PCCP

PERSPECTIVE

Simulating water with rigid non-polarizable models: a general perspective†

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Over the last forty years many computer simulations of water have been performed using rigid non-polarizable models. Since these models describe water interactions in an approximate way it is evident that they cannot reproduce all of the properties of water. By now many properties for these kinds of models have been determined and it seems useful to compile some of these results and provide a critical view of the successes and failures. In this paper a test is proposed in which 17 properties of water, from the vapour and liquid to the solid phases, are taken into account to evaluate the performance of a water model. A certain number of points between zero (bad agreement) and ten (good agreement) are given for the predictions of each model and property. We applied the test to five rigid non-polarizable models, TIP3P, TIP5P, TIP4P, SPC/E and TIP4P/2005, obtaining an average score of 2.7, 3.7, 4.7, 5.1, and 7.2 respectively. Thus although no model reproduces all properties, some models perform better than others. It is clear that there are limitations for rigid non-polarizable models. Neglecting polarizability prevents an accurate description of virial coefficients, vapour pressures, critical pressure and dielectric constant. Neglecting nuclear quantum effects prevents an accurate description of the structure, the properties of water below 120 K and the heat capacity. It is likely that for rigid non-polarizable models it may not be possible to increase the score in the test proposed here beyond 7.6. To get closer to experiment, incorporating polarization and nuclear quantum effects is absolutely required even though a substantial increase in computer time should be expected. The test proposed here, being quantitative and selecting properties from all phases of water can be useful in the future to identify progress in the modelling of water.

I. Introduction

Given the central role that water plays in life and in our everyday lives, the development of high quality interaction potentials for this ubiquitous material is of great interest. Even though water is a simple molecule from a chemical point of view (*i.e.*, is formed from just two hydrogen atoms and an oxygen atom) its behaviour is quite complex.[1–3] In fact it shows a number of anomalies in thermodynamic and transport properties, and exhibits a quite complex phase diagram. Besides this our knowledge of the interactions between molecules is far from complete.[4,5] These can be obtained 'on-the-fly', as in Car–Parrinello simulations,[6–9] or by fitting the results of high level *ab initio* calculations for clusters to an analytical expression.[10–12] Another route is to use an empirical potential whose parameters are fine-tuned so as to reproduce experimental properties[13,14] The main reason for describing water

using empirical potentials is the simplicity of the expressions that describe the energy of the system. The computational efficiency of the working expression allows one to simulate large systems over long time periods.

The area of computer simulations of water started with the pioneering work of Barker and Watts,[15] quickly followed by the work of Rahman and Stillinger[16] using the Ben-Naim Stillinger potential,[17] and proposing the ST2 potential a few years later.[18] In these three cases water was studied using classical statistical mechanics in conjunction with a simple rigid non-polarizable model to describe the water interactions. Since then a large number of different water models have been proposed, including rigid and flexible as well as polarisable and non-polarisable models. More than thirty years after these works, Guillot undertook an extensive review of the performance of different water models[19] with the suggestive title "A reappraisal of what we have learnt during three decades of computer simulations on water". Taking into account the large number of groups and studies dealing with computer simulations of water, the feeling is that progress in the area is slow. This is probably true, but in our opinion it should not lead to the conclusion that there has been no progress at all.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c1cp22168j

After listening to a talk dealing with computer simulations of water, it is somewhat straightforward to spoil the presentation of the speaker.[20] One could point out that the speaker is using a rigid model and water is after all flexible. If the author is using a flexible model it is possible to object that hydrogen is a light atom and therefore treating the high frequency intra-molecular normal models with classical statistical mechanics is not justified. One could argue that the parameters used in water potential models are typically obtained to reproduce some target properties at certain thermodynamic conditions and that there is no guarantee that the model can reproduce either all the experimental properties at the reference thermo-dynamic state or properties at different thermodynamic states. Similarly one could point out that the potential model used does not reflect changes in the chemical environment and therefore that the use of a polarizable model is advisable. But if the author is using a polarizable model one could argue that the effect of other molecules around a central molecule cannot be replaced by an effective electric field. These objections could be overcome by the use of a first principles (density functional) evaluation of the energy of the system. However, these "first principles" calculations are also approximate since the form of the functional is proposed *ad hoc* and dispersion forces are commonly neglected within this treatment. With this in mind it is not so surprising that the calculated melting point of ice I_h using the standard PBE and BLYP functionals is about 420 K.[21] When dispersive forces are included in a DFT treatment then the prediction of water properties[22] and of its melting point improves (now being 360 K).[23] Moreover, if the true potential energy surface (PES) is used for water, then one should use path integral simulations[24–29] to account for nuclear quantum effects, since only this way could one quantitatively reproduce water properties (assuming that the PES is accurate). We are led to conclude that any work dealing with the simulation of water must use certain approximations to describe water interactions. We believe that it is important to develop a phenomenological approach to assess the perfor-mance of water models. Rather than criticizing at an early stage the approximations used in the description of water, in our opinion, a better idea is to evaluate the performance of the water models by their ability to reproduce experimental properties of water. The number of properties and the range of thermodynamic conditions should be large enough to have an overall perspective of their capacity to describe real water. In summary, the question is not so much the approximations introduced to develop the water model, but instead, the real issue is how to assess the performance of such a model.

A first attempt to introduce a quantitative assessment of the performance of water was recently done by the authors.[30] In that paper we compared the results for four water models, namely TIP3P,[13] TIP4P,[13] TIP5P[31] and TIP4P/2005[32] (a model proposed after the Guillot's review). The scoring system was quite primitive, based only on the ordering of the relative performance of each model with respect to the others for each of the properties analysed. This introduced a serious bias because the evaluation of the performance was independent of the actual agreement with experiment (the higher score could in some cases be assigned not to the "best model" but to the "not so bad model"). Besides, the scoring system would be disturbed by the introduction of a new model in the competition (in fact, in this paper we have added SPC/E[14] to the list of models investigated). In this work the deviation from the experimental values will be used to provide a certain score for the performance of the model. Obviously, if the description of the PES of water is exact and nuclear quantum effects are included then one should reproduce all the experimental properties of water.

Thus the first goal of this paper is to provide a test to evaluate the performance of water models. Despite the intrinsic arbitrary nature involved in the selection of properties, we do hope that this test will be useful not only for assessing the performance of the water models included in this study, but also to evaluate the performance of other models. Besides, if the score obtained in the test increases in the future when new models are proposed, that would provide a clear sense of progress in the modelling of water. We shall apply this test to rigid non-polarizable models. The reason for this choice is that since they are widely used, a large number of properties have been already been computed thus making easier the implementation of the test. The numerical values obtained provide information about the overall agreement between model predictions and experiment. In this way, it is possible to discuss to what extent the models 'pass the exam' with satisfactory marks.

The selection of the target experimental properties is, of course, somewhat arbitrary. We have intended to cover a wide range of properties and thermodynamic states. Although a detailed account is presented below we give here for completeness a simple enumeration of the properties investigated grouped in 17 blocks: enthalpies of phase changes, critical point properties, surface tension, melting properties, orthobaric densities and temperature of maximum density (TMD), isothermal compressibility, gas properties, heat capacity at constant pressure, static dielectric constant, T_m–TMD–T_c ratios, densities of ice polymorphs, equation of state (EOS) at high pressure, self-diffusion coefficient, shear viscosity, orientational relaxation time, structure and phase diagram.

A second goal of this work is to try to rationalise the results of the test. Firstly, we intend to investigate why some models show a better performance than others. Besides, there are some properties for which all models fail. It is thus important to know how these results could be improved and what should be the necessary changes in the potential model and/or the simulation paradigm. In this way we believe that, although our test deals exclusively with rigid non-polarizable water models, the analysis of the results provides some guidance as to which properties may benefit of adding more complexity to the model (especially polarizability) and to the simulation methodology (path integral,[33–36] centroid molecular dynamics,[37] ring polymer dynamics[38,39]).

II. A test for water models

In this section we describe the test proposed to evaluate the performance of water models. In short, a number of properties are selected and the predictions of the different models will be compared to the experimental values. Since the aim is to compare the overall performance of the models for the

different phases of water, the comparison between simulation and experiment will include properties from the gas, liquid and solid phases of water. We shall not only include equilibrium thermodynamic properties, but also dynamic properties and phase transition predictions. For each property, each model will receive a certain number of points according to the proximity to the experimental values. The score ranges between ten (if the agreement between the predictions of the model and experiment is extremely good) and zero (if the predictions are very poor). More precisely, let us assume that for a certain property the prediction of a given water model adopts the value X, and the experimental value is $X_{\exp}$. The number of points assigned will be obtained from the expression:

$$ M = \min\left\{ \text{anint}\left[10 - \text{abs}\left(\frac{(X - X_{\exp}) \times 100}{X_{\exp}\, tol} \right) \right], 0 \right\}, \quad (1) $$

where the tolerance tol is given as a percentage and anint is the nearest integer function (equivalent to the round function in worksheets). Basically we evaluate the relative error of the estimate of a property for a given model. If the prediction is within 0.5 times the tolerance the score is ten points. If the deviation is between the 1.5 and 0.5 times the tolerance, the score is nine points, and so on. For a deviation larger than ten times the tolerance we assign zero points. Reasonable values of the tolerance for each property must be provided. Tolerances should reflect the uncertainty in the experimental value, the typical uncertainty of the calculated property when determined via computer simulation and finally the importance assigned to an accurate prediction of the property in the final scoring. We have found that reasonable values of the tolerances are 0.5, 2.5 or 5 per cent depending on the property. Besides providing an individual mark for each considered property we also provide the average of all the properties in each block and the total average over the blocks. This provides a global score for each model. It is worth mentioning that the evaluation procedure presented here has some similarities with the competition denoted as Industrial Fluid Properties Simulation Challenge, organised by the American Institute of Chemical Engineers (AIChE) and presented each year at the AIChE meeting.[40]

Let us now describe the models considered in this work. As mentioned in the Introduction we shall only consider rigid non-polarizable models. Among them we shall focus on the models more widely used in the literature. It is of interest to analyse to what extent these "commonly used" water models are able to describe water properties over a wide range of thermodynamic conditions. Rigid non-polarizable models can be typically classified into three different families, namely, models with three interaction sites, models with four inter-action sites and models with five interaction sites. Regardless of the number of sites it is always the case that a single Lennard-Jones interaction site is located on the position of the oxygen atom. The main difference between three, four and five sites models is the way in which the partial charges are distributed within the molecule. Common models with three interaction sites are TIP3P and SPC/E. In these models, a partial positive charge is placed on each of the hydrogen atoms

and the negative charge is located at the position of the oxygen atom. The model TIP3P was proposed by Jorgensen et al. in 1983.[13] The two parameters of the Lennard-Jones (LJ) interaction were chosen to reproduce the density of water at room temperature and pressure and the vaporisation enthalpy at room temperature. Thus, by design, TIP3P should reproduce these two properties. It is fair to say that TIP3P (or the slightly different version[41] used in CHARMM which also includes LJ centres on the hydrogen atoms) is probably the most popular model of water especially because it is quite often used to describe water interactions in systems including biological molecules (i.e., proteins or nucleic acids).

The second three-site model considered in this work is the SPC/E model.[14] This model has a good reputation among people performing simulations of water. There are two key differences between the SPC/E and TIP3P. The first one is that SPC/E does not use the experimental geometry of the water molecule in the gas phase. Rather it uses two simple values for the bond length and the bond angle. The bond length of the model is 1 Å (instead of the experimental value in the gas phase which amounts to 0.9578 Å) and a bond angle of 109.5° (instead of the experimental value of the bond angle in the gas phase which is 105.46 degrees). The differences in geometry between TIP3P and SPC/E may have some impact on the ability of these two models to account for the water properties. However, the main difference between SPC/E and TIP3P is the way the potential parameters of both models were obtained. In SPC/E the parameters were obtained so that the experimental value of the liquid density at room temperature and pressure is reproduced (as in TIP3P). In addition to that, the parameters of SPC/E were obtained to reproduce the experimental value of the vaporisation enthalpy of water when corrected by the so called self-polarization correction. The self-polarization term accounts for the fact that the dipole moment of the molecule of water in the gas phase is different from that in the liquid phase. A model which is not polarizable cannot account for this. The work to polarize a molecule from the dipole moment of the gas phase to the liquid phase value is called the polarization correction. Its expression is given by:

$$ \frac{E_{\text{pol}}}{N} = \frac{(\mu - \mu_{\text{gas}})^2}{2\alpha_{\text{p}}}, \quad (2) $$

where α_{p} is the polarizability of the water molecule, μ_{gas} is the dipole moment of the molecule in the gas phase and μ is the dipole moment of the model. The comparison between the performance of the TIP3P and the SPC/E models is interesting because it may show whether sacrificing the actual vaporisation enthalpy of water as a target property (substituting it by a 'corrected' value as in SPC/E) leads to an overall better potential model.

In this work two four site interaction models will be discussed: TIP4P and TIP4P/2005. In both models, the positive charges are located on the hydrogen atoms (as in TIP3P and SPC/E), but the negative charge is located not on the oxygen atom but along the H–O–H bisector. This charge distribution was used in the first water model proposed in 1933 by Bernal and Fowler.[42] This charge distribution is also used quite often when fitting the potential energy surface (PES) obtained from

first principles calculations to empirical expressions (see for instance the work in the groups of Clementi,[43] Jordan,[11] Xantheas[10]). TIP4P was proposed by Jorgensen *et al.* in 1983.[13] The parameters of the model were obtained to reproduce the density of the liquid (at room temperature and pressure) and the vaporisation enthalpy at ambient temperature. The comparison of the results for TIP3P and TIP4P will be of interest. Since both models use the same molecular geometry (*i.e.*, bond length and angle) and the target properties used to determine potential parameters are the same, then the comparison will reveal if the location of the negative charge on the H–O–H bisector of the TIP4P model improves the description of water with respect to a model where the negative charge is located on the oxygen atom. The other four site model considered in this work is TIP4P/2005. It was proposed by the authors six years ago.[32] TIP4P/2005 uses the same molecular geometry and charge distribution as TIP4P. The main difference is that different target properties were used to determine the potential parameters. In particular the parameters of the model were obtained to reproduce the room pressure isobar densities (not just the density at room temperature), and a couple of properties related with the density and stability of the ice polymorphs. As in SPC/E, the vaporisation enthalpy was not used as a target property. Rather, it was again assumed that the model should approximately reproduce the vaporisation enthalpy only when including the self-polarization term.[14,44] The comparison between TIP4P and TIP4P/2005 is of interest since it will illustrate whether the use of a Berendensen like approach (*i.e.* reproducing the density but not the vaporisation enthalpy at room temperature) yields an overall better water model.

The final model considered here is a five site model, TIP5P, which was proposed by Mahoney and Jorgensen in 2000.[31] Besides the positive charges being again placed on the hydrogen positions there are two negative charges located at the position of the so called "lone pair electrons". In fact TIP5P is the natural descendent of the popular ST2 model of Rahman and Stillinger.[18] TIP5P and ST2 connect with the idea widely presented in chemistry textbooks of the presence of sp^3 hybrids and lone pair electrons in water. The origin of this idea for describing water goes back to the initial applications of quantum mechanics applied to chemistry initiated by Linus Pauling.[45] The geometry of TIP5P is again taken from that of the gas phase. The parameters of the model were obtained to reproduce the vaporisation enthalpy of water and the location of the maximum in density of liquid water. The comparison between TIP5P and TIP4P is interesting since it illustrates whether the introduction of negative charges on the positions of the lone pairs electrons, somewhat in accordance with the "chemical intuition" improves the description of water. Our choice of rigid-non polarizable water models is not exhaustive. Many other water models have been proposed so far. Among the extensive list it is worth mentioning at least two: TIP4P-Ew proposed by Horn *et al.*,[46] which is similar in spirit to TIP4P/2005 and the NvdE model proposed by Nada and van der Eerden[47] which is a six-site model.

Table 1 shows the dipole and quadrupole moments of the models considered in this work. It can be seen that the dipole moments μ are in all cases higher than the dipole moment of

Table 1 Dipole moment (in 10^{-18} esu cm) and eigenvalues of the quadrupole tensor (in 10^{-26} esu cm^2) for different water models. The z axis is located along the H–O–H bisector, the x axis is parallel to the line joining the H, and the y axis is perpendicular to the plane of the molecule (with the origin at the centre of mass). For the liquid the multipolar moments were estimated either from a polarizable moment[51] or from a DFT calculation.[52] The magnitude of the quadrupole Q_T is defined as half the difference between Q_{xx} and Q_{yy}

Model	μ	Q_{xx}	Q_{yy}	Q_{zz}	Q_T	μ/Q_T
TIP3P	2.35	1.76	−1.68	−0.08	1.72	1.36
SPC/E	2.35	2.19	−1.88	−0.30	2.03	1.15
TIP4P	2.18	2.20	−2.09	−0.11	2.15	1.01
TIP4P/2005	2.305	2.36	−2.23	−0.13	2.30	1.00
TIP5P	2.29	1.65	−1.48	−0.17	1.56	1.46
Gas (Expt.)	1.85	2.63	−2.50	−0.13	2.56	0.72
Liq. (Pol. model)	3.09				3.21	0.96
Liq. (DFT)	2.95				3.27	0.90

the molecule in the gas phase. Thus, for non-polarizable models, the use of an effective dipole moment (larger in magnitude than that of the molecule in the gas phase) can be regarded as a possible way of accounting for polarization. Notice that for most of models μ is around 2.3 Debye. Notice also that the location of the negative charge is different for the different models proposed in this work and that leads to important differences in the quadrupolar tensor and of the quadrupole moment Q_T[48] (defined as half the difference of the two largest magnitude eigenvalues of the quadrupolar tensor[49,50]). Values of the dipole and quadrupole moment in the liquid phase were estimated from a polarizable model[51] or from a density functional calculation[52] (DFT). Now that the water models and the methodology used in this work to evaluate their performance has been described let us now enumerate the properties selected for judging their ability to predict water properties.

A. Block 1: enthalpy of phase change

The experimental value of the vaporization enthalpy has often been used to determine the values of the potential parameters. Certainly, models such as TIP3P, TIP4P and TIP5P reproduce the experimental value by design. However, models such as SPC/E and TIP4P/2005 reproduce the experimental value of the vaporization enthalpy only when the "*ad hoc*" polarization correction is used. In other words, these models do not reproduce the actual experimental values. We shall compare the vaporization enthalpy obtained with the different water models to the experimental values without introducing any kind of theoretical correction. Adding theoretical corrections[14,46] would bias the evaluation of the performance of the models. Since TIP3P, TIP4P and TIP5P reproduce the experimental value of the vaporization enthalpy they will obtain a high score for this property whereas SPC/E and TIP4P/2005 will have a lower score. Notice that if the polarization correction would be useful this should be reflected in the rest of the properties, so the overall performance of SPC/E and TIP4P/2005 would be enhanced. Notice also that the vaporization enthalpy is a measure of the internal energy of the liquid with respect to the vapour phase. A good water model should also be able to account for the properties of the solid phase. It seems then interesting to compare the internal energy of the

liquid with that of the solid phase. For this reason we have also included in the test the predictions for the melting enthalpy of ice I_h (the stable solid phase of water at ambient pressure). The value of the tolerance was set to 2.5 for the vaporization enthalpy and 5 for the melting enthalpy because the latter quantity is related to the difference between two relatively similar energies.

B. Block 2: critical point properties

The gas–liquid coexistence curve ends at a critical point. Properties such as the vaporisation enthalpy and the surface tension vanish at the critical point. The possibility of using the special properties of a fluid in the super-critical region could be particularly important in the case of water. Thus a correct description of the critical point seems important for the modelling of water. The experimental properties at the critical point are well known. After the introduction of the Gibbs ensemble,[53] Gibbs–Duhem[54] and the direct coexistence[55,56] techniques, the critical point has been determined for a number of water models. The block concerning the critical point should involve an analysis of the performance of three properties: critical temperature, critical density and critical pressure. Truncation of the potential, and system size effects may affect somewhat the computed critical point. For this reason, and also because of the sensitivity of the results to the model parameters, the values of the tolerance were chosen as 2.5 for the critical density and temperature and 5 for the critical pressure. It has been suggested that water may exhibit a second liquid–liquid critical point when super-cooled.[57–72] This is an interesting suggestion that has given rise to a lot of research. Although some indirect evidence has been obtained from experimental results,[71,73,74] its existence has not been demonstrated without ambiguity yet. For this reason we do not include this possible second critical point as a target property.

C. Block 3: surface tension

The surface tension of the liquid–vapour interface of water is large and this feature has important consequences. The number of simulations describing an interface between water (either pure or as solvent) or ice in contact with the vapour is growing.[56,75–88] We shall consider the value of the surface tension of liquid water at two temperatures—300 K and 450 K—in order to also evaluate the variation of the surface tension with temperature. The value of the tolerance has been fixed to 2.5, the main reason being that the typical uncertainty when determining the surface tension in computer simulation is about 3 per cent. Other interfacial free energies such as, for instance, the ice I_h–liquid interface,[89,90] could be included in this block. Since up to now it has only been evaluated[90] for TIP4P this property will not be included in the test.

D. Block 4: melting properties

The importance of ice is obvious when one takes into account that it covers the majority of the surface of Earth's poles, it may be found in clouds, thus playing a role in climatic and atmospheric issues,[91] not to mention its presence on other planets and moons of the solar system.[92] Understanding the nucleation (and/or melting) of ice seems also to be an important problem.[93–105] Therefore describing the location

of the I_h-water transition at room pressure seems to be important. It is somewhat surprising how little effort has been devoted to the determination of the melting point of water models. Up to a decade ago, the only attempts were those performed in the research groups of Haymet,[106–109] Clancy,[110] van der Eerden[111] and Tanaka.[112] During the last six years the work of our group,[113–117] along with that of others[118–124] has provided a reasonable estimate of the melting point of ice I_h for several water models. As another example, even though first principle calculations of water started twenty years ago, the estimate of the melting point for several common functionals used in DFT has been reported only recently.[21,23] Knowledge of the melting temperature is important in the study of ice nucleation using computer simulations. Moreover one of the characteristic anomalies of water is that, at melting, the density of the liquid is higher than that of ice I_h. Finally, the slope of the melting curve as given by dp/dT determines how the coexistence pressure changes with temperature. Describing this property correctly is important when it comes to describing freezing under pressure which is becoming increasingly important in studies related to food conservation.[125] Thus, the block of melting properties include four items: the melting temperature of ice I_h at room pressure, the densities of the coexistence phases and the slope of the coexistence curve. The tolerances chosen in this block are 0.5 for densities (they can be very accurately determined both experimentally and in simulations), 2.5 for the melting temperature (the typical uncertainty in computer simulations) and 5 for the dp/dT gradient.

E. Block 5: orthobaric densities and temperature of maximum density

The equation of state is one of the most interesting thermodynamic properties for any liquid. In the case of water, the relationship $\rho-T-p$ is even more important because of its peculiar behaviour. In fact, one of the hallmark properties of water is the existence of a maximum in density[126,127] when plotted as a function of temperature at a given pressure (some experimental work suggest that there is also a density minimum).[128] This maximum is found experimentally not only at room pressure (at which it is found to be about 4 Celsius degrees) but also for pressures up to 1500 bar.[129] Therefore to describe the behaviour of water in the low temperatures and super-cooled region[130] it seems to be crucial to reproduce the location of the experimental TMD. Reproducing the location of the TMD only guarantees that the water model shows a maximum in density at the correct temperature but it does not guarantee that the variation of density with temperature has the correct curvature. The experimental densities of liquid water at room pressure can only be measured up to 373 K (i.e., the boiling point). Water is a highly incompressible liquid and its density changes very little from say 1 bar to 20 bar.[19] Thus, reproducing the orthobaric densities (i.e., the liquid densities along the coexistence curve) is almost the same as reproducing densities along the room pressure isobar. For this reason we have decided to include in the test the orthobaric densities at three different temperatures, 298 K, 400 K and 450 K. This is an indirect way of testing if the curvature of the

EOS at constant pressure as a function of temperature is correct (or, in other words, it is an indirect test of the thermal expansion coefficient). From our experience, a bad prediction of the orthobaric densities at these three temperatures leads to poor estimates of surface tension and of the critical point temperature. Concerning the value of the parameter tolerance, we set the value 0.5 for orthobaric densities (they are usually obtained accurately both in experiment and in simulation). A value of 2.5 has been adopted for the tolerance of the TMD since its determination is computationally intensive and has larger error bars.[131–134]

F. Block 6: isothermal compressibility

We have included in the test the isothermal compressibility at room pressure at two different temperatures, namely 298 K and 360 K. The isothermal compressibility reflects how the density of the system changes with pressure. Furthermore, the isothermal compressibility is related to the value of the structure factor when the value of q in the reciprocal space tends to zero,[135–140] and there is an increasing interest in studying the aspect of the structure factor at low values of q. For these reasons, it seems worthwhile to include the isothermal compressibility in the test. Since the compressibility is obtained from volume fluctuations there is a considerable error in its determination by computer simulation (about four per cent[141,142]). Thus, the value of the tolerance has been set to five per cent.

G. Block 7: gas properties

Most of the water models used in this work were designed to reproduce properties of the liquid rather than properties of the gas. However, we believe that certain properties of the gas should be included in the test to illustrate the limitations of rigid non-polarizable models. Some recent studies on water clusters point out these deficiencies clearly.[143–146] In this block, we have considered the predictions for the vapor pressure at 350 K and 450 K and for the second virial coefficient at 450 K. The second virial coefficient of TIP3P and TIP4P has been obtained by Kofke and coworkers,[147–149] for SPC/E by several groups[147–151] for TIP4P/2005 by Baranyai et al.[152] and for TIP5P by Mahoney and Jorgensen.[31,153] The experimental value at 450 K is well known.[154] Strictly speaking vapor pressure cannot be regarded as a gas property since it is just the pressure at which, for a certain temperature, the chemical potential of the gas phase is identical to that of the liquid phase[155] (thus both phases are involved in its computation). Assuming that the gas behaves as an ideal gas then the vapor pressure is mostly determined by the chemical potential of the liquid. The vapor pressure is also regarded as an important property within the chemical engineering community. Therefore we believe its inclusion is worthwhile. We set the value of the tolerance parameter to 5. The inclusion of the vapor pressure is interesting since it may illustrate whether attempts to improve it lead to an overall prediction improvement.

H. Block 8: heat capacity at constant pressure

In the test we have also included the predictions for the heat capacity, C_p, at ambient pressure. We have considered two phases at slightly different temperatures. For liquid water, we consider its value at room temperature. For ice I_h we consider its value at 250 K. Since these two temperatures are relatively close, it seems interesting to know whether the models are able to describe the heat capacity of both the liquid and solid phase at these relatively similar conditions. As with other properties obtained through differentiation of a thermodynamic property (or its equivalent equation in terms of fluctuations), we give the highest value 5 to the tolerance parameter.

I. Block 9: static dielectric constant

Determining the dielectric constant, ε, of liquid water from computer simulations was, for quite a long time, a challenging problem. Basically long runs (2 ns for a preliminary estimate and at least 10 ns for a more precise one) were required and that was simply too much for the computers available on the eighties and part of the nineties. Besides, it took some time to understand how the dielectric constant should be computed depending on the periodic boundary conditions and on the way the long range coulombic forces are treated.[156–159] The dielectric constant is regarded as an important property to be reproduced since it measures the response of water under the action of an electric field. Also the dielectric constant is involved in the prediction of the activity coefficients of salts at extreme dilutions. For finite concentrations, the role of the dielectric constant as the guarantee for good predictions of the activity coefficient is not so clear since the activity coefficient is mostly determined by more direct (not so screened) ion–ion and ion–solvent interactions. The macroscopic constant is useful to predict the free energy change resulting of moving two ions that are far apart, but cannot be used to estimate the free energy change when moving ions at moderate or small distances.[160] On the other hand, the determination of the dielectric constant of ice has been for a long time a challenging problem.[161] Rick and coworkers made important progress in this area by using an extension of the algorithm proposed by Rahman and Stillinger[162] to evaluate the dielectric constant of ice I_h for SPC/E and TIP5P.[163,164] A different algorithm was proposed by Lindberg and Wang.[165] Quite recently, we have also computed the dielectric constant of TIP4P/2005 and TIP4P.[166,167] We have included as a test property the value of the dielectric constant of ice I_h at 240 K. As in the case of the heat capacity we believe that the inclusion in the test of the predictions of two different phases at two relatively close thermodynamic states may be quite useful. We have also included the ratio of the dielectric constant between ice I_h and water in the test. This ratio will determine the effect of an electric field on the melting temperature. The tolerance is set to 5 because of the uncertainty associated with the fluctuations formula used in the calculations and the long runs required for a satisfactory sampling.

J. Block 10: T_m–TMD–T_c ratios

The critical point and the triple point are singular points within the phase diagram of any liquid. It seems fair to judge a water model not only by the predictions for these particular points, but also by the extension of the liquid region. The ratio T_t/T_c defines the relative extent of the liquid range and seems

to be a property that should be included in the test.[168] Since for water the triple point temperature differs only by about 0.01 degrees from the normal melting temperature we shall assume that $T_t \simeq T_m$. Besides, since the maximum in density is an important water property it seems of interest to look at this property on a corresponding states perspective. For this reason we shall include in the test two new properties, the ratio TMD/T_c and the distance from the TMD to the melting point $T_{TMD} - T_m$. In water this difference amounts to 4 degrees and it is interesting to see if water models can account for the difference between these two characteristic temperatures. The tolerance of the ratios T_t/T_c and TMD/T_c should be at least that of the temperatures implied. Thus we have set it to 5. Since $T_{TMD} - T_m$ is a difference, it does not make sense to use a relative definition of the error and the X_{exp} and the factor 100 appearing in eqn (1) are dropped.

K. Block 11: densities of ice polymorphs

In our opinion, a good model to describe water should also be able to describe reasonably well the solid phase(s).[169] This point of view was first stated clearly by Whalley[170] and Morse and Rice[171] and was somewhat disregarded in the literature for many years. Although liquid water has received considerably more attention than ice (or ices), the number of studies dealing with ice have grown significantly over the last decade.[172–175] Thus we found it necessary to include some predictions for the properties of ices. We have chosen the density which is, by far, the easiest quantity to be obtained with experiments and in computer simulations. Thus we have included in the test the predictions for ice I_h (the least dense ice), ices II and V (moderately dense) and for the highly dense ice VI. The tolerance parameter 0.5 is the same as that used for the orthobaric densities.

L. Block 12: equation of state at high pressures

No doubt describing water at room temperature and pressure is important but quite often the weight given to this state to evaluate water models is too high. The behaviour of water at high pressures is very important in extensive research areas like chemical engineering and geosciences.[175–181] Thus we have decided to include the EOS of water at 373 K for pressures of 10 000 and 20 000 bar. Since the tested variable is a density, the tolerance is set to 0.5.

M. Block 13: self-diffusion coefficient

It is obvious that transport properties should also be considered in the test. A good candidate is the diffusion coefficient, D. It also seems interesting to investigate not only the value of D at ambient conditions but also its dependence with temperature. For this reason we include in the test predictions for D at 273 K, 298 K and 318 K at room pressure. The activation energy for diffusion obtained from an Arrhenius-like expression using just the values at 273 K and 318 K has also been included in the test. Since D varies over several order of magnitude with temperature we have considered $\ln(D)$ rather than D. For this reason, a low value (0.5) is assigned to the tolerance parameter for $\ln(D)$ while a larger value (5) is used for the activation energy.

N. Block 14: shear viscosity

Another important transport property is the viscosity (in particular the shear viscosity). The viscosity of water has been determined by computer simulation over the last few years by several groups.[182–187] Recently it has been calculated by Gonzalez and Abascal[188] and by Vrabec and coworkers[189] for a number of water models. Again, we have decided to also analyse the dependence of the viscosity with temperature (at room pressure) using the values at 298 K and 373 K. The calculation of the shear viscosity by computer simulation can be done by different methods but all of them are subject to large uncertainties due to the poor convergence of the quantities involved. Thus, we set the tolerance parameter to 5.

O. Block 15: orientational relaxation time

The diffusion coefficient and the viscosity are transport properties related with the motion of the center of mass of the water molecule. It is of interest to include in the test a dynamical property which measures some orientational relaxation time. There are several orientational times described in the literature. For bulk water the anisotropy of the orientational relaxation times is small[190] and in general $\tau_2^{HH} > \tau_2^{OH} > \tau_2^{\mu}$ being the values of τ_2^{HH} about 20 per cent larger than those of τ_2^{μ}. Here we shall include in the test the second order relaxation time of the HH vector τ_2^{HH} since this time has been calculated previously for all the water models considered in this work. For TIP4P/2005 was determined by Elola and Ladanyi,[191] for TIP5P by Rick,[50] for TIP4P and SPC/E by Kumar and Skinner[192] and for TIP3P by Spoel et al.[190] This relaxation time can be measured through NMR measurements. From the experimental results reported by Jonas et al.[193] a value of about 2.36 ps at room temperature and pressure for τ_2^{HH} can be estimated.[192] Given the large experimental uncertainty we set the tolerance parameter to 5.

P. Block 16: structure

Many models used the pair distribution functions as a target property in the fitting procedure to obtain the model parameters. The radial distribution functions are obtained trivially in computer simulations. Some further work is needed to obtain them from experimental diffraction results. Two common procedures to obtain radial distribution functions from experimental diffraction results are Reverse Monte Carlo[194] and EPSR Structure refinement[195]. Continuous progress in the area motivated that the experimental estimate of the height of the first peak of the O–O distribution function has been refined over the last decades. Narten and Levy[196] estimated its height to be 2.3. Later on it was estimated to be 2.75 by the groups of Soper and Gordon,[197,198] and corrected once again to the value of 2.3 after the work of Soper.[199] and Pettersson et al.[200] Experimental results are commonly obtained either from X ray diffraction or from neutron diffraction. To predict the X ray scattering from computer simulations[135,138] the electron density distribution should be known. Typically, it is approximated as the superposition of spherical electronic clouds centered on the atoms thus neglecting the deformation of the electronic cloud due to intramolecular or intermolecular bonds.[201] This problem does not appear in

neutron diffraction. In general thermodynamic properties of water are known experimentally with more accuracy than structural ones.[202] For this reason in our opinion, it is probably safer to fit potential parameters to well established thermodynamic properties. Despite these caveats, it is clear that a good model should reproduce the structure of water.[197,198,203] In fact, with the exception of TIP3P,[30] all the models considered in this work produce distribution functions in reasonable agreement with those obtained by inverting the diffraction data. Recently Pusztai et al.[204] have considered the ability of different water models to reproduce the neutron diffraction data obtained at ISIS (UK).[199] We have included in the test the goodness of the total scattering $\chi^2(F(Q))$ and the goodness to describe the different radial distribution functions of water $\chi^2(overall)$ considered by Pusztai et al.[204] (see their work for further details). The value of the tolerance parameter was set to 5 in eqn (1) (we did not include X_{exp} and the factor 100 since Pusztai et al. reported deviations with respect to experiment).

Q. Block 17: phase diagram

Until a few years ago, very little was known about the phase diagram (or even the melting point) of water models. The procedure to determine free energies[205–210] and the phase diagram of water via computer simulations has been described in detail.[113,208] Prescriptions to generate proton disordered configurations satisfying the Bernal–Fowler rules have also been proposed[163,211,212] In recent years we have evaluated the phase diagram for several water models,[30,32,113,117] among them TIP4P, SPC/E TIP4P/2005, TIP3P and TIP5P. We have observed significant differences in performance indicating that this is a stringent test of water models. For this reason, the ability of a certain water model to qualitatively predict the phase diagram of water seems to be a property to be considered for the test. However, in this case, it is very difficult to implement a numerical procedure to assign the corresponding scores. Despite this, we have decided to include this property in the test. To evaluate the performance we have used the following criterion: 2 points if ice I_h is the stable phase of the solid at the normal melting point (i.e., ice II does not appear as the stable phase), 2 points if ice III appears in the phase diagram, 2 points if ice V appears in the phase diagram, 2 points if ice VI appears on the phase diagram and 2 points if the transition pressures for the water–ice VII transition are predicted accurately. Although in the test described in this work the phase diagram prediction is treated as a single property, it is probably fair to recognize that its weight on the overall score should be higher since the global phase diagram is probably one of the most singular signatures of an interaction potential.

III. Results

In this section we present and discuss the scores obtained for the different models. In Table 2 the experimental values for the different properties considered in this work are given along with the results obtained from computer simulations of the respective water models. Since including all relevant references within the table would generate a rather large caption instead we shall describe here the sources of the data presented. Most of the experimental results for both liquid and solid water

presented were taken from the papers by Wagner and coworkers.[213–215] In particular, critical properties, melting properties, orthobaric densities, TMD, isothermal compressibilities, enthalpy changes, vapor pressures, heat capacities and EOS of state at high pressures were taken from these excellent compilations. The densities of the ice polymorphs were taken from the book of Petrenko and Whitworth[92] except for the density of ice II, which was taken from the recent work of Fortes et al.[216] Concerning transport properties the diffusion coefficients were taken from Prielmeir et al.[217] and from Mills[218] whereas viscosities were taken from Harris and Woolf.[219] The surface tension data were taken from the IAPWS release.[220]

The simulation results presented in Table 2 come from a variety of sources. Orthobaric densities, vapor pressures and critical properties were taken from Vega et al.[221] for TIP4P/2005, from Lísal et al. for TIP4P,[222] from Vega et al.[30] for TIP3P, from Lísal et al. for TIP5P[223,224] and from Errington and Panagiotopoulos[150] and Theodorou and coworkers[151] for SPC/E. Some of the data lacking in the previous references were obtained from Sakamaki et al.[225] Values for the surface tension were taken from Vega and de Miguel[75] for TIP3P, TIP4P, TIP4P/2005 and SPC/E. The surface tension of TIP5P was taken from the work of Chen and Smith.[79] Surface tensions for TIP4P/2005 have been evaluated independently by Alejandre and Chapela[86] and Mountain.[82] The melting properties of ice models were compiled by Abascal et al.[30,226] The values of the TMD were taken from Vega and Abascal[133] except for TIP5P, which was reported in the original reference presenting the model.[31] Isothermal compressibilities at ambient temperature were taken from the papers by Pi et al.[141] and by Jorgensen and Tirado-Rives.[227] At 360 K the data for all the models except TIP4P/2005 are new calculations performed specifically for this work. Enthalpy changes were taken from Vega et al.,[30] from Abascal et al.,[226] and from Jorgensen and Tirado-Rives.[227] Heat capacities of liquid water were taken from Jorgensen and Tirado-Rives,[227] from Abascal and Vega[32] and from Vega et al.[228] Heat capacities of ice I_h were only available for TIP4P/2005 model,[228] so for the rest of the models they have been evaluated in this work. Dielectric constants for liquid water were taken from Vega et al.,[30] except for SPC/E, which was taken from ref. 229. For ice I_h the dielectric constants are from Rick,[50,163,230] from Lindberg and Wang,[165] from MacDowell and Vega[166] and from Aragones et al.[167] The densities of the ice polymorphs are those reported by Vega et al.,[30] except for SPC/E, which were taken from Sanz et al.[113] The EOS at high pressures was taken from Vega et al.[30] The diffusion coefficients come from from Vega et al.[30] except for SPC/E that were taken from ref. 189. The shear viscosities were taken from Gonzalez and Abascal,[188] and from Vrabec et al.[189] Structural predictions were taken from Pusztai et al.[204] and phase diagram predictions from our previous works.[30,113]

We are now in a position to compare the performance of the water models considered in this work. Table 3 presents the scores obtained for each property for the five models investigated. What follows is a discussion of the results.

A. Enthalpy of phase change

Models such as TIP3P, TIP4P and TIP5P reproduce the experimental value of ΔH_v by design whereas SPC/E and

Table 2 Experimental and simulation data of different water models. Thermodynamic conditions as reported in each entry. The temperature of maximum density TMD, dielectric constants and diffusion coefficients as obtained at normal pressure. Melting enthalpies at the normal melting point of the model. Vaporization enthalpies as obtained at room T. For TIP3P the dielectric constant of ice I_h was obtained at 180 K (ice I_h melted at 240 K for this model). The asterisks for the ice densities of the TIP3P model indicate melting of the ices. The asterisks in the structure results for TIP3P and TIP5P indicate that these models were not considered in ref. 204

Property	Expt	TIP3P	SPC/E	TIP4P	TIP4P/2005	TIP5P	Tolerance (%)
Enthalpy of phase change/kcal mol^{-1}							
ΔH_{melt}	1.44	0.3	0.74	1.05	1.16	1.75	5
ΔH_{vap}	10.52	10.05	11.79	10.65	11.99	10.46	2.5
Critical point properties							
T_c/K	647.1	578	638.6	588	640	521	2.5
ρ_c/g cm^{-3}	0.322	0.272	0.273	0.315	0.31	0.337	2.5
p_c/bar	220.64	126	139	149	146	86	5
Surface tension/mN m^{-1}							
σ_{300K}	71.73	52.3	63.6	59	69.3	52.6	2.5
σ_{450K}	42.88	24.7	36.7	27.5	41.8	17.1	2.5
Melting properties							
T_m/K	273.15	146	215	232	252	274	2.5
ρ_{liq}/g cm^{-3}	0.999	1.017	1.011	1.002	0.993	0.987	0.5
ρ_{solid}/g cm^{-3}	0.917	0.947	0.95	0.94	0.921	0.967	0.5
dp/dT (bar K^{-1})	−137	−66	−126	−160	−135	−708	5
Orthobaric densities and TMD							
TMD/K	277	182	241	253	278	277	2.5
ρ_{298K}/g cm^{-3}	0.997	0.98	0.994	0.988	0.993	0.979	0.5
ρ_{400K}/g cm^{-3}	0.9375	0.868	0.916	0.895	0.93	0.859	0.5
ρ_{450K}/g cm^{-3}	0.8903	0.791	0.86	0.823	0.879	0.756	0.5
Isothermal compressibility (10^{-6}/bar)							
κ_T [1 bar; 298 K]	45.3	57.4	46.1	59	46	41	5
κ_T [1 bar; 360 K]	47	79.2	57.7	67.2	50.9	84	5
Gas properties							
p_v(350 K) (bar)	0.417	0.56	0.14	0.57	0.13	1.12	5
p_v(450 K) (bar)	9.32	11.72	5.8	13.3	4.46	21.8	5
B_2(450 K) (cm^3 mol^{-1})	−238	−476	−653	−396	−635	−320	5
Heat capacity at constant pressure/cal mol^{-1} K^{-1}							
C_p[liq 298 K; 1 bar]	18	18.74	20.7	20	21.1	29	5
C_p[ice 250 K; 1 bar]	8.3	*	14.9	14.7	14	15.1	5
Static dielectric constant							
ε[liq; 298 K]	78.5	94	68	50	58	91	5
ε[I_h; 240 K]	107	19	39	47	53	31	5
Ratio	1.36	0.20	0.57	0.94	0.91	0.34	5
T_m–TMD–T_c ratios							
T_m[I_h]/T_c	0.422	0.251	0.337	0.394	0.394	0.525	5
TMD/T_c	0.428	0.315	0.378	0.43	0.434	0.532	5
TMD–T_m (K)	4	36	26	21	26	3	5
Densities of ice polymorphs/g cm^{-3}							
ρ[I_h 250 K; 1 bar]	0.92	*	0.944	0.937	0.921	0.976	0.5
ρ[II 123 K; 1 bar]	1.19	1.219	1.245	1.22	1.199	1.285	0.5
ρ[V 223 K; 5.3 kbar]	1.283	*	1.294	1.294	1.272	1.331	0.5
ρ[VI 225 K; 11 kbar]	1.373	1.366	1.403	1.406	1.38	1.403	0.5
EOS high pressure							
ρ[373 K; 10 kbar]	1.201	1.211	1.213	1.216	1.204	1.223	0.5
ρ[373 K; 20 kbar]	1.322	1.34	1.338	1.344	1.321	1.355	0.5
Self-diffusion coefficient/cm^2 s^{-1}							
ln D_{278K}	−11.24	−10.2	−11.08	−10.78	−11.27	−11.41	0.5
ln D_{298K}	−10.68	−9.81	−10.58	−10.34	−10.79	−10.49	0.5
ln D_{318K}	−10.24	−9.67	−10.24	−9.92	−10.39	−9.94	0.5
E_a/kJ mol^{-1}	18.4	9.7	15.4	15.8	16.2	27	5
Shear viscosity/mPa s							
η[1 bar; 298 K]	0.896	0.321	0.729	0.494	0.855	0.699	5
η[1 bar; 373 K]	0.284	0.165	0.269	0.196	0.289	0.174	5
Orientational relaxation time/ps							
τ_2^{HH}[1 bar; 298 K]	2.36	0.8	1.9	1.4	2.3	1.6	5
Structure							
$\chi^2(F(Q))$	0	*	17.7	15.4	8.5	*	5
χ^2(overall)	0	*	22.2	24.1	14.8	*	5

TIP4P/2005 do not. It can be argued that introducing the self-polarization correction places the results of the latter models in agreement with experiment. However, as commented previously, we do not intend to introduce any correction to the results of models. Within the Born–Oppenheimer

approximation the PES does not depend on the mass of the nuclei. According to classical statistical mechanics there should be no isotopic effects on the vaporization enthalpy. The fact that, experimentally, isotopic effects on ΔH_v are important (it increases by about 0.4 kcal mol^{-1} when going

Table 3 Scores

Property	TIP3P	SPC/E	TIP4P	TIP4P/2005	TIP5P
Enthalpy of phase change					
ΔH_{melt}	0	0	5	6	6
ΔH_{vap}	8	5	10	4	10
Critical point properties					
T_c	6	9	6	10	2
ρ_c	4	4	9	9	8
p_c	1	3	4	3	0
Surface tension					
σ_{300K}	0	5	3	9	0
σ_{450K}	0	4	0	9	0
Melting properties					
T_m	0	1	4	7	10
ρ_{liq}	6	8	9	9	8
ρ_{solid}	3	3	5	9	0
dp/dT	0	8	7	10	0
Orthobaric densities and TMD					
TMD	0	5	7	10	10
ρ_{298K}	7	9	8	9	6
ρ_{400K}	0	5	1	8	0
ρ_{450K}	0	3	0	7	0
Isothermal compressibility					
κ_T [1 bar; 298 K]	5	10	4	10	8
κ_T [1 bar; 360 K]	0	5	1	8	0
Gas properties					
p_v[350 K]	3	0	3	0	0
p_v[450 K]	5	2	1	0	0
B_2[450 K]	0	0	0	0	3
Heat capacity at constant pressure					
C_p[liq 298 K; 1 bar]	9	7	8	7	0
C_p[ice 250 K; 1 bar]	0	0	0	0	0
Static dielectric constant					
ε[liq; 298 K]	6	7	3	5	7
ε[I_h; 240 K]	0	0	0	0	0
Ratio	0	0	4	3	0
T_m–TMD–T_c ratios					
T_m[I_h]/T_c	2	6	9	9	5
TMD/T_c	5	8	10	10	5
TMD–T_m	4	6	7	6	10
Densities of ice polymorphs					
ρ[I_h 250 K; 1 bar]	0	5	6	10	0
ρ[II 123 K; 1 bar]	5	1	5	8	0
ρ[V 223 K; 5.3 kbar]	0	8	8	8	3
ρ[VI 225 K; 11kbar]	9	6	5	9	6
EOS high pressure					
ρ[373 K; 10 kbar]	8	8	8	10	6
ρ[373 K; 20 kbar]	7	8	7	10	5
Self-diffusion coefficient					
ln D_{278K}	0	7	2	9	7
ln D_{298K}	0	8	4	8	6
ln D_{318K}	0	10	4	7	4
E_a	1	7	7	8	1
Shear viscosity					
η[1 bar; 298 K]	0	6	1	9	6
η[1 bar; 373 K]	2	9	4	10	2
Orientational relaxation time					
τ_2^{HH}[1 bar; 298 K]	0	6	2	9	4
Structure					
$\chi^2(F(Q))$	4	6	7	8	8
$\chi^2(overall)$	4	6	5	7	7

models in an effective manner through the values of the potential parameters. Since one uses experimental values of water as target for the properties for classical models the hope is that the parameters of the potential implicitly incorporate, to some extent, nuclear quantum effects. It is also clear that since the motion of the nuclei obey quantum mechanics rather than classical mechanics, sooner or later a classical description will fail.[231–236] Assuming that the potential parameters include, in an effective manner, nuclear quantum effects then the experimental value of the vaporization enthalpy of water could be used as the target value of the classical model. However, nothing indicates that best choice is a perfect match to this property. Let us now focus on the melting enthalpy. All three charge models significantly underestimate the melting enthalpy, that said the results of TIP4P/2005 are the best within this family. An explanation for this is not completely clear to us. One possible reason is related to the fact that a non-polarizable model cannot capture the presence of a some-what larger dipole moment in the ice I_h as compared to water. In fact, several studies suggest that the dipole moment of the molecule of water in ice I_h is slightly larger than in water. Obviously this cannot be described using these type of models. Again, the behaviour of TIP5P is different from that of three-point-charge models. This model overestimates the melting enthalpy even though the same dipole moment is used in both phases, contradicting the previous suggestion. It seems that when the negative charge is located on the lone pair electrons the ice phase becomes too stable. As stated by previous authors TIP5P is too tetrahedral. In some way the pair potential is imposing the geometry of the arrangement of the molecules in condensed matter. As first stated by Finney this may not be such a good idea after all.[237] As the three-point-charge models clearly show, in order to obtain a tetrahedral arrangement of molecules, there is no need at all to impose a tetrahedral distribution of charges within the molecule. The enhancement of the electronic density in the region of the lone pairs has been questioned some time ago[92,238] and recent highly accurate first principles electronic calculations do not show any indication of the enhancement. The values of the melting enthalpies may be relevant to understand the rate of ice nucleation in supercooled water. The difference in chemical potential between ice and water at a certain supercooling is related (approximately) to the enthalpy of melting through the Gibbs–Thomson equation.[239] Models with a high melting enthalpy should have a smaller size of the critical ice nucleus compared to those with a low melting enthalpy.[239,240]

B. Critical point properties

From the results given in Table 2 it can be seen that certain models (SPC/E, TIP4P/2005) are able to reproduce the critical temperature whereas the TIP3P, TIP4P, and TIP5P models fail in the prediction. It seems that models describing the vaporisation enthalpy of water (TIP3P, TIP4P and TIP5P) underestimate the critical temperature, whereas models that overestimate the vaporisation enthalpy (or that reproduce the vaporisation enthalpy of water only when including the polarisation correction) yield better predictions. The correlation between the vaporisation enthalpy and the critical temperature has

from water to tritiated water) provides a clear indication of the fact that nuclear quantum effects are indeed important in water. This is not surprising since nuclear quantum effects are important for light atoms (as H) and for strong inter-actions (as it is the case of the hydrogen bond). Since nuclear quantum effects are important in water, is there any hope in trying to reproduce experimental values within classical simu-lations? Quantum effects are included in rigid non-polarizable

already been pointed out by Guillot[19] and seems to be confirmed here. It seems that we are facing a brick-wall: when developing a simple rigid-non-polarizable model for water you must decide either to reproduce the vaporisation enthalpy or the critical temperature, since it is not possible to match both properties simultaneously. The somewhat sacred role played by the vaporization enthalpy when developing non-polarizable potential models is open to question. Describing other properties, the critical temperature for instance, is as legitimate as reproducing the vaporization enthalpy. The question is not to establish a discussion about whether it is more important to reproduce the vaporization enthalpy or other properties. Rather, the question is if the model resulting from fitting to the vaporization enthalpy is superior overall to that obtained by matching other properties. As will be shown later on, reproducing the critical point, with an adequate distribution of charges, seems to be the best choice, at least for water (for other molecules where many body forces are not so important as in water this observation may not hold). Notice that not all models reproducing the vaporisation enthalpy of water yield similar predictions for the critical temperature. Although TIP3P and TIP4P predict similar results (T_c is about 590 K) the critical temperature of TIP5P is significantly lower. Both TIP3P and TIP4P are three charge models (differing only in the location of the negative charge). It seems that, for three charge models, T_c does not depend much on the location of the negative charges. However, TIP5P is a four charge model, with the negative charges located on the position of the lone pair electrons. It seems that this charge distribution leads to a poor estimate of T_c. As for the critical density, TIP4P, TIP4P/2005 and TIP5P yield reasonable estimates whereas the location of the negative charge on the oxygen atom yields low critical densities. The vapor pressures of models that reproduce the vaporization enthalpy tend to be in better agreement with experiment than those of models overestimating the vaporization enthalpy of water (i.e. SPC/E and TIP4P/2005) which yield too low vapor pressures. The large enthalpy of vaporization is mostly responsible for a too low value of the chemical potential of the liquid and the consequence is a too low vapor pressure (at low temperatures the vapor behaves almost as an ideal gas so that its chemical potential is basically given the logarithm of the density). With respect to the critical pressure all models fail, significantly underestimating the critical pressure. Models that reproduce the critical temperature (SPC/E, TIP4P/2005) have vapour pressures that are too low, whereas models with more reasonable predictions of the vapour pressure (TIP3P, TIP4P) have a low critical temperature. In Table 3 the scores for the block are given. Overall, TIP4P models yield better predictions, followed by SPC/E, and with TIP3P and TIP5P obtaining the lowest scores.

C.   Surface tension

The results for the surface tension indicate that models matching the vaporisation enthalpy (TIP3P, TIP4P and TIP5P) result in rather poor predictions (the surface tension is too low) whereas models overestimating ΔH_v (SPC/E and TIP4P/2005) yield better predictions. Apart of this correlation, there should be other factors affecting the quality of the

predictions because the performance of TIP4P/2005 is significantly better than that of SPC/E despite the fact that both have similar values for ΔH_v. It seems that when the negative charge is located on the H–O–H bisector (as in TIP4P/2005) and not on the oxygen atom (as in SPC/E) the surface tension is better reproduced. Thus the surface tension seems to be sensitive to the way the charges are distributed within the molecules.

D.   Melting properties

Concerning the melting temperature, it is clear from Table 2 that three charge models tend to underestimate the experimental value. However, the deviation from experiment is not the same for all of the models: it is huge for TIP3P and much smaller for TIP4P/2005. The behaviour for three charge models can be rationalised[48] by considering the quadrupole moment $Q_T = 1/2(Q_{xx} - Q_{yy})$.[48,49] We have shown that a shift in the negative charge from the oxygen atom along the H–O–H bisector increases the magnitude of the quadrupole moment of the model (for a fixed value of the total dipole moment). Also, for three charge models, we have found that the value of T_m increases linearly[241] with the value of Q_T. This explains the higher value of T_m of TIP4P and TIP4P/2005 when compared with TIP3P and SPC/E. The correlation between T_m and Q_T observed for three charge models does not apply to a four charge model such as TIP5P. In fact, TIP5P has a low quadrupole moment but is able to reproduce the experimental melting temperature. Locating the negative charge on the lone pair electrons increases the stability of ice I_h. This is not so surprising since, in ice I_h, the molecules are located in an almost perfect tetrahedral arrangement which stabilises ice I_h. In summary, although the dipole moment of rigid non-polarizable models is similar (about 2.3D), the melting temperatures vary over a broad spectrum. Thus, charge distribution dramatically affects the melting point temperature.

As for the density predictions at the melting point, the predictions of TIP4P/2005 are quite good and the predictions of TIP3P, SPC/E and TIP4P are quite reasonable. The most striking behaviour is that of TIP5P for which the density of ice is much higher than the experimental value and very close to the density of the liquid. One is led to the conclusion that the location of the negative charge on the lone pair electrons considerably increases the density of ice I_h, adding extra stability which allows it to reproduce the experimental melting point. Concerning the predictions for the slope dp/dT of the melting curve, the predictions of TIP4P/2005, TIP4P and SPC/E are reasonable, TIP3P underestimates the experimental value by a factor of two, and TIP5P overestimates the experimental value by a factor of six. We have shown that the melting curve of ice I_h exhibits a negative pressure re-entrant melting[113] (i.e., the slope of the melting curve changes from negative to positive values). At the re-entrant point the slope is infinite. The possibility of re-entrant melting in water was suggested by Tammann as discussed by Bridgman[242] and found experimentally for tellurium.[243,244] The large slope of the melting point of TIP5P indicates that, at room pressure, the melting curve is close to the re-entrant point.[30] Taking all results into account

Table 4 Scoring summary

Property	TIP3P	SPC/E	TIP4P	TIP4P/2005	TIP5P
Enthalpy of phase change	4.0	2.5	7.5	5.0	8.0
Critical point properties	3.7	5.3	6.3	7.3	3.3
Surface tension	0.0	4.5	1.5	9.0	0.0
Melting properties	2.0	5.0	6.3	8.8	4.5
Orthobaric densities and TMD	1.8	5.5	4.0	8.5	4.0
Isothermal compressibility	2.5	7.5	2.5	9.0	4.0
Gas properties	2.7	0.7	1.3	0.0	1.0
Heat capacity at constant pressure	4.5	3.5	4.0	3.5	0.0
Static dielectric constant	2.0	2.3	2.3	2.7	2.3
T_m–TMD–T_c ratios	3.7	6.7	8.7	8.3	6.7
Densities of ice polymorphs	3.5	5.0	6.0	8.8	2.3
EOS high pressure	7.5	8.0	7.5	10	5.5
Self-diffusion coefficient	0.3	8.0	4.3	8.0	4.5
Shear viscosity	1.0	7.5	2.5	9.5	4.0
Orientational relaxation time	0.0	6.0	2.0	9.0	4.0
Structure	4.0	6.0	6.0	7.5	7.5
Phase diagram	2.0	2.0	8.0	8.0	2.0
Final score	2.7	5.1	4.7	7.2	3.7

it is clear that, although TIP5P reproduces the experimental melting point, this comes at a cost, since it incorrectly estimates the coexistence densities and the slope of the melting point. In Table 4 the global score for this block are presented. It seems that a reasonable prediction of melting properties can be obtained with TIP4P/2005 despite the fact that its prediction for the melting temperature is somewhat low.

E. TMD and orthobaric densities

The majority of models underestimate the experimental value of the TMD (see Table 2). Exceptions are TIP4P/2005 and TIP5P. This is not surprising since the location of the TMD was used as a target property when determining the parameters of both models. However their performance for the orthobaric densities are quite different. The predictions for TIP4P/2005 are excellent. On the contrary, the variation of the orthobaric densities with temperature is too sharp for TIP5P, having a deviation of about 15% at 450 K. A few years ago we found[133] that, for three charge models, the TMD is located about 25 K above T_m. Since TIP3P and SPC/E seriously underestimate T_m, it is not surprising that they also predict very low values for the TMD. But the dependence with temperature of the orthobaric densities is quite different for TIP3P and SPC/E. The former model fails completely while the results for the latter are reasonable. Overall, it seems that models predicting acceptable values of the critical point tend to result in better predictions for the orthobaric densities, whereas those underestimating T_c yield densities that are too low. Notice that, taking into account the different correlation of the TMD (with T_m in three charge models) and the orthobaric densities (with T_c) there are large variations in the scores obtained by the different models. Only TIP4P/2005 gives an overall satisfactory score in this block (Table 4).

F. Isothermal compressibility

The best results for the isothermal compressibilities are obtained for the SPC/E and TIP4P/2005 models. The performance of the other models is not so good. We do not have a simple explanation to rationalise these results. Certainly both SPC/E and TIP4P/2005 rely on the self-polarisation correction for ΔH_v but it is not clear how this may affect the quality of the predictions for κ_T. Models having good predictions for the isothermal compressibility are more likely to describe the EOS at high pressures. We shall see that this is indeed the case. We have not included in the test the location of the minimum in compressibility at room pressure which experimentally is located at about 318 K. This behaviour is reproduced by TIP4P/2005 with a good estimate of the location of the temperature of the minimum. There is some indication that the other models also have a minimum in κ_T but located at lower temperatures.[141] The existence and location of the minimum is relevant when it comes to understand the behaviour of super-cooled water. Experimentally, it is found that for temperatures below the minimum the values of the compressibility increase dramatically and it has been suggested by Speedy and Angell[245] that they diverge at the homogeneous nucleation limit of super-cooled water.

G. Gas properties

All the models predict overly negative values for the second virial coefficient, with the TIP5P results being not so bad. Similar comments may be made for the vapour pressures, with TIP3P and TIP4P providing the 'best' estimates. Kiss and Baranyai have shown that these models are unable to predict the energy of water in small clusters.[144] However, TIP4P models are able to predict the arrangement of molecules in small clusters rather well, although values of the energy of formation of the cluster are incorrectly predicted. These results are not at all surprising. Non-polarizable models that are optimised for condensed matter simulations cannot reproduce the properties of the gas phase because of the enhanced value of the dipole moment with respect to that of the gas phase. A model with a fixed charge distribution cannot mimic nature where the dipole moment changes in the molecule from a value of 1.85 D in the gas phase to a value in the range 2.7–3.1 in condensed phases. It is to be expected that the introduction of polarizability would dramatically improve the performance for the properties of this block.

H. Heat capacity at constant pressure

The water models considered in this work predict values for C_p that are too high. Models that account for the vaporisation enthalpy, such as TIP3P or TIP4P, overestimate C_p by about 5–10% whereas models that overestimate the vaporisation enthalpy overestimate C_p by about 15 per cent. The behaviour of TIP5P is striking: it overestimates C_p by about 50 per cent. Since TIP3P, TIP4P and TIP5P match the vaporisation enthalpy, the failure of TIP5P in predicting C_p must be related with the way the charges are distributed in the molecule. It seems that, in this model, properties vary with temperature far too quickly (C_p simply reflects how the enthalpy changes with temperature at constant pressure). This was also the case for the orthobaric densities. Overall, one has the feeling that C_p can be reproduced reasonably, but not perfectly, with rigid non-polarizable models. Since C_p is related to enthalpy fluctuations, it seems that classical statistics and quantum statistics provide quite different values for these fluctuations, being lower when nuclear quantum effects are included. Thus the apparent good agreement exhibited by certain water models for the liquid phase is somewhat fortuitous.

In this work we have also calculated the heat capacity of ice I_h at 250 K for the selection of models. It can be seen in Table 2 that the heat capacity of the solid phase is overestimated by about 75%. How is it possible that upon lowering the temperature by just 50 degrees, going from liquid water to ice I_h (both condensed phases showing a relatively similar short range structure) the results deteriorate so much? The answer to this question is often something like this: "water models are designed to work for liquid water at room temperature and pressure and one should not expect that they should be reliable for other phases and conditions". We disagree with this statement. Firstly, the value C_p for the liquid phase is not commonly used as a target property when fitting the potential parameters. Secondly, the selected temperatures and the two phases considered, ice I_h and water, are not so different as to justify the strong failure of the predictions for the solid phase (notice that all of the models fail in a similar way in describing C_p of ice I_h). We have recently shown[228] that the model TIP4PQ/2005, a minor modification of TIP4P/2005 intended to be used in path integral simulations, nicely reproduces C_p for both liquid water and ice I_h at any temperature. The conclusion is that nuclear quantum effects are required to describe the heat capacity of both liquid and (especially) solid water.[246,247] The stronger influence of these quantum effects on the heat capacity of ice I_h with respect to the liquid is probably due to the absence in the former phase of translational contributions which transform into high frequency librational modes and these clearly require a quantum treatment.

I. Static dielectric constant

The discussion of the dielectric constant is somewhat similar to that presented for the heat capacity. Predictions of the dielectric constants for liquid water at room temperature and pressure are presented in Table 2. It is worthwhile recalling the expression of the dielectric constant for a rigid non-polarizable model when using Ewald sums under conducting boundary conditions:[156–159]

$$\varepsilon = 1 + \frac{4\pi\rho}{3kT}\mu^2 G, \qquad (3)$$

where the polarisation factor G (also denoted as the finite size Kirkwood factor[229]) is defined as

$$G = \frac{\langle M^2 \rangle}{N\mu^2}, \qquad (4)$$

and ρ is the number density. It is clear that (all other magnitudes being constant) the larger the value of the dipole moment the larger the dielectric constant. The majority of the models considered in this work (the exception being TIP4P having a dipole moment of 2.19 D) has a dipole moment of about 2.30 D. Despite this, they predict quite different values for the dielectric constant. Thus, the polarisation factor G, appearing in eqn (4) must be quite different for these models. As noted by Steinhauser et al.[248] and Guillot,[19] G is related to the relative orientation between molecules in the sample.[249] and not to the site–site correlation functions. Models with similar site–site distribution functions $g_{OO}(r)$, $g_{OH}(r)$ or $g_{HH}(r)$, may differ significantly in G. Some time ago Steinhauser and coworkers pointed out that water models have quite different G which could be useful when it comes to developing improved water models.[248] These observations have also been considered by Guillot.[19] From the results in Table 2 it seems that four site (TIP4P-like) models tend to yield low values of ε, three site models predict increased ε (the performance of SPC/E being better and the value of TIP3 is somewhat high), and the five-site TIP5P provides quite reasonable predictions. Let us examine the results of the dielectric constant at room pressure for ice I_h at 240 K. Until recently the evaluation of $\varepsilon(I_h)$ has received little attention, whose study was pioneered by Rick and co-workers.[50,163,230] Recently we have evaluated this property for a number of water models.[166,167] Because at 240 K TIP3P ice I_h melts in this work we have evaluated the dielectric constant of TIP3P at 180 K (details are similar to those described in ref. 167). The results are presented in Table 2. The dielectric constant of solid water is underestimated by about 80 per cent by TIP3P, 60 per cent by SPC/E, 50 per cent by TIP4P and TIP4P/2005 and 70 per cent by TIP3P. So we are again forced to formulate a similar question as in the case of C_p: how is it possible that just in 50 degrees and moving from water to ice I_h that the agreement deteriorates in such a dramatic manner? One could once again repeat the standard answer: "water potential models are designed to work for liquid water at room temperature and pressure and one should not expect that they should be reliable for other phases and conditions". Let us now try to investigate this question further by analysing the ratio between the dielectric constants of ice I_h and water.

The experimental value of the ratio ε (ice, 240 K)/ε (liq, 298) is of about 1.4, whereas the predictions of TIP3P and TIP5P are of about 0.2–0.3, improving somewhat for SPC/E (close to 0.6) and increasing to 0.9 for TIP4P models. It seems that something is really very wrong in the dielectric constant of water models in condensed phases. The dipole moment of water in condensed phases cannot be measured directly but ab initio calculations for liquid water yield a dipole moment higher than 2.7 D for the molecule in the fluid phase and of about 3.1 for ice I_h (although the exact values depend on the details of the calculation[29,51,52,250–253] and on the criterion

used to distribute the electronic cloud between the molecules of the system). This is consistent with the dipole moment of 2.7 D found for the molecule in the hexamer cluster.[254] Rigid non-polarizable models have dipole moments around 2.3 D. The value of 2.3 D seems appropriate to reproduce the energy of water in the fluid phase (either exactly or slightly over-estimating) when the interaction between molecules is given by a Coulombic law and a LJ interaction. The case of the water octamer described by the TIP4P model is particularly illustrative. The model reproduces rather well the energy of the octamer cluster,[255] even though the dipole moment of the molecule in the model is 2.19 D and that of the molecule in the cluster is above 2.7 D.[254] Nature obeys the Schrodinger equation and, within this formalism, it is possible to have the correct interaction energy while having molecules with a dipole moment higher than 2.7 D. Assuming that rigid non-polarizable models correctly describe the structure of liquid water, they would never be successful in reproducing the dielectric constant since their values of the dipole moments, dictated by energetic criteria, are too small compared to the true value. This idea was suggested by Guillot and Guissani.[256] The case of water shows clearly that it may be dangerous to force simple models with discrete charges to have the same dipole moment as those obtained from first principle calculations. It is probably a better idea to force the models to have similar energies to those found experimentally (allowing small deviations from the experimental values may pay off when regarding the overall performance). In summary, it seems that the dielectric constant is one of the properties that cannot be described by a rigid non-polarizable model. There is a further indication that this is the case. For the TIP4P and TIP4P/2005 models, the dielectric constant is not reproduced neither for water nor for ice I_h. However, it seems that the failure of these models has a simple explanation. In fact, by using the value of G obtained from TIP4P models and using a dipole moment of about 2.7 for the liquid and of about 3.1 for ice I_h, then quite reasonable predictions are obtained for the dielectric constant of both phases.[167] Moreover, this is also fulfilled for the ices, III, V and VI. In this way it is possible to qualitatively describe how the dielectric constant changes in the solid forms of water.[167]

A final remark. We have found that the polarisation factor G is essentially the same for TIP4P and TIP4P/2005. A similar remark was made by Steinhauser and coworkers[248] for SPC and SPC/E. Since the ratio of the dipole to the quadrupole moment is identical for SPC and SPC/E and quite similar for TIP4P and TIP4P/2005 this suggests that, for three charge models, the dielectric constant can be written as

$$\varepsilon = 1 + \frac{4\pi\rho}{3kT}\mu^2 G(\mu/Q_T). \qquad (5)$$

The key idea behind this expression is that, for three charge models, the factor G depends only on the dipole/quadrupole ratio. This ratio is essentially the same for TIP4P and TIP4P/2005. This ratio is also the same for SPC and SPC/E. That allows us to rationalise the variation of the dielectric constant within three charge models. The idea of including the quadrupole moment in correlations describing the dielectric constant of water was first proposed by Rick.[50] Nuclear quantum effects

should not significantly influence the values of the dielectric constant. The electronic quantum effects are more likely responsible for the failure in the predictions of the dielectric constant. When solving the Schrodinger equation it is possible to describe simultaneously both the cohesion energy of water and the polarisation of a certain configuration (which is probably consistent with molecules having a dipole moment higher than 2.7 D). It is not possible with rigid non-polarizable models to reproduce both, the cohesion energy and the polarisation of a certain configuration. In our opinion first principle calculations will likely defeat rigid non-polarizable models in the estimate of the dielectric constants[253] providing consistent values for the fluid and solid phases of water.

J. T_m–TMD–T_c ratios

The ratio of the triple point (or the melting point temperature) to the critical temperature gives an idea of the liquid range of a fluid.[168] The lower its value the larger the temperature range over which the fluid phase appears in the phase diagram. It changes significantly from one substance to another, being about for 0.23 for propane, 0.5 for noble gases and 0.7 for carbon dioxide. For water the value of this ratio is of 0.428, thus water has a rather large liquid range. The temperature of the maximum in density of water at room pressure is another important point within the phase diagram of water. The physics of super-cooled water[257] has two important temperatures: the melting temperature indicating where super-cooled water begins to exist, and the maximum in density of water which signals that the response function (i.e., the coefficient of thermal expansion) behaves in an unusual manner (i.e., it becomes negative) so that the density decreases when the liquid is cooled. For water, the temperature difference between the TMD and the T_m is just four degrees. It seems also interesting to analyse the ratio TMD/T_c. In Table 2 the results for these three properties are presented. TIP4P models predict quite well the value for T_m/T_c. The ratio is too high for TIP5P (and probably the same will be true for models locating the negative charge on the lone pair electrons such as ST2). The value of this ratio is quite low for TIP3P. However, the stable solid phase at melting (at normal pressure) for TIP3P is ice II with a melting point of about 220 K (see Vega et al.[30]). If this value were to be included then T_m/T_c would be about 0.45. For SPC/E the stable solid phase at melting is also ice II but its melting point is only 1 degree above that of ice I_h, so the ratio is adequately described by the value of the ice I_h melting temperature. Values of the TMD/T_c follow similar trends to those presented for T_m/T_c. Concerning the difference between the TMD and T_m most of the models predict a value of about 25 K. The only exception is TIP5P. For this model the value of this difference is about 10 K when Ewald sums are implemented to determine its properties and of 5 K when the TMD is located in simulations with truncated Coulombic interactions. We should mention that computer simulation results are sensitive to the treatment of the long range coulombic interactions. For this reason some models have been reparametrized to be used with Ewald sums.[50,258] The global evaluation of this block reveals that the TIP4P models provides a good description of the relative location of the different singular

points, followed by TIP5P and SPC/E, and finally by TIP3P which gives somewhat poor predictions.

K. Densities of ice polymorphs

Before discussing the results of this block, let us justify the choice of the selected temperatures used for the comparison. According to the third law of thermodynamics the coefficient of thermal expansion is zero at zero temperature. For this reason the density of solids does not change much with temperature at low temperatures. In fact, the densities of ices are essentially constant from 0 K to about 100 K, and start to decrease significantly with temperature only for temperatures above 125 K. In classical statistical mechanics the density of a solid increases as the temperature decreases all the way to 0 K. For this reason if one compares the densities obtained from classical calculations to experimental values for temperatures below 100 K even good models describing the density of that ice polymorph at higher temperatures will fail. This has been illustrated in our recent work.[231,234] Quantum statistics should be used to obtain good agreement with experiment at temperatures below 100 K. This remark is also relevant for *ab initio* calculations. The density obtained from an energy minimisation for a solid structure should be higher than the experimental one, unless the effect of the vibrations of the solid structure are incorporated in the description. For this reason most of the temperatures selected for the comparison are above 200 K. The only exception is ice II, for which a reliable experimental estimate of its density has recently been reported at 123 K. Overall TIP4P models (especially TIP4P/2005) yield good estimates for the polymorphs of water, the results of SPC/E being reasonable except for ice II. The densities predicted by the TIP5P model are too high for all of the ice phases. Once again, locating the negative charge on the lone pair electrons results in a model that is too tetrahedral, with densities too high for tetrahedral structures such as the ices. The problem with TIP3P is different. For some of the ices considered the solid is mechanically unstable and melts at the studied temperature. This model is certainly not adequate when it comes to describing the solid phases of water (not to mention other problems as the behavior of antifreeze proteins in water).

L. EOS at high pressures

The predictions for the density of water at 10 000 bar and 20 000 bar at 373 K are presented in Table 2. We have chosen the temperature of 373 K instead of room temperature because at 298 K the fluid phase exists only up to a pressure of about 10 000 bar. The results of the evaluation are presented in Table 3. The predictions are excellent for TIP4P/2005, very good for SPC/E, good for TIP3P and TIP4P and rather poor for TIP5P.

M. Self-diffusion coefficient

Before commenting the results for the self-diffusion coefficient it is important to stress that it was not included as a target property for any of water models considered in this work. The results for SPC/E and TIP4P/2005 are in excellent agreement with experiment. This is a clear indication that the prediction

of the diffusion coefficient is substantially improved when the model predicts a vaporisation enthalpy around 10–15 per cent larger than the experimental value. Models that match the vaporisation enthalpy overestimate D at room T, by a factor of 2 for TIP3P, by 50 per cent for TIP4P and by a small amount for TIP5P. Thus the value of the diffusion coefficient seems to be sensitive to the position of the negative charge. The dependence of D with T of TIP5P is peculiar. It provides acceptable values for D at room temperature but the dynamics is somewhat slow at 278 K and significantly faster than experimental values at 318 K. This indicates that the activation energy associated with the Arrhenius-like behaviour of D in this range of temperatures is not reproduced at all by TIP5P (see Table 2). This is also the case of TIP3P. In contrast, TIP4P, SPC/E and TIP4P/2005 provide more or less acceptable predictions for E_a. In summary, concerning the self-diffusion coefficient predictions, it is clear that some models fail completely and other models are successful. The sensitivity of this property to different details of the water model makes it quite useful in developing potential models. In retrospect, one is led to conclude that the diffusion coefficient has not received the attention it should deserve as a target property.

A final warning is related to system size effects when determining the diffusion coefficient. In general the diffusion coefficient increases with system size.[259] If the size of the simulated system is about 500 molecules one is not far from the thermodynamic limit (a rough estimate is that it would increase by about ten per cent). That would not influence very much the scores. For the majority of models it would slightly reduce the score since they already overestimate the diffusion coefficient of water. The only exception is TIP4P/2005 that underestimates the diffusion coefficient so the inclusion of finite size effects could bring the predictions into closer agreement with experiment.

N. Shear viscosity

The results for the viscosity, η, follow similar trends to those already discussed for the self-diffusion coefficient. Again, excellent results are provided by TIP4P/2005 and are quite satisfactory by SPC/E. The rest of the models (all of them matching the experimental vaporisation enthalpy) yield quite low values of the viscosity. The global score obtained for the viscosity (Table 4) is quite similar to that obtained for the diffusion coefficient D. This is not so surprising. According to the Stokes–Einstein relation:

$$D = \frac{kT}{6\pi\eta d}, \qquad (6)$$

where d is the "effective" hydrodynamic radius. According to this relation the diffusion coefficient and the viscosity are not independent of each other. In fact models overestimating the diffusion coefficient by a factor of two underestimate the viscosity approximately by a factor of two also. Thus if the diffusion coefficient is predicted correctly it is likely that the predictions for the viscosity are good. However, an accurate determination of the viscosity requires runs at least one order of magnitude longer that those required to determine the self-diffusion coefficient accurately. This reinforces the idea that the diffusion coefficient is a good target property to consider

when modelling water and that it should be included in future developments.

O. Orientational relaxation time

The orientational τ_2^{HH} relaxation time of the different models is presented in Table 2. The best agreement with experiment is obtained by model TIP4P/2005 followed by SPC/E. The relaxation times of TIP4P and TIP5P are similar and too low as compared to the experimental value. The worst prediction is that of TIP3P which is between two and three times smaller than the experimental value. The relaxation time correlates well with the shear viscosity. Models with low viscosities tend to have low orientational relaxation times. This can be explained by using the Stokes–Einstein–Debye equation.[260] The behavior of the diffusion coefficient and orientational relaxation time may be important to understand rates of ice nucleation in supercooled water.

P. Structure

Recently Pusztai et al.[204] have compared the total scattering ($\chi^2(F(Q))$) of SPC/E, TIP4P and TIP4P/2005 to the results of neutron diffraction experiments. They have also compared the ability of these three water models to predict the experimental radial distribution functions $\chi^2(overall)$. A first conclusion of their work is that the results for all of the models considered (among others SPC/E, TIP4P and TIP4P/2005) were reasonable when compared to experiment. Unfortunately neither TIP3P nor TIP5P were considered. It is commonly accepted that TIP3P provides poor predictions for water structure[30] as compared to the other models.[261,262] For this reason we assigned to TIP3P less points than those obtained by the model scoring the poorest for this block. It is also commonly accepted that the predictions of TIP5P are reasonable. In fact when using X-rays, the diffraction spectrum of TIP5P seems to be comparable to that of TIP4P/2005. For this reason we assigned to TIP5P the same score as TIP4P/2005. An analysis similar to that performed by Pusztai et al.[204] comparing neutron diffraction results with TIP5P predictions would be quite useful. The scores obtained by the structure predictions are presented in Table 3. Overall TIP4P/2005 predicts reasonably well the structure, as TIP5P, followed by TIP4P and SPC/E. A comparison between experimental results and simulation predictions for the oxygen–oxygen radial distribution function can be found in ref. 30. A more extensive comparison including all radial distribution functions would be an interesting topic or research for further studies.

Q. Phase diagram

Although it is difficult to translate phase diagram predictions into a number we have decided to include this property in the evaluation test. In fact, the study of the phase diagram played a fundamental role in the development of TIP4P/2005. The scores are given in Table 4. TIP4P and TIP4P/2005 are able to qualitatively predict the phase diagram of water (the main difference between them is that the phase diagram of TIP4P/2005 is shifted by about 20 K to higher temperatures, improving the agreement). The rest of the models—TIP3P, SPC/E and TIP5P—fail in that respect. It is clear that matching the

vaporisation enthalpy (or not) has nothing to do with the ability of a model to describe the phase diagram of water. In fact, TIP4P, TIP3P and TIP5P reproduce the vaporisation enthalpy of water and their predictions are quite different. Also SPC/E and TIP4P/2005 predict similar values for the vaporisation enthalpy and they yield quite different phase diagrams. The fact that TIP4P and TIP4P/2005 provide reasonable estimates indicates that the key factor regarding the quality of phase diagram predictions is the charge distribution in the water model. The key to understanding the phase diagram of a certain molecular solid is the fact that the relative stability between solid phases is quite sensitive to the orientational dependence of the interaction energy. In the fluid phase the molecules present a number of different relative orientations. In the case of the solid phases, molecules undergo vibrations/librations with respect to certain selected relative orientations. This is perhaps one specific reason why a model optimized only for liquid water at room temperature is unlikely to be particularly good for an ice and vice versa. For molecular solids, the phase diagram yields information about the orientational dependence of the potential energy. Since all of the water models considered carry a LJ centre on the oxygen, the orientational dependence of the potential is due to the electrostatic contribution. Let us recall that the water models investigated in this work have similar values of the dipole moment. However they differ significantly in the quadrupole Q_T. This suggests that the quadrupole moment may be involved in the ability to predict phase diagrams. In fact, we have shown[263] that the ability to predict the phase diagram of rigid non-polarizable models is determined by the ratio of the dipole to the quadrupole moment. Models that yield good phase diagram predictions have a ratio dipole/quadrupole moment close to one. For TIP4P models this ratio is about 1, and it takes larger values for SPC/E and still much larger for TIP3P and TIP5P. What is the experimental value of this ratio? For an isolated molecule the ratio is very low, namely, 0.7. First principles calculations suggest that this ratio increases to 0.9–0.95 in liquid water. These results indicate that the ratio dipole/quadrupole of TIP3P, SPC/E and TIP5P is too large and that affects their ability to predict the phase diagram.

In the nineteen seventies/eighties a number of studies were performed for models for simple molecules with point dipoles and/or point quadrupoles.[49,264,265] It was clear from these studies that the orientational structure of the fluid, energetics and dielectric properties were quite sensitive to the balance between dipolar and quadrupolar forces. It is somewhat surprising that this discussion did not transfer much to the area of modelling water. The word dipole moment is often found when discussing water models, however very little is said about the value of the quadrupole moment. Finney and coworkers already pointed out the importance of the quadrupole in the modelling of water.[237,266] Watanabe and Klein[267] a few years later proposed a model of water where the quadrupole was explicitly considered in the determination of the potential parameters, though, in retrospective, their idea of exactly reproducing the experimental value of the quadrupole moment of water did not yield a good model. Also Rick, when looking for an empirical expression to describe the dielectric constant

of water models in the liquid phase, ended with an expression that included both the dipole and the quadrupole.[230] In recent work we were forced to consider the quadrupole when describing the correlation[241] between T_m of ice I$_h$ and the quadrupole moment Q_T and also when describing the ability to describe phase diagrams.[48,263] Also in other recent papers the importance of the quadrupole in the modelling of water is increasing.[268] In summary the phase diagrams of water is quite different for different water models, and the key to success seems to be related to with having a value of the ratio dipole to quadrupole moment of about one. For rigid non-polarizable models this is achieved when the negative charge is located on the H–O–H bisector at a distance close to that of TIP4P models.

IV. Discussion

Now that a detailed discussion of the results for each property and model has been presented it is pertinent to provide a global view of the results. The discussion of the results consists of two sections; firstly a comparison of the performance of the different rigid non-polarizable models will be presented. After which we shall discuss the limits of rigid non-polarizable models when it comes to the description of water.

A. Comparison of rigid non-polarizable models

The global results obtained by rigid non-polarizable models are presented in Table 4. The total score obtained by the water models is of about 3 for TIP3P, 4 for TIP5P, 5 for TIP4P and SPC/E and 7 for TIP4P/2005. The models that do not reproduce exactly the vaporisation enthalpy of water (TIP4P/2005 and SPC/E) obtain the highest scores. The comparison between TIP4P and TIP4P/2005 is interesting in this respect. Both models have almost the same charge distribution. The main difference is that the vaporisation enthalpy is used as a target property for TIP4P but it was not used as target property in TIP4P/2005. For essentially all properties (except for the the properties involving a gas phase) the performance of TIP4P/2005 is better than that of TIP4P and the average scoring differs by more than 2 points. Similar comments apply to the comparison between TIP3P and SPC/E. The central idea of SPC/E was to provide a theoretical reasoning justifying that having a vaporisation enthalpy higher than the experimental value could be useful. Comparing the performance of SPC/E (5 points) to that obtained by TIP3P (3 points) one must conclude that Berendsen's *et al.*[14] suggestion was indeed a very good one. We recall that we have not included the Berendsen correction in the results and, thus, SPC/E has a lower score than TIP3P for ΔH_v. But, as expected, this is largely compensated by the improvement in other properties. This is a first conclusion of our work: sacrificing an exact match of the vaporisation enthalpy of water results in overall higher scores.

On the other hand, the considerable difference in the scores obtained by TIP4P/2005 and SPC/E provides a first indication of the superiority of the TIP4P-like charge distribution with respect to that of SPC-like one. For models that match the vaporisation enthalpy of water (TIP3P, TIP4P and TIP5P) there are also significant differences. These three models were developed by Jorgensen and coworkers, following a similar

strategy and methodology. The variation of the score must be due to the way in which the negative charge is distributed within the molecule. The score obtained by TIP3P is only 3. Thus, TIP3P can be regarded as the worst model of water among those considered in this work. It is hard to justify its use nowadays. It may be argued that most of force-fields for biomolecular simulations were designed to work using TIP3P. For a long time that was probably the best thing to do, but it seems clear now that new force-fields of should be built around better water models.[269–278] Locating the negative charge on the lone pair electrons, as in TIP5P (and the same applies to the historically important ST2 model) seems to be a small step forward. The performance of TIP5P for liquid water at room temperature and pressure is quite good, but it deteriorates very quickly once one moves away from these conditions. One could argue that this should occur for any model. In our opinion this is only partially true. Even admitting that none of the non-polarizable models describe all thermodynamic conditions, one should recognise that a model like TIP4P/2005 obtains a global score over 7 whereas TIP5P obtains roughly half of this score. The fact that the degradation of properties of TIP5P occurs very quickly as one moves from room temperature and pressure, is in our opinion, an indication that locating all the negative charge on the lone pair electrons seriously deteriorates the performance of a water model. However a very interesting idea behind the development of TIP5P should not be overlooked: the model was designed to reproduce the maximum in density at room temperature. The best results (among models matching the vaporisation enthalpy of water) are obtained by TIP4P. This model obtains an score of 5 points (very similar to that of SPC/E) which is an improvement over the performance of TIP3P and TIP5P. As in the comparison TIP4P/2005-SPC/E we attribute the improvement to the way one distributes the charges in the model which significantly affects its performance. A second conclusion of the test is the superiority of the TIP4P-like charge distribution for water models.

It is not difficult then to put all the pieces together. The charge distribution of TIP4P seems to be adequate. The idea of Berendsen *et al.*[14] of overestimating the vaporisation enthalpy of water seems also to be useful when it comes to improving the performance of a water model. Why not use Berendens's approach for a TIP4P like model? The result is a model close to TIP4P/2005. If an improvement of about 2 points is achieved by changing the target value of the vaporisation enthalpy (see the global scores of TIP3P and SPC/E) and an additional gain of about 2 points could be obtained by locating the negative charge on the H–O–H bisector instead of on the oxygen (see the improvement from TIP3P to TIP4P), then such model could have a global score close to 7. This is roughly the global score of TIP4P/2005. In the design of the parameters of TIP4P/2005 we also tried to reproduce as closely as possible the maximum in density of water at room pressure (as was done for TIP5P) and the phase diagram of water (which essentially forces the TIP4P charge distribution). Thus, in a sense, the development of TIP4P/2005 borrowed ideas used in the design of previously proposed water models.

We may summarize the results by pointing out that not all rigid non-polarizable water models have the same ability to

describe the properties of water. It is also true that the result obtained by the best model, about 7, is still far from the maximum of 10 points. It is interesting now to discuss the possible limits of rigid non-polarizable water models in the description of the water properties.

B. Limitations of rigid non-polarizable models

From the results presented so far it is clear that rigid non-polarizable models cannot describe all properties of water successfully. The best results are obtained with TIP4P/2005 so it is useful to focus our attention on the results of this model in order to analyse the limits of current non-polarizable models. We should mention that by "limits of non-polarizable models" we really mean "limits of classical simulations of non-polarizable models". It is worth pointing out that for any property described above (including those for which all common water models fail) it is possible to design a "special purpose" rigid non-polarizable model which reproduces the experimental value of the target property. However it is highly likely that, after evaluating the performance of this special purpose model with the test proposed in this work, the global score will be rather low. Therefore a "limit of a rigid non-polarizable models" just indicates that improving the description of a certain property can only be done at the cost of decreasing the overall score. We shall now present what, in our opinion, are the limits of rigid non-polarizable models:

• Limitation 1. Properties of the gas phase

Properties of the gas phase, including properties of clusters and virial coefficients, cannot be reproduced by rigid non-polarizable models.[144] The electronic cloud of the molecule of water changes significantly with the environment (being different in the isolated molecule, in the dimer, in small clusters, in the liquid phase, and in the ices). Those changes, which appear naturally in an electronic structure calculation, cannot be reproduced by non-polarizable models. When the non-polarizable model is designed to reproduce the properties of the liquid then it must fail for the gas phase. It is likely that the inclusion of many body forces (polarization, three body forces) will solve this problem.[279,280]

• Limitation 2. Critical pressure

Although the vapour pressure is not a "one phase property", since it depends on the properties of the liquid and those of the fluid, it seems that vapour pressures and the critical pressure represent a limit for rigid non-polarizable models. Models having better predictions for the vapour pressure have a low critical temperature, thus yielding low critical pressures. Models reproducing the critical temperature yield low vapour pressures. All rigid non-polarizable models underestimate the value of the critical pressure. It is likely that including polarization will help to solve this problem.

• Limitation 3: Simultaneous matching of the vaporisation enthalpy and the critical temperature

All models discussed in this work fail in describing both properties simultaneously. Certainly one can design a "special purpose" model reproducing both properties[150] but its global score would probably be low. Again, it is likely that including polarization will help to solve this problem.

• Limitation 4. Simultaneous matching of the melting temperature and the maximum in density

For most of the rigid non-polarizable models, the difference between the melting temperature and the TMD is of about 25 K compared to the experimental value of 4 K. The only exception is TIP5P for which this difference is about 10 K. But as a consequence the density of ice and several other properties are poorly predicted. We have commented that there is evidence that the dipole moment of ice I_h is slightly larger than that of liquid water. It is possible that a polarizable model captures the increase in the dipole moment and that could give to the solid phase the small extra stability needed to increase the melting temperature. Once again, only the inclusion of polarization could help to solve the problem

• Limitation 5: Heat capacity

Classical simulations of rigid non-polarizable models cannot quantitatively describe the heat capacity of water. Nuclear quantum effects should be incorporated to describe this property accurately. In fact, for liquid water at room T and p all models yield values higher than the experimental value. For ice I_h at 250 K and room pressure all models fail dramatically in describing C_p, overestimating it significantly. Any further success in describing C_p at room T and p must be regarded as being fortuitous rather than due to any intrinsic merit of the model. Including polarization will not solve the problems in the prediction of C_p. The inclusion of nuclear quantum effects (through, for instance, path integral simulations) may solve the problem. Since nuclear quantum effects are somewhat included through the value of the parameters for water models designed for classical simulations, a reparameterization of the model is needed for models designed for path integral simulations. Besides the inclusion of nuclear quantum effects allows us to study isotopic effects on the properties of water.[232,281]

• Limitation 6: The third law of Thermodynamics

Classical simulations do not not satisfy the third law of Thermodynamics: the heat capacity remains finite even at 0 K, the density keeps growing as the temperature decreases, and the entropy goes to minus infinity as the temperature tends to zero. Experimentally C_p goes to zero, the density remains approximately constant for temperatures below 120 K and the entropy tends to a finite value (zero for proton ordered ices, about $R \ln(3/2)$ for proton disordered phases[282] or a slightly lower value when there is only partial proton disorder[283]). These limitations are due to the classical treatment rather than to the use of rigid-non-polarizable models. This would also apply to polarizable models when studied with classical simulations. When nuclear quantum effects are incorporated (through path integral simulations) in a rigid non-polarizable model then simulations would satisfy the third law.

• Limitation 7: Dielectric constant

Rigid non-polarizable models cannot describe the dielectric properties of the condensed phases of water (liquid and ices). All models (even those that are successful for liquid water at room T and p) fail in predicting the dielectric constant of ice I_h at 240 K. For most of the models the dielectric constant of ice I_h is about half that of water, in clear contrast to experiment where both phases have similar dielectric constants at the melting point. The only exception are TIP4P models which predict a similar constant for ice I_h and liquid water

(although their values are not satisfactory). Interestingly, if the dielectric constant of TIP4P/2005 is scaled by the square (see eqn (3)) of the ratio of the dipole moment of water in condensed phases (2.7–3.1) to the dipole moment of the model (2.3) then the simulation results are able to describe reasonably well the dielectric constant of water, ice I$_{\text{h}}$ and the rest of the ices.[167] Rigid non-polarizable models have a dipole moment of about 2.3 Debyes. If the true dipole moment of water in condensed phases is larger than 2.7 Debyes (and all evidence points to this[254]) then there is no way a rigid non-polarizable model can describe the dielectric constant of the condensed phases of water. Any apparent success in describing the dielectric constant for the liquid phase must be due to an incorrect orientational dependence (as given by the polarization factor G). The inclusion of nuclear quantum effects cannot solve this problem. Only including polarization, so that the models have much larger dipole moments, can solve this problem.

• Limitation 8: Extremely high pressure region of the phase diagram

We have seen that rigid non-polarizable models can describe the phase diagram of water at least qualitatively. There are however several exceptions. Obviously these models cannot mimic the dissociation of the water molecule, which seems to happen in the high pressure phase of water ice X where the hydrogen atom moves to the central position between two oxygen atoms. Also, the transition pressures between water and ice VII are overestimated by a factor of two by rigid non-polarizable models, and these models fail significantly in describing the density of ices VII and VIII.[113,173,284,285] Further work is needed to understand the origin of this failure. For ice VIII the shortest hydrogen bond O–O distance is longer than the shortest non-bonded O–O distance[286] (for ice VII they are identical). This suggests that probably for the models described in this work the description of the repulsion between non-hydrogen bonded molecules is not correct. That may explain the failure in describing the densities of ices VII and VIII. Modifying the expression for the repulsive part of the potential[150,279,287,288] or including anisotropy in the repulsive part of the potential may be required to improve the performance. A successful rationalization of many important structural aspects of water and ice has been made on the basis of the detailed nature of the repulsive region.[289–291] It is somewhat surprising that rigid non-polarizable models can qualitatively describe the phase diagram of water, since polarization effects and nuclear quantum effects are neglected. Notice however that even though nuclear quantum effects are important to determine one phase properties (i.e. heat capacities) their impact on phase transitions is much smaller if both phases are affected by nuclear quantum effects in a similar manner. Notice also that although polarization effects are important to determine one phase properties such as the dielectric constant, their impact on phase transition is much smaller if both phases present similar dipole moments. That explains the relative success of some rigid non-polarizable models in describing phase diagrams.

• Limitation 9. Chemical limits

Obviously the models used in this work cannot deal with problems in which chemical reactions are involved, say electron transfer, dissociation, pH determination and so on. Also the models of this work cannot provide direct results for IR or for Raman spectra.

C. Mapping of quantum theory into classical simulations

To clarify the origin of the limitations of rigid non-polarizable models it is interesting to write the expression of the energy obtained from say a DFT calculation and to compare it with the expression of a rigid non-polarizable model. The DFT expression of the energy is:[292]

$$U_{\text{DFT}} = E[\rho_{\min}(\mathbf{r}); \mathbf{R}_A] - NE_{\text{H}_2\text{O}}. \tag{7}$$

$$E[\rho(\mathbf{r}; \mathbf{R}_A)] = \frac{-1}{2} \sum_{i=1}^{N_e} \int \Psi_i(\mathbf{r}) \nabla^2 \Psi_i(\mathbf{r}) d\mathbf{r} + E_{\text{XC}}[\rho(\mathbf{r})]$$

$$+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 - \sum_{A=1}^{M} \int \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \rho(\mathbf{r}) d\mathbf{r}, \tag{8}$$

where $\rho(\mathbf{r})$ is the electronic density at point $\mathbf{r}$ approximated by the sum of the contributions of different orbitals Ψ_i, i.e., $\rho(\mathbf{r}) = \sum_{i=1}^{N_e} |\Psi_i(\mathbf{r})|^2$. The term E_{XC} is the exchange correlation functional (which is not known exactly). The interaction energy, U_{DFT}, for a system of N molecules of water is obtained in a DFT calculation as the difference between the energy of the system at a certain configuration E and that of N isolated water molecules ($E_{\text{H}_2\text{O}}$). The electronic density for a certain configuration of the nuclei $\mathbf{R}_A$ is obtained by minimizing the functional $E(\rho)$ subject to an orthonormality condition between orbitals.

For the rigid non-polarizable models considered in this work the energy U_{rnp} is given as:

$$U_{rnp} = \sum_i \sum_j 4\varepsilon[(\sigma/R_{ij})^{12} - (\sigma/R_{ij})^6]$$

$$+ \sum_i \sum_j \sum_\alpha \sum_\beta \frac{q_{i\alpha} q_{j\beta}}{R_{i\alpha j\beta}}, \tag{9}$$

where the indices i and j run over the N molecules of water and the α, β indices over the partial charges of each molecule. It is clear that such different mathematical expressions cannot yield identical results for all thermodynamic properties for all thermodynamic states.[235,236] Louis and coworkers have discussed in detail the issue of describing the properties of a Hamiltonian by another simpler Hamiltonian[235,236] introducing the concepts of representativity and transferability. The representativity is the possibility of reproducing as many properties as possible of the complex Hamiltonian at a certain thermodynamic state by the simpler Hamiltonian. The transferability is the possibility of using the same simple potential to reproduce properties of the complex Hamiltonian at different thermodynamic states. Thus the failure of rigid non-polarizable models in describing simultaneously the vapour and the liquid is a transferability problem and the problem in describing C_{p} is a representativity problem. In fact, the Hamiltonian used in path integral simulations is different from that used in classical simulations (the classical simulation is recovered when using a single bead $P = 1$). For this reason if one forces the classical Hamiltonian to reproduce the energy of the quantum simulation, one should not expect the fluctuations in the enthalpy (which determine C_{p}) between both systems to become identical.

Matching the energy is possible, matching both the energy and their fluctuations is asking for too much. A similar line of reasoning may also be applied to the dielectric constant.

V. Conclusions and outlook

In this work a test has been proposed to evaluate the performance of water models. We have applied the test to rigid-non-polarizable models obtaining scores (out of a maximum score of 10) ranging from about 3 (TIP3P) to about 7 (TIP4P/2005). Thus although none of the water models considered here is perfect, some water models are clearly better than others. The TIP4P/2005 can be regarded as a small variation on the first model of water, proposed by Bernal and Fowler in 1933.[42] Thus it has taken about 80 years to optimise the parameters and to analyse the capacity of this potential model.[293] No doubt it is a reasonable model of water. Taking into account its simplicity (a few charges plus a LJ centre) it is somewhat surprising how many properties can be described. The overall score of TIP4P/2005 (about 7 points) in the test proposed in this work is probably not far from the maximum score that can be obtained for a rigid non-polarizable model. However there is still room for a modest improvement. Including anisotropy in the repulsive part of the potential would certainly be beneficial (a possibility is to include LJ centres also on the hydrogens and not just on the oxygen atom). Also, replacing the repulsive part of the LJ potential by an exponential function (as suggested by quantum chemistry) may also be beneficial at high pressures. Increasing the number of charges could also improve the results. Charge distributions like that used in the six site model of Nada and van der Eerden deserve further studies.[47] However our impression is that those modifications would not increase the number of points in the test above, say, 7.6. The reason for this "feeling" is that these changes do not address the real deficiencies of rigid non-polarizable models: the lack of polarization and the neglect of nuclear quantum effects. To obtain a significant improvement in the score these issues should be addressed. In any case the test proposed in this work could be useful in the future to determine the real limit (in score) of a rigid non-polarizable model. To help the implementation of the test for other water models, or for other different choices of the tolerances we provide the results of Tables 2–4 in a Worksheet Excel format as ESI.†

The lack of polarizability in these models prevents an accurate description of the properties of the gas phase, of the critical pressure, of the dielectric constant and of a simultaneous description of the vaporisation enthalpy and critical temperature. The fact that these models are used within classical statistical mechanics prevents them from describing the heat capacity (even at room temperature) and also the description of certain properties (including the equation of sate) at low temperatures (say below 120 K) not to mention the structure which is most likely severely affected by nuclear quantum effects. After considering the deficiencies it seems timely to consider possible areas of research to go one step further in the modelling of water.

A. Including nuclear quantum effects

The inclusion of nuclear quantum effects will improve the description of water properties. This is true regardless of whether the potential energy of the system is obtained from an empirical expression or from electronic structure calculations. Because of the low mass of the hydrogen nuclei, classical simulations of an accurate potential energy surface cannot reproduce the experimental properties of water, especially at low temperatures. Future modelling of water should take into account the impact of nuclear quantum effects in water not only in thermodynamic but also in transport properties.[38,294] Since the procedure to perform path integral simulations (both for flexible and rigid models[27,234,295]) is now well established and some simulation packages already incorporate path integral simulations (AMBER[296] for instance) we forecast important advances on this area, the main limitations being the computer time and the existence of an accurate description of the PES of water.

B. Including polarization: electronic structure calculations

When solving the electronic Schrodinger equation the changes in the electronic charge distribution (polarization) occur in a natural way. If the Schrodinger equation could be solved exactly in condensed matter the problem of water modelling would be solved. But, due to computational limitations, this is not the case and one should use simpler ways to approach the problem of electronic structure, for instance DFT calculations. For current computational standards DFT calculations in condensed matter are still quite intensive. It is possible nowadays to perform DFT simulations for about 100 molecules lasting about 10 ps (using classical statistical mechanics to describe the motion of the nuclei). In fact, recent progress has been made over the last few years in this area by determining the vapour liquid equilibria,[297,298] the ice VII–ice VIII and water–ice VII coexistence[299,300] or the water–ice I_h equilibria.[21] A serious problem with DFT calculations is that dispersion forces are usually missing although this is changing in more recent implementations.[22,301] Another problem is that the functional is only approximate. That may explain why some results are somewhat deceptive (i.e., the critical temperatures are quite low[297] and the melting temperatures can be as high as 420 K). In any case this should be an area of active research. Of particular interest would be to determine the relative energy between the solid phases of water at 0 K[170,302] from DFT calculations[303–307] and the determination of the phase diagram of water. If current functionals are not successful new functionals should be proposed. Progress in this area is expected in the forthcoming years.

C. Including polarization: simplified approaches

An alternative to costly DFT calculations is to introduce the polarizability without solving the Schrodinger electronic equation. The need to include polarization to describe water properties was already advocated in the seventies[266,308–311] More recently models like the TIP4P-FQ of Rick et al.,[312] the POL3 model of Caldwell and Kollman,[313] the POL5 of Stern et al.,[153] the BSV model,[314] the MCHDO of Saint-Martin et al.,[315,316] the TIP4P-pol2 of Siepmann et al.,[317] the AMOEBA model of Ren and Ponder,[318] the charge on spring model of Yu and van Gunsteren,[319] the Gaussian charge polarizable model of Paricaud et al.,[279] the TTM models of Xantheas and

coworkers,[10,320] the polarizable model of Baranyai and Kiss,[285] the three body model of Skinner et al.,[280] the charge transfer model of Lee and Rick,[321] the TIP4P-QDP models of Bauer and Patel[322] and the model of Jordan and coworkers,[11] are only but a few examples of polarizable models proposed in the last two decades. The parameters of the polarizable models are obtained by either fitting experimental properties or via ab initio calculations for water clusters. Polarizable models should significantly reduce the problems of transferability exhibited by rigid non-polarizable models and, in principle, should obtain a higher score than that obtained by a good non-polarizable model. However, that should not be taken for granted (for instance, just to mention two examples, the melting point of POL3 is of 180 K[323] whereas that of TIP4P-FQ is of 303 K[120]). Besides, some representativity problems may still exist for empirical polarizable model since this is the price one pays when the exact solution of the Schrodinger equation is replaced by a simpler empirical methodology. The area of the modelling of water mixtures and ions in solution (not considered in this paper) would also greatly benefit from the introduction of polarizability in the simulations[324–326] since then the molecules would be sensitive to the chemical environment.

D. Including flexibility

In this work we have been concerned with rigid water models. It can be argued that the molecular vibrations induce fluctuations in the molecular dipole moment which increase its average value with respect to the counterpart rigid model.[327] This typically affects the results by increasing the critical temperature,[328] the surface tension[328,329] and the dielectric constant.[330] It is to be seen whether these improvements are consistent and do not imply poorer predictions for other properties. If the overall effect corresponds simply to an increase in μ, the same effect could also be achieved by a rigid model with a dipole moment similar to the average μ of the flexible one. If we intend to use classical simulations then we see little advantage in introducing flexibility. The intramolecular vibrations are basically quantum so the way they are treated within classical simulations is incorrect. Moreover, introduction of flexibility does not correct the problems found in rigid non-polarizable models. More in particular it does not solve the problem of polarization. Also, performing classical simulations of a flexible model does not solve the problem of the existence of nuclear quantum effects in water either. Third law properties are not recovered and the predictions of the heat capacities worsen (there will be a contribution of $1/2 R$ to C_p for each intramolecular degree of freedom which is totally wrong). The point of view that there is little advantage of using flexible models within classical simulations has been addressed before by van Gunsteren and coworkers.[331] Of course if one is interested in the study of intramolecular vibrations (for instance to determine IR or Raman spectra) then rigid models are not at all useful and a flexible model would be necessary.[332,333]

Things are different if one calculates the true PES of water whilst including nuclear quantum effects. In this case of course the electronic cloud changes, and molecular geometry changes would appear in a natural way. There is no doubt that, in a full quantum treatment of water, the molecule should be flexible,

and only in this way one could obtain a score of ten points in a test such as that proposed in this work.

E. Computational efficiency

Let us now discuss how the computer time increases when going from the rigid non-polarizable models to more sophisticated ones. We shall arbitrarily assign the value of one to the computational cost of classical simulations for a rigid non-polarizable model. An important feature is that the highest frequency sampled by the simulation changes from about 800 cm^{-1} for rigid models (the frequency of the intermolecular librational moves) to about 3800 cm^{-1} for flexible models (the OH stretching frequency). Thus the computational cost increases by a factor of 5 for flexible models since the 1 fs time step (commonly used for rigid models) should be replaced by a time step of 0.2 fs (commonly used for flexible models). Including nuclear quantum effects increases the computer time by a factor of P, where P is the number of replicas required to sample properly the quantum degrees of freedom. Typically P is chosen as $P > (h\nu)/(kT)$ where ν is the maximum frequency to sample. According to that, for $T > 250$ K the computational cost increases by a factor of 7 for rigid models and by a factor of 35 for flexible ones (the computational overhead being even larger at lower temperatures). If some kind of polarizability is included in the model, then there must be a factor of about 6 in the computational cost, which is a rough estimate of the increased cost associated with empirical models requiring a self-consistent approach to obtain the energy of a certain configuration[334] (which typically requires six iterations), or by a factor of at least 1000 if an approximate procedure to solve the Schrodinger equation (DFT) is required. The results of the computer time required by different approaches to water modelling are presented in Table 5. The computer time increases by more than five orders of magnitude when going from the simple rigid non-polarizable model to models that include nuclear quantum effects in which the energy is evaluated by DFT on the fly. Between these two limits there are a range of different possibilities. Introducing computational tricks[335] that reduce the differences in computational times would be greatly beneficial. For instance, in fluctuating charges models, polarizability is introduced but the computational overhead is only of two[153] (instead of the factor of 6 for other polarizable models). Also tricks have been proposed by Manolopoulos and coworkers[336] to reduce the computational cost of polarizable models of water within path integral simulations. Developments aimed at reducing the computational cost of DFT calculations would also be welcome. The area of algorithms and methodology aimed to reduce the computational cost of modelling water with more sophisticated treatments are required and we anticipate that this will be an active area of research in the future. Thus the computer times presented in Table 5 should be regarded as upper limits of the computational overhead since when implementing new special algorithms/methodologies the overhead will indeed be reduced.

F. Coarse graining

Finally there is growing interest in developing "coarse grained" water models.[337–345] There is no clear definition of what should be

Table 5 Computational cost of performing simulations for water. The computational cost assigned to classical simulations of rigid non-polarizable models is set to one. Models are divided into two families. Models where the energy of the system is obtained from an empirical expression (whose parameters were determined either fitting experimental results or *ab initio* results for clusters), and models where electronic structure calculations are carried out to evaluate it. If the model is flexible the computational cost increases by a factor of 5 due to the smaller time step required. If nuclear quantum effects are included the computational cost increases by a factor of 7 for rigid models and of 35 for flexible models (number of beads required to deal with nuclear quantum effects). If polarizability is introduced within an empirical potential the computational cost increases by a factor of 6. Finally we assume that evaluating the energy for a certain configuration from DFT calculations is 1000 times more expensive than its evaluation for an empirical potential

Potential	Flexibility	Quantum	Polarizability	Computational cost
Empirical	—	—	—	1
Empirical	—	—	√	6
Empirical	—	√	—	7
Empirical	√	—	—	5
Empirical	—	√	√	$7 \times 6 = 42$
Empirical	√	—	√	$5 \times 6 = 30$
Empirical	√	√	—	$5 \times 35 = 175$
Empirical	√	√	√	$5 \times 35 \times 6 = 1050$
DFT	√	√	—	$1000 \times 5 \times 35 \times 1 = 175\,000$
DFT	√	—	—	$1000 \times 5 \times 1 = 5000$
DFT	—	√	—	$1000 \times 1 \times 7 \times 1 = 7000$
DFT	—	—	—	$1000 \times 1 \times 1 \times 1 = 1000$

understood by a "coarse grained" model. All models that reflect water interactions in an approximate manner can be considered to be "coarse grained". It is common practice to denote as "coarse grained" water models those that are simpler and therefore computationally faster than the rigid non-polarizable models presented in this work. It is unlikely that "coarse grained" models of water can improve the global score obtained by the best rigid non-polarizable models. However for certain applications it may be enough that they describe certain (but not all) properties of water with sufficient accuracy (for the same reason it may be reasonable to choose a rigid non-polarizable model that, although not the best from a global point of view, is reasonable for a selected set of properties of interest[346]). The lower computational cost of coarse-grained models allow us to sample times and system-sizes not currently affordable with rigid non-polarizable models. Let us just describe some coarse-grained models of water. In some models the charges have been replaced by short ranged directional sites as in the models developed by Kolafa and Nezbeda[338,339,347,348] which can be used along with Wertheim's[349] TPT1 perturbation theory.[350,351] The same spirit is behind the Mercedes–Benz model of water[352,353] which induces tetrahedral ordering through short range directional attractive forces. In other cases directional forces, aimed to induce tetrahedral arrangements, are introduced by including three body forces as in the mW model of Molinero and Moore.[341] Another possibility is including several water molecules within a unique interaction site as in the model of Zhe, Cui and Yethiraj.[342] Finally, there are models where the discrete partial charges are replaced by ideal multipoles.[354,355] There is no doubt that the area of coarse graining of water is an area of rapidly growing interest.

Significant progress along these lines in the future can be anticipated. The hope is that the score of 7 points obtained by a rigid non-polarizable model of water on the test proposed in this work is improved by more sophisticated ways of describing water. Although the payback will be the computational overhead.

Acknowledgements

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