

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2004 issue.

NOTES

Tracing the phase diagram of the four-site water potential (TIP4P)

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(Received 26 March 2004; accepted 15 April 2004)

We present here the phase diagram for one of the most popular water models, the four-point transferable intermolecular potential (TIP4P) model. We show that TIP4P model, does indeed provide a qualitatively correct description of the phase diagram of water. The melting line of the five-point transferable intermolecular potential (TIP5P) at low pressures is also presented. © 2004 American Institute of Physics. [DOI: 10.1063/1.1759617]

Water plays a key role in our relation to Nature. It provides the substrate where all biological processes occur, it is the most common of all solvents and it exists on Earth as gas, liquid and solid. Hence the importance of having a good pair potential for water. Most of the water models that have been developed so far have been tailored to liquid water properties¹ but its performance for predicting solid phase properties have received less attention.^{2,3} We present here the phase diagram for one of the most popular water models, the TIP4P proposed by Jorgensen *et al.*¹ In this model a Lennard-Jones (LJ) interaction site is located on the oxygen, two positive charges are located on the hydrogens and a negative charge is located 0.15 Å away from the oxygen along the H–H bisector.

Initial solid configurations were obtained by using crystallographic data (taken from Ref. 4 and references therein). This is all what is needed in the case of the proton ordered ices (II, IX, and VIII). For the proton disordered ices (I, Ic, IV, VI, VII, and XII), the oxygens were placed on the lattice points, and hydrogen disordered configurations with no net dipole moment and satisfying the ice rules were generated by using the algorithm of Buch *et al.*⁵ For ices III and V which present a certain degree of proton ordering⁶ we generalized the algorithm of Buch *et al.*⁵ to generate initial configurations with biased occupation of the hydrogen positions. Isotropic NpT Monte Carlo simulations were performed for the liquid phase. Anisotropic NpT Monte Carlo simulations (Rahman–Parrinello-type) were used for the solid phases. 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 electrostatic forces beyond the cutoff as in other studies of water.⁷ The number of particles used in the simulations ranged from (288 to 600) and was chosen for each solid phase so as to fit at least twice the

cut-off distance in each direction. The free energy of the liquid phase was evaluated 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 free energy is known⁸). The free energies of the solid phases were evaluated by using the Einstein crystal methodology of Frenkel and Ladd⁹ as described elsewhere.¹⁰ For the ordered ices, the Frenkel and Ladd procedure yields directly the free energy. For the disordered ices a certain averaging over disordered configurations is needed. We found that differences in free energy of several configurations were small and lie within the statistical error bars. Accordingly, we typically evaluated the free energy from a single Einstein crystal calculation and added the Pauling entropy, $S/R = \ln(\frac{3}{2})$, which accounts for the degeneracy resulting from the possible hydrogen bond arrangements consistent with the ice rules. For the partially ordered ices (III and V) the Pauling entropy is not adequate. Rather, we extended the method of Howe and Whitworth,¹¹ in order to account for partial disorder as found in ice III and V.⁶ Once the free energy for a certain state was known we used thermodynamic integration to compute it for other thermodynamic conditions. In this way it was possible to locate at least one coexistence point for each coexistence line. Gibbs–Duhem¹² simulations (i.e., a numerical integration of the Clapeyron equation) using a fourth-order Runge–Kutta integration were used to obtain the full coexistence curve between two coexistence phases.

The phase diagram of the TIP4P obtained in this way is presented in Fig. 1. For the TIP4P model we locate the melting temperature of ice I at $p = 1$ bar to be $T_m = 232(5)$ K, in good agreement with a previous estimate by Gao *et al.*, who found $T_m = 238(6)$ K.² The vapor equilibria of the TIP4P model has been presented elsewhere.¹³ As it can be seen the phase diagram of the TIP4P model presents a qualitative agreement with experiment. Ices I, II, III, V, VI, VII, and VIII were found to be stable phases for the TIP4P model (as

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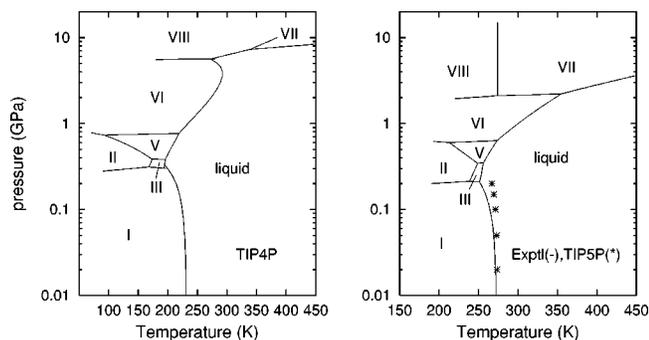


FIG. 1. Phase diagram of H₂O. Left: simulation results for the TIP4P model (due to numerical uncertainties the three coexistence lines do not meet exactly at the same point in the liquid-I-III triple point). Right: experimental values (lines) and simulation results of the melting curve of ice I for the TIP5P model (symbols). Only the stable phases have been included in the diagrams.

they indeed are for real water). Also in agreement with the behavior of real water, the calculations indicated that 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. In both cases the free energy difference found between the considered phases was smaller than the typical uncertainty of our free energy calculations. At a pressure of one bar, our results confirm that the stable solid phase of TIP4P is the proton disordered structure I (or eventually Ic). At very low temperatures (18 K) the proton ordered XI like (antiferroelectric) structure is more stable, in good agreement with recent estimates by Rick and

TABLE I. Entropy and molar volume changes for several coexistence lines at the calculated triple points compared with the corresponding experimental values (taken from Ref. 16).

Triple point	Transition		$\Delta S / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$		$\Delta v / (\text{cm}^3 \cdot \text{mol}^{-1})$	
	From	To	Expt.	Simulation	Expt.	Simulation
liquid-I-III	L	I	-16.8	-16.4	2.434	2.81
	L	III	-15.3	-15.1	-0.839	-0.63
	I	III	1.6	1.3	-3.273	-3.44
liquid-III-V	L	III	-18.0	-14.4	-0.434	-0.21
	L	V	-18.3	-14.3	-1.419	-1.17
	III	V	-0.3	0.1	-0.985	-0.96
liquid-V-VI	L	V	-19.1	-16.1	-0.949	-0.47
	L	VI	-19.2	-16.2	-1.649	-1.19
	V	VI	-0.1	-0.1	-0.700	-0.72
I-II-III	I	II	-3.2	-1.8	-3.919	-3.77
	I	III	0.7	1.3	-3.532	-3.49
	II	III	3.9	3.1	0.387	0.28
II-III-V	II	III	5.1	3.1	0.261	0.22
	II	V	4.8	3.2	-0.721	-0.74
	III	V	-0.3	0.1	-0.982	-0.96

Haymet.³ Certain deficiencies of the TIP4P model are visible in Fig. 1, especially concerning the freezing of water into the high density ices VIII and VII which occurs at too high pressures. Also re-entrant behavior (not found experimentally) is found for the water-ice VI coexistence line of the TIP4P model. In Table I entropy and volume changes at phase transitions are reported. The TIP4P does a good job although there is some room for improvement.

Our results show that computer simulations are a valuable tool for the study of the ices (both stable and metastable) and of the phase diagram of water. The phase diagram of water, with its rich polymorphism of solid phases offers a wonderful opportunity to test and improve the current models of water so widely used in the simulation of biological systems. As an example in Fig. 1 the melting line of ice I (the proton disordered hexagonal ice) is presented for the TIP5P model.¹⁴ Its melting temperature was found to be $T_m = 274(5)$ K in good agreement with experiment and with a previous estimate by Nada and van der Eerden,¹⁵ namely $T_m = 270(7)$ K (although these authors found the proton ordered phase to be more stable when Ewald sums were not included). The ability of the TIP5P model to predict the rest of the phase diagram remains to be tested.

ACKNOWLEDGMENTS

This project has been financed by Grant Nos. FIS2004-06227-C02-02 and BFM2001-1017-C03-02 of Direccin General de Investigacion. A Ramon y Cajal contract (L.G.M.) and a FPU Ph.D grant (E.S.) are gratefully acknowledged. We thank R. Garcia and C. McBride for technical help.

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