The melting point of hexagonal ice (Ih) is strongly dependent on the quadrupole of the water models†

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It is shown that quadrupolar interactions play a determinant role in the melting temperatures of common water models and that there is a simple relationship between the strength of the quadrupolar forces and the position of the negative charge; our conclusion is that acceptable predictions for the melting temperature can only be obtained when the negatively charged site is shifted from the oxygen atom towards the hydrogens.

Rigid models have enjoyed considerable success in the investigation of water properties. Their simplicity enables their use in the investigation of new water properties. In recent years there has been a growing interest (experimental and theoretical) in the study of condensed phases of water.[1–7] In particular, the thermodynamic stability of the different ice polymorphs has been determined[8] for the first time for two rigid water models: SPC/E[9] and TIP4P.[10] Unexpectedly, the results showed very different predictive ability for the two models exhibiting similar liquid properties. The predictions for TIP4P were quite satisfactory while the results yielded by SPC/E were significantly worse. The responsibility of the failure of SPC/E was soon attributed to the placement of the negative charge at the oxygen position.[8] However a deeper investigation of the question is important as SPC/E is still one of the most commonly used water models. In this communication, we will study the variation of the hexagonal ice (Ih) melting temperature for these and other successful rigid water models. In particular we intend to relate it to changes in the dipole and quadrupole moments of the models.

In this work we deal with rigid models carrying a Lennard-Jones (LJ) center (at the oxygen atom) and three charged sites. These types of model are the most widely used in computer simulations of liquid water so they have also been the first models investigated in the solid state. Thus, the ice Ih melting temperature (T_m) of three-charge models is now known with relative accuracy.[11] Besides, these models share many geometric features so that (as will be shown later) simple expressions may be written for the dipole and quadrupole moments. This will enable an analysis of the relative importance of these interactions in determining the melting temperature. The set of models investigated include well known water models (such as SPC/E, TIP4P, SPC[12] and TIP3P[10]) and also other promising models recently proposed (namely, TIP4P-Ew,[13] TIP4P/Ice,[14]

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† The HTML version of this article has been enhanced with colour images.

and TIP4P/2005[15]). Formally, these models have the same functionality even when they are usually denoted as three-site (SPC, SPC/E, and TIP3P) or four-site models (TIP4P-like). The distinction vanishes when one considers that the negative charge is placed at a site M located at a distance d_{OM} from the oxygen atom. When $d_{OM} = 0$ the LJ center collapses into the negative site and a three-site model is obtained.

For the models considered in this work, it is trivial to show that the dipole moment is given by

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

where q_H is the hydrogen charge, d_{OH} the bond length, and 2θ the bond angle. Fig. 1 shows the ice Ih melting temperatures as a function of the dipole moment μ of the models. The results for the T_m seem almost uncorrelated with the dipole moment. But this should be taken with some caution as the dipole moment of these models is very similar, around 2.3 D, despite their difference in d_{OM}. Anyway, the noticeable constancy of the dipole moments of successful water models indicates that this model property is almost unequivocally determined by the properties used to fit the model parameters (the use of the vaporization enthalpy as a target fitting property is probably related to this fact). Despite that the results for SPC and SPC/E may indicate some dependence of T_m on μ, it is clear from Fig. 1 that other parameters are more determinant of the final value for T_m. In particular, notice that the results of Fig. 1 are more or less grouped according to the molecular geometry: three site models (with $d_{OM} = 0$) yield very low melting
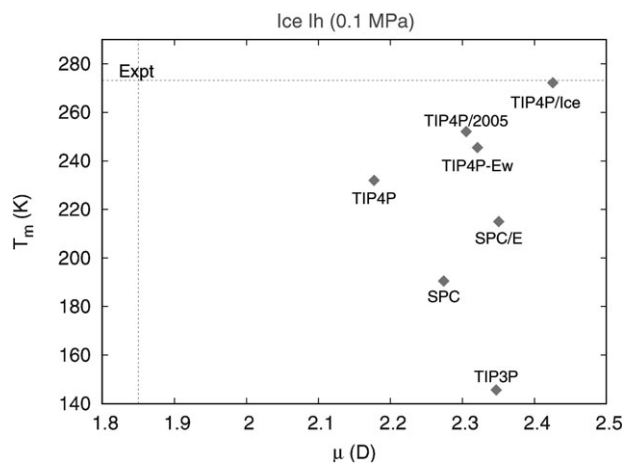
Fig. 1 Melting temperature of ice Ih at 0.1 MPa for three-charge models as a function of μ. The experimental result is depicted at the gas phase value for μ.

temperatures while TIP4P-like models (with $d_{OM} > 0.1$) are closer to experiment.

Let us analyse the dependence of T_m on the next term in the multipole expansion of the electrostatic energy, the quadrupole tensor. The magnitude of the components of this tensor are dependent on the system coordinates. Given the symmetry of the water molecule it seems natural to choose the line bisecting the HOH angle as the Z axis. Another natural decision is to make a second axis coplanar with the molecular plane so it would be parallel to the line joining the hydrogens. Let us denote it as the X-axis. Consequently, the Y-axis would be normal to the molecular plane. At this point, the origin of coordinates is still undefined. For this choice of molecular axes the off-diagonal components are null and the xx and yy components carry different signs so that Q_{zz} is quite small (the quadrupole tensor is traceless). Then, a significant measure of strength of the quadrupolar interactions is[16–18]

$$Q_T = (Q_{xx} - Q_{yy})/2, \qquad (2)$$

which may be written in terms of the molecular parameters as

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

Notice that Q_T does not depend on the position of the negative charge. Besides, even though the particular values of Q_{xx}, Q_{yy}, and Q_{zz} depend on the origin of coordinates, Q_T does not. Moreover, for a certain choice of the origin, $Q_{xx} = -Q_{yy}$, and, thus, $Q_{zz} = 0$. The distance from the oxygen atom to this "natural" origin of coordinates is

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

In this way, for three-charge water models, *the quadrupolar interactions are proportional to a single quantity, Q_T.* Thus, we may unambiguously plot T_m in terms of a single scalar quantity (Q_T) representing the "quadrupole moment" much in the same way as we depicted T_m in Fig. 1 as a function of the dipole moment μ. The corresponding plot is shown in Fig. 2. The figure shows a strong correlation between the melting temperatures and Q_T. Contrary to the dipole moment case, the models exhibit large differences in their Q_T values. The sensitivity of T_m to the quadrupole moment is evident. In Fig. 2 we have also depicted the experimental gas phase value for Q_T.[19] It can be seen that models approaching the experimental melting temperature of ice Ih carry a quadrupole moment similar to the experimental value for the isolated molecule (notice that *ab initio* calculations indicate that the quadrupole moment in the liquid phase is equal[20] or moderately larger[21,22] than in the gas phase). Fig. 2 shows that the larger the differences from the experimental Q_T, the larger are the departures from the experimental T_m. In other words, the ice Ih melting temperature gives a strong indication of the possible values of the effective Q_T in three-charge water models. It may be argued that not all the water properties can be reproduced by the water models, and, thus, that one should sacrifice some of them at a certain degree. But a departure from the experimental melting temperature exceeding 100 K (as in TIP3P) or even around 60–80 K (as in SPC and SPC/E) seems too large. Especially, when there is not a
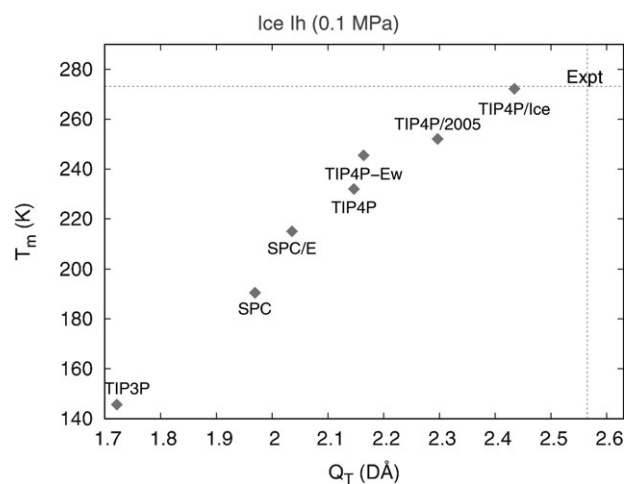
Fig. 2 Melting temperature of ice Ih at 0.1 MPa for three-charge models as a function of Q_T.

clear counterpart, *i.e.* when there are not significant improvements in other properties with respect to models providing a more or less reasonable T_m. Besides, the quadrupole moment is not just one more of the many properties to be accounted for by a water model. It is well known that variations in the dipole and quadrupole moment may have a serious influence on the structural/dielectric properties of simple charged models.[23–25] In the case of water, the same has been demonstrated by Carnie and Patey[16] using a simple model made of hard spheres with embedded dipoles and quadrupoles. Moreover, it has recently been reported that the structure of the different ice polymorphs seem to be sensitive to the details of the molecular models.[26] In summary, the poor results for the melting temperature of ice Ih and the departures from the experimental quadrupole moment indicate that the quadrupole forces are not adequately represented in some water models. This throws some doubt on the generalized use of such models except in problems where the ability of the model to reproduce the experimental results has been explicitly demonstrated.

Since eqn (3) indicates that Q_T does not depend on d_{OM}, it may seem at first contradictory that the poor results of SPC, SPC/E and TIP3P (for which $d_{OM} = 0$) are attributed to their Q_T values. This is a consequence of the fact that all the models have similar μ. To clarify this point let us we substitute q_H in eqn (3) from its value in eqn (1). Then, it may be seen that Q_T is related to the dipole moment through

$$Q_T = \frac{3(d_{OH}\sin\theta)^2}{4(d_{OH}\cos\theta - d_{OM})}\mu \qquad (5)$$

If μ is approximately constant (as in the models of this work) and the geometric parameters d_{OH} and θ are fixed, Q_T depends only on the distance d_{OM}. Low values of d_{OM} result in low quadrupole moments. In this way, the correlation found between the melting temperatures and the quadrupole moments may also be extended to d_{OM}. In particular, as $d_{OM} = 0$ for TIP3P, this model has a very low value of the quadrupole moment and, thus, a low T_m. SPC and SPC/E also have $d_{OM} = 0$ but, since the bond length and angle in these models are larger than those for TIP3P, the quadrupole moments of SPC

and SPC/E are somewhat larger than the TIP3P values. This is the reason why the melting temperatures yielded by SPC and SPC/E are higher than the TIP3P prediction (though still too low). Eqn (5) and Fig. 2 indicate clearly that the substantial increase of the melting temperature in TIP4P-like models with respect to three-site models is due to the shift of the M site from the oxygen position towards the hydrogens which (at constant μ) results in considerably larger quadrupole moments.

Data in Fig. 2 cannot appear completely aligned because the models have different Lennard-Jones parameters (ε and σ) and slightly different dipole moments as well. We have attempted to separate the different contributions by fitting the melting temperatures to the following expression

$$
\begin{aligned}
T_{\mathrm{m}} \simeq {} & T_0 + T_\varepsilon(\varepsilon/k_{\mathrm{B}} - \varepsilon^{\mathrm{ref}}/k_{\mathrm{B}}) + T_\sigma(\sigma - \sigma^{\mathrm{ref}}) \\
& + T_\mu(\mu - \mu^{\mathrm{ref}}) + T_{Q_T}(Q_T - Q_T^{\mathrm{ref}}),
\end{aligned} \tag{6}
$$

where the quantities carrying the superscript ref are the parameters of a reference water model for which we used TIP4P/2005. Accordingly, the fitting parameter T_0 is quite close to the melting temperature for this model. The coefficients T_ξ and the predicted melting temperatures are given in Table 1. The deviations of the fitted values with respect to the simulated data are within the estimated uncertainties of the latter. Besides, it should be noticed that the coefficients T_ε and T_σ are similar to the reported values of the derivatives of the melting temperature with respect to ε and σ for TIP4P.[27] Although the dependence of T_{m} on μ and Q_T cannot be completely separated—q_T and μ are coupled through eqn (5)—the coefficients T_μ and T_{QT} give an approximate idea of the relative influence of the dipole and quadrupole moments. The fact that T_{Q_τ} doubles T_μ confirms the large influence of the quadrupole moment on the melting temperature of the three-charge water models.

Several papers have shown the importance of quadrupolar forces in water.[16,28–30] Also, several water models have emphasized the importance of the quadrupole moment.[31,32] But a direct demonstration of their effects in an experimental property has not yet been reported. It is known that the dielectric constant of water is quite sensitive to the quadrupole moment.[16,17] However, the effects of the quadrupole is opposite to that of the dipole so that similar dielectric constants may be obtained with different balances between dipole and quadrupole moments. In this work we show that the melting temperature of ice Ih increases with both the dipole and the quadrupole moments. Since the more popular three-charge water models show very similar dipole moments, the melting temperature provides an unambiguous link between the strength of the quadrupolar forces and experiment. We conclude that, in order to yield acceptable predictions for the ice Ih melting temperature, the effective quadrupole moment of these types of model should be of the same order as the experimental value for the gas phase and models not fulfilling this condition are not able to reproduce with a minimum accuracy the experimental melting temperature of hexagonal ice. Thus, the failure of certain models to account for this property is a consequence of their low quadrupole moments which, in turn, is a consequence of placing the negatively charged site at the oxygen atom.

Acknowledgements

References

1 C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer and J. L. Finney, *Science*, 2006, **311**, 1758.
2 M. Martin-Conde, L. G. MacDowell and C. Vega, *J. Chem. Phys.*, 2006, **125**, 116101.
3 P. Jedlovszky, L. Partay, P. N. M. Hoang, S. Picaud, P. von Hessberg and J. N. Crowley, *J. Am. Chem. Soc.*, 2006, **128**, 15300.
4 S. Picaud, *J. Chem. Phys.*, 2006, **125**, 174712.
5 G. A. Tribello, B. Slater and C. G. Salzmann, *J. Am. Chem. Soc.*, 2006, **128**, 12594.
6 T. Loerting, C. G. Salzmann, K. Winkel and E. Mayer, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2810.
7 T. Head-Gordon and S. W. Rick, *Phys. Chem. Chem. Phys.*, 2007, **9**, 83.
8 E. Sanz, C. Vega, J. L. F. Abascal and L. G. MacDowell, *Phys. Rev. Lett.*, 2004, **92**, 255701.
9 H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269.
10 W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, *J. Chem. Phys.*, 1983, **79**, 926.
11 R. G. Fernández, J. L. F. Abascal and C. Vega, *J. Chem. Phys.*, 2006, **124**, 144506.
12 H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren and J. Hermans, in *Intermolecular Forces*, ed. B. Pullmann, Reidel, Dordrecht, 1981, p. 331.
13 H. W. Horn, W. C. Swope, J. W. Pitera, J. D. Madura, T. J. Dick, G. L. Hura and T. Head-Gordon, *J. Chem. Phys.*, 2004, **120**, 9665.
14 J. L. F. Abascal, E. Sanz, R. García Fernández and C. Vega, *J. Chem. Phys.*, 2005, **122**, 234511.
15 J. L. F. Abascal and C. Vega, *J. Chem. Phys.*, 2005, **123**, 234505.
16 S. L. Carnie and G. N. Patey, *Mol. Phys.*, 1982, **47**, 1129.
17 S. W. Rick, *J. Chem. Phys.*, 2005, **122**, 94504.
18 T. Ichiye and M. L. Tan, *J. Chem. Phys.*, 2006, **124**, 134504.
19 J. Verhoeven and A. Dymanus, *J. Chem. Phys.*, 1970, **52**, 3222.
20 Y. Tu and A. Laaksonen, *Int. J. Quantum Chem.*, 2005, **102**, 888.
21 L. Delle Site, A. Alavi and R. M. Lynden-Bell, *Mol. Phys.*, 1999, **96**, 1683.
22 P. L. Silvestrelli and M. Parrinello, *J. Chem. Phys.*, 1999, **111**, 3572.
23 G. P. Morriss and P. T. Cummings, *Mol. Phys.*, 1982, **45**, 1099.
24 E. Lomba, M. Lombardero and J. L. F. Abascal, *J. Chem. Phys.*, 1989, **91**, 2581.
25 E. Lomba, M. Lombardero and J. L. F. Abascal, *Mol. Phys.*, 1989, **68**, 1067.

Table 1 Fit of the ice Ih melting temperatures[14,15,27] (in K) to eqn (6). The parameters of the TIP4P/2005 model are used as a reference ($\varepsilon^{\mathrm{ref}}/k_{\mathrm{B}} = 93.2$ K, $\sigma^{\mathrm{ref}} = 3.1589$ Å, $\mu^{\mathrm{ref}} = 2.3051$ D, and $Q_T^{\mathrm{ref}} = 2.2968$D Å). The coefficients of the fit are: $T_0 = 252.5$, $T_\varepsilon = -2.273$, $T_\sigma = -505$, $T_\mu = 133.4$, and $T_{Q_T} = 270.2$

Model	T_{m}	T_{m}(fit)	Diff.
TIP3P	145.6	144.7	0.9
SPC	190.5	190.5	−0.0
SPC/E	215.0	218.6	−3.6
TIP4P	232.0	231.8	0.2
TIP4P-Ew	245.5	241.7	3.8
TIP4P/2005	252.1	252.5	−0.4
TIP4P/Ice	272.2	272.4	−0.2

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Phys. Chem. Chem. Phys., 2007, **9**, 2775–2778 | 2777

26 C. Vega, C. McBride, E. Sanz and J. L. F. Abascal, *Phys. Chem. Chem. Phys.*, 2005, **7**, 1450.

27 C. Vega, E. Sanz and J. L. F. Abascal, *J. Chem. Phys.*, 2005, **122**, 114507.

28 E. R. Batista, S. S. Xantheas and H. Jonsson, *J. Chem. Phys.*, 2000, **112**, 3285.

29 S. W. Rick, *J. Chem. Phys.*, 2004, **120**, 6085.

30 G. A. Tribello and B. Slater, *Chem. Phys. Lett.*, 2006, **425**, 246.

31 K. Watanabe and M. L. Klein, *Chem. Phys.*, 1989, **131**, 157.

32 M. L. Tan, L. Lucan and T. Ichiye, *J. Chem. Phys.*, 2006, **124**, 174505.

2778 | *Phys. Chem. Chem. Phys.*, 2007, **9**, 2775–2778

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