

# Can simple models describe the phase diagram of water?

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## Abstract

The melting point of ice  $I_h$  for the TIP3P, SPC, SPC/E, TIP4P, TIP4P/Ew and TIP5P models has been determined by computer simulation. It has been found that the melting points of ice  $I_h$  for these models are 146, 190, 215, 232, 245 and 274 K respectively. Thus from the models of water available so far only TIP5P reproduces the experimental melting point of water. The relative stability of ice II with respect to ice  $I_h$  at the normal melting point has also been considered. Ice II is more stable than ice  $I_h$  for the TIP3P, SPC, SPC/E and TIP5P models. Only for the TIP4P and TIP4P/Ew models is ice  $I_h$  more stable than ice II at low pressures. The complete phase diagram for the SPC/E, TIP4P and TIP5P models has been computed. It has been found that SPC/E and TIP5P do not correctly describe the phase diagram of water. However, TIP4P provides a qualitatively correct description of the phase diagram of water. A slight modification of the parameters of the TIP4P model yields a new model, denoted as TIP4P/ice, which reproduces the experimental melting point of water and provides an excellent description of the densities of all ice phases.

## 1. Introduction

Water is, without a shadow of a doubt, an essential molecule. For this reason an improved understanding of its physical properties is clearly an important problem. In the liquid phase water presents a number of anomalies when compared to other liquids [1, 2]. In the solid phase it exhibits one of the most complex phase diagrams, having thirteen different solid structures, nine of them being thermodynamically stable and four of them being metastable. The experimental study of the phase diagram of water has spanned the entire 20th century, starting with the pioneering work of Tammann and Bridgman [3, 4] up to the discovery of the latest known phase of water, ice XII [5]. The existence of several types of amorphous phase at low temperatures [6, 7] and the possible existence of a liquid–liquid phase transition in water [8] has also been the focus of much interest in the last two decades.

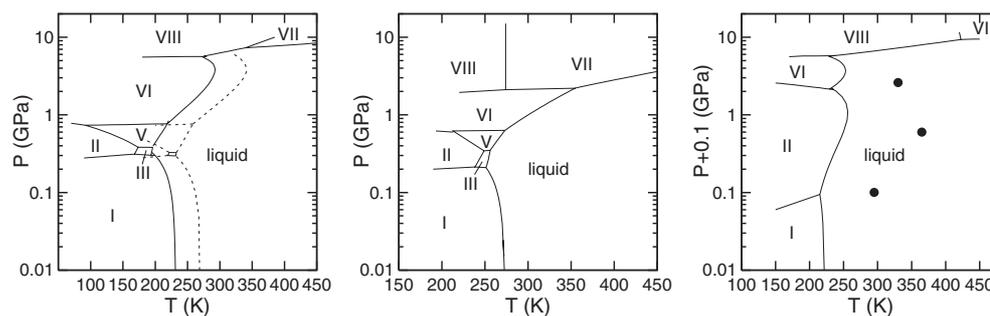
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Water is also challenging from a theoretical point of view. The first computer simulations of water were performed by Barker and Watts [9] and by Rahman and Stillinger [10] in the early 1970s. For obvious reasons computer simulations of water have focused mostly on the liquid state. In the most popular models [11], water is treated classically, often as a rigid non-polarizable molecule with the positive charge located on the hydrogen atom and a Lennard-Jones interaction site located on the oxygen atom. Differences appear in the location of the negative charge. When the negative charge is located on the oxygen atom one has the family of models with three interaction sites formed by TIP3P [12], SPC [13], and SPC/E [14]. When the negative charge is located on the H–O–H bisector the model has four interaction sites, as is the case of TIP4P [12], and the new potential TIP4P/Ew [15]. When the negative charge is located on the ‘lone pair electrons’ one has a model with five interaction sites as with TIP5P [16]. Values of the parameters for these potential models were chosen to reproduce the experimental values of the density and enthalpy of vaporization of liquid water at room temperature [17]. The ability of these models to describe the fluid–solid and solid–solid equilibria is largely unknown (more is known about the vapour–liquid equilibrium [11]). Studies of the solid phases and/or the fluid–solid equilibria are scarce [18–20]. Early work by Morse and Rice [18] showed clearly that the old potential models of the 1970s do not correctly describe the densities of the ices. Haymet *et al* [21, 22] have studied the fluid–ice  $I_h$  interface. Baez and Clancy [23] undertook the first attempt to determine the phase diagram for a water model: SPC/E. The melting temperature of ice  $I_h$  for other different potential models have been determined recently by several groups, including the work of Tanaka *et al* [24] and that of Nada and van der Eerden [25].

Taking into account the importance of water, and the question of whether the current models of water can be used to describe the solid phases (ices) or even to predict the phase diagram, a systematic study has been undertaken [26–33] of the solid state behaviour of the liquid ‘water models’.

## 2. Simulation details

The equation of state of liquid and solid water was obtained by using the NpT Monte Carlo technique. The Lennard-Jones (LJ) interaction was truncated at 8.5 Å and a long-range correction to the energy was added [34]. To deal with electrostatics the Ewald summation method was employed, truncating the real space sum at 8.5 Å. For the liquid phase isotropic NpT simulations were used, whereas for the solid phases anisotropic NpT simulations (Parrinello Rahman like) were performed [35]. For proton ordered solids the initial configurations were taken from crystallographic data. For proton disordered ices the configurations were generated using the procedures proposed [28, 36] to guarantee that the Bernal–Fowler rules are satisfied [37] and that the simulation box has zero or very small dipole moment (typically smaller than 0.9 Debye for the whole system which has between 300 and 600 molecules depending on the type of solid). The residual free energy of the liquid was computed by following a thermodynamic path in which the charges are gradually switched off so that the water models transform into the LJ model (for which the residual free energy is known [38]). For example for the TIP4P model at  $T = 300$  K and  $p = 1$  bar (where the density of the model is  $\rho = 0.994$  g cm<sup>-3</sup>) we obtained an excess Gibbs free energy of  $-6.09$  kcal mol<sup>-1</sup>, which is in good agreement with the previous estimate of Jorgensen *et al* [39] (i.e.  $-6.1$  kcal mol<sup>-1</sup> at  $T = 298$  K). The free energy of the solids was evaluated using the Einstein crystal method of Frenkel and Ladd [40] as implemented for angular molecules by Vega and Monson [41]. For disordered solid phases, the Pauling entropy  $S/R = \ln(3/2)$  or its extension to partial ordered [28] is added to account for the degeneracy resulting from the possible hydrogen bond



**Figure 1.** Phase diagram of water as obtained from experiment (centre), for the SPC/E model (right) and for the TIP4P and TIP4P/ice models (left). Left side, solid lines (TIP4P), dashed lines (TIP4P/ice). Right side, lines: coexistence line of SPC/E; symbols: stability limit of the ice phases (note the shift of 0.1 GPa in  $p$  for this model).

arrangements, consistent with the ice rules. Once an initial coexistence point between two phases is found the coexistence line is traced out using the Gibbs–Duhem integration proposed by Kofke [42] (which is basically a numerical integration of the Clapeyron equation). This was performed for both the SPC/E and the TIP4P models of water. The information obtained in this way can be very useful when it comes to producing the phase diagram for a different potential model. For this purpose one can use ‘Hamiltonian’ Gibbs Duhem integration which allows one to determine the melting line of a model potential starting from the melting line of a distinct potential model. Details of just how this procedure can be applied to models of water have been reported elsewhere [32].

### 3. Results

#### 3.1. Mechanical stability. Density predictions.

NpT simulations have been performed for ice  $I_h$ ,  $I_c$ , II, III, IV, V, VI, VII, VIII, IX, XI and XII (only ice X was not considered) for the thermodynamic conditions reported in table 11.1 of the book by Petrenko and Whitworth [2] using the SPC/E, TIP4P, TIP4P/Ew, TIP4P/ice and TIP5P water models. A detailed list of the thermodynamic states considered can be found elsewhere [26, 31]. The TIP4P/ice is a new water model proposed recently by our group to describe ice phases. It is essentially a TIP4P-like model with slightly different parameters [33]. For these conditions it was found that the ices were mechanically stable for all of the water models (with the exception of ice VII which melted spontaneously, but was stable at higher pressures). It was found [30] that at constant pressure ices can be superheated up to 90 K above the equilibrium coexistence point [30, 43], where the chemical potential and pressure of both phases become identical (see figure 1). Superheating a solid is a rare phenomenon in experimental work, but it is the rule when performing simulations of bulk solid phases (i.e. having no interfaces or defects). It was also found that amorphous phases of water can be obtained at low temperatures. In fact at constant temperature a high-density amorphous phase is obtained by compressing ice  $I_h$  to pressures above those of the melting line, and by expanding ices VII and VIII to pressures below those of the melting line [29].

Concerning the predictions of the densities for ice phases it was found that SPC/E, TIP4P and TIP4P/Ew overestimate the experimental density by about 2–3%. This degree of agreement is remarkable considering that these models were not designed to study solid phases. The

**Table 1.** Melting properties of ice  $I_h$  at  $p = 1$  bar for different models.  $T_m$  is the melting temperature (K);  $\rho_l$  and  $\rho_{I_h}$  are the coexistence densities ( $\text{g cm}^{-3}$ ) of liquid water and ice;  $\Delta H$  is the melting enthalpy ( $\text{kcal mol}^{-1}$ );  $\Delta V$  is the volume change at melting ( $\text{cm}^3 \text{mol}^{-1}$ );  $dp/dT$  is the slope of the coexistence curve ( $\text{bar K}^{-1}$ ). Results for NvdE were taken from Nada and van der Eerden [25].

Model	SPC	SPC/E	TIP4P	TIP4P/Ew	TIP5P	NvdE	TIP4P/ice	Exptl
$T_m$	190.5	215	232	245.5	273.9	271	272.2	273.15
$\rho_l$	0.976	1.019	0.991	0.987	0.982	0.989	0.985	0.999
$\rho_{I_h}$	0.934	0.950	0.940	0.936	0.967	0.917	0.906	0.917
$\Delta H$	0.62	0.74	1.00	1.05	1.75	1.53	1.29	1.44
$\Delta V$	-0.83	-1.28	-0.99	-0.99	-0.28	-1.43	-1.59	-1.61
$dp/dT$	-162	-112	-183	-181	-929	-156	-120	-135

TIP5P model overestimates the ice densities by about 7%. The TIP4P/ice model yields the best results, with an error of 1%.

### 3.2. Melting points for ice $I_h$

In table 1 the melting point and coexistence densities of ice  $I_h$  for SPC, SPC/E, TIP4P, TIP4P/Ew, TIP5P, NvdE, and TIP4P/ice are given. For TIP3P (not included in the table) and SPC the deviation of the melting temperature from experiment is greater than 80 K. For SPC/E and TIP4P the deviations are 58 and 40 K respectively. TIP4P/Ew is an improvement over TIP4P and melts at only 28 K below the experimental value. Models designed to reproduce the density and vaporization enthalpy of liquid water, in general, yield too low melting temperatures and too low melting enthalpies (with TIP5P being the only exception). The only three models reproducing the melting point of water are TIP5P, the model of Nada and van der Eerden (denoted here as NvdE) and TIP4P/ice. TIP5P yields poor predictions of the coexistence densities and of the slope ( $dp/dT$ ) of the coexistence curve. NvdE and TIP4P/ice (designed to reproduce melting properties) provide good agreement with experiment. The model of Nada is computationally more expensive than TIP4P/ice since it requires the determination of 30 distances versus the TIP4P/ice that requires the determination of only 10. TIP4P/ice reproduces ice densities (see the previous section) and the phase diagram of water (see the next section) better than any other water potential model proposed so far, although the performance of NvdE remains to be seen. No model reproduces exactly the melting enthalpy of ice  $I_h$ , although the NvdE and the TIP4P/ice provide a quite good estimate.

### 3.3. Phase diagram

The phase diagrams for SPC/E, TIP4P, and TIP4P/ice have been computed. Preliminary results for TIP5P can be found elsewhere [32]. All solid structures of water apart from ice X were considered. Results are presented in figure 1. The main conclusions from figure 1 are as follows.

- The SPC/E model incorrectly predicts the phase diagram of water. TIP5P provides a similar phase diagram [32]. In both cases ice II becomes so stable that it dominates the phase diagram. In fact ices III and V disappear from the phase diagram (they are less stable than ice II). The same is true for ice  $I_h$  (for these two models ice  $I_h$  is only stable at negative pressures). The stable solid phase at the normal melting pressure ( $p = 1$  bar) for these models is ice II. The melting temperature at  $p = 1$  bar of ice II is between one (SPC/E) and eight degrees (TIP5P) above those calculated for ice  $I_h$  as reported in table 1.

- The TIP4P model is able to qualitatively describe the phase diagram of water. The phase diagram of TIP4P/ice is similar to that of TIP4P but shifted to higher temperatures by about 40 K (providing better agreement with experiment).
- The free energy differences between ice  $I_h$  and  $I_c$ , and between ice V and ice XII, were smaller than our statistical uncertainty, so a definitive conclusion about their relative stability cannot be established.
- All models failed to describe the high-pressure region of the phase diagram (i.e., the freezing to ices VII and ices VIII). The melting pressures of ices VII and VIII from the simulations are too high by a factor of two or more when compared to experiment. At low temperatures the proton disordered ice  $I_h$  transforms into a proton antiferroelectric [44] ordered structure (ice XI like). For TIP4P the transition was located at  $T = 18$  K. For SPC/E the transition was located at  $T = 84$  K. For TIP5P it occurs at a temperature of about 180 K. These results are in agreement with those from Rick [20]. For other models (NvdE, SPC, TIP4P/ice, TIP4P/Ew) it remains to be studied whether this transition also occurs.
- All models of water predict the existence of re-entrant behaviour (i.e., a change of slope of the melting curve in the  $p$ - $T$  diagram) for the ices of moderate density (II–VI). This possibility was first suggested by Tammann a century ago. The difference in compressibility between liquid water and ices provokes this re-entrant behaviour [26, 32].
- The phase diagram is a stringent test for any water model. A good model of water should provide at least a reasonable description of the solid phases as was first suggested by Morse and Rice [18], Whalley [45] and Finney [46]. For this reason the study of ices may be useful in improving current liquid water potentials. The location of the negative charge appears to be the crucial factor when determining the aspect of the phase diagram. For models locating the negative charge on the oxygen (SPC, SPC/E, TIP3P) or on the ‘lone pair electrons’ (TIP5P), it is found that ice II becomes too stable and dominates the phase diagram of water. Notice that in the quantum mechanical calculations of Clementi *et al* [47] the negative charge was finally located on the H–O–H bisector (as in the TIP4P, TIP4P/Ew and TIP4P/ice models). In the very first model of water, proposed by Bernal and Fowler [37] in 1933, the negative charge was also located on the H–O–H bisector. By looking again at figure 1 the question arises: why did we decide to move the negative charge from there?

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