Properties of ices at 0 K: A test of water models

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The properties of ices I_h, II, III, V, and VI at zero temperature and pressure are determined by computer simulation for several rigid water models (SPC/E, TIP5P, TIP4P/Ice, and TIP4P/2005). The energies of the different ices at zero temperature and pressure (relative to the ice II energy) are compared to the experimental results of Whalley [J. Chem. Phys. **81**, 4087 (1984)]. TIP4P/Ice and TIP4P/2005 provide a qualitatively correct description of the relative energies of the ices at these conditions. In fact, only these two models provide the correct ordering in energies. For the SPC/E and TIP5P models, ice II is the most stable phase at zero temperature and pressure whereas for TIP4P/Ice and TIP4P/2005 ice I_h is the most stable polymorph. These results are in agreement with the relative stabilities found at higher temperatures. The solid-solid phase transitions at 0 K are determined. The predicted pressures are in good agreement with those obtained from free energy calculations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2774986]

I. INTRODUCTION

Taking into account the importance of water, it is not surprising that thousands of simulation studies of water have been performed since the pioneering works of Barker and Watts[1] and Rahman and Stillinger.[2] Besides, since water is the medium where life takes places, describing water interactions is also important when performing simulation studies of biological molecules in solution. For this reason the search of a water potential that describes in a satisfactory way its properties has been a very active area of research in the last years.[3,4] Many water potentials have been proposed in the literature. The potential parameters are typically obtained to match the experimental density and enthalpy of vaporization of real water. In this way some successful potentials have been proposed. This is the case of SPC,[5] SPC/E,[6] TIP4P,[7] and TIP5P.[8] In these models[3] water is treated classically as a rigid nonpolarizable molecule with the positive charge often located at the hydrogen atoms and a Lennard-Jones (LJ) 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 such as TIP3P,[7] SPC, and SPC/E. When the negative charge is located on the H-O-H bisector the model has four interaction sites, as is the case of TIP4P. When the negative charge is located on the "lone pair electrons" one has a model with five interaction sites as TIP5P.

The emphasis when developing potentials has been the ability of the potential to reproduce the properties of liquid water. The existence of several types of amorphous phases at low temperatures,[9–11] and the possible existence of a liquid-liquid phase transition in water[12–15] has extended the interest in water to the low temperature region. The study by computer simulation of the solid phases of water has received less attention. The experimental study of the properties of ices and of the phase diagram of water has spanned the entire 20th century, starting with the pioneering work of Tammann and Bridgman[16–21] up to the recent discovery of ices XII, XIII, and XIV.[22,23] Compared to the liquid, the study of ices by computer simulation has been more limited. In 1982 Morse and Rice[24] performed a systematic study of the ability of the water potential models available in the seventies to reproduce the properties of several water polymorphs. Since then the interest in determining ice properties from computer simulation has been growing steadily.[25–43] It seems of interest to study by computer simulation the performance of the different water potentials to describe the properties of the solid phases of water (ices) as this may help to improve our understanding of water interactions.

Motivated by this our group has studied in a systematic way the performance of SPC/E, TIP4P, and TIP5P to describe the properties of ices.[44–50] We have found that SPC/E and TIP5P yield a bad prediction of the phase diagram of water.[44,51] In fact, for these models, ice II was more stable than ice I_h at normal pressure and, besides, ices III and V were found to be metastable phases. Moreover, the melting temperature predicted by SPC/E models was quite low.[50] With respect to their ability to reproduce the densities of the different solid polymorphs, it has been found that SPC/E and TIP5P overestimate the density of ices by about 3% and 8%, respectively.[44,49] The failure of these models is in contrast with the success of the TIP4P model[7] which is the natural descendent of the very first model of water proposed by Bernal and Fowler.[52] In fact, the TIP4P model is able to predict reasonably well the phase diagram of water.[44] It predicts ice I_h as the stable solid phase at ambient pressure. The prediction of the densities for the different solid phases of water appears as reasonable (it overestimates the experimental densities by about 2%).[49] The main failure of the model seems to be a melting point about 40 K below the experimental value.[31,44,53–56] In view of these results, it was more or less obvious that the parameters of the TIP4P model could be modified slightly to yield improved performance. It is with

this idea in mind that the TIP4P/Ice (Ref. 57) and TIP4P/2005 (Ref. 58) models were proposed. TIP4P/Ice (Ref. 57) reproduces the melting temperature of water and TIP4P/2005 reproduces the maximum in density of liquid water at room pressure (the impossibility of reproducing simultaneously the temperature of maximum density and the melting point for nonpolarizable models has been reported recently[59]). Besides providing good phase diagrams the two new models TIP4P/Ice and TIP4P/2005 predict quite well the densities of the different ice polymorphs; the typical deviation with respect to the experiment is about −1% for TIP4P/Ice (Ref. 57) and about 1% for TIP4P/2005.[58]

In 1984 Whalley determined the experimental values of the energies of different ice polymorphs (relative to that of ice I_h) at zero temperature and pressure.[60] The goal was to provide data that could be useful to validate different water potentials. As stated in his article "effective potentials that are used to simulate water ought to be tested on the many phases of ice before being treated as serious representations of liquid water". In another subsequent work published in 1987, Handa, Klug, and Whalley determined the relative energies of the ices at zero pressure for a temperature close to 150 K. In this article the zero temperature, zero pressure energies of ices I_h, II, III, V, and VI will be determined for several water models. In particular, we shall consider SPC/E, TIP5P, and TIP4P/2005 and TIP4P/Ice. Our interest is to check whether these simple models are able to describe the experimental values of the relative energies of the different ice polymorphs. A second benefit of the study is that it will allow us to determine the transition pressures at zero temperature between the different ice polymorphs (the same was already illustrated by Whalley using experimental data). We shall focus our attention mainly on the transition between ice I_h and ice II. This is especially important since as stated above ice II has been found to be more stable than ice I_h at the melting point for the models SPC/E and TIP5P and it would be of interest to establish whether this is also true at zero temperature and pressure. An extra benefit of this zero temperature calculations is that they allow us to test in an indirect way the validity of previous free energy calculations. Indeed the coexistence pressures at zero temperature obtained from free energy calculations should be in agreement with those obtained from the direct determination of the properties of the ices at zero temperature and pressure.

II. PROPERTIES AT ZERO TEMPERATURE

The third law of thermodynamics states that for a pure substance the entropy becomes zero at 0 K provided the substance appears in a perfectly ordered crystalline form. It is then important to clarify several issues related with the properties of the systems when they approach 0 K. The first concerns the limiting behavior of the thermodynamic properties at 0 K and the appearance of the coexistence lines between two phases at 0 K (see Ref. 61 for interesting annotations on the low temperature phase stability in connection to the Third Law of Thermodynamics). It is also important to know how a classical statistical mechanics treatment affects the results at these conditions. Finally, we want to discuss here possible methods for the calculation of coexistence properties between two phases at 0 K. In particular, we are interested in the calculation of the coexistence pressure. If we denote as H, V, and S the molar values of the enthalpy, volume and entropy, respectively, then the Clapeyron equation can be written as

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta S}{\Delta V}. \tag{1}$$

This means that the slope of a certain coexistence curve is the entropy change ΔS divided by the volume change ΔV. In general, the difference in volume between two coexisting solid phases is not zero even at zero temperature. The entropy change depends on the considered transition. According to the Third Law of Thermodynamics, the entropy of a perfectly ordered solid is zero at 0 K. Thus, solid-solid phase transitions between perfectly ordered phases show zero slope at 0 K. When one or both of the solid phases are not completely ordered, they have residual entropy at zero temperature and then the slope of the coexistence curve is not null even at zero temperature. It is well known that a number of solid phases of water present residual entropy at zero temperature.[62] This is the case of ice I_h, III, V, and VI. In these structures the oxygen is located on a lattice but the hydrogen atoms are disordered. However ice II is proton ordered and then it has zero entropy at 0 K. Thus, the coexistence curves ice I_h-ice II, III-II, V-II, and VI-II present nonzero slope when approaching 0 K.

The idea of Whalley was to estimate the differences in energy between ices at 0 K from the known experimental values of the coexistence pressures at that temperature. Let us briefly summarize the procedure used by Whalley. At zero temperature the condition of chemical equilibrium between two phases, labeled as phase A and B, respectively, is given by

$$U_A(p_{eq}, T=0) + p_{eq}V_A(p_{eq}, T=0) = U_B(p_{eq}, T=0) + p_{eq}V_B(p_{eq}, T=0), \tag{2}$$

where U is the (molar) internal energy and p_{eq} is the coexistence pressure. Hence, phase transitions between solid phases at zero temperature occur with zero enthalpy change. In the following we shall drop the $T=0$ K indication but it should be understood that the thermodynamic analysis in the rest of this section is only valid at 0 K. The change of internal energy at the equilibrium pressure between phases A and B can be obtained from the previous expression as

$$U_B(p_{eq}) - U_A(p_{eq}) = p_{eq}[V_A(p_{eq}) - V_B(p_{eq})]. \tag{3}$$

This equation can be further transformed. Let us define $\Delta X = X(B) - X(A)$ where X is a certain thermodynamic property. If one assumes that the isothermal compressibility κ_T does not depend on pressure, it follows[60] that

$$\Delta U(p=0) = -p_{eq}\Delta V(p=0) + \tfrac{1}{2}p_{eq}^2\Delta(V\kappa_T). \tag{4}$$

This equation was used by Whalley to estimate $\Delta U(p=0)$ from the knowledge of $\Delta V(p=0)$, p_{eq} and $\Delta(V\kappa_T)$. Notice that whereas Eq. (3) is exact, Eq. (4) contains an approximation. The previous equation can be simplified even further if

one assumes (which is a quite good approximation for ices) that $\Delta(V\kappa_T)=0$. Then it follows

$$\Delta U(p=0) = -p_{eq}\Delta V(p=0). \quad (5)$$

In summary, Eq. (3) is exact, Eq. (4) is an approximation which will be denoted here as first order approximation, and Eq. (5) is another approximation which will be referred to as zero order approximation. The nice feature of the zero order approximation is that it allows us to estimate the coexistence pressure from the values of ΔU and ΔV at zero pressure

$$p_{eq} = -\Delta U(p=0)/\Delta V(p=0). \quad (6)$$

In this study we shall perform classical Monte Carlo simulations at 0 K for several water models and for several solid structures. The coexistence pressures will be obtained either exactly from Eq. (2) (i.e, equating the enthalpies of the two phases at coexistence) or more simply from the zero order approximation Eq. (6).

Before continuing it seems important to discuss the properties of systems at 0 K when treated with classical statistical mechanics. Of course thermodynamic relations such as the Clapeyron equation are still valid within a classical treatment (thermodynamics relations also hold for classical systems except for the laws related to the third principle of thermodynamics). However, within classical statistical mechanics ΔS is in general different from zero at 0 K. This is because the entropy is not null at 0 K. In fact, within classical statistical mechanics the entropy diverges to $-\infty$ as the temperature approaches zero.[63] This can be seen by using the following reasoning. As shown in Fig. 2, in a classical treatment, the residual heat capacity at constant pressure (C_p^{res}) is not zero even at 0 K (the slope of the residual internal energy U remains finite up to 0 K). The heat capacity for a rigid water model has two contributions: the ideal term $(6R/2)$ and the residual contribution, which we have seen that is also finite and positive. Therefore, within a classical statistical mechanics formalism, C_p is finite and positive at 0 K. The entropy at a given temperature can be computed as

$$S(T) = S(T=0) + \int_0^T \frac{C_p}{T} dT. \quad (7)$$

As C_p is finite and positive, the term C_p/T diverges as the temperature approaches zero. On the other hand the entropy increases with the temperature or, what is the same, the entropy decreases as the temperature is lowered. As C_p/T diverges at 0 K and the entropy decreases as the temperature goes down, the entropy must go to minus infinite as the temperature approaches zero. However, in spite of this divergence of the entropy at 0 K, the differences in entropy between different solid phases remain finite. For instance, for hard spheres the entropy goes to minus infinity when the density tends to that of close packing whereas the difference in free energy between the fcc and hcp close packed structures remains finite.[64–66] As a consequence, the coexistence lines between solid phases will present a nonzero slope in the p-T plane.

III. SIMULATION DETAILS

Simulations have been performed for the SPC/E, TIP5P and the two recently proposed models TIP4P/Ice and TIP4P/2005 models. Since SPC/E (Ref. 6) and TIP5P (Ref. 8) have been often described in the literature we shall just refer to the original references. TIP4P/Ice (Ref. 57) and TIP4P/2005 (Ref. 58) correspond to slight modifications of the TIP4P (Ref. 7) model. The main differences between TIP4P and TIP4P/Ice is a larger value of the charge located on the H atoms and a larger value of the dispersion energy of the LJ interaction site. The parameters of the TIP4P/2005 are just intermediate between those of TIP4P and TIP4P/Ice. *NpT* Monte Carlo (MC) simulations have been performed for the following solid structures of water: ice I_h, II, III, V, and VI. In the simulations described in this work the LJ potential was truncated at 8.5 Å for all the phases. Standard long range corrections were added to the LJ energy. Ewald sums were used to deal with the long range electrostatic forces. The real part of the electrostatic contribution was also truncated at 8.5 Å. The screening parameter and the number of vectors of reciprocal space considered had to be carefully selected for each crystal phase.[67,68] The number of molecules used for ice I_h, II, III, V, and VI was 288, 432, 324, 504, and 360, respectively. These system sizes guarantee that the smallest edge of the simulation box is always larger than twice the cutoff in the potential.

Since the considered solid structures are not cubic [I_h (hexagonal), II (trigonal), III and VI (tetragonal) and V (monoclinic)] anisotropic *NpT* MC simulations (Parrinello-Rahman like[69,70]) were necessary for the solid phases, thus allowing both the shape and the relative dimensions of the unit cell to change. For the proton disordered phases (I_h and VI) the algorithm of Buch *et al.*[71] was used to generate an initial configuration where the hydrogens are disordered (but not the oxygens) and satisfying the ice rules[52,62] with a negligible dipole moment. The remaining disordered polymorphs, ice III and ice V, required some additional care as they are known to exhibit only partial disorder.[72] In view of this, the algorithm given in Ref. 71 was generalized[46] to construct an initial configuration with biased occupation of the hydro-

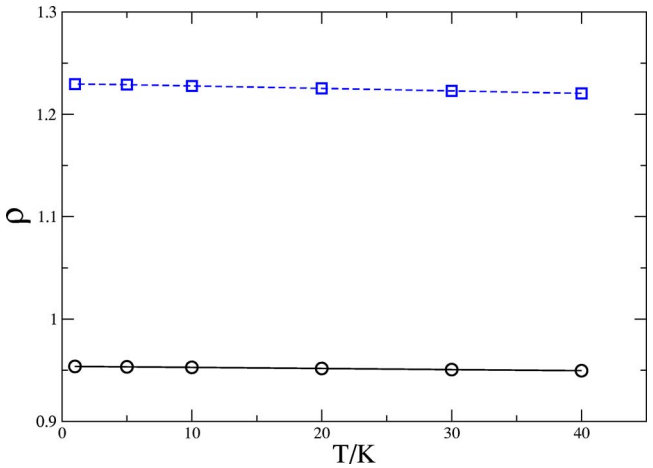

FIG. 1. (Color online) Densities (in g/cm^3) of ice I_h (solid line and open circles) and of ice II (dashed line and open squares) for the TIP4P/2005 model of water along the $p=0$ isobar.

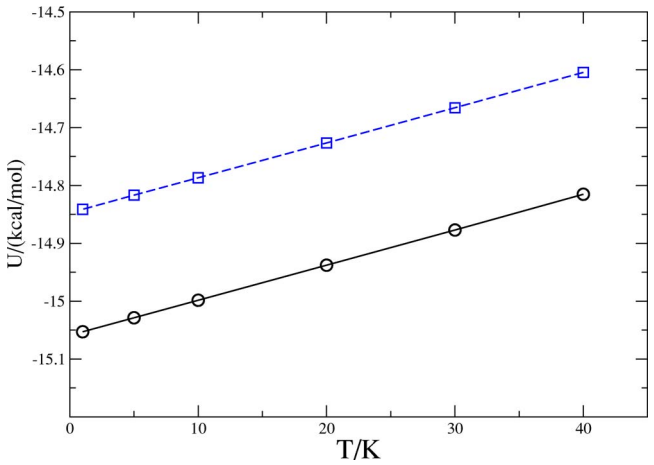

FIG. 2. (Color online) Residual internal energies of ice I_h (solid line and open circles) and of ice II (dashed line and open squares) for the TIP4P/2005 model of water along the $p=0$ isobar.

gen positions. Ice II presents proton ordering and thus crystallographic information was used to generate an initial solid configuration.[73]

To obtain the zero temperature-zero pressure properties, several consecutive Parrinello-Rahman *NpT* simulations (at zero pressure) were performed between 40 K and 1 K. The simulation started at 40 K and after a run of about 20 000 cycles for equilibration plus 40 000 cycles to obtain thermodynamic averages the temperature was changed to a lower value (a cycle is defined as a trial move per particle plus a trial volume change). The final configuration of a run was used as the initial configuration of the next run at a lower temperature. Figure 1 shows the densities of TIP4P/2005 along the zero pressure isobar. In Fig. 2 the residual energies of TIP4P/2005 along the zero pressure isobar are presented. As it can be seen in both figures, these properties vary linearly with temperature. Hence, the properties at 0 K can be obtained by fitting the simulation results to a straight line. Notice that the nonzero slope of the results presented in Figs. 1 and 2 are due to the classical treatment of the model. According to the Third Law of Thermodynamics, both the coefficient of thermal expansion α and the heat capacity C_p should go to zero as the temperature goes to zero. For the particular case of SPC/E simulations were also performed for other isobars (besides the zero pressure isobar). In particular, for ices I_h and II, simulations were performed for the following pressures $p=-500, -1000, -1500, -2000, -2500$ bar (the reasons for choosing negative pressures in the case of the SPC/E will be clarified in the next section).

In this work we have also performed Gibbs-Duhem simulations[74,75] to determine the coexistence line between ices I_h-II for the models SPC/E, TIP5P, TIP4P/2005, and TIP4P/Ice. Gibbs-Duhem simulations allow us to determine the coexistence line between two phases provided that an initial coexistence point is known. The Gibbs-Duhem technique is just a numerical integration (using simulation results to estimate the volume and enthalpy change between phases) of the Clapeyron equation. For the I_h-II coexistence line initial coexistence points for a number of water models are available from a previous work.[50] For the integration of the Clapeyron equation a fourth-order Runge-Kutta method algorithm is employed. Typically six to seven temperatures were chosen to integrate the coexistence line between ices I_h and II from 150 K up to temperature of about 20 K. The rest the of simulation details (size of the system, cutoff, anisotropic scaling) were identical to those used in the *NpT* simulations along the isobars. In Table I the results of the Gibbs-Duhem simulations along the I_h-II coexistence line are presented. For each model, the coexistence properties at selected temperatures (the initial temperature, one or two intermediate temperatures and the final temperature) are given. We report the equilibrium pressure, volume change, enthalpy

TABLE I. Simulation results for the transition between ices I_h and II as obtained from the Gibbs-Duhem simulations. The changes in the properties of the coexisting phases are calculated as the values for ice II minus those for ice I_h. The change in volume is given in cm^3/mol, the enthalpy change in kcal/mol, the entropy change in cal/K and the slope dp/dT in bar/K. The initial coexistence point was taken from Ref. 50.

T/K	p/bar	ΔV	ΔH	ΔS	(dp/dT)
TIP4P/Ice					
180	2790	−0.224	−0.0906	−0.503	5.21
120	2490	−0.229	−0.0587	−0.489	4.95
60	2210	−0.233	−0.0300	−0.500	4.98
10	1960	−0.236	−0.0050	−0.498	4.90
TIP4P/2005					
160	2900	−0.218	−0.0849	−0.530	5.64
80	2470	−0.226	−0.0405	−0.506	5.20
20	2160	−0.230	−0.0092	−0.457	4.62
SPC/E					
150	−498	−0.234	−0.1122	−0.748	7.43
90	−940	−0.238	−0.0660	−0.735	7.17
20	−1430	−0.241	−0.0140	−0.683	6.57
TIP5P					
150	−587	−0.209	0.0186	0.124	−1.37
90	−500	−0.207	0.0122	0.136	−1.52
25	−391	−0.205	0.0041	0.163	−1.85

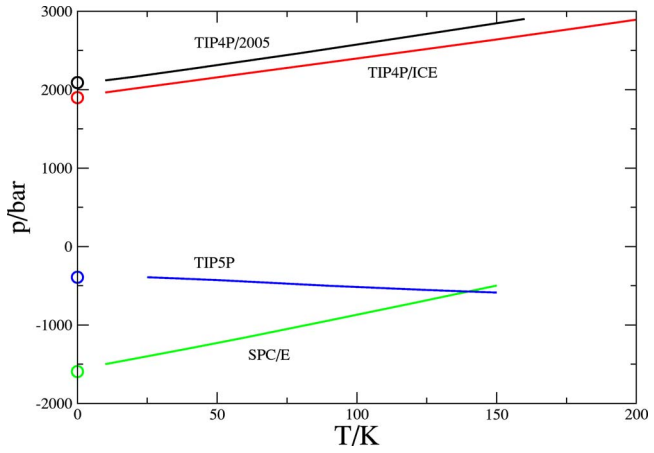

FIG. 3. (Color online) Coexistence lines between ices I_h and II as obtained from Gibbs-Duhem simulations for TIP4P/2005, TIP4P/Ice, SPC/E, and TIP5P models (solid lines). The symbols represent the coexistence pressures as obtained from the properties of the systems at zero temperature.

change, entropy change, and slope of the melting curve. A simple inspection of Table I shows that the enthalpy change of the transition goes to zero when the temperature approaches zero. The entropy change also varies along the transition although it does not tend to zero when the temperature vanishes. The slope of the coexistence line does not change much with temperature so that the coexistence lines between these two solid phases do not deviate much from a straight line. Thus, the coexistence pressure at 0 K may be simply obtained by extrapolation of the results at a slightly higher temperature. The properties along the I_h-II coexistence line as obtained from Gibbs-Duhem simulations are plotted in Fig. 3.

IV. RESULTS

Let us start by presenting the results for the properties of the different ices at zero pressure and temperature. In Table II the internal energies and densities are given for the TIP4P/Ice, TIP4P/2005, SPC/E, and TIP5P models. The internal energies differ significantly from one model to another. The higher internal energies (i.e., the less negative value) correspond to TIP5P. This can be understood since the parameters of this model were chosen to match the experimental enthalpy of vaporization. The order of magnitude of the energies of SPC/E and TIP4P/2005 are similar because these models reproduce the experimental enthalpy of vaporization only when a self-polarization term is taken into account.[6] Finally, the lowest values (i.e., the largest in absolute value) are given by the TIP4P/Ice because this model provides an enthalpy of vaporization much higher than the experimental one (even when the self-polarization term is added) which is required to match the ice I_h experimental melting temperature.[57] In Table II the results corresponding to the ice polymorph with the lowest energy at zero temperature and pressure are presented in bold characters. For TIP4P/Ice and TIP4P/2005 ice I_h is the structure with the lowest energy. However for SPC/E and TIP5P the lowest internal energy corresponds to ice II. Thus, for TIP4P/2005 and TIP4P/Ice ice I_h is the stable phase at zero pressure and temperature whereas for SPC/E and TIP5P the stable phase is ice II.

Let us now compute the coexistence pressures between the different ice phases. It is interesting to analyze first the performance of the zero order approximation given by Eq. (6). According to this approximation, in order to determine the coexistence pressure it is sufficient to know the internal energy and density at zero density and pressure. Within this approximation, the coexistence pressure at 0 K for the ice I_h-ice II line is −1590 bar for the SPC/E model. For the same model we have obtained by computer simulation the properties of ices I_h and II at several pressures along the zero temperature isotherm. From these results it is possible to determine exactly the location of the phase transition at zero temperature (from the condition of equal enthalpy between the two phases). In Fig. 4 the enthalpies of SPC/E for these two ices are shown. The enthalpies of ices I_h and II cross at a pressure of about −1570 bar. This is the coexistence pressure obtained in a rigorous way. As it can be seen both estimations agree quite well which guarantees that the error introduced by the zero approximation is small. For this reason it will be used in the rest of this work to determine the coexistence pressures.

The coexistence pressures calculated within the zero order approximation are presented in Table III. We leave aside for the moment the comparison with the experimental coexistence pressures. The first thing to note from the results of

TABLE II. Properties of several ice polymorphs at $T=0$ K and $p=0$ for popular water models.

Ice	TIP4P/Ice	TIP4P/2005	SPC/E	TIP5P
		U (kcal/mol)		
I_h	**−16.465**	**−15.059**	−14.691	−14.128
II	−16.268	−14.847	**−14.854**	**−14.162**
III	−16.140	−14.741	−14.348	−13.320
V	−16.049	−14.644	−14.169	−13.101
VI	−15.917	−14.513	−13.946	−12.859
		ρ(g/cm^3)		
I_h	0.938	0.954	0.981	1.045
II	1.212	1.230	1.279	1.326
III	1.169	1.184	1.181	1.200
V	1.277	1.297	1.325	1.383
VI	1.363	1.385	1.413	1.471

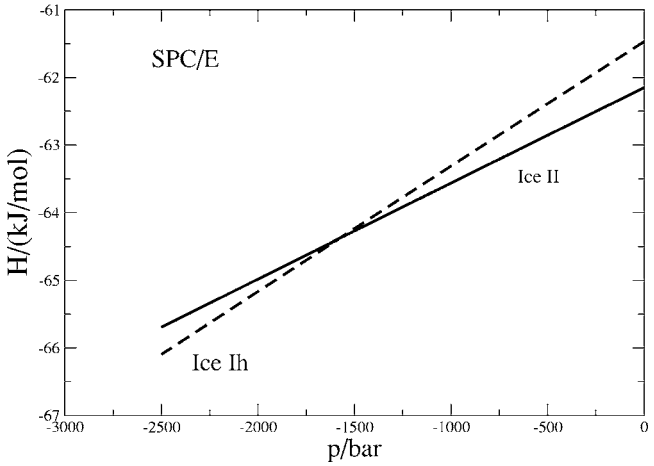

FIG. 4. Enthalpies of ices I_h and II at zero temperature for the SPC/E model of water.

Table III is that the coexistence pressure between ice I_h and ice II occurs at negative pressures for SPC/E and TIP5P. In fact, for the SPC/E model at zero temperature, ice I_h is more stable than ice II only at pressures below −1590 bar. For TIP5P the situation is not as dramatic as that for SPC/E, ice I_h being more stable than ice II at pressures below −390 bar. For TIP4P/2005 and TIP4P/Ice the I_h-II transition occurs at positive pressures so that ice I_h is more stable than ice II for a certain range of positive pressures. A second important question is to analyze whether the coexistence pressures obtained from zero Kelvin calculations agree with the results from Gibbs-Duhem simulations. This is a severe test since any error in the free energy calculation of the solid phases or in the determination of the initial coexistence point or in the Gibbs-Duhem integration along the coexistence line gives rise to discrepancies. Therefore the comparison constitutes a cross check of the calculations. In Table IV the coexistence pressures for the TIP4P/2005 model extrapolated to 0 K from the Gibbs-Duhem simulations are compared to the values predicted from the zero Kelvin calculations. The agreement is satisfactory. This provides further evidence of the correctness of the phase diagram computed for TIP4P/2005. It is also interesting to point out that the melting temperature of ice I_h obtained from free energy calculations was found in agreement with the melting temperature obtained from direct fluid-solid coexistence runs[55] and from surface melting simulations.[56] Therefore the melting temperatures as determined from free energy calculations seem to be correct for this model (and for other models as well). This type of cross checking is worth taking into account especially that free energy calculations of molecular solids are somewhat involved.[44,76–80] In summary, the above commented calculations provide further evidence of the validity of the phase diagram computed for the TIP4P/2005. Because of this, and considering that some coexistence lines (II-V, V-VI, and II-VI) have been extended to lower temperatures than those previously reported for this model, we present in Fig. 5 the resulting phase diagram of TIP4P/2005 including the new coexistence points.

TABLE IV. Coexistence pressures at 0 K (in bar) for TIP4P/2005 as obtained from extrapolation of the Gibbs-Duhem coexistence lines and from the analysis of the properties of the ices at zero temperature.

Phases	Gibbs-Duhem	Equation (6)
I_h-II	1990	2090
I-III	3600	3630
II-V	11530	11230
II-VI	9080	8530
V-VI	5990	6210

We now focus on the coexistence pressure between ices I_h and II for different water models. We have also plotted in Fig. 3 the predicted pressures using the calculations at 0 K (circles). It may be seen that these predictions agree quite well with the extrapolated values of the Gibbs-Duhem simulations for the I_h-II coexistence line. Therefore, both set of results are mutually consistent. It is clear that ice II is more stable than ice I_h at zero temperature and pressure for the SPC/E and TIP5P models. For the TIP5P model the slope of the I_h-II line is negative (this is because for this model the enthalpy of ice II is higher than that of ice I_h along the coexistence curve). This is an anomalous behavior since for the rest of the models the enthalpy of ice I_h is higher than that of ice II along the coexistence curve. Because of the negative slope the transition pressure between ices I_h and II at high temperatures (for instance at the temperature of the normal melting point) is lower than at 0 K. In summary, for TIP5P at positive pressures ice II would be more stable than ice I_h at any temperature up to the melting point. For the SPC/E model the stability of ice I_h increases with temperature. Since for this model the ice I_h melting point is around 215 K,[55,59] either ice I_h does not appear on the phase diagram at positive pressures or appears just in a very small region of

TABLE III. Coexistence pressures (in bar) between solid phases at $T=0$ K. The experimental values were taken from Whalley (Ref. 60). d is a measure of the departures of the predictions for a given model from the experimental values (see the text).

Phases	Experimental	TIP4P/Ice	TIP4P/2005	SPC/E	TIP5P
I_h-II	140±200	1900	2090	−1590	−390
I_h-III	2400±100	3580	3630	4600	15250
II-V	18500±4000	12120	11230	58270	79600
II-VI	10500±1000	8920	8530	28410	40690
III-V	3000±100	2920	3060	4530	4610
V-VI	6200±200	6210	6210	11010	12950
d		4	4	8	26

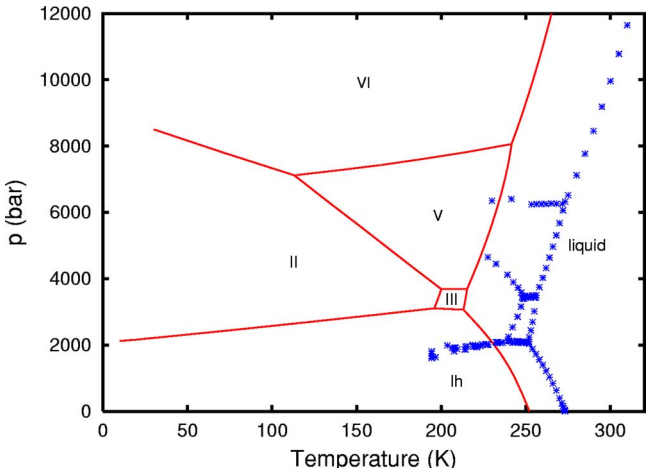

FIG. 5. (Color online) Phase diagram of the TIP4P/2005 model of water as obtained from free energy calculations and the Gibbs-Duhem simulations

the phase diagram in the vicinity of the melting point. On the contrary, for TIP4P/Ice and TIP4P/2005 the transition between ice I_h and ice II occurs at positive pressures at any temperature in accordance with the experimental observation. Thus, the calculations in the region close to 0 K reinforce previous reports about the dependence of the relative stability of these ice polymorphs on the water models.[44,59]

Let us finally compare the computer simulation results for these models to the experimental data. First of all we compare the transition pressures between ices at 0 K (see Table III). In order to give a numerical value more or less representative of the accuracy of the results and, taking into account the disparity of the values, we have calculated the mean weighted deviations

$$d = (1/N) \sum w |p_{\text{model}} - p_{\text{expt}}| \tag{8}$$

using the inverse of the experimental uncertainty as a weighting function w. The results for TIP5P do not agree with the experimental values. The d value indicates that the departures of the TIP5P predictions from the experimental equilibrium pressures are (in average) more than 25 times larger than the experimental uncertainty. The only exception is the ice I_h-II transition for which the difference with respect to the experimental value is relatively small. The same applies, although to a minor extent, to the coexistence pressures yielded by the SPC/E model. The predictions for TIP4P/2005 are quite similar to those for TIP4P/Ice so we shall use the latter model for our discussion. As it can be seen, the calculations for the TIP4P/Ice model are in reasonable agreement with the experimental values. Although the largest difference with experiment is that for the II-V coexistence, the discrepancy is in this case only slightly larger than the experimental uncertainty. The differences for the other solid-solid lines are lower than 2000 bar. The more significant departures appear when ice I_h is one of the coexistence phases (i.e., I_h-II and I_h-III transitions). In the case of the I_h-II coexistence the model overestimates the equilibrium pressure by about 1800 bar, a value considerably larger than the experimental uncertainty. Taking into account the simplicity of the model (rigid, nonpolarizable, and classical) the predictions appear as quite reasonable. Probably the predictions of the TIP4P/Ice and TIP4P/2005 models represent the limit of what can be achieved by simple water models.

Finally we present the relative energies of the ice phases at 0 K. The energy of ice II will be taken as the zero of energies so that all the energies will be referred to that of ice II. In Table V the relative energies (with respect to that of ice II) of the different ice polymorphs (at zero temperature and pressure) are presented. Again, the predictions for TIP5P and SPC/E do not agree with experiment. These models predict rather poorly the relative energies of the different ice polymorphs. Therefore it is not surprising that they yield poor predictions for the phase diagram of water. In particular, the positive value of the relative energy of ice I_h, indicates that ice II is more stable than ice I_h at the considered thermodynamic state as commented before. The relative energies predicted by the TIP4P/Ice and TIP4P/2005 are quite satisfactory. For both models, the difference of the predicted energies with respect to the experimental values is (in average) lower than 0.1 kcal/mol. Both models predict that the internal energy of ices at zero temperature and pressure increases in the order I_h, II, III, V, and VI which is in agreement with experiment. It is indeed gratifying that such simple models are able to capture the ordering of the energies of the ice phases. The correct ordering guarantees a qualitatively correct phase diagram. The relative energy of ices III, V, and VI with respect to ice II is described quite well by these models. The main discrepancy is related to the energy of the ice I_h with respect to ice II. This relative energy is found to be negative both in experiment and in the TIP4P/2005 and TIP4P/Ice models (so that ice I_h is the most stable

TABLE V. Relative internal energies (in kcal/mol) of several ice polymorphs with respect to ice II at zero temperature and pressure for the TIP4P/Ice, TIP4P/2005, SPC/E, and TIP5P water models. For comparison, the experimental measurements of Whalley (Ref. 60) are also included, d is the mean deviation with respect to the experimental results [calculated as in Eq. (8) with $w=1$ and with the pressures replaced by the relative internal energies].

Phase	TIP4P/Ice	TIP4P/2005	Exp.	SPC/E	TIP5P
I_h	−0.197	−0.212	−0.014	0.163	0.034
II	0	0	0	0	0
III	0.128	0.106	0.201	0.506	0.842
V	0.219	0.203	0.213	0.686	1.061
VI	0.351	0.334	0.373	0.908	1.303
d	0.07	0.08		0.37	0.62

TABLE VI. Relative internal energies (in kcal/mol) between ices at zero pressure for temperatures around 150 K. Experimental results were taken from Ref. 81 except for ice XII that were taken from Ref. 82. Ice VIII melted for the SPC/E model at zero pressure and a temperature of 124 K.

Ice	T(K)	TIP4P/Ice	TIP4P/2005	Exp.	SPC/E	TIP5P
I_h	162	–0.194	–0.209	0.004	0.164	0.038
II	162	0.000	0.000	0.000	0.000	0.000
III	143	0.132	0.112	0.230	0.511	0.874
V	144	0.231	0.218	0.235	0.704	1.083
VI	143	0.354	0.338	0.352	0.918	1.313
XII	150	0.304	0.295	0.307	0.830	1.277
VIII	124	1.903	1.798	0.650	—	2.449

phase at zero temperature and pressure). However, the difference between the experimental value and the one obtained in the simulation is larger for this polymorph than for the other ices. Thus, the stability of ice I_h with respect to the rest of the polymorphs (ices II, ices III, V, and VI) is overestimated in the TIP4P/Ice and TIP4P/2005 models. It is worth mentioning that whereas the density of ice I_h in TIP4P/Ice is around 0.93 g/cm^3, the densities of the rest of ices are in the range $1.20-1.36$ g/cm^3. This important difference in density may affect the zero point energies (not taken into account in classical simulations) which can also be different in low density (I_h) and high density ices (II, III, V, VI). It may also have some effect on the effective dipole moment of the water molecule in such a different environments. Further work (e.g., path integral simulations or evaluation of the phonon dispersion curve, inclusion of polarizability) is needed to clarify the origin of this feature.

Up to now we have compared the relative internal energies between ices at 0 K. However, in a later work, Whalley *et al.*[81] also reported the relative internal energies of the different ices at zero pressure and temperatures around $T=150$ K. These were determined from calorimetric measurements. In Table VI the relative internal energies at zero pressure are compared for the different ices. Notice that the temperature at which the comparison is made is not the same for all solid phases. As before we take as zero energy that of ice II at 162 K. Then the displayed result for the experimental energy of, let us say, ice III (0.23 kcal/mol) means that the internal energy of ice III at zero pressure and 143 K is 0.23 kcal/mol higher than that of ice II at 162 K (the zero of energies). As it can be seen in Table VI the experimental energies reported by Whalley *et al.* from calorimetric measurements are quite similar to those given at 0 K. Both sets of experimental results are mutually consistent and they also show that the difference in internal energies between ices at zero pressure does not depend much on temperature. The relative energies for the different water models presented in Table VI are quite similar to those already discussed for the 0 K case. In addition to the energies of ices I_h, II, III, V, and VI, the internal energies of ice VIII and XII are also given (those of ice XII were taken from Ref. 82). TIP4P/Ice and TIP4P/2005 again describe quite well the energy of ice XII. However none of the models predicts correctly the energy of ice VIII. The energy of ice VIII for all models is much higher that found in experiment. This may explain why ice VIII appears in the phase diagram of SPC/E and TIP4P at a much higher pressure that found in experiment.[44]

V. CONCLUSIONS

In this work the properties (density and internal energy) of ices I_h, II, III, V, and VI at zero temperature and pressure have been obtained from computer simulations. The following models have been considered, namely, SPC/E, TIP5P, TIP4P/Ice, and TIP4P/2005. It is found that ice II is the most stable phase at 0 K for SPC/E and TIP5P models. Ice I_h is the most stable phase for TIP4P/2005 and TIP4P/Ice models. The phase transitions between the different solid phases occurring at 0 K have also been calculated. Only TIP4P-like models predict the equilibrium pressures reasonably well. Besides, the coexistence pressures calculated using the properties at 0 K agree quite well with those obtained from Gibbs-Duhem simulations (with an initial point obtained from free energy calculations). Both sets of results are fully consistent which is a guarantee of the validity of the free energy calculations and phase diagram predictions. It was mentioned above that Gibbs-Duhem simulations require an initial coexistence point which is typically obtained from free energy calculations. Since the transition pressures determined from the zero order approximation are in good agreement with those obtained from Gibbs-Duhem simulations, one could (naively) think that free energy calculations may not be needed to determine solid-solid coexistence lines. In principle, one could determine the transition pressure at 0 K from the zero order approximation (or better from the isoenthalpic condition) and then use it as the initial point to perform Gibbs-Duhem integration starting at 0 K. Unfortunately, this is not possible. The reason is that at 0 K both ΔH and T are null so that its ratio (ΔS) which certainly adopts a finite value cannot be determined. Gibbs-Duhem simulations can start from 0 K, but only if ΔS is known. Obviously, ΔS can only be obtained through free energy calculations. In summary, although runs at 0 K enable to check the consistency of phase diagram calculations, they do not allow by themselves to draw the phase diagram of a certain model.

The relative energies of the different polymorphs have been computed and compared to the experimental values reported by Whalley more than 20 years ago.[60] In general the relative energies between ices are quite small (about 0.2 kcal/

mol). For this reason their correct prediction is a quite difficult test to pass for water models. Besides water models pass the test with quite different marks! TIP5P fails completely in predicting the relative energy of the different ices polymorphs. The results of SPC/E, although better than those for TIP5P, are not satisfactory either. The relative energies predicted by TIP4P/Ice and TIP4P/2005 agree reasonably well with experiment, the main difference being an over stabilization of ice I_h. Further work is needed to clarify the origin of this discrepancy for TIP4P-like models although it is likely that quantum effects and polarizability may be responsible of the difference. It would be of interest to determine the relative stability between ices[83] from first principles (i.e., *ab initio* calculations) although very precise calculations would be required.

As to why some models are more successful than others we have shown recently that the balance between dipolar and quadrupolar forces varies significantly among the water models, and that this has a deep effect on the appearance of the phase diagram.[84,85] Notice that in order to predict the phase diagram correctly two conditions are required. First, the relative stability of the different ices should be predicted correctly (this guarantees a good description of the solid-solid coexistence lines). The calculations presented in this work illustrate that this is indeed achieved by TIP4P/2005 and TIP4P/Ice models. Second, the relative stability of the ices with respect to the liquid should also be described correctly. This second aspect is not discussed in this work. We just should point out that TIP4P/2005 and TIP4P/Ice predict[50,55] a melting point for ice I_h of about 252 K and 272 K, respectively (to be compared with the experimental value of 273.15 K). Therefore these models describe also quite well the relative energy of the ices with respect to the liquid, the error in the melting point of these models being about 20 K and 1 K, respectively. In the case of the TIP4P/2005 the critical temperature[86] and surface tension[87] of water are reproduced with extraordinary accuracy. Therefore, TIP4P/2005 is able to provide a coherent view of the phase diagram of water from the low temperature limit up to the critical point. Probably, significant further improvement can only be achieved by the addition of polarizability[88] and quantum effects.[89,90]

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