Ice: A fruitful source of information about liquid water

J.L.F. Abascal *, R. García Fernández, L.G. MacDowell, E. Sanz, C. Vega

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

Abstract

The recent calculation by computer simulation of the phase diagram involving the solid phase of water has triggered a number of new simulation experiments with somewhat unexpected results. Firstly, it has been shown that this is a severe test of the potential models. The results yielded by TIP4P and derived models are, in general, in fair agreement with experiment. But the differences between the experimental phase diagram and the computer simulation for the three site models (SPC, SPC/E and TIP3P) and for the five site model TIP5P are significant. In this paper we show how this information can be useful to develop improved potentials. We discuss the difficulties in fitting different properties and analyze the reasons that led us to the proposal of two different models: TIP4P/Ice and TIP4P/2005. The first model was intended to reproduce the melting temperature of hexagonal ice while the second one was designed as a general model.
© 2007 Published by Elsevier B.V.

1. Introduction

Given the importance of water, a great effort has been devoted to the development of accurate potential models. A recent review [1] discusses the results yielded by more than forty different models. Such a number is indeed indicative of the importance of water but, at the same time, it suggests that none of them is satisfactory for a wide range of thermodynamic conditions. However, if one is only interested in the condensed phases of water the number reduces considerably. It has been shown that simple models with a permanent dipole moment may account satisfactorily for the liquid properties since an enhanced dipole reproduces in an averaged way the polarization effects characteristic of the dense water phases. In an attempt to simplify further the models, most of them are also rigid. The most successful of these rigid non-polarizable models are SPC [2] (and its reparametrization SPC/E [3]), TIP3P [4], and TIP4P [4]. In these simple models a single Lennard–Jones (LJ) interaction site is located at the position of the oxygen atom. There are three charged sites. Two of the charges are positive (q_H) and are placed at the hydrogen atoms. The negative site is

coincident with the oxygen atom in three site models as SPC, SPC/E and TIP3P. In four site models as TIP4P, the center of the negative charge (denoted the M site) is placed at some distance d_{OM} (0.15 Å in TIP4P) from the oxygen along the H–O–H bisector. Recently, the higher performance of computers has allowed to increase the number of sites of the models as in the five-site model TIP5P [5,6] (in which two partial charges are placed at the positions of the "lone electron pairs") and the six-site model of Nada and van der Eerden [7] (NvdE).

Contrarily to the view that water models when used in computer simulation yield similar results, the prediction of the phase diagram shows that their ability to describe the phase diagram of water is not similar in any way. In general, TIP4P-type models yield a qualitatively correct phase diagram [8–11]. The exception is TIP4P-Ew [12] for which the stability of ice II is overestimated [11]. As a consequence ice III becomes metastable and the stability domain of ice V is severely reduced to a small range of temperatures and pressures. The situation is even worse for SPC/E [9] where ice III, ice V and even ice I_h are metastable with respect to ice II (ice I_h being thermodynamically stable only at negative pressures). Therefore the relative stability of ice II plays a central role in establishing whether the prediction of the phase diagram for a given model is acceptable or not. In this paper we show how this information can be useful to develop improved potentials. We discuss the difficulties in fitting different properties

---

* Corresponding author.
  E-mail address: abascale@quim.ucm.es (J.L.F. Abascal).

and analyze the reasons that led us to the proposal of two new models: TIP4P/Ice [10] and TIP4P/2005 [11].

2. Simulation details

The simulations have been performed with the Monte Carlo technique. For the liquid phase, isotropic NpT simulations were used, whereas for the solid phases anisotropic NpT simulations (Parrinello Rahman like) were performed [13]. The Lennard–Jones interaction was truncated at 8.5 Å and a long range correction to the energy was added [14]. To deal with electrostatics the Ewald summation method was employed with the real space sum truncated at 8.5 Å.

For the calculation of the phase diagrams we have used several techniques. For TIP4P and SPC/E we used a combination of free energy calculations and Gibbs–Duhem integration [9]. The residual free energy of the liquid was computed by following a thermodynamic path in which the charges are gradually switched off so that the water models transform into a LJ system (for which the residual free energy is known [15]). Initial configurations for proton ordered solids were obtained using the crystallographic data. For proton disordered ices, the configurations were generated using a procedure [16,17] to guarantee that the Bernal–Fowler rules are satisfied [18] and that the simulation box has zero or very small dipole moment. The free energy of the solids was evaluated using the Einstein crystal method of Frenkel and Ladd [19]. For disordered solid phases, the Pauling entropy $S/R = \ln(3/2)$ is added to account for the degeneracy resulting from the possible hydrogen bond arrangements, consistent with the ice rules. Once an initial coexistence point between two phases is found, the whole coexistence line is traced using the Gibbs–Duhem integration proposed by Kofke [20,21]. Basically it consists in the numerical integration of the Clapeyron equation

$$\left(\frac{dp}{dT}\right) = \frac{\Delta H}{T \Delta v} \tag{1}$$

For the other models (TIP3P, SPC, TIP5P, TIP4P-Ew, TIP4P/Ice and TIP4P/2005) we used the "Hamiltonian" Gibbs Duhem integration [21–23] which allows one to determine the shift in coexistence curves due to changes in the potential. A brief summary of the technique follows. Let us write a path between a reference potential u_{ref} and the potential of interest u by defining $u = (1 - \lambda)u_{ref} + \lambda u_{new}$ where λ changes from zero to one. We can use λ as a new intensive thermodynamic variable. Following the same steps leading to the classical Clapeyron equation it is easy to write the generalized relationships

$$\frac{dT}{d\lambda} = \frac{\Delta x_g}{\Delta s} \tag{2}$$

and

$$\frac{dp}{d\lambda} = -\frac{\Delta x_g}{\Delta v}, \tag{3}$$

where

$$x_g = \frac{1}{N} \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{N,p,T,\lambda}, \tag{4}$$

and s, v are the entropy and volume per molecule, respectively, and U the total energy of the system. The integration of these equations makes possible to calculate the shift in the coexistence temperature (pressure) produced by a change in the interaction potential at constant pressure (temperature). To obtain the rest of the coexistence curves we proceed with the usual Gibbs–Duhem technique.

Finally, the results for the melting temperatures of all the models have been cross-checked with those calculated using a direct coexistence of the solid–liquid interface [24,25]. We used molecular dynamics simulations of boxes containing liquid water and ice in contact. The implementation is based in the analysis of the evolution of the total energy along NpT simulations at different temperatures. If the trial temperature is considerably higher than the T_m the solid region melts quickly and the drift of the total energy is positive. The temperature is then reduced until, for a given value, the drift of the total energy along the simulation is null or negative. The uncertainty in the determination of the melting temperature is strongly dependent on the simulated time. We have shown that in order to reduce the uncertainty to about 2 K the simulations should be of the order of 10 ns long. We have compared the direct coexistence results with our own T_m determinations using a free energy route. We have found [24,26] a very good agreement between the results of both methodologies, the differences being around 3 K for a number of water models: SPC/E, TIP4P, TIP5P, TIP5P-E, TIP4P-Ew, TIP4P/2005, TIP4P/Ice and NvdE.

3. Predictions for the solid phases of water

In this section we analyze the results obtained for the solid phases of water of the most popular water models. Although, for completeness, we include in the figures the results for TIP4P/Ice and TIP4P/2005, these models are actually a consequence of the conclusions obtained in our analysis of the results for the other models. Thus, the parametrization leading to TIP4P/Ice and TIP4P/2005 and the predictions of these models will be analyzed in the next section.

3.1. Phase diagram

Predictions for the dense region of the phase diagram have been reported in Refs. [9] (SPC/E and TIP4P), [23] (TIP3P, SPC and TIP5P), [10] (TIP4P/Ice) and [11] (TIP4P-Ew and TIP4P/2005). TIP4P provides a qualitatively correct description of the phase diagram, Ices I_h, II, III, V, VI, VII and VIII were found to be stable phases for the TIP4P model (as they indeed are for real water). As in real water, ice IV and ice IX are clearly metastable phases in TIP4P. We could not resolve either the relative stability of ices I_h and I_c or that of ices V and XII since the free energy differences were smaller than our typical uncertainties. Concerning the SPC/E model, we found that ices II,VI,VII,VIII are stable solid phases while ices IV and IX are metastable. Major defects of the predictions for SPC/E are that ices III and V are metastable and that the stable phase at $p = 1$ bar is ice II instead of ice I_h. The appearance of the phase diagram for the SPC/E model at low pressures arises from the extraordinary
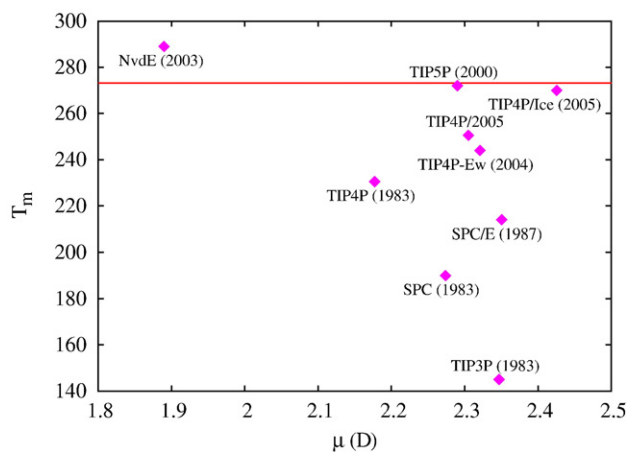
Fig. 1. Melting temperature of ice I_h for several water models as a function of the dipole moment. The year in which the model was proposed is indicated in brackets.

stability of ice II. Analyzing one by one the differences between TIP4P and SPC/E models it was found that the only difference of TIP4P with respect to SPC/E that reduces the stability of ice II with respect to its competitors (ice I_h, III, V) is the location of the negative charge.

The relative stability of ice I_h with respect to ice II has also been considered for other models. It turns out that for SPC, TIP3P and TIP5P the stable phase at the normal melting point is ice II so that ice I_h is not a thermodynamically stable phase. TIP4P-Ew shows an intermediate behavior between that for models with the negative charge at the oxygen and TIP4P: ice II takes over the region of moderately high pressures so that ice III becomes metastable and the interval of stability of ice V is reduced to a marginal range of temperatures and pressures. It is interesting to point out that the distance d_{OM} in TIP4P-Ew is 0.125 Å (to be compared with 0.15 Å for TIP4P and 0 for SPC/E). This explains that the situation for TIP4P-Ew is less dramatic than for SPC/E but still not satisfactory.

In summary, the calculation of the phase diagram has shown that this is a severe test for the water potential models.

Contrarily to the view that water models when used in computer simulation yield similar results, the prediction of the phase diagram shows that their ability to describe the phase diagram of water is not similar in any way. The only model yielding a qualitative agreement with experiment is TIP4P. But, despite the satisfactory appearance of the TIP4P phase diagram, the departures from experiment of the melting points of ices I_h III, V, and VI are above 40 K. This clearly indicated that there was room for improvement.

3.2. Melting properties of ice I_h

The melting temperatures of ice I_h (T_m) of these water models are displayed in Fig. 1. It seems reasonable that the molecular dipole moment μ may influence the melting properties. This is especially true when one considers the dependence of μ on d_{OM} for three charged site models (SPC, SCP/E, TIP3P, TIP4P and derived models)

$$\mu = 2q_H(d_{OH}\cos\theta - d_{OM}), \qquad (5)$$

and takes into consideration the enormous influence of d_{OM} in the phase diagram as we commented above. However, Fig. 1 indicates that, apparently, T_m is uncorrelated with μ. In fact, the permanent dipole moment of these models is always around 2.3 D because the enlargement (or reduction) in the distance between the centers of the negative and positive charges is compensated by a decrease (increase) of the molecular charges. For instance, in TIP3P (for which $d_{OM}=0$) $q_H=0.417e$ leading to $\mu=2.347$ D. The hydrogen charge increases to $0.524e$ in TIP4P-Ew but the dipole moment remains almost the same, $\mu=2.321$ D, due to the shift of the negative charge towards the hydrogens ($d_{OM}=0.125$ Å). Thus, what we essentially see in Fig. 1 reflects the importance of other factors at almost constant μ. In particular, Fig. 1 shows that the results are more or less grouped according the molecular geometry. Three site models (TIP3P, SPC, SPC/E) systematically yield very low melting temperatures. The T_m's predicted by four site models (TIP4P-

Table 1
Melting properties of ice I_h at $p=1$ bar for different models

Model	TIP3P	SPC	SPC/E	TIP4P	TIP4P-Ew	TIP4P/2005	TIP4P/Ice	TIP5P	NvdE	Experimental
T_m (K)[a]	145.6	190.5	215	232.0	245.5	252.1	272.2	273.9	290	273.15
ρ_l (g/cm^3)	1.017	0.991	1.011	1.002	0.992	0.993	0.985	0.987	1.004	0.999
ρI_h (g/cm^3)	0.947	0.934	0.950	0.940	0.936	0.921	0.906	0.967	0.915	0.917
H_l (kcal/mol)	−11.69	−11.64	−12.49	−10.98	−12.02	−12.17	−13.31	−10.33	−10.07	–
H_{I_h} (kcal/mol)	−11.99	−12.22	−13.23	−12.03	−13.07	−13.33	−14.60	−12.08	−12.09	–
ΔH (kcal/mol)	0.30	0.58	0.74	1.05	1.05	1.16	1.29	1.75	2.02	1.44
dp/dT (bar/K)	−66	−115	−126	−160	−164	−135	−120	−708	−169	−137
T_c (K)[b]	580	593.8	638.6	588.2	628	640	705	521.3	–	647.1
T_m/T_c	0.251	0.321	0.337	0.394	0.391	0.394	0.386	0.525	–	0.422

T_m, melting temperatures; ρ_l and ρI_h, coexistence densities of liquid water and ice; H_l and H_{I_h}, enthalpies of liquid and ice (we have not included the 3RT term arising from the translational and rotational kinetic terms); $\Delta_m H$, melting enthalpy; dp/dT, slope of the coexistence curve. We also include for comparison the critical temperatures of the models and the ratio T_m/T_c.
[a] Melting properties taken from Refs. [23] (TIP3P, SPC, SPC/E, TIP4P, TIP4P-Ew), [11] (TIP4P/Ice), and [10] (TIP4P/2005). The melting temperature of NvdE has been taken from Ref. [26] and the rest of melting properties for this model are results of this work.
[b] Critical temperatures from Refs. [27] (SPC, SPC/E), [28] (TIP4P), [29] (TIP4P-Ew, TIP4P/2005, TIP4P/Ice), and [30] (TIP5P). The liquid–vapor coexistence properties of TIP3P have not yet been reported and will be discussed in a forthcoming publication.

like) are much closer to the experimental value. As the difference between these two groups of models is essentially the distance d_{OM}, one may observe again the great influence of this parameter in the ice properties. Finally, it is to be noticed that when the models have the same geometry (SPC, SPC/E) – or a similar one (TIP4P-like models) – it is clear that T_m noticeably increases with μ. In Fig. 1 we have also displayed the year in which the models were proposed. It can be seen a more or less continuous improvement along the years. Interestingly, until 2003, the progress was "blind", i.e., the authors did not know the melting point of their models. This means that the improvement was a side effect of changes in the model parameters and that other water properties were the target quantities in these parameterizations.

Table 1 shows the melting properties of ice I_h for these models. The coexistence density of the liquid phase is fairly well reproduced by all the models (the departures from experiment are always smaller than 2%). But the coexistence density of the solid phase is systematically overestimated. The differences with respect to the experimental value are clearly more than 3% for TIP3P, SPC/E and TIP5P. TIP4P-Ew and SPC give more reasonable predictions, with departures of around 2%. The results for the melting enthalpies are also very poor in general with deviations over 50% for TIP3P, SPC and SPC/E while TIP4P and TIP4P-Ew reduce the difference to 30%. TIP5P gives a slightly smaller departure from experiment (around 20%) although this model overestimates the melting enthalpy. All the previous quantities can be combined using the Clapeyron equation to yield dp/dT, i.e., the slope of the coexistence curve. The predictions for this property are extremely variable. TIP5P and TIP3P furnish very poor predictions; the result for the former is about 5 times larger than the experimental one while dp/dT for TIP3P is about one half the experimental value. Compared with them, the results for SPC, SPC/E, TIP4P and TIP4P-Ew may be denoted as acceptable because the departures are smaller than a 20%. In summary, none of the models gives satisfactory melting properties. The better predictions correspond to TIP4P and TIP4P-Ew but even for these models the overall agreement is not satisfactory enough (we recall that the results for the recently proposed TIP4P/2005 and TIP4P/Ice models will be discussed later in this paper). The predictions deteriorate for all the three site models TIP3P, SPC and SPC/E. Thus, the quality of the results for the melting temperatures is indicative of the rest of the melting properties for three and four site models. TIP5P, with a rather different geometry, gives non-balanced predictions: an excellent result for the melting temperature together with an extremely poor value for Δv which translates in a unusually large slope of the coexistence curve.

In Table 1 we have also included the results for the critical temperature and the ratio T_m/T_c. Beyond the particular values of T_c we would like to remark here that the results for the ratio T_m/T_c can again be grouped according to the molecular geometry. TIP4P-like models produce a ratio of around 0.39 and the three site models give $T_m/T_c \simeq 0.33$. These values are smaller than the experimental ratio which is 0.422. TIP5P shows again a peculiar behavior as the ratio (0.525) is higher than the experimental one.

4. The search for improved water potentials

The results presented in the previous section triggered a simple question: can this information be used to improve the water potential? But the answer to a simple question is not necessarily simple. The goodness of the parametrization relies on the functional describing the force field and on the target quantities used to minimize the difference between the predicted values and the experimental ones. In accordance with the origin of the question, there are several obvious choices. We should try the TIP4P geometry for the new water potential as it provides a compromise between simplicity and prediction ability. Also, obvious target properties are the melting point of ice I_h and the phase diagram. As the Hamiltonian Gibbs–Duhem integration allows one to calculate the variation of a coexistence temperature due to a change in the potential, there is no problem to calculate the derivatives of the ice I_h melting temperature with respect to any of the potential parameters (the depth ϵ and width σ of the Lennard–Jones interaction, the distance d_{OM} and the hydrogen charge q_H). The quality of a phase diagram is a rather abstract quantity. To put it in numbers we selected the stability domain of ice II. Our numerical implementation consisted in the calculation of the derivatives of the liquid–ice III and ice II–ice III coexistence temperatures at 300 MPa with respect to the potential parameters. But what we actually fitted to the experiment was the difference between these two coexistence temperatures which provides the stability range of ice II at that pressure.

Apart of these solid properties it is necessary to include typical liquid properties. Common choices are the liquid density at ambient conditions and the vaporization enthalpy. Although the calculation of the temperature of maximum density is very costly in computer time it is particularly representative of the water behavior so we decided to include it among the target quantities of our fit. As the number of target quantities should be larger than the number of parameters, one or two additional properties have to be chosen. Since the density of the different ice polymorphs is systematically overestimated and it is rather sensitive to the potential model (the departures for ice II reach 0.12 g/cm³ for TIP5P [11]) we included the density of ice II in the fitting properties. But we anticipate that this is not a crucial choice and that many other thermodynamic properties could work as well.

For the fitting procedure, a first order expansion of the quantities as a function of the parameters is made. As an example, the melting temperature of a model can be written in terms of the corresponding value for a reference model and the derivatives with respect to the potential parameters

$$T_m \simeq T_m^{ref} + \frac{\partial T_m}{\partial \epsilon}(\epsilon - \epsilon^{ref}) + \frac{\partial T_m}{\partial \sigma}(\sigma - \sigma^{ref}) + \frac{\partial T_m}{\partial q_H}(q_H - q_H^{ref})$$
$$+ \frac{\partial T_m}{\partial d_{OM}}(d_{OM} - d_{OM}^{ref}). \tag{6}$$

We calculated the derivatives with respect to a parameter $\xi = (\epsilon/k)/K$, $\sigma/Å$, $d_{OM}/Å$, q_H/e) as

$$T_\xi = \frac{\partial T_m}{\partial \xi} \simeq \frac{\Delta T_m}{\Delta \xi}. \tag{7}$$

We obtained the following values for the liquid-I_h TIP4P coexistence curve, $T_\epsilon = -1.764$ K, $T_\sigma = -504$ K, $T_{q_H} = 1462$ K, and $T_{d_{OM}} = -811$ K. Eq. (6) provides an excellent estimation of the melting temperature for TIP4P-like models with deviations with respect to the simulated values of 1 K or less. However, it gives a rather poor estimation for TIP3P. This is because the large differences in q_H and d_{OM} lead to large but mutually cancelling contributions increasing the importance of higher order corrections to Eq. (6).

We used a non-linear fit to minimize the sum of the differences between the estimated quantities and the experimental data using weighting factors to account for the disparity in the values of the target properties. Although a wide variety of parameters can be obtained by modifying the weight factors, none of them fit satisfactorily the overall quantities. In particular, *it is impossible to simultaneously fit the melting temperature of ice I_h and the enthalpy of vaporization $\Delta_v H$*. TIP4P, which was designed to match the experimental result for $\Delta_v H$, has a melting temperature about 40 K below the experimental value. In 1987, Berendsen suggested that a self-energy correction [3] should also be included if a comparison is made between the properties of the liquid state and the gas phase. This was the basis for the proposal of the successful SPC/E model that improved the overall predictions of its predecessor SPC. Since then, there has been a growing acceptance of Berendsen's arguments [1]. Accordingly, in our fit we will include the self-energy term in the calculation of $\Delta_v H$. The correction depends on the polarizability α and on the difference between the dipole moment of the model μ_l and that of the gas phase μ_g. It may be approximated by

$$\Delta E^{pol} = (\mu_l - \mu_g)^2 / 2\alpha. \qquad (8)$$

Table 2 shows that the inclusion of the correction in the fitting procedure (as done for TIP4P-Ew) yields parameters that provide a significant improvement of the melting temperature. Indeed, our fitting procedure indicated that an increase of the enthalpy of vaporization results in a better agreement not only of T_m but also of the rest of properties. In fact, it is possible that most of the improvement found for the TIP4P-Ew model [12] with respect to TIP4P is a consequence of the inclusion of the self-energy correction. Incidentally, we also observe in the table that TIP4P-Ew gives a wrong prediction of the relative stability of ices II and III at 320 MPa while TIP4P gives a satisfactory
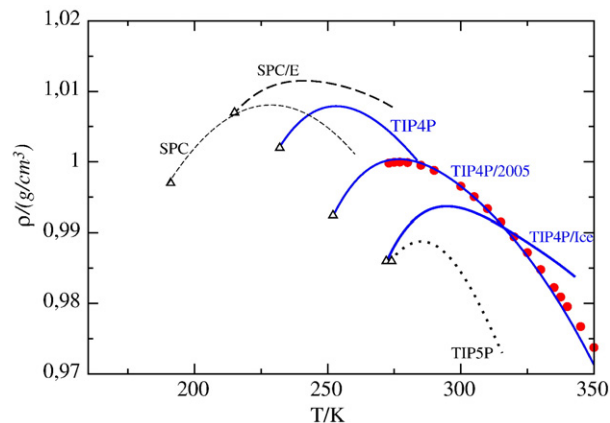

Fig. 2. Densities at 1 bar. The triangle ending the lines represents the liquid density at the melting point. The full circles are the experimental data.

account of this property. But the parameters of TIP4P and TIP4P-Ew are very similar with the exception of d_{OM} (0.15 Å in TIP4P to 0.125 Å in TIP4P-Ew). The disappearance of ice III from the stable phases can be attributed to the decrease of the distance d_{OM}. The extraordinary large dependence of the ice II–ice III coexistence temperature on d_{OM} is also to be noticed: the derivative is −4400 K/Å.

It is not surprising that the temperature of maximum density T_{TMD} seems also to be linked to the melting temperature (Fig. 2). The peculiarity here is the noticeable constancy of the difference $T_{TMD} - T_m$ within the different groups of water models. For three site models the maximum in density occurs between 26 K and 37 K above the melting temperature [31]. The difference $T_{TMD} - T_m$ reduces to about 21–27 K in four site models [11,31] (TIP4P, TIP4P-Ew, TIP4P/Ice and TIP4P/2005). This behavior has two consequences. Firstly, it is not necessary to include the cumbersome calculation of T_{TMD} in the fit as it can be estimated from the melting temperature. But, as long as the difference $T_{TMD} - T_m$ is much larger than the experimental value, *it is also impossible to simultaneously fit the melting temperature of ice I_h and the temperature of maximum density*.

The dilemma posed by the relation between T_m and $\Delta_v H$ on one hand and between T_m and T_{TMD} on the other cannot be solved and forces one to design the water potential "à la carte". The only potential yielding a melting temperature close to the experiment (TIP5P) furnishes extremely poor values for other

Table 2
Essential features of the different TIP4P models

Model	TIP4P	TIP4P-Ew	TIP4P/2005	TIP4P/Ice	Experiment
$\Delta_v H$	**10.65**	11.76 (**10.58**)	11.99 (10.89)	13.49 (11.84)	10.52
T_m	232.0	245.5	252.1	**272.2**	273.15
T_{TMD}	253	273	**278**	295	277
Ice II domain	25	−105	17	12	8
T_c	588	628	640	705	647.1
T_{TMD}/T_c	0.430	0.435	0.434	0.418	0.428

We typed in bold font the characteristic property determining the parametrization of the model. The stability range of ice II has been calculated as the difference between the liquid–ice III and ice II–ice III coexistence temperatures at 3200 bar. Temperatures are given in Kelvin and $\Delta_v H$ in kcal mol^{-1}. Values in brackets include the self-polarization correction (Eq. (8)) to the enthalpy of vaporization.

melting properties and for the densities of the ice polymorphs. Moreover ice I_h is a metastable solid at those conditions as ice II is the thermodynamically stable form for TIP5P. So we believed that the enthalpy of vaporization could be sacrificed for the sake of a good agreement for the melting temperature (see Table 2). As by design the resulting model was intended to reproduce several ice properties we denoted it as TIP4P/Ice. In fact, as Table 1 shows, TIP4P/Ice not only matches the experimental melting temperature but also provides excellent predictions for the rest of melting properties. TIP4P/Ice also provides the closest to experiment phase diagram of all the water models reported until now [10]. However it is important to stress that despite the excellent prediction for the melting temperature of ice I_h, the rest of the solid–liquid coexistence temperatures are slightly underestimated by TIP4P/Ice. Probably this is because the dipole moment of ice is larger than that of liquid water, the effect being more important for the more dense polymorphs. This could also be related with low melting enthalpy values found in general for the models of this work. In fact, the result for TIP4P/Ice (which gives the best prediction for the melting enthalpy) is still 10% below the experimental value. As for the ice polymorphs densities, TIP4P/Ice gives a signed mean deviation from experiment (for ten different polymorphs) of only -0.009 g/cm^3 to be compared with 0.070 g/cm^3 for TIP5P [10]. Although TIP4P/Ice was not designed to accurately describe the liquid state properties, its predictions are acceptable. For instance, it overestimates the critical temperature but the departure from the experimental value is the same than that for TIP4P (which underestimates T_c), a model usually considered as describing satisfactorily the liquid water properties. In summary TIP4P/Ice is a specialized potential which provides reasonable predictions also for the liquid state.

A different approach was followed for the parametrization of TIP4P/2005. In this case we wanted a general model. In order to get a better agreement with the enthalpy of vaporization, the condition of a perfect match for the melting temperature should be relaxed. Interestingly the mid-point between these two requirements implies a better agreement for the temperature of maximum density. We then increased the weight factor associated to this latter property. As commented above, $T_{TMD} - T_m$ is about 25 K for TIP4P models. Thus, we did not try to fit T_{TMD} but we chose a target T_m in the range 250–255 K. The value for the resulting model was 252 K and a rigorous calculation of the temperature of maximum density led to $T_{TMD} = 278$ K, only 1 K over the experimental result [11]. Interestingly, the agreement is not limited to the temperature of the maximum density. TIP4P/2005 gives excellent results for the densities at 1 bar. The averaged difference with the experiment is 7×10^{-4} g/cm^3, lower than the statistical uncertainty in the simulations. As a consequence, derived properties as the thermal expansion coefficient, α_p, and the isothermal compressibility, κ_T, are essentially coincident (i.e., within the statistical uncertainty) with the experimental data. The excellent predictions for the thermodynamic properties extend to very high temperatures and pressures. For instance, the maximum deviation between simulation and experiment for the 473 K isotherm up to 30000 bar is only a 0.45% (and 0.9% at $T = 573$ K, $p = 40000$ bar).

TIP4P/2005, also yields a very satisfactory phase diagram. It is similar to that for TIP4P/Ice but slightly shifted towards lower temperatures (about 20 K). Despite that, it improves noticeably the TIP4P phase diagram. In fact, the phase diagram of TIP4P/2005 is essentially midway between those for TIP4P and TIP4P/Ice. This is indeed a general behavior of these models. For instance, the mean signed deviated of ten ice polymorphs is 0.007 g/cm^3 which is just the mean value between the results 0.023 and -0.009 g/cm^3 for TIP4P and TIP4P/Ice. Regarding the melting properties, TIP4P/2005 gives a well balanced set of predictions that result in an excellent value for the slope of the coexistence curve. Finally, it is to be noted that TIP4P/2005 also accounts satisfactorily for other types of properties as the self-diffusion coefficient, the static dielectric constant and the liquid structure.

There are some other points in Table 2 that deserve mention. First, the relation between the maximum density temperature and the critical temperatures. Since, at low temperatures, the densities at 1 bar are very close to the liquid branch of the coexistence curve, it seems reasonable that the 1 bar isochore determines in some way the quality of the liquid branch of the liquid–vapor envelope at higher temperatures. But the results of Table 2 are beyond this quite general statement. For all the TIP4P-like models for which data are available, the ratio T_{TMD}/T_m is between 0.418 and 0.435. More importantly, the constancy of this ratio is accompanied by its agreement with the experimental value, 0.428. As a consequence, the excellent T_{TMD} yielded by TIP4P/2005 translates into a very satisfactory critical temperature [29].

5. Conclusions

In this work we have seen that the study of the properties of the different ice polymorphs threw some light on the properties of liquid water and has served to design improved water models. The conclusions of our study are the following:

– The distance between the oxygen atom and the center of the negative charge has a profound influence on the ice properties. This is particularly true for the melting temperatures and for the relative stability of ice II. (Incidentally, we note that there is a report indicating that the structure of proton ordered ices is also sensitive to the differences in the water models [32]). Three site models (for which $d_{OM} = 0$) give very poor results for the properties of the solid phases of water. Our study suggest that the distance d_{OM} should be 0.15 Å or slightly higher in order to get acceptable results.
– The inclusion of the self-polarization term to account for the different dipole moments of the liquid and vapor phases in the fitting of the enthalpy of vaporization leads to potential models that significantly improve the melting properties. Besides it also improves the liquid properties. In fact TIP4P/2005 (and also TIP4P-Ew) gives better predictions than TIP4P for all the liquid properties (thermodynamic properties, diffusivity, dielectric constant) investigated until now. This new study gives then an additional support to Berenden's arguments leading to the proposal of SPC/E.

– Different water properties are related and the differences (or ratios) in several cases deviate from the experimental values. For instance, the difference between the temperature of maximum density and the melting temperatures are about 25 K for TIP4P models and a little bit larger for three site models. As a consequence, in designing water potentials, one has to select which properties are better reproduced by the model and which ones should be sacrificed.

– In particular, several models can be obtained with our fit, all of them with $d \geq 0.15$ Å and, thus, leading to more or less acceptable phase diagrams. TIP4P is the potential model we obtain when the fit put the emphasis in the vaporization enthalpy (neglecting the self polarization correction). TIP4P/2005 is a new model obtained when the larger weight factor is given to the temperature of maximum density and the self polarization correction is included. Finally, TIP4P/Ice is the resulting model when the main target property is the melting temperature. We would like to mention also that a similar potential to TIP4P-Ew is obtained when the fit put the emphasis in the vaporization enthalpy (with the self polarization correction included) but the relative stability of ice II is not taken into account.

– Overall, the two new potentials, TIP4P/Ice, TIP4P/2005 are the only models that accurately predict the melting properties of ice I_h, the densities of the ice polymorphs and the complete dense region of the phase diagram. Besides, TIP4P/2005 gives unprecedented predictions for the liquid state essentially matching the temperature of maximum density and the liquid branch of the liquid-vapor coexistence curve which results in an excellent prediction for the critical temperature.

Acknowledgments

References

[1] B. Guillot, J. Mol. Liq. 101 (2002) 219.
[2] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, J. Hermans, in: B. Pullmann (Ed.), Intermolecular Forces, Reidel, Dordrecht, 1981, p. 331.
[3] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, J. Phys. Chem. 91 (1987) 6269.
[4] W.L. Jorgensen, J. Chandrasekhar, J.D. Madura, R.W. Impey, M.L. Klein, J. Chem. Phys. 79 (1983) 926.
[5] M.W. Mahoney, W.L. Jorgensen, J. Chem. Phys. 112 (2000) 8910.
[6] S.W. Rick, J. Chem. Phys. 120 (2004) 6085.
[7] H. Nada, J.P.J.M. van der Eerden, J. Chem. Phys. 118 (2003) 7401.
[8] E. Sanz, C. Vega, J.L.F. Abascal, L.G. MacDowell, J. Chem. Phys. 121 (2004) 1165.
[9] E. Sanz, C. Vega, J.L.F. Abascal, L.G. MacDowell, Phys. Rev. Lett. 92 (2004) 255701.
[10] J.L.F. Abascal, E. Sanz, R. García Fernández, C. Vega, J. Chem. Phys. 122 (2005) 234511.
[11] J.L.F. Abascal, C. Vega, J. Chem. Phys. 123 (2005) 234505.
[12] H.W. Horn, W.C. Swope, J.W. Pitera, J.D. Madura, T.J. Dick, G.L. Hura, T. Head-Gordon, J. Chem. Phys. 120 (2004) 9665.
[13] M. Parrinello, A. Rahman, J. Appl. Phys. 52 (1981) 7182.
[14] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1987.
[15] J.K. Johnson, J.A. Zollweg, K.E. Gubbins, Mol. Phys. 78 (1993) 591.
[16] V. Buch, P. Sandler, J. Sadlej, J. Phys. Chem., B 102 (1998) 8641.
[17] L.G. MacDowell, E. Sanz, C. Vega, J.L.F. Abascal, J. Chem. Phys. 121 (2004) 10145.
[18] J.D. Bernal, R.H. Fowler, J. Chem. Phys. 1 (1933) 515.
[19] D. Frenkel, A.J.C. Ladd, J. Chem. Phys. 81 (1984) 3188.
[20] D.A. Kofke, Mol. Phys. 78 (1993) 1331.
[21] D.A. Kofke, J. Chem. Phys. 98 (1993) 4149.
[22] R. Agrawal, D.A. Kofke, Phys. Rev. Lett. 74 (1995) 122.
[23] C. Vega, E. Sanz, J.L.F. Abascal, J. Chem. Phys. 122 (2005) 114507.
[24] R. García Fernández, J.L.F. Abascal, C. Vega, J. Chem. Phys. 124 (2006) 144506.
[25] C. McBride, C. Vega, E. Sanz, L.G. MacDowell, J.L.F. Abascal, Mol. Phys. 103 (2005) 1.
[26] J.L.F. Abascal, R. García Fernández, C. Vega, M.A. Carignano, J. Chem. Phys. 125 (2006) 166101.
[27] J.R. Errington, A.Z. Panagiotopoulos, J. Phys. Chem., B 102 (1998) 7470.
[28] M. Lísal, W.R. Smith, I. Nezbeda, Fluid Phase Equilib. 181 (2001) 127.
[29] C. Vega, J.L.F. Abascal, I. Nezbeda, J. Chem. Phys. 125 (2006) 034503.
[30] M. Lísal, J. Kolafa, I. Nezbeda, J. Chem. Phys. 117 (2002) 8892.
[31] C. Vega, J.L.F. Abascal, J. Chem. Phys. 123 (2005) 144504.
[32] C. Vega, C. McBride, E. Sanz, J.L.F. Abascal, Phys. Chem. Chem. Phys. 7 (2005) 1450.