Quantum, intramolecular flexibility, and polarizability effects on the reproduction of the density anomaly of liquid water by simple potential functions

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The ability of simple potential functions to describe the properties of liquid water at a range of thermodynamic state points has been explored. These simple potential function models represent a water molecule by a set of sites, either rigid or flexible relative to each other, that interact with a simple, generally classical, Hamiltonian, which has parameters that are empirically determined. Calculations on several models that include intramolecular flexibility, electronic polarization or quantum mechanical effects have been performed. The consequences of altering these parameters have been systematically examined to determine factors of importance in reproducing properties of pure liquid water. It is found that simple four-site models that incorporate classical intramolecular flexibility or electronic polarization do not improve the description of the density anomaly of liquid water. Quantum statistical mechanical path integral calculations on the classical rigid nonpolarizable TIP5P model [J. Chem. Phys. **112**, 8910 (2000)] and the classical flexible nonpolarizable TIP4F model indicate that although quantum mechanical effects destructure the rigid model, they improve the radial distribution and energy distribution properties of the flexible model. In addition, although quantum effects make the density behavior of the rigid model worse, they improve the density behavior of the flexible model. Path integral calculations have also been performed on quantum D_2O TIP5P water; this leads to a temperature of maximum density that is higher and to a more structured liquid than results from calculations on quantum H_2O TIP5P water. A similar effect is seen with calculations on a five-site rigid model, TIP5P(PIMC), which was parameterized using path integral rather than classical Monte Carlo calculations. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1418243]

I. INTRODUCTION

Prior to 1983, Monte Carlo (MC) and molecular dynamics (MD) calculations for liquid water generally used the BNS, MCY, and ST2 potential functions.[1] These seminal models were developed with limited computational resources and do not accurately reproduce thermodynamic and structural properties of liquid water, particularly the density, in calculations in the isothermal–isobaric (NPT) ensemble.[2] In 1983, the TIP3P model was introduced and demonstrated that the energy and density could be accurately reproduced within the framework of three-site models, although at the expense of losing structure beyond the first peak in the oxygen–oxygen (OO) radial distribution function (rdf).[2] At about the same time, the SPC model[3,4] demonstrated that the structure beyond the first peak of the OO rdf could be better reproduced, but with a slight sacrifice in the density. The four-site TIP4P model,[2] by moving the site of the negative charge 0.15 Å off the oxygen along the hydrogen–oxygen–hydrogen (HOH) bisector and by appropriate choice of parameters, is able to reproduce both the structure and thermodynamic properties of liquid water to high accuracy at a single state point. These models, along with the SPC/E model[5] and the ST2 model,[6] are currently the most com-

monly used water models. These models are known as simple potential function models since they represent a water molecule by a set of sites, either rigid or flexible relative to each other, that interact with a simple, generally classical, Hamiltonian, which has parameters that are empirically determined. They were developed in conjunction with liquid-state calculations, generally at 25 °C and 1 atm, and have been used successfully to study a wide variety of properties of liquid water,[7,8] often at conditions far from their original parameterization.[9–11]

Among the most well known of the peculiar properties of liquid water is the behavior of its density as a function of temperature and pressure, $\rho(T,P)$.[12–17] Liquid water at standard pressure exhibits a temperature of maximum density (TMD) at 4.0 °C, and this maximum is shifted to lower temperatures as the pressure is increased. In addition, the density is nearly constant between −15 °C and +25 °C and falls off more gradually than for other liquids between 25 °C and 100 °C. Although some of the commonly used water models have a TMD, none is successful at quantitatively reproducing $\rho(T)$ in the temperature region of interest.[18–27] More accurate results may be achievable by considering additional interaction sites, electronic polarization, intramolecular flexibility or quantum mechanical effects. Recently, the TIP5P

model was developed and included optimization of the position of the negative charges along the lone-pair directions.[28] TIP5P water reproduces the structural and thermodynamic properties at 25 °C and 1 atm as well as the best previously existing models. In addition, the density maximum near 4 °C at 1 atm is reproduced and the average error in the density over the 100 °C temperature range from −37.5 °C to 62.5 °C is only 0.006 g cm⁻³. At 25 °C and 1 atm, the TIP5P model is also found to have a dielectric constant[28] of 81.5 ±1.6 and a diffusion constant[29] of 2.62±0.04 ×10⁻⁵ cm²/s, both of which represent an improvement relative to three and four-site models that do not include an energy correction.[5,28–30] For a discussion of the polarization self energy correction, see Refs. 5 and 30 and Sec. III of Ref. 29.

The inclusion of polarizability is thought to be a mechanism to model water under an even wider range of conditions than the bulk liquid phase at 25 °C and 1 atm. For example, the heterogeneities and anisotropies of water near solid or gaseous interfaces, near ions, or near biomolecules are better described by a water model with rapidly responsive electronic degrees of freedom.[31–37] Intramolecular flexibility has been put forth as a mechanism to model certain vibrational properties of water and the deformations of water near perturbations.[35–47] Although many of these phenomena involve water effected by ions, solutes, or surfaces, pure water is known to undergo significant changes in dipolar, dielectric, and geometric properties as a function of temperature and pressure.[7,8] In addition to these classical effects, the contribution of quantum mechanical effects to the properties of water have been studied.[4,6,48–63] Calculations can include quantum mechanical effects by adding quantum corrections to classical calculations[48–50] or by using mixed quantum/classical simulations,[52] *ab initio* molecular dynamics,[53] or path integral techniques.[54–62]

Although intramolecular flexibility, electronic polarization, and quantum mechanical effects help in the reproduction of certain properties relative to classical rigid nonpolarizable models, these effects do not generally lead to models with improved thermodynamic, structural and dielectric properties.[35,36,38,40,53,59] Their influence on the behavior of water at a range of thermodynamic state points has not to our knowledge been examined in a systematic manner. To begin to elucidate these effects, several models have been examined in which the features of the underlying model have been systematically varied. Classical Monte Carlo calculations have been performed on TIP4F, a four-site flexible model, and classical molecular dynamics calculations have been performed on Dang97, a four-site dipole polarizable model. The results of these calculations are compared with the results for the TIPnP models. Quantum mechanical effects have been examined by performing quantum statistical mechanical path integral calculations on both rigid and flexible models. The next section reviews the potential functions, the relevant theory, and computational details. In Sec. III, the results of the classical calculations for the TIP4F and Dang97 models are presented. In Secs. IV and V the dependence of the structural and thermodynamic properties is given for the TIP5P and TIP4F models, respectively, as a function of quantum

TABLE I. Monomer geometry and parameters for the water models.

	TIP5P	TIP4F	Dang97	TIP5P(PIMC)
$q_H(e)$	0.241	0.511	0.519	0.251
$q_O(e)$	⋯	⋯	⋯	⋯
$q_L(e)$	−0.241	−1.022	−1.038	−0.251
σ_O (Å)	3.12	3.27	3.234	3.12
ε_O (kcal/mol)	0.16	0.10	0.1825	0.16
α_L (Å³)	⋯	⋯	1.444	⋯
r_{OH} (Å)	0.9572	0.9572	0.9572	0.9572
θ_{HOH} (deg)	104.52	109.5	104.5	104.52
r_{OL} (Å)	0.70	0.175	0.215	0.70
θ_{LOL} (deg)	109.47	⋯	⋯	109.47
k_{OH} (kcal mol⁻¹ Å⁻²)	⋯	600.0	⋯	⋯
k_{HOH} (kcal mol⁻¹ rad⁻²)	⋯	75.0	⋯	⋯
k_{OL} (kcal mol⁻¹ Å⁻²)	⋯	900.0	⋯	⋯
k_{HOL} (kcal mol⁻¹ rad⁻²)	⋯	50.0	⋯	⋯

path discretization. Section VI presents some further path integral results on two rigid five-site models that examine the isotopic effect and the effect of reparameterizing a model to quantum rather than classical calculations. Finally, Secs. VII and VIII present a discussion and the conclusion.

II. REVIEW OF THE MODELS, THEORY, AND COMPUTATIONAL DETAILS

TIP5P is a rigid nonpolarizable five-site model[28] and its defining parameters are presented in Table I. Also presented in Table I are parameters defining TIP4F, a flexible nonpolarizable four-site model in which the flexibility is modeled by classical harmonic energy terms,[64] Dang97, a rigid four-site polarizable model in which the flexible electronic degrees of freedom are modeled by variable dipoles,[34] and TIP5P(PIMC), a five-site model with the same geometry as the TIP5P model that was parameterized with path integral rather than classical calculations. Note that for TIP4F water, the oxygen-interaction site distance is larger than in TIP4P water and the HOH angle is increased such that its value in the liquid phase ends up approximately equal to the value for TIP4P water.[2] For Dang97 water, there is a single polarizable site, which is located on the massless charge site, and the oxygen-interaction site distance is larger than in TIP4P water in order to better reproduce the gas phase dipole and quadrupole moments.[34]

The potential part of the model Hamiltonian is given in Eq. (1),[33,34,65,66]

$$U = \sum_a U_a + \sum_{a \neq b} U_{ab} + U_{POL},$$

$$U_a = \sum_{bonds} k_r (r - r_{eq})^2 + \sum_{angles} k_\theta (\theta - \theta_{eq})^2,$$

$$U_{ab} = \sum_{ij} \frac{q_i q_j e^2}{r_{aibj}} + 4\varepsilon_O \left[\left(\frac{\sigma_O}{r_{aObO}} \right)^{12} - \left(\frac{\sigma_O}{r_{aObO}} \right)^6 \right],$$

$$U_{POL} = -\frac{1}{2} \sum_a \vec{p}_a \cdot \vec{E}_a^q, \tag{1}$$

where a and b are indices representing the molecules, i and j are indices representing the atoms, and the remaining vari-

ables represent their standard quantities. The intramolecular energy for the TIP5P, TIP5P(PIMC), and Dang97 models is a constant, taken to be zero, and the polarization energy for the TIP5P, TIP5P(PIMC), and TIP4F models is likewise taken to be zero.

The classical statistical mechanical calculations described in Sec. III for the TIP4F model were performed with the Metropolis Monte Carlo algorithm[67] using the BOSS program, version 3.8,[68] and the standard protocols including periodic boundary conditions.[28] At each step a single particle was randomly chosen, translated and rotated, and had its intramolecular degrees of freedom modified. Attempted volume moves were performed every five passes and intermolecular interactions were truncated with 9 Å spherical cutoffs based on the OO separation. The calculations involved 267 TIP4F water molecules in a periodic box and were run for up to several hundred million configurations at the lowest temperatures to ensure proper equilibration and averaging.

For polarizable models, technical difficulties lead to extremely long calculations for the standard single particle move Monte Carlo algorithm.[69] Thus, the classical statistical mechanical calculations reported in Sec. III for the Dang97 model were performed with a standard molecular dynamics algorithm,[70] using POLDYN,[71] a modified version of the molecular dynamics program AMBER.[72] There were 550 molecules in a periodic box with 9 Å spherical cutoffs, the time step was 1.0 fs and the temperature and pressure coupling were 0.1 ps and 0.2 ps, respectively. The molecular dynamics calculations were run for between several hundred ps and ≈ 1.5 ns, with the averaging period consisting of up to ≈ 1 ns at the lowest temperatures; convergence diagnostics were monitored as in the Monte Carlo calculations.

The quantum statistical mechanical calculations described in Secs. IV–VI were performed with the standard classical Monte Carlo algorithm applied to discretized path integrals. By taking advantage of the well known isomorphism between a quantum statistical mechanical N body problem and a classical statistical mechanical $N*P$ body problem,[18,54–56,59] where P is the discretization of the quantum polymer representing the classical point particle, the N particle partition function can be written in the discrete, or primitive, representation as

$$Q = \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{3NP/2} \int \prod_{i=1}^{N} \prod_{s=1}^{P} dr_{is}$$

$$\times \exp\left\{ -\beta \sum_{s=1}^{P} \left[\frac{1}{2} \kappa \sum_{i=1}^{N} (r_{is+1} - r_{is})^2 \right.\right.$$

$$\left.\left. + \frac{1}{P} V(r_{1s} \cdots r_{Ns}) \right] \right\}. \tag{2}$$

Each quantum particle i of mass m is discretized into P beads, with r_{is} being the position of bead s on particle i. By convention, bead $N+1$ is identical to bead 1. The harmonic constant $\kappa = mP/\beta^2\hbar^2$ mediates interactions between successive beads on the same atom. The interatomic potential $V(r_{1s} \cdots r_{Ns})$ is moderated by a factor of P and acts only between correspondingly labeled beads of different atoms.

Path integral calculations were performed on the TIP5P, TIP5P(PIMC), and TIP4F models in the isothermal–isobaric ensemble at a pressure of 1 atm at temperatures every 25 °C between -50 °C and 100.0 °C with several discretizations and at elevated pressures every 2000 atm up to 6000 atm for the TIP5P and TIP4F models. Results are reported for discretizations P equal to 1, 5, and 10, with the classical limit corresponding to $P=1$. At selected state points, calculations for other discretizations were performed to monitor convergence as a function of discretization. These indicate that for the bulk phase properties reported here, the highest discretizations reported are sufficient to capture the essential quantum mechanical effects. As pointed out previously,[28] NPT MC calculations are a good choice for computing liquid densities because there is no uncertainty in the implementation of the ensemble, and because the temperature and pressure controls are exact. Periodic boundary conditions were used with a smaller cubic sample of 125 water molecules (unless otherwise noted) with 7 Å spherical cutoffs owing to the increased computational demands.

The starting coordinates for each calculation came from a box equilibrated at 25 °C and 1 atm or at closer conditions. Volume changes were attempted every ≈ 500 configurations, and their magnitudes as well as the ranges for molecular translations and rotations were adjusted to yield acceptance rates of $\approx 40\%$. For the TIP5P and TIP5P(PIMC) models, solvent moves consisted of translating and rotating a single molecule as well as moving the different beads of that molecule with respect to each other while maintaining the correct molecular geometry. For the TIP4F model, intramolecular degrees of freedom were also modified. All path integral Monte Carlo calculations were performed with a modified version of the BOSS program, version 3.8;[68] modifications were tested by reproducing results of previous path integral calculations on the SPC, ST2, and TIP4P models and reproducing isotopic shifts in path integral calculations on those models.[59,60,62] Convergence diagnostics were monitored, and error estimates were obtained by the batch-means procedure.[73] In spite of the small box size, the calculations required up to several hundred million steps of equilibration and averaging due to the slow equilibration of the quantum degrees of freedom.

III. RESULTS FOR CLASSICAL CALCULATIONS

The development of the polarizable Dang97 model is described elsewhere,[34] while the development and properties of the flexible TIP4F model are briefly reviewed here.[64] Results for both models are then presented.

A. The development of the TIP4F model

The methodology behind the development of the TIP4F model of liquid water is similar to that for the development of previous models.[2,28,74] Criticisms of flexible water models have included that they typically do not properly describe the dependence of the change in dipole moment on molecular geometry[37,39,75,76] and that geometric flexibility should be included only in polarizable models.[30,40] While such criticisms are valid, the effect of flexibility on the density anomaly is of

TABLE II. Average geometric properties of TIP4F.

State point	μ (D)	r_{OH} (Å)	θ_{HOH} (deg)
Gas phase, 0 K	1.85	0.9572	109.5
Gas phase, 25 °C	1.93	0.959	107.3
Liquid, 25 °C	2.32	0.977	104.3

interest, particularly since three-site models that refrain from using an energy correction fail to reproduce a reasonable TMD.[27]

The gas phase geometry of TIP4F water listed in Table I and Table II differs from that of TIP4P water since the oxygen-interaction site distance and the HOH angle have been increased. Intramolecular flexibility is modeled with classical harmonic energy terms as presented in Table I.[74] The calculated vibrational constants, obtained by setting the massless charge site to have a large mass in order to separate its motion from those of the other atoms, are 2371, 3837, and 3958 cm^{-1}, as compared to experimental values of 1594, 3656, and 3755 cm^{-1}. The gas phase dipole moment of 1.85 D is approximately equal to the experimental gas phase value. In the pure liquid at 25 °C, the bond lengths increase ≈ 0.02 Å and the bond angle decreases to approximately the value for TIP4P water. The geometric deformation, the importance of which has been described previously,[38] causes the dipole moment to increase to 2.32 D, approximately equal to the value for the TIPnP models. The global minimum for the TIP4F dimer has $r_{OO} = 2.67$ Å and a net interaction energy of -6.36 kcal/mol.

Table III presents computed thermodynamic properties from pure liquid calculations at 25 °C and 1 atm. The experimental results are well reproduced by TIP4F water, although not quite as well as by the TIP4P or TIP5P models. The heat of vaporization is slightly high, and the heat capacity is too high due to the classical modeling of intramolecular flexibility. Figure 1 presents the OO rdf for TIP4F water and compares it to results for the TIP4P and TIP5P models and to experiment.[77,78] Note that the experimental results are not those used in the original TIP5P paper.[28] Recent experiments,[78] performed after and independent of the development of the TIP5P model, indicate that the first peak of the OO rdf is sharper and located shorter OO distance than previous experimental results,[28,77] in excellent agreement with the TIP5P results.[78(b)] Figure 1 also shows that the second peak of the OO rdf for the TIP4F model is shifted inward relative to both the new and old experimental values and values calculated with the rigid TIP4P and TIP5P models. In
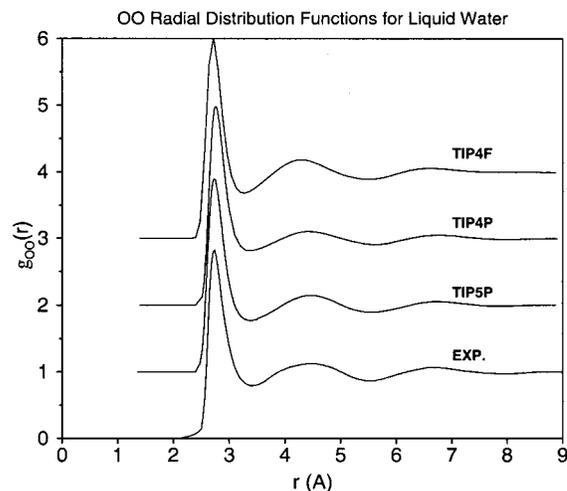
FIG. 1. OO radial distribution functions for water at 25 °C and 1 atm.

addition, structure is not lost and is slightly more pronounced than in the TIP4P and TIP5P models. Similar results are seen for the other two rdfs.

B. The density results for TIP4F and Dang97

The energies and densities for both the flexible TIP4F model and the polarizable Dang97 model at a range of temperatures are presented in Table IV and the density profile for both models is presented in Fig. 2. For these four-site models, both classical flexibility and electronic polarizability make the density profile worse over the entire temperature range, relative to the TIP4P model. At low temperatures, the density maximum for both TIP4F water and Dang97 water shifts to a much lower temperature and may not exist above -50 °C. For both models, the difference in the density between the lowest temperature calculations may not statistically significant due to slow equilibration. At high temperatures, the density decreases slightly more rapidly with increasing temperature for both models than does the density of TIP4P water. The present results agree with previous analyses that the addition of electronic polarization does not introduce abnormalities into the temperature dependence of the properties of liquid water and does not properly describe the temperature dependence of its thermodynamic properties.[20,79]

The pressure dependence of the thermodynamic properties has also been examined for the TIP4F and Dang97 models and the data are also presented in Table IV. For models

TABLE III. Calculated and experimental properties for liquid water at 25 °C and 1 atm.

	TIP4F	TIP4P	TIP5P[a]	TIP5P(PIMC)	Expt.[a]
ρ (g/cm^3)	0.998±0.001	1.001±0.001	0.999±0.001	0.997±0.002	0.997
$-E_{inter}$ (kcal/mol)	12.16±0.01	10.06±0.01	9.87±0.01	9.94±0.01	9.92
ΔH_{vap} (kcal/mol)	10.78±0.01	10.65±0.01	10.46±0.01	10.53±0.03	10.51
C_p (cal/mol deg)	32.4±0.6	20.4±0.7	29.1±0.8	19.0±0.5	18.0
$10^6 \kappa$ (atm^{-1})	41±3	60±5	41±2	57±5	45.8
$10^5 \alpha$ (deg^{-1})	82±10	44±8	63±6	42±5	25.7

[a]See Ref. 28.

TABLE IV. Intermolecular energy (kcal/mol) and density (g/cm^3) for TIP4F and Dang97 water.

$T(°C)$	P (atm)	$-E_{inter}$, TIP4F	ρ, TIP4F	$-E_{inter}$, Dang97	ρ, Dang97
−50.0	1	14.239±0.007	1.0475±0.0004	11.269 ± 0.005	1.0358±0.0009
−25.0	1	13.585±0.008	1.0369±0.0006	10.804 ± 0.007	1.0251±0.0007
0.0	1	12.844±0.009	1.0159±0.0007	10.322 ± 0.006	1.0148±0.0009
25.0	1	12.165±0.017	0.9942±0.0012	9.801 ± 0.007	0.9962±0.0014
50.0	1	11.470±0.016	0.9726±0.0013	9.330 ± 0.008	0.9742±0.0012
75.0	1	10.816±0.013	0.9447±0.0010	8.871 ± 0.005	0.9480±0.0011
100.0	1	10.156±0.018	0.9071±0.0014	8.402 ± 0.008	0.9156±0.0010
25.0	2000	12.429±0.013	1.0681±0.0012	9.985 ± 0.011	1.0611±0.0013
25.0	4000	12.658±0.018	1.1234±0.0015	10.055 ± 0.010	1.1094±0.0020
25.0	6000	12.758±0.018	1.1737±0.0007	10.165 ± 0.013	1.1518±0.0014

such as TIP4P and TIP5P, application of pressure at 25 °C leads the intermolecular energy to decrease slightly and the density to increase too rapidly.[28,80(a)] Similar effects for the energy are seen with the flexible and polarizable models. The rate of increase of the density with increasing pressure, however, is in slightly better agreement with experimental results for both the TIP4F and Dang97 models than for the TIP4P or TIP5P models.[28]

IV. RESULTS OF PATH INTEGRAL MC CALCULATIONS ON THE TIP5P MODEL

The path integral calculations on the rigid TIP5P model show that the liquid-phase thermodynamic and structural quantities converge fairly rapidly as a function of increasing discretization. For example, results at 25 °C and 1 atm as well as results at other state points except perhaps those with the lowest temperatures indicate that a discretization of $P = 5$ is sufficient to reproduce properties computed with much larger P.

Table V presents the energy and density for the classical and quantum calculations on TIP5P water at a range of thermodynamic state points. As has been noticed previously,[58–62] the energies for the quantum calculations are smaller in magnitude than those for the corresponding classical calculations. Thus, since quantum molecules bind to each other less well than do the corresponding classical molecules, the den-

sity tends to be lower, as is seen at the higher temperatures. The energy difference between the quantum and classical results is larger at lower temperatures. The energy for classical TIP5P water decreases too rapidly as the temperature is decreased, and this is moderated and in better agreement with the experiment for the quantum mechanical calculations.[27,28] The results for the density are also plotted in Fig. 3 and indicate that the density profile for the quantum calculations on the rigid model is noticeably worse. The TMD near the experimental value for classical TIP5P water, presented here for 125 molecules and previously for larger boxes,[28] is shifted to a much lower temperature. For $P = 5$, there is a maximum at ca. −25 °C while for $P = 10$ the maximum is lost, although the results at the lowest two temperatures for $P = 10$ are not significantly different and may not be completely converged.

As a function of increasing pressure, the density of TIP5P water increases somewhat too rapidly, as can be seen in Table V for 125 molecules and as was reported previously

TABLE V. (a) Intermolecular energy (kcal/mol) for classical and quantum calculations on TIP5P water. (b) Density (g/cm^3) for classical and quantum calculations on TIP5P water.

$T(°C)$	Pressure (atm)	Classical, $P = 1$	Quantum, $P = 5$	Quantum, $P = 10$
(a)				
−50.0	1		−9.824±0.010	−9.494±0.011
−25.0	1	−11.718±0.002	−9.236±0.009	−9.032±0.008
0.00	1	−10.704±0.019	−8.778±0.006	−8.733±0.018
25.0	1	−9.924±0.012	−8.399±0.018	−8.324±0.015
50.0	1	−9.308±0.009	−8.012±0.010	−7.972±0.013
75.0	1	−8.824±0.023	−7.649±0.026	−7.615±0.026
100.0	1	−8.300±0.020	−7.319±0.032	−7.288±0.020
25.0	2000	−9.918±0.023	−8.597±0.010	−8.524±0.009
25.0	4000	−9.955±0.017	−8.692±0.012	−8.631±0.007
25.0	6000	−9.991±0.018	−8.739±0.011	−8.631±0.011
(b)				
−50.0	1		0.9766±0.0011	0.9857±0.0012
−25.0	1	0.9502±0.0002	0.9843±0.0010	0.9845±0.0013
00.0	1	0.9695±0.0008	0.9708±0.0007	0.9704±0.0016
25.0	1	0.9716±0.0015	0.9497±0.0010	0.9527±0.0031
50.0	1	0.9574±0.0012	0.9231±0.0021	0.9221±0.0020
75.0	1	0.9373±0.0016	0.8962±0.0020	0.8939±0.0031
100.0	1	0.9055±0.0049	0.8600±0.0053	0.8621±0.0033
25.0	2000	1.0596±0.0034	1.0497±0.0022	1.0464±0.0014
25.0	4000	1.1214±0.0027	1.1131±0.0023	1.1118±0.0012
25.0	6000	1.1864±0.0025	1.1684±0.0014	1.1655±0.0012
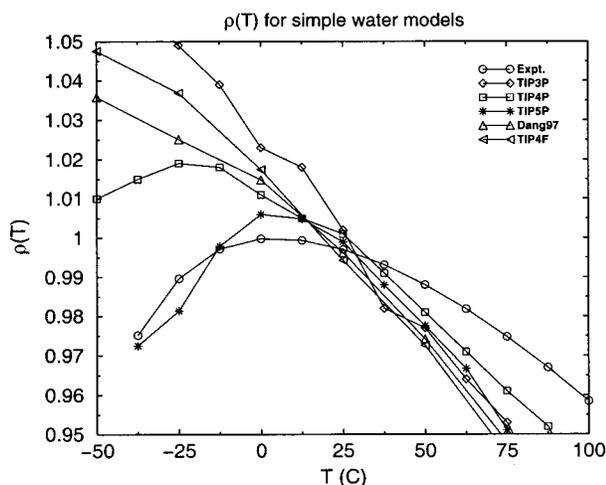
FIG. 2. Density of water models vs experiment as a function of temperature at 1 atm.

J. Chem. Phys., Vol. 115, No. 23, 15 December 2001

Reproduction of the density anomaly of liquid water   10763
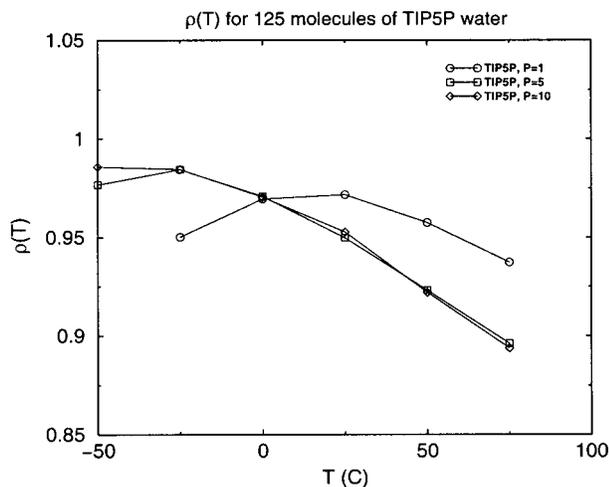
FIG. 3. Density of quantum calculations on the rigid TIP5P water model as a function of temperature at 1 atm.

FIG. 5. Distributions of individual water-water interaction energies for quantum calculations on rigid TIP5P water at 25 °C and 1 atm. Units for the ordinate are number of molecules per kcal/mol.

for 512 molecules.[28] Although the inclusion of quantum effects decreases the density, its effect is nearly independent of pressure. Similarly, although quantum effects modify the energy, the energy decreases only slightly more in the quantum calculations than in the classical calculations as the pressure is increased.

The OO rdfs for the classical and quantum calculations at 25 °C and 1 atm are presented in Fig. 4. Quantum mechanical effects tend to destructure the liquid,[58–60] as is seen with the TIP5P OO rdf. Similar effects are seen in the other rdfs and also in the energy pair distribution functions, the latter of which are presented in Fig. 5. The characteristic hydrogen bonding peak is shifted to higher energy and structure in the profile is partially lost. For both the radial distribution and energy distribution functions, qualitatively similar effects are seen at other temperatures and pressures.

V. RESULTS OF PATH INTEGRAL MC CALCULATIONS ON THE TIP4F MODEL

The path integral calculations on the flexible TIP4F model converge more slowly as a function of increasing dis-

cretization than those for the rigid model, and thus it is difficult to establish an appropriate discretization level. Nevertheless, results at a range of temperatures and pressures indicate that a discretization of $P=5$ captures the majority of the quantum contribution of the idealized continuous path integral calculation. Results for $P=10$ are near those for $P=5$, while calculations of several hundred million Monte Carlo steps with $P=20$ failed to converge.

Although quantum mechanical effects destructure both the radial distribution and energy pair distribution function for the rigid model, the results are very different for the flexible model, as seen in Figs. 6 and 7. Figure 6 presents the OO rdf for the TIP4F model. Structure is not lost but is modified. This is in agreement with previous results[61,62] for path integral calculations of flexible water models in which structure in the rdfs was not lost as much as in corresponding calculations on rigid models. The heights of the peaks and valleys are very similar for the classical and quantum calculations. It is noteworthy that the positions of the peaks are

FIG. 4. OO radial distribution functions for quantum calculations on the rigid TIP5P water model at 25 °C and 1 atm.
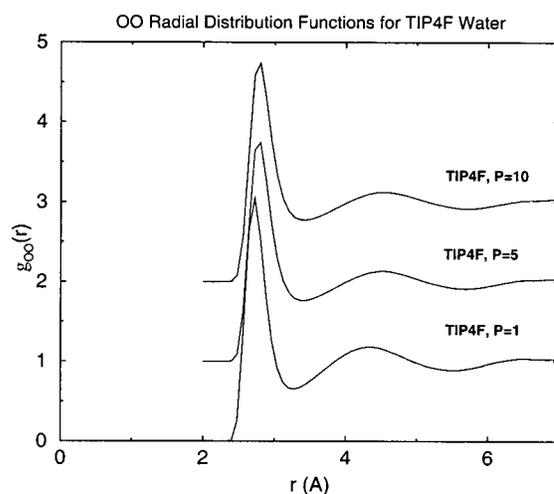
FIG. 6. OO radial distribution functions for quantum calculations on the flexible TIP4F water model at 25 °C and 1 atm.

Water–water energy pair distribution for TIP4F water
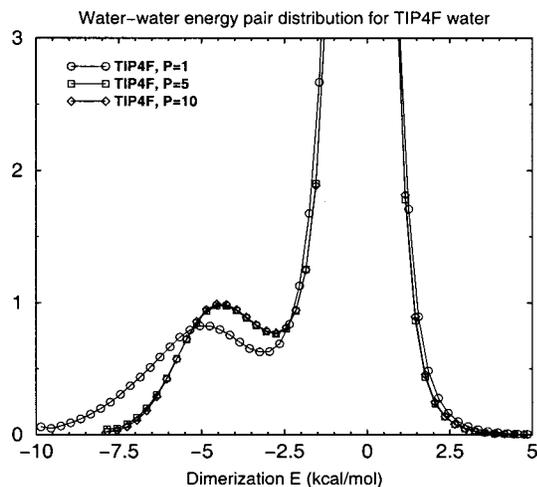
FIG. 7. Distributions of individual water–water interaction energies for quantum calculations on flexible TIP4F water at 25 °C and 1 atm. Units for the ordinate are number of molecules per kcal/mol.

TABLE VI. (a) Intermolecular energy (kcal/mol) for classical and quantum calculations on TIP4F water. (b) Density (g/cm^3) for classical and quantum calculations on TIP4F water.

$T(°C)$	Pressure (atm)	Classical, $P=1$	Quantum, $P=5$	Quantum, $P=10$
(a)				
−50.0	1	−14.505±0.007	−11.504±0.008	−10.980±0.007
−25.0	1	−13.839±0.008	−10.819±0.011	−10.716±0.008
00.0	1	−13.144±0.010	−10.365±0.009	−10.152±0.007
25.0	1	−12.365±0.020	−9.852±0.015	−9.747±0.010
50.0	1	−11.528±0.019	−9.359±0.015	−9.369±0.012
75.0	1	−10.972±0.022	−8.885±0.012	−8.875±0.009
100.0	1	−10.223±0.020	−8.441±0.012	−8.430±0.017
25.0	2000	−12.592±0.016	−10.046±0.011	−10.060±0.011
25.0	4000	−12.760±0.020	−10.163±0.009	−10.200±0.011
25.0	6000	−12.863±0.021	−10.221±0.012	−10.190±0.013
(b)				
−50.0	1	1.0560±0.0005	0.9548±0.0007	0.9536±0.0006
−25.0	1	1.0326±0.0006	0.9604±0.0009	0.9463±0.0006
00.0	1	1.0190±0.0007	0.9441±0.0008	0.9396±0.0005
25.0	1	0.9948±0.0013	0.9301±0.0010	0.9236±0.0006
50.0	1	0.9660±0.0016	0.9071±0.0011	0.9051±0.0009
75.0	1	0.9444±0.0016	0.8794±0.0010	0.8783±0.0006
100.0	1	0.9074±0.0017	0.8494±0.0011	0.8476±0.0013
25.0	2000	1.0652±0.0012	1.0118±0.0007	1.0127±0.0007
25.0	4000	1.1209±0.0012	1.0780±0.0005	1.0746±0.0005
25.0	6000	1.1653±0.0010	1.1274±0.0006	1.1255±0.0007

shifted outward in the quantum calculation relative to the classical calculation. Comparison with Fig. 1 indicates that this partially corrects an error introduced with the classical TIP4F model, in which the position of the second peak is shifted too much inward. Similar effects are seen in the OH and HH rdfs. Figure 7 presents the energy pair distribution functions. As with the rigid model, the hydrogen-bonding band is shifted to slightly higher energy. However, the band remains distinct in agreement with previous results that indicate that although the hydrogen bonding in quantum water is less energetically favorable, quantum effects can lead to more structured hydrogen bonding with flexible molecules.[61] Thus, quantum phenomena have a very different effect in flexible models than rigid models; problems with the classical flexible model associated with its being too flexible are improved.

Table VI presents the energy and density for the classical and quantum calculations on TIP4F water. For the flexible model, as with the rigid model, the energy difference between the classical and quantum calculations is larger at lower temperatures. In a manner similar to the results for TIP5P, the rate of decrease of the energy is moderated at low temperatures upon the inclusion of quantum effects. The difference between the densities for the quantum and classical results is qualitatively different from that for the rigid model, as illustrated in Fig. 8. The shape of the density profile for calculations on a box of 125 molecules agrees with the results for a box with 267 molecules, as seen by comparison with Fig. 2. In Fig. 8, for $P=5$ there is a maximum at ca. −25 °C, while for $P=10$ there is none. Although it is not clear by examining the underlying data which result is more reliable (low temperatures require a higher discretization, which takes longer to equilibrate), it is clear that $|\partial\rho/\partial T|$ is significantly smaller for the path integral calculations in the low temperature region. In contrast to the improvement for the density profile at low temperature, the trend for the flexible model at higher temperatures is the same for both the quantum and the classical models. As a function of increasing pressure, the TIP4F model behaves in a manner similar

to the TIP5P model, i.e., although the magnitude of the energy and density are modified, their behavior as a function of pressure is not.

VI. ISOTOPIC SUBSTITUTION FOR TIP5P AND THE TIP5P(PIMC) MODEL

The effect of isotopic substitution in quantum calculations of liquid water has been examined,[58–60] and a model has been developed by fitting parameters to the results of quantum calculations.[62] The present section reports the results of calculations to determine the effect on the density

$\rho(T)$ for 125 molecules of TIP4F water
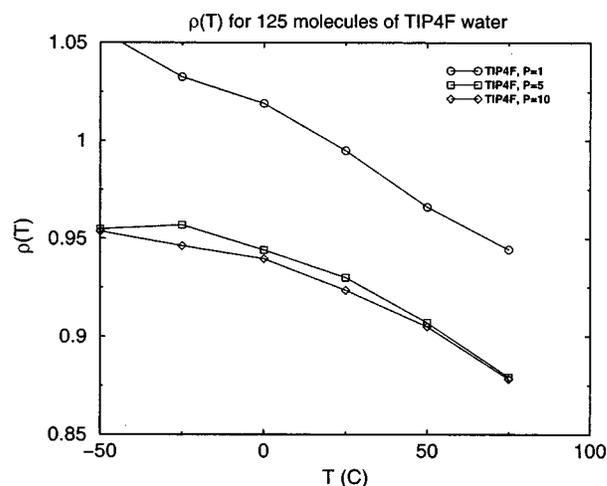
FIG. 8. Density of quantum calculations on the flexible TIP4F water model as a function of temperature at 1 atm.

TABLE VII. Intermolecular energy (kcal/mol) and density (g/cm^3) for quantum calculations on D$_2$O TIP5P water and TIP5P(PIMC) water.

$T(°C)$	P (atm)	E, D$_2$O TIP5P	ρ, D$_2$O TIP5P	E, TIP5P(PIMC)	ρ, TIP5P(PIMC)
−50.0	1	−10.778 ± 0.004	0.9468 ± 0.0005		
−25.0	1	−9.999 ± 0.008	0.9758 ± 0.0011	−11.325 ± 0.014	0.9659 ± 0.0020
0.0	1	−9.441 ± 0.010	0.9797 ± 0.0015	−10.470 ± 0.009	0.9889 ± 0.0009
25.0	1	−8.930 ± 0.012	0.9607 ± 0.0019	−9.978 ± 0.009	0.9785 ± 0.0010
50.0	1	−8.513 ± 0.011	0.9376 ± 0.0026	−9.518 ± 0.012	0.9677 ± 0.0016
75.0	1	−8.130 ± 0.010	0.9125 ± 0.0024	−9.069 ± 0.010	0.9419 ± 0.0015

profile of isotopic substitution and of the development of a quantum version of the TIP5P model that is parameterized with path integral calculations.

A. The effect of isotopic substitution on the density profile of TIP5P

Differences between liquid H$_2$O and liquid D$_2$O have been examined experimentally and theoretically.[6,18,60,63] Several lines of evidence, e.g., relative melting points, boiling points and TMDs as well as leading quantum corrections in theoretical treatments, concur that D$_2$O is the more structured liquid.[60] Calculations on quantum D$_2$O TIP5P water have been performed by modifying the mass in the harmonic constant $\kappa = mP/\beta^2\hbar^2$; the results for the energy and density are presented in Table VII. A comparison with Table V shows that, in agreement with results previously reported,[60] calculations on quantum D$_2$O lead to intermolecular energies and densities that generally have a larger magnitude. Although not presented, the radial and energy distribution functions are more structured for quantum D$_2$O than quantum H$_2$O. In addition, Fig. 9 indicates that, in agreement with experiment,[14] the TMD for quantum D$_2$O TIP5P water is higher than that for quantum H$_2$O TIP5P water. The ratio of $T_{max}(D_2O)/T_{max}(H_2O)$ appears to be larger than the experimental value of 1.026,[18] although statistical noise near the maxima make the precise determination of this ratio difficult. It also appears that, in agreement with experiment,[14] the en-

velope of the density profile is sharper for quantum D$_2$O TIP5P water than for quantum H$_2$O TIP5P water, although the low temperature at which quantum H$_2$O TIP5P water has its maximum makes quantitative comparison difficult.

B. The development of the TIP5P(PIMC) model

In view of the derivation of TIP5P to reproduce experimental properties of water, addition of quantum effects reduces the agreement with experiment. Thus, we have developed a modified model, TIP5P(PIMC), that is suitable for use in path integral calculations and that largely restores the quality of the results. The approach for creation of the TIP5P(PIMC) model is similar to that for previous models,[2,28] with the exception that path integral calculations rather than classical statistical mechanics calculations were used. The defining parameters are given in Table I; only the magnitude of the partial charge was altered, otherwise the parameters are identical to those for TIP5P water. This restores the density and intermolecular energy to the desired higher magnitudes. A previous model developed with the aid of quantum calculations also demonstrates the need to increase the dipole moment relative to the corresponding classical model, although in that case the dipole moment was increased by modifying the geometry.[62]

For development of TIP5P(PIMC) water, calculations were performed with a discretization of $P = 5$ and 216 molecules in a periodic box with intermolecular interactions truncated at 9 Å. Using a set of partial charges with magnitude 0.251 rather than 0.241 e, a density of 0.997 ± 0.002 g/cm^3 and an intermolecular energy of −9.94 ± 0.01 kcal/mol were obtained at 25 °C and 1 atm, as listed in Table III. Also presented in Table III are the fluctuational properties, calculated either from finite difference approximations to the derivatives or from the fluctuational formula, as discussed previously.[28] Note that the results for the energy and density are better than for the classical TIPnP models and the heat capacity is better than for the classical TIP5P model. These differences in the energy and density are near the noise level in the present calculations and are at the level of imprecision defined by varying such parameters as the number of molecules and method of dealing with boundary conditions. For example, the computed bulk phase properties change by only a few percent and computed diffusion constants increase by only ≈ 0.2 cm^2/s when reaction field or Ewald techniques are used to model the boundary conditions.[80(b)]
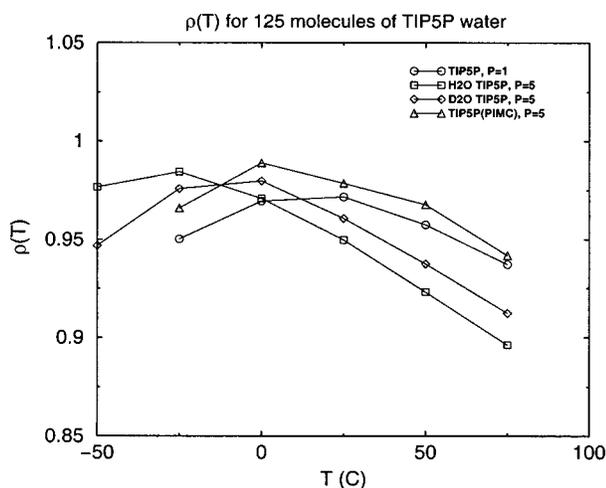
FIG. 9. Density profile of D$_2$O quantum calculations on TIP5P water and of H$_2$O quantum calculations on TIP5P(PIMC) water compared with classical and H$_2$O quantum calculations on TIP5P water at 1 atm.
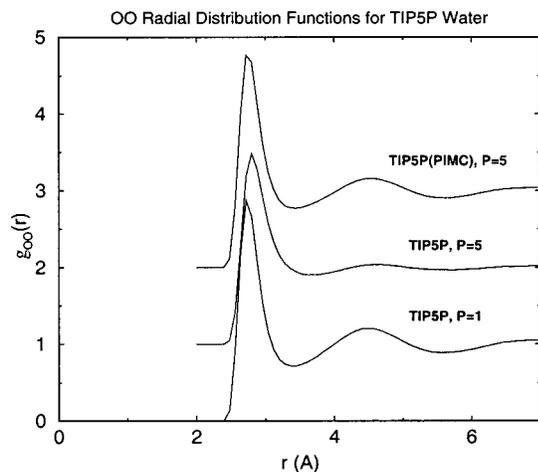
FIG. 10. OO radial distribution functions for TIP5P water and TIP5P(PIMC) water at 25 °C and 1 atm.

In addition to the ability of TIP5P(PIMC) to reproduce the thermodynamic properties, it is able to reproduce well the radial distribution functions (rdfs). One example of the rdfs is presented in Fig. 10; as is seen, the rdfs are more structured than those obtained by quantum calculations on TIP5P water and are slightly less structured than those from classical calculations on TIP5P water. The distance to the first peak, shifted out slightly upon the introduction of quantum effects, is shifted back inward toward the value for classical calculations on TIP5P. Recent experimental results indicate that the position and magnitude of this first peak are remarkably well reproduced by TIP5P water;[78] these are also well reproduced by TIP5P(PIMC) water in path integral calculations. Thus, TIP5P(PIMC) water reproduces the structural and thermodynamic properties in quantum calculations with a quality comparable to that of TIP5P water in classical calculations.

C. The effect of developing a model with path integral calculations

Path integral calculations similar to those presented in Sec. IV for the TIP5P model were performed for the TIP5P(PIMC) model. In particular, a temperature scan was performed for a periodic cube of 125 molecules. The energy and density for TIP5P(PIMC) water from those calculations are presented in Table VII, and the density profile for TIP5P(PIMC) water is presented in Fig. 9 along with that for TIP5P water. As noted previously,[28] there is size-dependence for the TMD such that for classical TIP5P water it increases from ≈4 to 12 to 20 °C for periodic cubes with 512, 216, and 125 molecules and cutoffs of 9, 8, and 7 Å. The TMD is increased for TIP5P(PIMC) relative to discretized TIP5P in view of the larger partial charges; however, it is ≈20 °C below the value for classical TIP5P water for the cube with 125 molecules. In a further refinement one could push the TMD for the PIMC model to higher temperature by increasing the oxygen to lone-pair site distance.[28]

VII. DISCUSSION

Liquid water is anomalous not only in the existence of its TMD but also in the relatively gradual change of its energy and density as a function of increasing temperature and pressure. Many water models fail to describe these changes adequately. There are two regimes for liquid water, considering both the anomalous properties and the ability of simple potential functions to reproduce these properties. One regime is at moderate temperatures and pressures where the TMD occurs; the other is at more extreme conditions of temperature and pressure.[81–83] Although there are several methods to improve the behavior in the first regime, i.e., by increasing the complexity of the charge distribution[28] or increasing the magnitudes of the partial charges,[5] there is no simple solution to improve the behavior at a wider range of state points. The reproduction of thermodynamic properties far from the state points of original parameterization is sensitive to the fluctuational behavior of the model, and a general feature of simple water models is that the fluctuational properties are not modeled as well as the underlying thermodynamic quantities.[5,27,28]

It should be noted that, with the exception of TIP5P water, the parameterization of the other models discussed here did not include reproduction of the density maximum. Although modifying the parameters of the TIP4F or Dang97 models may lead to some improvement in the low temperature results, that neither model improves upon the description of water at a wide range of state points is not surprising. The changes in water structure as the state point is varied are subtle.[7,8] The fact that both models yield poorer density behavior than the best rigid nonpolarizable models is evidence that their relatively simple modeling of intramolecular flexibility or electronic polarization is not adequate.

It has been suggested that in order to improve the description of liquid water at a range of state points, more sophisticated potential functions are needed.[22,83] The present work supports that conclusion. Furthermore, the needed sophistication is not achieved by including polarization, intramolecular flexibility or quantum mechanical effects *per se*, but instead requires full consideration of the underlying physical phenomena with an emphasis on accurate modeling of the electronic degrees of freedom. Within the framework of nonpolarizable potentials, the success for the density profile of increasing the potential function complexity is seen as one proceeds through the TIPnP series. Another example of improvement through increased complexity involves the modeling of the vapor–liquid coexistence curve. Although it is often suggested that a polarizable potential will in principle describe both the gas phase and the liquid phase since its parameterization uses data from both phases,[84] it has been shown that several simple polarizable models that have been parameterized to both gas and liquid data are not acceptable at modeling the intermediate region.[83] On the other hand, by modeling the quantum mechanical charge-magnitude dependence on the overlap integrals with a coupling between the Lennard-Jones terms and the electronic degrees of freedom a better description of the intermediate region can be achieved.[83] In general, the intermediate region is sensitive to fluctuations, and if the parameter fitting is to orthogonal sets

of data in two different regions, the intermediate region will not be well described.

The importance of quantum mechanical effects on the properties of liquid water has led to a variety of methods for their incorporation.[4,48–50,59,60,62] Attempts to include quantum mechanical effects that consider differing vibrational contributions between the liquid and gas phase[4,49] or perturbative semiclassical corrections[48,50] should be distinguished from path integral methods,[59,60,62] since the latter typically involve a quantum calculation on a potential that was developed for classical calculations. This leads to modification of properties such as the energy, density and vibrational spectra in a characteristic way relative to the corresponding classical calculations on the same model.[62] The parameterization of a water model with quantum statistical mechanical calculations requires that the molecules be made more attractive by, e.g., increasing the dipole moment, either by modifying the geometry[62] or by increasing the magnitudes of the charges as with TIP5P(PIMC) water.

Increasing the magnitudes of the partial charges structures the liquid, as was described in Sec. VI and as is seen by comparing results for SPC and SPC/E.[5] Thus, considering that SPC/E has a TMD while SPC does not,[21,27] and that the PPC model[23] employs a polarization correction and has been reported to have a TMD, it is not surprising the TIP5P(PIMC) model has an improved density behavior in the low temperature region relative to path integral calculations on the TIP5P model. The reparameterized model has properties more similar to classical calculations on the original model than do quantum calculations on the original model. Comparisons[58–61] between classical calculations and quantum calculations on a given water model are not as relevant as comparisons between two related models, one of which is classically parameterized and the other of which is quantum mechanically parameterized. The issue of fair comparison has been raised before in the context of classical flexible models.[38] The TIP5P(PIMC) model is not a replacement for the TIP5P model. The increased computational expense of path integral calculations would render biomolecular and low temperature applications often impractical, and it is unnecessary in situations where no new insight is obtained. Classical calculations may be viewed as being associated with an implicit parameter renormalization to account for their approximate nature. It is well known that the simple nonpolarizable models have dipole moments lower than the most conservative estimates for the liquid phase value.[5,7,8,28,85] Viewing classical calculations as involving a parameter renormalization implies that the liquid-phase dipole moments for the quantum mechanically parameterized model should be closer to the experimental value. Thus, the increase in dipole moment to 2.39 D for TIP5P(PIMC) water from 2.29 D for the TIP5P model is in the right direction.

The importance of incrementally modifying existing models should also be emphasized. Incorporating many new effects into a single model[35,36] leads to difficulties in determining what features of the model are responsible for what observed properties of the model. The TIP5P model represents incremental improvement over the prior TIP3P and TIP4P models and yields an improved density profile for a

well understood reason.[28] Incremental improvements allow one to isolate those variables responsible for the improved or worsened reproduction of the properties of interest. This is particularly important when the consequence of a potential modification is not readily discernable.

It should be noted that after this work was completed, we learned of success with another more electronically complex model, TIP4P-FQ,[32] which is a four-site polarizable model with variable charges. It yields an average liquid state dipole moment of 2.62 D and has now been shown to have a density maximum near the experimental value.[86]

VIII. CONCLUSION

The consequences of including intramolecular flexibility, electronic polarization, and quantum mechanical effects in simple models of liquid water for the reproduction of the thermodynamic and structural properties at a range of thermodynamic state points has been examined. Particular attention has been focused upon the reproduction of the density anomaly. Both the four-site classically flexible TIP4F model and the dipole-polarizable Dang97 model do not improve the description of either the density maximum or thermodynamic properties at high temperatures in comparison with the rigid, nonpolarizable TIP4P model. Path integral calculations on TIP4F water and TIP5P water indicate that the high temperature behavior of the density is not improved by the inclusion of quantum mechanical effects. For quantum calculations on flexible TIP4F water, the density maximum is shifted to a higher temperature relative to classical calculations and the radial distribution and energy distribution functions are improved. Thus, the introduction of quantum mechanical effects alleviates some of the problems created by adding classical flexibility to simple water models, reinforcing the idea that real water is more like rigid water models than classical flexible water models. Improvements are not seen for path integral calculations on the rigid TIP5P model. As expected, for this model, the radial distribution and energy distribution functions are destructured relative to classical calculations and the density profile is worse. Path integral calculations on quantum D_2O TIP5P and TIP5P(PIMC), a modification of the TIP5P model in which the results of quantum calculations were fit to experimental data, indicate that in both cases the liquids are more structured than from calculations on quantum H_2O TIP5P and that in both cases the density profile is improved.

Thus, the inclusion of intramolecular flexibility, electronic polarization or quantum effects does not immediately lead to better reproduction of the thermodynamic properties of bulk water at a range of thermodynamic state points. At state points not far from 25 °C and 1 atm, improvement of the relatively crude modeling of the electrostatics, in going, for example, from TIP3P to TIP4P to TIP5P, is more beneficial than the simple inclusion of classical flexibility, polarizability, or quantum effects. Further improvement for water models is expected to require more sophisticated description of the electronic degrees of freedom with balanced treatment of any partial charge model and polarizability and with attention paid to their effect on the fluctuational properties.

ACKNOWLEDGMENTS

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