

## Phase Diagram of Water from Computer Simulation

E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell

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

(Received 18 November 2003; published 22 June 2004)

The phase diagram of water as obtained from computer simulations is presented for the first time for two of the most popular models of water, TIP4P and SPC/E. This Letter shows that the prediction of the phase diagram is an extremely stringent test for any water potential function, and that it may be useful in developing improved potentials. The TIP4P model provides a qualitatively correct description of the phase diagram, unlike the SPC/E model which fails in this purpose. New behavior not yet observed experimentally is predicted by the simulations: the existence of metastable reentrant behavior in the melting curves of the low density ices (I, III, V) such that it could be possible to transform them into amorphous phases by adequate changes in pressure.

DOI: 10.1103/PhysRevLett.92.255701

PACS numbers: 64.70.Kb, 61.50.Ks, 64.70.Dv, 87.15.Aa

Water is present on Earth as a gas, a liquid, and a solid (as ice I). It provides the substrate where all biological processes occur and it is the most common of all solvents. Most of the water models that have been developed so far have been tailored to mimic liquid water properties [1,2]. The unique polymorphism of the solid phases of water was documented long ago by Tammann and Bridgman [3]. Nine stable and another four metastable solid phases have been reported [4–7]. For this reason, it has been recognized that the prediction of freezing [8–11] and high pressure properties constitute a severe test [12].

After 30 years of computer simulations of water [13] we present here a comparison of the high pressure phase diagram for two of the most popular models of water, namely, the TIP4P and the SPC/E. The TIP4P model was proposed by Jorgensen *et al.* [1] In this simple model a single Lennard-Jones (LJ) interaction site is located at the position of the oxygen atom. Two positive point charges are located in the positions of the hydrogen atoms, and a negative charge is located 0.15 Å away from the oxygen along the H-O-H bisector in the direction of the positive charges. This geometry was originally suggested by Bernal and Fowler [14]. In the SPC/E model, first proposed by Berendsen *et al.* [2], the LJ interaction site and the negative charge are located at the position of the oxygen atom. Positive charges are located on the hydrogen atoms (at a distance of 1 Å from the oxygen and forming a tetrahedral angle). Both models simplify the true interaction between water molecules (i.e., they neglect molecular flexibility, polarizability, quantum effects, etc.) but do have the advantage of economy and one may wonder how far it is possible to go with such simple models.

In our simulations, the pair potential was truncated for all phases at 8.5 Å. Standard long range corrections to the LJ energy were added. Ewald sums were employed for dealing with the electrostatic interactions. Isotropic isobaric isothermal (NpT) Monte Carlo simulations were performed for the liquid phase. Anisotropic

NpT Monte Carlo simulations (Rahman–Parrinello-like) were used for the solid phases [15].

In Table I, NpT Monte Carlo simulation results for the TIP4P and SPC/E models are compared to experimental results for the densities of liquid water and of all known ice phases (except Ice X which cannot be described with these models [6]). For the disordered phases I, Ic, IV, VI, VII, and XII, we used the algorithm of Buch *et al.* [19] to generate a starting configuration having no net dipole moment and where the hydrogens (but not the oxygens) are disordered and satisfy the ice rules. The remaining disordered phases, ice III and ice V, required some additional care, as they are known to exhibit only partial disorder [20]. We generalized the algorithm given in Ref. [19] in order to generate an initial configuration with biased occupation of the hydrogen positions. Both TIP4P and SPC/E overestimate the experimental ice densities by about 2%. Predictions of TIP4P and SPC/E for the internal energy (see Table I) are quite different, being much lower for the SPC/E model. For the SPC/E, Berendsen *et al.* suggested adding the polarization energy which amounts to 1.25 kcal mol<sup>-1</sup>. When this is done, the internal residual energies of SPC/E and TIP4P are similar, although differences are still visible. Taking as a reference the internal energy of the liquid state, the internal energies of ices I and II (for the thermodynamic states of Table I) are -2.01, -2.73 (in kcal mol<sup>-1</sup>) for the TIP4P whereas they amount to -1.78 and -2.92 for the SPC/E model. Obviously these differences should be reflected in the phase diagram.

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 TIP4P transforms into the LJ model (for which the residual free energy is known [21]). The free energy of the solids was evaluated with the Einstein crystal method of Frenkel and Ladd [22] as implemented for angular molecules by Vega and Monson [23,24]. For disordered solid phases, the Pauling entropy,  $S/R = \ln(3/2)$ , is added to account for the

TABLE I. Densities and residual internal energies of the known ice phases as obtained from NpT simulations for the TIP4P and SPC/E models. The experimental data of ices are taken from Ref. [6], except that of ice VII, taken from Ref. [16]. Simulation results from Ref. [17] (labeled with an asterisk) have also been included. For ice I we have also included (labeled with an asterisk) the density of the SPC/E model reported by Gay *et al.* [18].

Phase	$T/K$	$p/\text{GPa}$	exptl.	$\rho/(\text{g cm}^{-3})$		$U/(\text{kcal mol}^{-1})$	
				TIP4P	SPC/E	TIP4P	SPC/E
Liquid	300	$10^{-4}$	0.996	0.994	1.000	-9.87	-11.15
Liquid*	301	$10^{-4}$	0.996	0.992	0.997	-9.82	-11.09
I	250	0	0.920	0.937	0.944	-11.89	-12.93
I*	250	0	0.920		0.947		
Ic	78	0	0.931	0.964	0.971	-13.15	-14.22
II	123	0	1.170	1.220	1.245	-12.61	-14.08
III	250	0.28	1.165	1.175	1.171	-11.58	-12.62
IV	110	0	1.272	1.314	1.300	-12.29	-12.23
V	223	0.53	1.283	1.294	1.294	-11.75	-12.71
VI	225	1.1	1.373	1.406	1.403	-11.65	-12.53
VII	300	10	1.880	1.832	1.822	-8.56	-9.42
VIII	10	2.4	1.628	1.674	1.679	-11.47	-12.31
IX	165	0.28	1.194	1.210	1.219	-12.49	-13.70
XII	260	0.5	1.292	1.314	1.313	-11.35	-12.29

degeneracy resulting from the possible hydrogen bond arrangements consistent with the ice rules [25]. Thermodynamic integration allowed one to obtain the free energies for other thermodynamic states. It was then possible to locate one point of the coexistence line. From this point, the whole melting curve was calculated by using the Gibbs-Duhem method [26,27]. For the TIP4P model, we located the melting temperature of ice I at  $p = 1$  bar to be  $T_m = 232(7)$  K, in agreement with the value  $T_m = 238(6)$  estimated by Gao *et al.* [9]. If the proton charge of the TIP4P model is changed from  $0.52e$  to  $0.5474e$  the experimental melting temperature of water  $T_m = 273.15$  K is reproduced by the new model, but then the coexistence densities deteriorate slightly. For the SPC/E model we located the melting temperature of ice I at  $p = 1$  bar to be  $T_m = 215(7)$  K [a rough estimate by Bryk and Haymet [28] was  $T_m = 225(5)$  K].

For the proton ordered phases ice II, VIII, IX, and the antiferroelectric analogous of ice XI [29] no degeneracy entropy is required. The partially disordered phases III and V [20] required some additional care because the Pauling degeneracy entropy is no longer adequate. We extended the method of Howe and Whitworth [30] to account for the degeneracy entropy in these ices.

Figure 1 shows the phase diagram of the TIP4P model. Ices I, II, III, V, VI, VII, and VIII are found to be stable phases for the TIP4P model (as they indeed are for real water). As in real water ice IV and ice IX are clearly metastable phases for the TIP4P model. We could not resolve either the relative stability of ices I and Ic or that of ices V and XII since the free energy differences were smaller than our typical uncertainties. At a pressure of 1 bar, our results confirm that the stable solid phase of

TIP4P at melting is the proton disordered structure I (or eventually Ic). Concerning the SPC/E model, we found that ices II, VI, VII, VIII are stable solid phases while ices IV and IX are metastable. A major defect of the SPC/E model is that it predicts that ices III and V are metastable which is in clear disagreement with experiment. It also predicts a I-II-liquid triple point at  $T = 215.2$  K,  $p = -60$  bars. The stable phase at  $p = 1$  bar for the SPC/E model is ice II which melts at  $T = 216$  K. A small change in the free energy could introduce ice I in the phase diagram of the SPC/E model but only for a very narrow range of pressures. In summary, although both models show similar performance when describing liquid water, it is clear that such similarity breaks down when the global phase diagram is considered, TIP4P providing a better description of the phase diagram than SPC/E. The appearance of the phase diagram for the SPC/E model at low pressures arises from the extraordinary stability of ice II. Analyzing one by one the differences between TIP4P and SPC/E models (dipole moment, bond length, and angle, location of the negative charge and LJ parameters) it was found that the only difference of TIP4P with respect to SPC/E that reduces the stability of ice II with respect to its competitors (ice I, III, V) is the location of the negative charge. This is the key factor to understanding the differences in the phase diagram between both models at low pressures. Pair potentials obtained from quantum chemistry calculations [31] locate the negative charge on the H-O-H bisector and not on the oxygen atom, and this Letter shows that this is important to obtain a qualitatively correct phase diagram of water.

A surprising feature found in the melting curves of both TIP4P and SPC/E models is the existence of

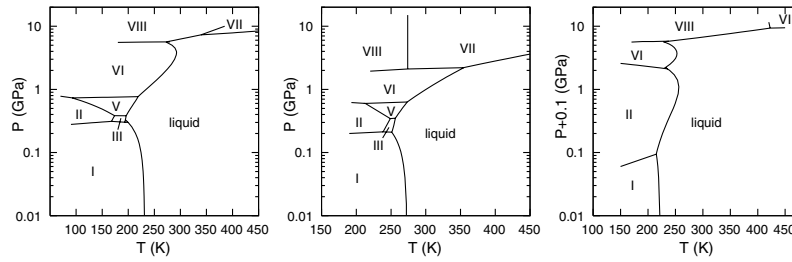


FIG. 1. Phase diagram of H<sub>2</sub>O. Left: simulation results for the TIP4P; right: simulation results for the SPC/E; middle: experimental phase diagram. For the SPC/E the coexistence pressures have been shifted by 0.1 GPa to include results for ice I (which appears for the SPC/E model at slightly negative pressures). Only the stable phases have been included in the diagrams.

reentrant behavior (i.e., a change of sign in the slope of the melting curve in the  $p$ - $T$  diagram). Tammann speculated with this possibility a century ago (as quoted by Bridgman in p. 553 of Ref. [3]). We shall discuss the origin of this behavior. In Fig. 2 the equation of state of TIP4P water and ices I, III, V, VI, and VIII at a temperature of 225 K is shown. Ices exhibit low compressibilities. Liquid water is far more compressible, and at high pressures water becomes more dense than any of the low density ices, namely I, III, V, and VI. Water is never more dense than the high density ice VIII. The ratio of the entropy change and the volume change determines the slope of a coexistence line,  $dp/dT$ . For freezing lines the entropy change is always negative. However, for the low density ices the volume change at freezing is negative at low pressures and positive at high pressures. This provokes reentrant behavior [24] which is clearly visible in the liquid-ice VI coexistence line of the TIP4P model (Fig. 1) (and in some melting curves of the SPC/E model). We obtained such a reentrant behavior in the freezing line of all low density ices (although occurring in the metastable regions). In Fig. 3 an enlarged view of the phase diagram of the TIP4P model in the central region of pressures is presented. The change of slope of the

liquid-ice III and liquid-ice V lines is clearly visible. More surprisingly the liquid-ice I also undergoes a change of slope at negative pressures (around  $-1500$  bars). Henderson and Speedy [32] suggested this change of slope of the liquid-ice I coexistence line by extrapolating their experimental measurements at negative pressures to lower values. Although this reentrant behavior has never been observed in nature, the curvature of the experimental [5] water freezing lines (liquid-ice I, liquid-ice III, and liquid-ice VI) suggest this possibility. Apparently, the reentrant behavior is frustrated in the experimental melting lines because a new ice polymorph appears when the reentrant point is approached. Thus, this work gives a new view of the “anomalous” slope of the experimental liquid-ice I coexistence line as the only ice phase for which the upper part of the reentrant melting line lies in a thermodynamically stable region. Some time ago Mishima *et al.* [33] were able to melt ice I at very low

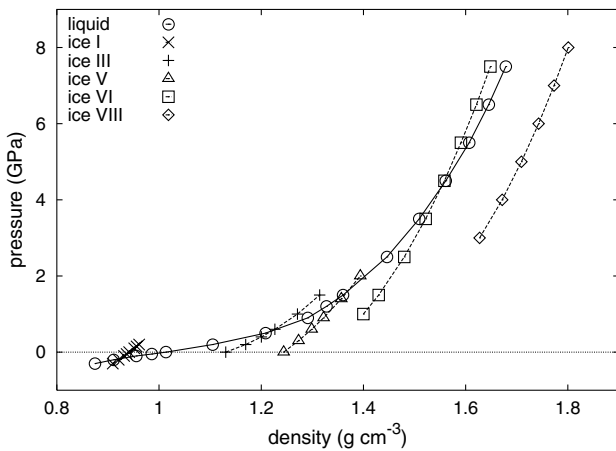


FIG. 2. Isotherms of several H<sub>2</sub>O phases at  $T = 225$  K as obtained from NpT Monte Carlo simulations of the TIP4P model.

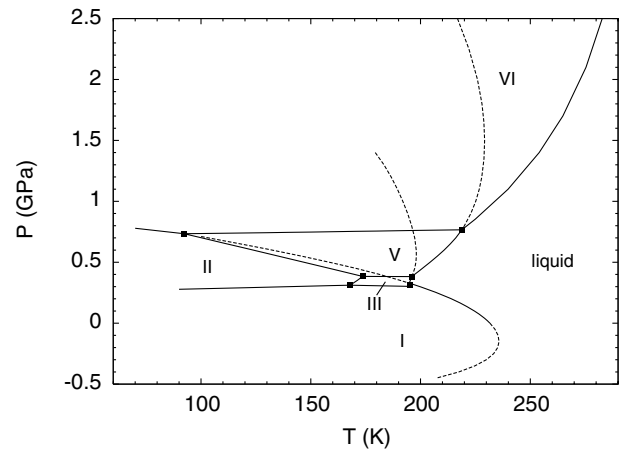


FIG. 3. Detailed view of the central part of the phase diagram of TIP4P water. For the liquid-ice III and liquid-ice V coexistence lines, reentrant behavior is observed although the upper part of the reentrant lies in metastable regions. The liquid-ice I line is also reentrant but, in this case, the upper part of the reentrant corresponds to the thermodynamically stable region and the turning point occurs at negative pressures (about  $-0.15$  GPa and 235 K for TIP4P). Solid line: coexistence lines; dashed lines: metastable coexistence lines.

temperatures ( $T = 77$  K) transforming into a high density amorphous phase. Also ice IV melted into supercooled water when decreasing the pressure [34]. We decided to study this type of melting under pressure for the TIP4P model in three different cases. First, we compressed ice I at 77 K for the TIP4P and found melting to an amorphous phase at  $p = 12\,000$  bars as found previously by Tse and Klein [35] and in agreement with experiment [33]. Second, we compressed ice III at  $T = 196$  K and found spontaneous melting at  $p = 40\,000$  bars (which confirms the reentrant behavior presented in Fig. 3). Finally, we attempted to melt ice I at  $T = 230$  K by applying negative pressures but, rather, we found that at  $p = -8500$  bars the system spontaneously sublimated into a mechanically unstable vapor.

The high pressure phase diagram, with its rich polymorphism of solid phases offers a wonderful opportunity to improve the current models of water. The TIP4P model is able to capture the main features of the experimental phase diagram of water while SPC/E is not. Notice that a nontetrahedral model (TIP4P) exhibits all the tetrahedral arrangements of the ice phases. The slope of the melting lines of ice I, III, V, and VI has its origin in the approach of a reentrant point (where both liquid and solid coexistence phases present the same density). The results of this work suggest that amorphous/liquid phases can be obtained experimentally by applying pressure, not only for ice I as already shown by Mishima *et al.* [33] at very low temperatures, but also to ice III (and V), or by applying negative pressure to ice I at temperatures close to the triple point. It may be worthwhile to search experimentally for these possibilities.

This project has been financed by Grants No. FIS2004-06227-C02-02 and No. BFM2001-1017-C03-02 of the Spanish Dirección General de Investigación. A FPU Ph.D. grant (E.S) and a Ramón y Cajal contract (L.G.M) are gratefully acknowledged. We would like to thank R. García and C. McBride for technical help. We also thank D. Frenkel, J.-P. Hansen, and E. de Miguel for a critical reading of the manuscript.

- 
- [1] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
  - [2] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).
  - [3] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **47**, 441 (1912).
  - [4] B. Kamb, in *Structural Chemistry and Molecular Biology*, edited by A. Rich and N. Davidson (W. H. Freeman, San Francisco, 1968), pp. 507–542.
  - [5] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University Press, London, 1969).

- [6] V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford University Press, Oxford, 1999).
- [7] C. Lobban, J. L. Finney, and W. F. Kuhs, *Nature (London)* **391**, 268 (1998).
- [8] L. A. Baez and P. Clancy, *J. Chem. Phys.* **103**, 9744 (1995).
- [9] G. T. Gao, X. C. Zeng, and H. Tanaka, *J. Chem. Phys.* **112**, 8534 (2000).
- [10] S. W. Rick and A. D. J. Haymet, *J. Chem. Phys.* **118**, 9291 (2003).
- [11] H. Nada and J. P. J. M. van der Eerden, *J. Chem. Phys.* **118**, 7401 (2003).
- [12] J. L. Finney, J. E. Quinn, and J. O. Baum, in *Water Science Reviews 1*, edited by F. Franks (Cambridge University Press, Cambridge, United Kingdom, 1985).
- [13] A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **55**, 3336 (1971).
- [14] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).
- [15] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, San Diego, 1996).
- [16] R. J. Hemley, A. P. Jephcoat, H. K. Mao, C. S. Zha, L. W. Finger, and D. E. Cox, *Nature (London)* **330**, 737 (1987).
- [17] D. van der Spoel, P. J. van Maaren, and H. J. C. Berendsen, *J. Chem. Phys.* **108**, 10220 (1998).
- [18] S. C. Gay, E. J. Smith, and A. D. J. Haymet, *J. Chem. Phys.* **116**, 8876 (2002).
- [19] V. Buch, P. Sandler, and J. Sadlej, *J. Phys. Chem. B* **102**, 8641 (1998).
- [20] C. Lobban, J. L. Finney, and W. F. Kuhs, *J. Chem. Phys.* **112**, 7169 (2000).
- [21] J. K. Johnson, J. A. Zollweg, and K. E. Gubbins, *Mol. Phys.* **78**, 591 (1993).
- [22] D. Frenkel and A. J. C. Ladd, *J. Chem. Phys.* **81**, 3188 (1984).
- [23] C. Vega, E. P. A. Paras, and P. A. Monson, *J. Chem. Phys.* **96**, 9060 (1992).
- [24] C. Vega and P. A. Monson, *J. Chem. Phys.* **109**, 9938 (1998).
- [25] L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
- [26] D. A. Kofke, *J. Chem. Phys.* **98**, 4149 (1993).
- [27] C. Vega, J. L. F. Abascal, C. McBride, and F. Bresme, *J. Chem. Phys.* **119**, 964 (2003).
- [28] T. Bryk and A. D. J. Haymet, *J. Chem. Phys.* **117**, 10258 (2002).
- [29] E. R. Davidson and K. Morokuma, *J. Chem. Phys.* **81**, 3741 (1984).
- [30] R. Howe and R. W. Whitworth, *J. Chem. Phys.* **86**, 6443 (1987).
- [31] O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.* **64**, 1351 (1976).
- [32] S. J. Henderson and R. J. Speedy, *J. Phys. Chem.* **91**, 3069 (1987).
- [33] O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **310**, 393 (1984).
- [34] O. Mishima and H. E. Stanley, *Nature (London)* **392**, 164 (1998).
- [35] J. S. Tse and M. L. Klein, *Phys. Rev. Lett.* **58**, 1672 (1987).