

## Dipole-Quadrupole Force Ratios Determine the Ability of Potential Models to Describe the Phase Diagram of Water

José L. F. Abascal and Carlos Vega

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

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We show that, in order to yield an acceptable phase diagram for water, the key ingredient is the relative strength of the dipolar and quadrupolar forces. We also demonstrate that for three-point-charge water models the relative strength of the dipolar to quadrupolar forces is determined by the position of the negative charge. This provides a theoretical background—supported by the experiment—to our knowledge of the water interactions which at present is essentially dominated by empirical models. In addition, it can be quite useful in the development of improved water models with a more physical basis.

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Despite the effort devoted to the knowledge of the molecular interactions in water, it is significant that the more successful general purpose water models are still empirical models. Moreover, it is usually perceived that these models yield very similar results [1]. The recent calculation of the phase diagram for several water models has shown that the ability of the water models to describe it is not similar in any way. This provides a unique opportunity to investigate the reasons of the distinct behavior of different models and, thus, to provide a more physical background to our knowledge of the interactions in water.

In this work we deal with rigid, nonpolarizable models as SPC/E [2] and TIP4P [3]. In these simple models a single Lennard-Jones (LJ) interaction site is located at the position of the oxygen atom. Besides, these are three-point-charge models. Two positive charges are placed at the hydrogen atoms ( $q_H$ ). The negative site is coincident with the oxygen atom in SPC/E. In TIP4P the center of the negative charge (the  $M$  site) is placed at a distance  $d_{OM} = 0.15$  Å from the oxygen along the H-O-H bisector. These empirical potentials account for a number of properties of the liquid [1] and amorphous phases [4] of water. It seemed to us that it would be interesting to know whether these models are able to describe the complex dense region of the water phase diagram (fifteen crystalline solids have been reported [5]). Free energy calculations for the fluid and solid phases can be used for the determination of phase diagrams by computer simulation [6–10]. These calculations for TIP4P and SPC/E and other recently proposed three-point-charge models as TIP4P/Ice [11], TIP4P-Ew [12], and TIP4P/2005 [13] have shown to be a severe test of potential models. Besides, the melting points obtained using the free energy route have been confirmed by alternative calculations [14,15]. In general, TIP4P-type models yield a qualitatively correct phase diagram [8,11,13] (Fig. 1) and a good description of amorphous phases [16]. The exception is TIP4P-Ew for which the stability of ice II is overestimated [13] (Fig. 2). 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 [8] (Fig. 2) where ice III, ice V, and even ice  $I_h$  are metastable with respect to ice II. 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 Letter we try to establish the key ingredient that leads to a good phase diagram prediction.

The dipole moment of three-point-charge models as the ones described above is given by:

$$\mu = 2q_H(d_{OH} \cos\theta - d_{OM}), \quad (1)$$

where  $d_{OH}$  is the bonding distance and  $2\theta$  is the H-O-H angle. The value of the dipole moment for several water models is presented in Table I. There is no correlation between the overstability of ice II and the strength of the dipolar interactions. In fact, TIP4P and TIP4P/Ice (which both yield a satisfactory phase diagram) have the smallest and the highest value of the dipole moment, respectively. We already noted in the past [8] that a shift of the  $M$  site

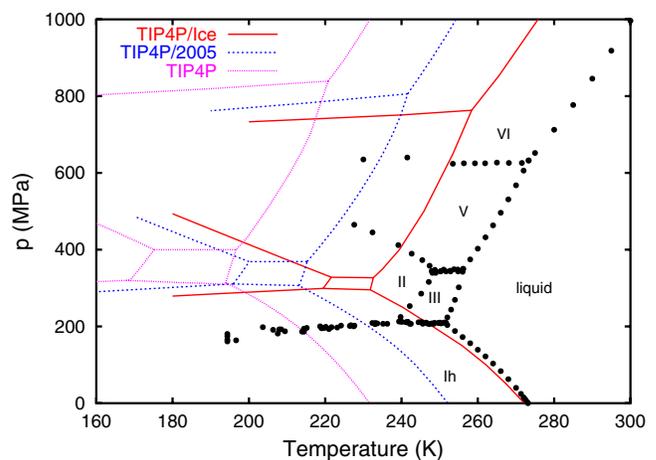


FIG. 1 (color online). Phase diagram of TIP4P [8], TIP4P/2005 [13], and TIP4P/Ice [11] models. Full circles are the experimental data. The labels denote the stable regions of the ice polymorphs in the experimental phase diagram and (by similarity) of the water models.

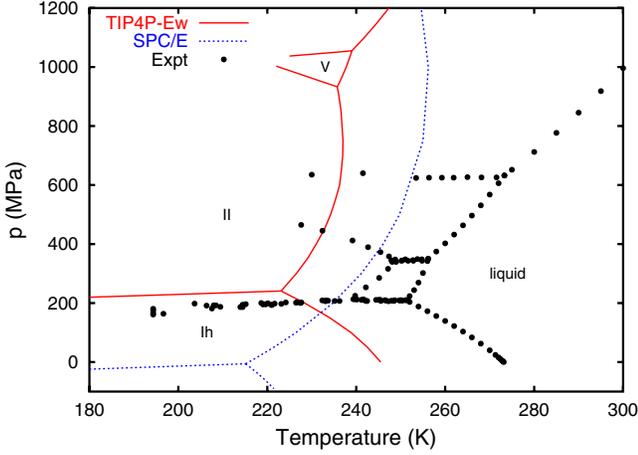


FIG. 2 (color online). Phase diagram of TIP4P-Ew and SPC/E. The labels denote the stable regions of the polymorphs for TIP4P-Ew. For SPC/E the liquid-Ih-II triple point occurs at negative pressure.

from its position in TIP4P in the direction of the oxygen atom deteriorated the phase diagram. Changing the value of  $d_{OM}$  affects not only the dipole moment but also the higher multipole moments of the molecule. As for the quadrupolar tensor, the off-diagonal components are null. Besides, we follow the suggestion of Carnie and Patey [17] and Rick [18], who chose to use  $Q_T = (Q_{xx} - Q_{yy})/2$ . For three-point-charge water models, it is trivial to show that  $Q_T$  is independent on the reference system provided that the  $y$  axis is normal to the molecular plane and that the  $x$  axis is parallel to the line joining the hydrogens

$$Q_T = (3/2)q_H d_{OH}^2 \sin^2 \theta. \quad (2)$$

Given the invariance of  $Q_T$  it seems natural to use a reference system for which the only nonzero components of the quadrupolar tensor are  $Q_{xx} = Q_T$  and  $Q_{yy} = -Q_T$  (the tensor is traceless). In this way a single quantity  $Q_T$  is enough to represent the strength of the quadrupolar inter-

TABLE I. Dipole and quadrupole moments (see the text) for several three-point-charge models. Debye units ( $1 \text{ D} = 10^{-18} \text{ esu}$ ) are used for  $\mu$ , and  $Q_T$  is given in Buckingham (D Å). The last column refers to the degree of overstabilization of ice II in the phase diagram of the corresponding model.

Model	$\mu$ (D)	$Q_T$ (D Å)	$\mu/Q_T$ (Å <sup>-1</sup> )	Overstability of ice II
TIP4P/Ice	2.425	2.434	0.996	Null
TIP4P/2005	2.305	2.297	1.004	Null
TIP4P	2.177	2.147	1.014	Null
TIP4P-Ew	2.321	2.164	1.073	Medium
SPC/E	2.350	2.035	1.155	Strong
SPC	2.274	1.969	1.155	Strong
TIP3P	2.347	1.721	1.363	Strong
Gas (Experiment)	1.85	2.565	0.91	...

actions in three-point-charge water models. The “natural” reference system yielding such a simple expression for the quadrupolar tensor is obtained when the origin of coordinates is located on the H-O-H bisector at a distance:

$$d_{\text{origin}} = \frac{d_{OH} \cos \theta + d_{OM}}{2} - \frac{d_{OH}^2 \sin^2 \theta}{4(d_{OH} \cos \theta - d_{OM})} \quad (3)$$

from the oxygen atom. But notice that the use of such a “natural” reference system is not strictly required since  $Q_T$  may be calculated as  $Q_T = (Q_{xx} - Q_{yy})/2$  which is independent on the origin of coordinates. Data in Table I show some correlation between  $Q_T$  and the relative stability of different ices. It seems that, in general, the anomalously enhanced stability of ice II can be associated to low  $Q_T$  values. But the behavior of TIP4P and TIP4P-Ew is somewhat puzzling as  $Q_T(\text{TIP4P-Ew}) > Q_T(\text{TIP4P})$  while the aspect of the phase diagram predicted by TIP4P is much closer to experiment than that of TIP4P-Ew. Besides, it is quite surprising that TIP4P, TIP4P/2005, and TIP4P/Ice give a qualitatively similar phase diagram [8, 11, 13] despite the different strength of their quadrupolar interactions.

The key to solve this puzzle is given in Table I. Models predicting correctly the relative stability of ices (those represented in Fig. 1) have a ratio  $\mu/Q_T$  very close to 1.00 (in Å<sup>-1</sup> units). A small departure from this value—as in TIP4P-Ew—means an overstabilization of ice II and larger differences lead to unacceptable phase diagrams as that for SPC/E (see Fig. 2). Notice that the ratio  $\mu/Q_T$  depends on the distance from the  $M$  site to the oxygen atom but not on the molecular charges

$$\frac{\mu}{Q_T} = \frac{4(d_{OH} \cos \theta - d_{OM})}{3(d_{OH} \sin \theta)^2}. \quad (4)$$

Thus, for a family of models with fixed values of  $d_{OH}$  and  $\theta$ , the relation dipolar-quadrupolar interactions in three-point-charge models is *exclusively* determined by the position of the negative charge. As a result of our analysis we may then conjecture that the deterioration of the phase diagram may be ascribed to an increase of the ratio dipolar to quadrupolar forces.

The Hamiltonian Gibbs-Duhem integration [19–21] allows us to determine the shift in coexistence curves due to changes in the potential. Thus, for water, it is possible to analyze the effect on the phase diagram of a change in  $d_{OM}$  (i.e., a change in  $\mu/Q_T$ ) while keeping constant the rest of the parameters ( $d_{OH}$ ,  $\theta$ ,  $\sigma_{LJ}$ , and  $\epsilon_{LJ}$ ). Notice that  $d_{OM}$  determines  $\mu/Q_T$  but not the particular values of  $\mu$  and  $Q_T$ . Since water models differ little in the value of the dipole moment and more significantly in  $Q_T$  (see Table I), we adapt  $q_H$  to the changes in  $d_{OM}$  so that the resulting  $\mu$  is kept constant. Our implementation of the technique and the simulation details were given in our previous work where the melting point of ice  $I_h$  was determined for several water potentials [20]. Let us simply recall that standard long range corrections to the LJ energy were added (after trun-

cation at 8.5 Å), Coulombic forces were treated using Ewald sums, and anisotropic NpT runs were used for the solid phases [22]. As a reference model we use the TIP4P/2005 potential [13]. This model has provided excellent results for the solid densities, phase diagram (including vapor-liquid [23] equilibria), and for the temperature of maximum density of liquid water. In summary, starting from the coexistence lines for TIP4P/2005, we calculate the coexistence lines for models with the same dipole moment and other model parameters but with different values of  $Q_T$ . To keep  $\mu$  constant, both the atomic charges and  $d_{OM}$  are changed simultaneously. For instance, for  $d_{OM} = 0.1546, 0.125, 0$  the corresponding values of  $q_H$  that give  $\mu = 2.305$  D (the dipole moment of TIP4P/2005) are  $q_H = 0.5564, 0.5207, \text{ and } 0.4096$ , respectively, so that the ratio  $\mu/Q_T$  adopts the values 1.0036, 1.0724, and 1.3634, respectively. The model with  $d_{OM} = 0$  has a higher  $\mu/Q_T$  than that of the SPC/E model (for which  $d_{OM}$  is also null) due to the different bond length and angle. The distance  $d_{OM} = 0.09$  Å for the TIP4P geometry produces in fact a ratio  $\mu/Q_T$  which is very close to that of SPC/E.

The effect on the phase diagram of a variation of the ratio dipolar to quadrupolar forces while keeping constant the LJ parameters is summarized in Fig. 3. There we show the shifts of the coexistence points when  $d_{OM}$  changes from 0.1546 Å (the value for TIP4P/2005) to 0.125 Å (the value for TIP4P-Ew). The shifts of the melting temperatures of ices Ih, III, V, and VI are small and very similar for the different ice forms (between 20 and 30 K). In other words, the overall liquid-solid envelope is shifted towards lower temperatures. The fact that these proton disordered ices behave similarly against the liquid suggests that the relative stability of these polymorphs is not affected by the quadrupolar forces in a significant way. On the contrary,

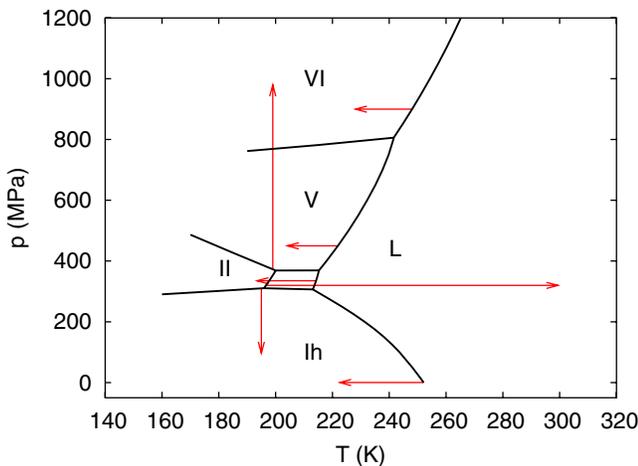


FIG. 3 (color online). Shifts of some coexistence points when the distance  $d_{OM}$  changes from 0.1546 Å to 0.125 Å (bond length and angle, LJ parameters and  $\mu$  are kept constant). The phase diagram of the starting model (TIP4P/2005) is represented by solid lines. The arrows represent the shifts in temperature or pressure of the coexistence points.

the coexistence between proton ordered ice II and the proton disordered ices is strongly influenced by changes in the quadrupolar forces. The ice II-ice V coexistence pressure increases by about 600 MPa when going from  $d_{OM} = 0.1546$  Å to  $d_{OM} = 0.125$  Å. At the same time, ice II extends its stability domain at the expense of ice Ih (the coexistence pressure decreases by about 200 MPa). Although these shifts in the coexistence pressure are not large enough to make ices Ih and V metastable in the final model, the stability domains of these polymorphs are severely reduced. The most dramatic change in the phase diagram is due to the large increase in the ice II-ice III coexistence temperature (around 100 degrees). As a consequence of the enhanced stability of ice II, ice III becomes a metastable phase so that the form in coexistence with the liquid at 300 MPa is ice II and not ice III (the calculation of the melting point of ice II at 300 MPa gives  $T_m = 220$  K).

The results shown in Fig. 3 unambiguously confirm the sensitivity of the phase diagram to the ratio dipole to quadrupole forces. Moreover, the phase diagram of the final model (with the parameters of TIP4P/2005 but with a  $d_{OM}$  identical to that for TIP4P-Ew) has a strong similarity with that of TIP4P-Ew. This demonstrates that the failure in the TIP4P-Ew phase diagram is caused by the position of the  $M$  site and not by the values of the dipole moment nor the Lennard-Jones parameters. We have extended our calculations to smaller  $d_{OM}$  values. The results follow similar trends as those presented in Fig. 3. For a model with the same  $\mu/Q_T$  ratio as SPC/E, not only ice III but also ice Ih and V are metastable (ice Ih would be stable only at negative pressures). These calculations are in complete agreement with the findings for SPC/E and confirm that the position of the negative charge is determinant in the quality of the phase diagram. The exigence of the prediction of the stability of ice III is probably a too severe requirement for a water potential given its small experimental stability domain. But the strong dependence of the ice II-ice III coexistence temperature on  $d_{OM}$  greatly reduces the acceptable  $d_{OM}$  values. For instance, for  $d_{OM} = 0.14$  Å at 300 MPa the melting temperature of ice III is already almost 70 degrees below the ice II-ice III coexistence temperature. Clearly, the range of acceptable  $d_{OM}$  values is quite narrow.

The effect of the ratio  $\mu/Q_T$  on the relative stability of ices for popular water models is shown in Fig. 4 where we represent the difference between the melting temperatures of ices Ih and II at 300 MPa. It can be seen that the relative stability of these ice polymorphs is strongly correlated (almost linearly) with the ratio dipole to quadrupole moments.

Three-point-charge models with a different balance of dipolar and quadrupolar forces may yield predictions of similar quality for the liquid state. But in this work we have shown that the stability of the ice polymorphs is strongly sensitive to the position of the  $M$  site (which, in turn, can be mapped onto the ratio  $\mu/Q_T$ ). Interestingly, the coexis-

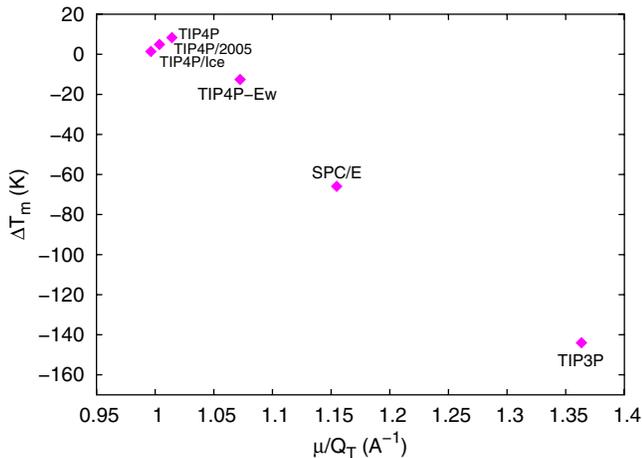


FIG. 4 (color online). Difference between the melting temperature of ice Ih and that of ice II at 300 MPa as a function of the ratio  $\mu/Q_T$ .

tence points for which we detect a marked sensitivity always involve the proton ordered ice II. Notice that in liquid and in proton disordered ices there is always a great number of available orientations. Thus, although the dipole and quadrupole interactions are distinctly sensitive to the relative molecular orientation, the final outcome of any magnitude is an average over many different orientations. In contrast, the fixed orientations in a proton ordered phase make it particularly sensitive to the distinct orientational dependence of the dipolar and quadrupolar forces. These statements suggest that the atom-atom distribution functions of the ordered ices should also be more sensitive to the details of the models than those for the proton disordered forms. In fact, they do [24] and it would be of interest to determine them experimentally to further test the performance of the difference water potentials.

In summary, a ratio  $\mu/Q_T$  around  $1.0 \text{ \AA}^{-1}$  or less seems to be a condition for a good phase diagram prediction (incidentally, this condition is fulfilled by the early water model of Bernal and Fowler [25]). Although in this work we focus on three-point-charge water models, the conclusion may be quite general. In fact, for TIP5P [26]—with  $\mu/Q_T = 1.46$ —ices  $I_h$  and III are again metastable with respect to ice II. The central role played by the ratio of dipolar and quadrupolar forces to describe real water has been suggested elsewhere [17,27]. The unique opportunity offered by ices to test and improve water models has also been noticed [5,28]. In this work we have shown how the determination of the phase diagram brings out relevant information about the delicate balance of dipolar and quadrupolar forces in real water. The relative stability of the ice polymorphs is the first experimental property with a demonstrated sensitivity to the relative strength of dipolar and quadrupolar interactions and therefore can be quite useful in the development of future potential models for the water molecule.

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