	10.575 (4)
	TIP5P [22]	12.084 (3)	11.823 (7)	11.367 (8)	11.041 (8)	10.735 (7)	10.46 (1)
	TIP5P-E [22]	12.03 (3)	11.67 (3)	11.27 (2)	10.924 (7)	10.633 (4)	10.377 (4)
	Expt [58]	11.18	11.0372	10.9029	10.7732	10.6483	10.5176
C_p (cal/molK)	TIP4P [38]	23	23.2	23.3	21.8	20.7	21.4
	TIP4P-Ew [3]	24.2 (3)	21.9 (3)	20.8 (3)	20.1 (3)	19.6 (3)	19.2 (3)
	TIP5P [22]		43.0 (2)	39.4 (3)	33.8 (5)	30.9 (8)	29.1 (8)
	TIP5P-E [22]	19 (2)	22 (1)	32 (3)	31 (2)	29 (1)	27.2 (6)
	Expt [58–60]	23.47	19.34	18.38	18.17	18.048	18.004
$10^5 \alpha$ (deg ⁻¹)	TIP4P [38]	−37.2	−11.6	33.8	66.3	39.8	44
	TIP4P-Ew [3]	−8.7 (3)	−5.3 (3)	−2.4 (3)	−0.1 (3)	1.8 (3)	3.4 (3)
	TIP5P [22]		−12.5 (1)	−10.5 (3)	−3.2 (5)	3.3 (7)	6.3 (6)
	TIP5P-E [22]	1.2 (21)	1.1 (14)	−5.0 (30)	−1.8 (22)	1.8 (9)	4.9 (6)
	Expt [59]		−9.674	−3.712	−0.705	1.185	2.558
$10^6 \kappa$ (atm ⁻¹)	TIP4P [38]	43.9	51.5	44.1	45.4	52	60.3
	TIP4P-Ew [3]	54.3			48.9		48.1
	TIP5P [22]		17 (1)	24 (1)	31 (1)	36 (1)	41 (2)
	TIP5P-E [22]	18 (3)	29 (3)	48 (4)	52 (4)	53 (3)	52 (3)
	Expt [59]		71.88	58.27	51.56	47.86	45.85

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Table 3. continued

Property	Model	235.5 K	248 K	260.5 K	273 K	285.5 K	298 K
D_{self} (10^{-9} m ² /s)	TIP4P [61]						3.31 (8)
	TIP4P-Ew [3]	0.172 (1)			1.179 (1)		2.335 (4)
	TIP5P [53]	0.070 (8)	0.14 (2)	0.43 (3)	1.01 (2)	1.87 (8)	2.62 (4)
	TIP5P-E [22]	0.09 (2)	0.17 (2)	0.48 (5)	1.2 (1)	1.9 (1)	2.8 (1)
	Expt [62,63]			0.66	1.1	1.64	2.3
ε	TIP4P						
	TIP4P-Ew [3]	81.9 (5.2)			70.8 (1.4)		63.9 (0.9)
	TIP5P [22]				92 (2)		82 (2)
	TIP5P-E [22]				95 (14)	90 (9)	92 (14)
	Expt [64]				87.74	83.02	78.3
τ_{nmr} (ps)	TIP5P [22]	69 (7)					1.58 (5)
	TIP5P-E [22]	63 (10)	28 (2)	10.3 (9)	4.1 (3)	2.3 (1)	1.55 (4)
	Expt [65]					3.44	2.46
Property	Model	310.5 K	323 K	335.5 K	348 K	360.5 K	373 K
ρ (g/cm ³)	TIP4P [38]	0.991	0.981	0.971	0.961	0.952	0.931
	TIP4P-Ew [3]	0.9908 (3)	0.9843 (3)	0.9771 (3)	0.9688 (3)	0.9594 (3)	0.9492 (3)
	TIP5P [53]	0.989 (1)	0.978 (2)	0.967 (2)	0.9512 (9)		
	TIP5P-E [22]	0.9926 (6)	0.9827 (6)	0.9714 (6)	0.9586 (7)		
	Expt [58,59]	0.99362	0.98838	0.98207	0.97527	0.96737	0.95869
$\Delta_{\text{vap}}H$ (kcal/mol)	TIP4P [38]	10.47	10.29	10.11	9.96	9.82	9.65
	TIP4P-Ew [3]	10.444 (4)	10.297 (4)	10.155 (4)	10.018 (4)	9.875 (4)	9.73 (4)
	TIP5P [22]	10.207 (6)	9.967 (3)	9.744 (6)	9.519 (7)		
	TIP5P-E [22]	10.133 (3)	9.910 (3)	9.697 (3)	9.493 (5)		
	Expt [58]	10.3986	10.264	10.1286	9.9993	9.8619	9.7206

C_p (cal/mol K)	TIP4P [38]	22.2	22.4	21.2	19.4	20.5	
	TIP4P-Ew [3]	18.9 (3)	18.7 (3)	18.6 (3)	18.5 (3)	18.5 (3)	18.5 (3)
	TIP5P [22]	27.6 (3)	27 (1)	25.9 (9)	25.9 (8)		
	TIP5P-E [22]	26.6 (5)	25.5 (9)	24.9 (5)	24 (1)		
	Expt [58–60]	17.995	18.004	18.024	18.054	18.096	18.151
$10^5 \alpha$ (deg $^{-1}$)	TIP4P [38]	77.4	81.3	82.4	76.4	129.2	
	TIP4P-Ew [3]	4.6 (3)	5.5 (3)	6.3 (3)	7.0 (3)	7.6 (3)	8.3 (3)
	TIP5P [22]	8.7 (5)	9.2 (11)	11.0 (10)	12.7 (7)		
	TIP5P-E [22]	6.9 (10)	9.1 (13)	10.6 (9)	11.8 (14)		
	Expt [59]	3.648	4.567	5.379	6.121	6.821	7.498
$10^6 \kappa$ (atm $^{-1}$)	TIP4P [38]	44.2	50.1	50.1	55.3	63.2	78.6
	TIP4P-Ew [3]		49.4		53.6		59.9
	TIP5P [22]	47 (1)	56 (4)	59 (3)	65 (3)		
	TIP5P-E [22]	58 (3)	60 (3)	64 (4)	67 (4)		
	Expt [59]	44.91	44.76	45.22	46.22		49.65
D_{self} (10^{-9} m 2 /s)	TIP4P [61]						
	TIP4P-Ew [3]		3.822 (4)		5.637 (4)		7.709 (4)
	TIP5P [53]	3.70 (9)	4.74 (8)	6.33 (7)	6.78 (10)		
	TIP5P-E [22]	3.88 (6)	5.2 (2)	6.4 (2)	8.0 (2)		
	Expt [62,63]	3.07	3.95	4.96	6.08		
ϵ	TIP4P						
	TIP4P-Ew [3]		60.0 (0.7)		54.1 (0.7)		48.7 (0.6)
	TIP5P [22]		75 (2)		69 (2)		
	TIP5P-E [22]	80 (2)	77 (9)	80 (2)	72 (1)		
	Expt [64]	74.11	69.91	66.17	62.43		
τ_{nmr} (ps)	TIP5P [22]				0.47 (2)		
	TIP5P-E [22]	1.03 (3)	0.74 (1)	0.58 (1)	0.44 (2)		
	Expt [65]	1.92	1.66	1.41	1.12		

5. CONCLUSIONS

The 4- and 5-site transferable intermolecular potential water models for use with truncated cut-offs and Ewald summation electrostatic treatments are reviewed. The use of Ewald summation techniques is found to lower the energy and change the molecular properties of the model. These changes in the molecular properties are within the error of the original model or have significantly improved upon them, when the models have been parameterized taking into account long-range electrostatics using Ewald techniques.

TIP4P-Ew has been found to reproduce the density curve considerably better than TIP4P. Better agreement between the new parameterization and the original TIP4P model was also found for the enthalpy of vaporization and self-diffusion coefficient, as seen in Table 3. The TIP4P-Ew water model reproduces the density curve and the slope of the enthalpy of vaporization, as seen in Figs 2 and 3, respectively, better than any of the water models reviewed. The TIP4P-Ew model has been tested in BOSS [54], AMBER [55], GROMACS [56], and CHARMM [57]. Table 3 summarizes the calculated properties of the TIP4P, TIP4P-Ew, TIP5P, and TIP5P-E water models along with the experimental values; a review of the presented data shows that the Ewald re-parameterizations of the original 4- and 5-site models have moderate to significant improvements in the calculated properties.

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