The phase diagram of water at negative pressures: Virtual ices

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The phase diagram of water at negative pressures as obtained from computer simulations for two models of water, TIP4P/2005 and TIP5P is presented. Several solid structures with lower densities than ice Ih, so-called virtual ices, were considered as possible candidates to occupy the negative pressure region of the phase diagram of water. In particular the empty hydrate structures sI, sII, and sH and another, recently proposed, low-density ice structure. The relative stabilities of these structures at 0 K was determined using empirical water potentials and density functional theory calculations. By performing free energy calculations and Gibbs–Duhem integration the phase diagram of TIP4P/2005 was determined at negative pressures. The empty hydrates sII and sH appear to be the stable solid phases of water at negative pressures. The phase boundary between ice Ih and sII clathrate occurs at moderate negative pressures, while at large negative pressures sH becomes the most stable phase. This behavior is in reasonable agreement with what is observed in density functional theory calculations. © 2009 American Institute of Physics. [DOI: 10.1063/1.3182727]

I. INTRODUCTION

Water has a rich and intriguing chemistry the study of which is as old as science itself.¹ In the solid phase it exhibits a wide variety of crystalline phases,² while liquid water is the most commonly employed solvent in chemistry and biology.

Ever since the pioneering works of Barker and Watts³ and Rahman and Stillinger⁴ 40 years ago, simulation studies of water have been an important area of research. To simulate water it is essential to choose a potential model that correctly describes the interactions between molecules. In recent years we have tested the ability of water potential models to describe the phase diagram of water^{5–7} and found that widely used potential models such as SPC/E (Ref. 8) or TIP5P (Ref. 9) fail in their description of the phase diagram. However, TIP4P (Ref. 10) provides a reasonable prediction which can be further improved with only a slight modification of the potential parameters. The resulting model, which reproduces a number of water properties including the phase diagram, has been denoted TIP4P/2005.¹¹

So far the phase diagram of water has been computed only for positive pressures, which leads one to wonder what kind of solid phases could be found in the phase diagram for water at negative pressure. Experimentally negative pressure corresponds to a situation where a solid is either under tension¹² or in the meniscus of a confined liquid (due to the change in pressure across a curved interface) in certain conditions.^{13,14} Bridgmann¹⁵ states in his classic paper that, if the temperature is kept constant, pressure driven phase transitions are accompanied by an increase in the density. Hence, on the phase diagram, the phase that appears above the coexistence line will always have a higher density than the phase below the line. This rule implies that, upon decreasing the pressure, any new phases that may appear below ice Ih, should have a lower density than ice Ih. Experimentally there is no known ice with a density lower than ice Ih. Therefore the ices appearing at negative pressures (with a density lower than ice Ih) can be denoted virtual ices, the word virtual indicating that these ices have not been found experimentally.

In addition to the 15 known solid phases, there are a number of studies based on simulation, where the possible existence of new ice polymorphs has been reported.^{16–19} For instance, Fennell and Gezelter¹⁶ reported the existence of two new virtual ices named ice i and ice i', with a density lower than ice Ih. These two ices are possible candidates to occupy the negative region of the phase diagram. Other virtual ices are the networks formed by water molecules in the hydrate structures. Clathrate hydrates are inclusion compounds in which a guest molecule occupies the cavities formed by a host water lattice.^{20,21} Their structures consist of a three-dimensional framework of hydrogen-bonded water molecules within which are incorporated a smaller number of relatively inert "guest" molecules. Typical guest molecules include natural gas molecules such as methane, ethane, and propane or small molecules composed of atoms from the first two rows of the Periodic Table such as hydrogen or carbon dioxide. These inclusion compounds are common on earth (in particular, methane hydrate can be found in large quantities in coastal regions) and are attracting interest in the research community^{22–27} (both experimental and simulation) partly as a future energy resource and partly as possible gas storage materials. Hydrates are classified as sI, sII, and sH according to the arrangement of the water molecules, the particular structure adopted depends upon the guest molecules present. These three empty hydrate structures (without

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FIG. 1. Initial configuration of hydrate type sI with disordered proton and 368 water molecules.

any guest molecules) all have a lower density than ice Ih and are therefore considered here to be potential virtual ices which may occupy the phase diagram at negative pressures. Experimentally, it is not possible to study the empty hydrates, since they are thermodynamically stable (at positive pressures) only when they contain a guest molecule. However, it is possible to study by computer simulation all these virtual ices (including the empty hydrates) as long as they are mechanically stable (even though they may not be thermodynamically stable). It is not possible to access the chemical potential of an empty hydrate experimentally so typically in van der Waals-Platteeuw theory²⁸ an approximate method is used to calculate this quantity. Here we demonstrate a method by which this chemical potential may be determined accurately. This method of calculation is in the same spirit as those employed in recent work by Monson et al.^{29,30} who tested the predictions of van der Waals theory against those of more accurate GCMC (Grand Canonical Monte Carlo) simulation to see what effect the various approximations of the van der Waals-Platteeuw theory had on the estimation of the hydrate guest occupancies.

The main goal of this paper is to determine by computer simulation the phase diagram of water at negative pressures, considering as possible solid phase candidates the empty hydrate structures sI, sII, sH, and the structure proposed recently by Fennell and Gezelter.

II. STRUCTURES

In this work we consider the empty hydrate phases as possible phases of ice and so our focus is on the number of water molecules that form the unit cell rather than the size and type of the cavities of which it is composed. Structure type sI (Ref. 31) has a cubic unit cell with 46 water molecules. The simulation box used in this work contained $2 \times 2 \times 2$ unit cells—a total of 368 molecules (see Fig. 1).



FIG. 2. Initial configuration of hydrate type sII with disordered proton and 1088 water molecules.

For the sII structure,³² which has cubic symmetry, we used a $2 \times 2 \times 2$ supercell of unit cells. Each unit cell contains 136 water molecules and so the total number of molecules used in the configuration was 1088 (see Fig. 2) Finally, the sH phase³³ has hexagonal symmetry and a unit cell that contained 34 water molecules. Our configuration consisted of a $3 \times 2 \times 2$ supercell which contained 408 water molecules (see Fig. 3). In all cases a fully proton disordered configuration which satisfied the Bernal and Fowler³⁴ rules was used.

The structure proposed by Fennell and Gezelter¹⁶ was found accidentally when performing crystallization studies for liquid water.³⁵ At temperatures below the melting point of the soft sticky dipole (SSD) (Ref. 36–39) water model, Fennell and Gezelter observed a solid phase that did not correspond to the most experimentally stable phase; namely, ice Ih. Instead they found a new polymorph they named *ice i*—and a slightly different variant denoted as *ice i'*. In our study we employed the configurations for ice i and *i'* provided by in the additional material published by Fennell and Gezelter.¹⁶ In these configurations there are 1024 water molecules (see Fig. 4). Notice that ices i and *i'* are new and as yet undiscovered solid phases, which bear no relation to ice Ih and that in these two structures the protons are ordered.

III. WATER MODEL POTENTIALS

Two models are used in this work to describe the interaction between water molecules. The first one is the TIP4P/



FIG. 3. Initial configuration of hydrate type sH with disordered proton and 408 water molecules.



FIG. 4. Initial configuration of ice i with ordered proton and 1024 molecules. The presence of large octogonal pores leads to a polymorph that is less dense than ice I_h .

2005 model, which was recently proposed by Abascal and Vega.¹¹ In this model water is treated as rigid and nonpolarizable. Positive charges are located on the positions of the H atoms, an LJ interaction site is located on the oxygen atom, and the negative charge is located at a distance d_{OM} from the oxygen along the H–O–H bisector. We have chosen this model because it provides a good description of the phase diagram at positive pressures. It also reproduces the density maximum of liquid water and a number of other water properties.^{11,40,41}

The second model considered in this work is the TIP5P model, which was proposed in 2000 by Mahoney and Jorgensen.⁹ This model is also rigid and nonpolarizable, with positive charges on the hydrogen atoms and a LJ site located on the oxygen atom. The main difference from the TIP4P/ 2005 model is that negative charges are located on the "lonepair" electrons at a distance of d_{OL} from the oxygen. This model is the modern version of the ST2 (Ref. 42) models used in the 1970s. The parameters of this model were fitted to reproduce thermodynamic properties of liquid water like the density maximum. Although TIP5P fails in describing the phase diagram of water, we have decided to include it in this study since it has been suggested¹⁶ that for this model ice i'is the stable solid structure at the normal melting point. However, ice II was not considered by Fennell and Gezelter¹⁶ so it would be of interest to check whether or not ice II is the stable solid phase for this model at the normal melting point.

A comparison of the performance of these two models in describing water's properties has been published recently.⁴¹

IV. METHODOLOGY

Initial solid configurations for sI, sII, and sH were obtained from crystallographic data.⁴³ For the proton disordered ices (sI, sII, and sH), the oxygens were placed on the lattice points, and proton disordered configurations with no net dipole moment which satisfied the Bernal and Fowler³⁴ rules were obtained using the algorithm proposed by Buch *et al.*⁴⁴ and elaborated upon by MacDowell *et al.*⁴⁵ For the proton ordered (ices i and *i'* proposed by Fennell and Gezelter) we took the initial configuration from the additional material given in their paper.¹⁶ An initial solid configuration for ice II was obtained from crystallographic data from the paper of Lobban *et al.*⁴⁶ For ice XI the antiferroelectric structure described in the paper of Davidson and Morokuma⁴⁷ was used.

NpT Monte Carlo simulations^{48,49} Anisotropic (Rahman-Parrinello-like) were used for all solid structures. The pair potential was truncated for all phases at 8.5 Å and standard long range corrections to the LJ energy and pressure were added. $\overline{}^{50,51}$ Ewald sums were employed for the electrostatic forces with the real part of the electrostatic contribution truncated at 8.5 Å. The importance of an adequate treatment of the long range Coulombic forces when dealing with water simulations has been pointed out in recent studies.⁵² The screening parameter and the number of vectors of reciprocal space considered had to be carefully selected for each crystal phase.^{50,51} The free energies of the solid phases were evaluated by using the Einstein molecule approach proposed by Vega and Noya⁵³ and extended to molecular systems by Noya et al.^{54,55} This method is a variant of the Einstein crystal methodology of Frenkel and Ladd⁵⁶ which, for proton ordered ices (ice i and ice i'), directly yields the free energy. For proton disordered ice phases one must add the Pauling³ entropy, S/R = ln(3/2) if free energies are to be recovered.

Once the free energy for a certain state point was known we used thermodynamic integration to compute it for other thermodynamic conditions.^{55,58} In this way it was possible to locate at least one coexistence point for each coexistence line. Gibbs–Duhem⁵⁹ simulations, using a fourth-order Runge-Kutta integration,⁶⁰ were used to obtain the full coexistence curve between two coexistence phases. Finally, as a consistency check the coexistence lines obtained by Gibbs-Duhem simulations were extended up to 0 K, and compared to the predictions obtained from 0 K NpT simulations. Recently Aragones et al.⁶¹ and Kataoka and Yamada⁶² showed that it is possible to determine phase transitions at 0 K from NpT simulations at 0 K, and that the transitions determined in this way should be in agreement with those obtained from free energy and Gibbs-Duhem integration calculations. Hence, this constitutes a severe cross check of the calculations.

To determine the properties of the virtual ices at 0 K and zero pressure Parrinello–Rahman NpT simulations were performed between 200 and 1 K. Simulations were started at high temperatures (and zero pressure) and the system was then cooled in a series of consecutive runs. The final configuration of a run was used as the initial configuration of the next, lower-temperature run. The properties at 0 K were obtained by fitting the simulation results to a straight line.

As an additional check on the 0 K energetics DFT was used to optimize structures by minimizing the energy with respect to the volume and the coordinates. The CASTEP code was used to calculate the energies using the PW91 functional

TABLE I. Properties of several ice polymorphs at T=0 K and p=0 bar for TIP4P/2005 and TIP5P models. The data marked with an asterisk are taken from Ref. 61. The structures in bold are those with the lowest internal energy.

	U	ho (g/cm ³)		
Phase	(kcal/mol)			
	TIP4P/2005 model			
II^*	-14.847	1.230		
XI	-15.079	0.955		
Ih^*	-15.059	0.954		
ice i	-14.752	0.894		
ice i'	-14.758	0.894		
sI	-14.815	0.845		
sII	-14.836	0.832		
sH	-14.740	0.813		
	TIP5P model			
II^*	-14.162	1.326		
XI	-14.267	1.047		
Ih*	-14.128	1.045		
ice i	-14.175	0.984		
ice i'	-14.176	0.984		
sI	-13.837	0.920		
sII	-13.898	0.911		
sH	-13.760	0.888		

at the gamma point, with a plane wave cutoff of 500 eV and ultrasoft pseudopotentials as used in previous studies.^{63,64} All the cell parameters used are larger than 10 Angstroms and since ice is an insulating, molecular solid sampling at the Gamma point is appropriate.

For the empirical model simulations and DFT calculations, the zero point energy was not considered. Nevertheless, our own DFT calculations suggest that zero point energy is a minor contribution to total energy *differences* between ice phases.

V. RESULTS

In Table I the internal energies and densities of the various ice phases at 0 K and zero pressure are presented. The internal energies obtained from TIP4P/2005 are different from those of TIP5P. This is mainly due to the fact that TIP5P reproduces the vaporization enthalpy of water. The same is true for the original TIP4P model.¹⁰ However, by design TIP4P/2005 (as SPC/E) reproduces the vaporization enthalpy of water only when the self polarization term introduced by Berendsen *et al.*⁸ is included.^{11,40} The data marked in bold correspond to the phases with the lowest internal energy (i.e., the most stable phase at 0 K and zero pressure). In both models, ice XI, the proton ordered phase of ice Ih, is the phase with the lowest internal energy.

At zero temperature the condition of chemical equilibrium between two phases, labeled as phases A and B, respectively, is given by

$$U_A(p_{eq}, T=0) + p_{eq}V_A(p_{eq}, T=0)$$

= $U_B(p_{eq}, T=0) + p_{eq}V_B(p_{eq}, T=0),$ (1)

where U_A and U_B are the molar internal energies and V_A and

 V_B are the molar volumes of phases A and B, respectively.

The conditions at which transitions from the most stable phase at 0 K and zero pressure to other solid structures (either occurring at positive or negative pressures) will occur can be estimated by using the zero-order approximation described by Aragones *et al.*⁶¹ and first proposed by Whalley.⁶⁵ Coexistence pressures can be estimated from the zero-order approximation as

$$p_{\rm eq} \approx \frac{-\Delta U(p=0)}{\Delta V(p=0)}.$$
 (2)

The zero-order approximation assumes that the differences in molar energy and molar volume between the two phases are independent of pressure and equal to the differences observed at zero pressure. As shown by Whalley⁶⁵ and Aragones et al.⁶¹ the zero-order approximation works reasonably well and provides one with a quick estimate of the transition pressures between ices at 0 K from only a knowledge of their energies and densities at 0 K and zero pressure. Since the densities of ices i, i' and sI, sII, and sH presented in Table I are lower than that of ice XI (or ice Ih) they could, according to Bridgman's prescription, be found as stable phases at negative pressures. In the TIP4P/2005 model, using the zeroorder approximation one finds the following transitions: at 0 K and room pressure ice XI is the stable solid phase. On decreasing the pressure ice XI transforms into sII at a pressure of -3639 bar and at -7775 bar sH becomes the most stable phase. Hence, for the TIP4P/2005 model, ices i, ice i'and sI are not thermodynamically stable at 0 K, because at no pressure do they become the phase with the lowest chemical potential.

For the TIP5P model the situation is somewhat different. At zero pressure ice XI is the most stable phase while at pressures below -3430 bar ice *i'* becomes the most stable (although it is important to note that the energies of ice i and ice *i'* are almost identical). A transition from ice *i'* to sII then occurs at -7883 bar and a further transition from sII to sH at -11411 bar. Thus both models predict that, as the pressure is decreased, the structure goes through the sequence XI \rightarrow sII \rightarrow sH. The main difference between the predictions of TIP4P/2005 and TIP5P is the presence of ice *i'* as a stable phase between ices XI and sII. We shall discuss later on whether DFT calculations support the existence of ice *i'* as a stable phase of water at negative pressures.

Although one can obtain interesting conclusions from the results at 0 K, it is desirable to determine the phase diagram for finite temperatures as well. This requires free energy calculations at finite temperatures for a certain reference state and thermodynamic integration to obtain the free energy surface. In Table II the free energies, calculated at 200 K and 1 bar, of the different solid phases computed in this work are reported. At this low pressure the Gibbs free energy is to all intent and purposes identical to the Helmholtz free energy (any differences are observed only the in fifth significant figure). For this reason, it is clear that at 200 K and 1 bar, ice Ih is the most stable phase of the TIP4P/2005 (the proton ordered ice XI is stable from 0 K up to 25 K approximately). This is gratifying since experimentally, ice Ih is the most stable phase at these conditions. For the TIP5P

TABLE II. Helmholtz energies, A_{sol} , of the virtual ices (ice i, ice i', sI, sII, and sH) and of several water polymorphs (Ih, II, and XI) for different potential models using the Einstein molecule method. (See details in the Refs. 53 and 54). For all phases, the thermodynamic conditions were 200 K and 1 bar. In all simulations we have taken the coupling parameters of the springs (Ref. 55) like $\Lambda = 1$ Å and $\Lambda_E/(k_BT/Å^2) = \Lambda_{E,a}/(k_BT)$ $= \Lambda_{E,b}/(k_BT) = 25000$. For proton disordered structures the Pauling (Ref. 57) entropy Rln (3/2) has been included in A_{sol} . The structure with the lowest free energy is presented in bold. For the pressure and temperature considered the difference between the Gibbs free energy and the Helmholtz free energy is very small (of the order of 0.001 in Nk_BT units).

Phase	Ν	ho (g cm ⁻³)	$\frac{A_{\rm sol}}{Nk_BT}$	Phase	Ν	ho (g cm ⁻³)	$\frac{A_{\rm sol}}{Nk_BT}$		
TIP4P/2005 model				TIP5P model					
II	432	1.175	-25.563	II	432	1.254	-23.054		
XI	360	0.928	-25.898	XI	360	0.994	-22.827		
Ih	432	0.928	-26.252	Ih	432	0.992	-22.968		
ice i	1024	0.874	-25.315	ice i	1024	0.934	-22.827		
ice i'	1024	0.874	-25.327	ice i'	1024	0.934	-22.829		
sI	368	0.819	-25.672	sI	368	0.871	-22.317		
sII	1088	0.807	-25.720	sII	1088	0.862	-22.420		
sH	408	0.788	-25.528	sH	408	0.840	-22.156		

model, the stable phase at 200 K and 1 bar is ice II. Hence, the stable phase at the normal melting point of the TIP5P potential is neither ice Ih, or any of the other virtual ices considered in this work (including Fennell and Gezelter's structures). Notice again that the free energies of the two structures proposed by Fennell and Gezelter, ice i and ice i', are quite similar. For this reason we shall only consider the ice i' structure in the rest of this study. As can be seen in Table II for the TIP5P model at 200 K and 1bar, the free energy of ice i (or ice i') is higher than the free energies of ices Ih or II. It is interesting to note that the free energy difference between ice sI and Ih at 200 K and 1 bar is 0.23 kcal/mol for TIP4P/2005 and is 0.26 kcal/mol for TIP5P. This difference in free energy—evaluated at the melting point----enters directly in the van der Waals-Platteeuw theory of hydrates. The value calculated here at 200 K is expected to be very similar to the free energy difference at the melting point.

Once the value of the free energy was determined for a certain reference state, thermodynamic integration was used to explore other states and to locate an initial point for each coexistence line. Coexistence points are obtained by equating the chemical potentials between two phases at a certain temperature and pressure. Using Gibbs–Duhem⁵⁹ simulations we can then obtain the coexistence curves between two phases and thus draw the phase diagram for each model. These phase diagrams are shown in Fig. 5.

The melting lines of the ices at negative pressures are presented. For pressures below -3000 bar it is not possible to determine the melting lines, because the liquid becomes mechanically unstable and transforms quickly into a vapor phase. This is due to the fact that the melting curve is intersecting the spinodal line of the vapor-liquid equilibrium curve and simulations of the liquid within the NpT ensemble are not possible.⁶⁶ The phase diagram for the TIP4P/2005 model is quite similar to the experimental one at positive pressures. Ice XI is stable at very low temperatures and small pressures, and transforms into ice Ih when heated to a temperature of about 25 K (the ice XI to ice Ih transition is



FIG. 5. Phase diagrams in the region of negative pressures for the TIP4P/ 2005 model (a) and for TIP5P model (b). In both diagrams, the dashed line indicates room pressure. The open circles correspond to the values of coexistence pressure at 0 K estimated using the differences of energies and volumes at 0 K and the zero-order approximation.

TABLE III. Relative energy values at 0 K and 0 bar using the antiferroelectric ice XI as reference structure (proton ordered phase of ice Ih). The number of molecules used in the calculations is N. The density is given in g cm⁻³ and ΔU_0 K is given in kcal/mol. The relative energies of ice i and ice i' are quite similar so that we present results only for ice i.

Fase	DFT			TIP4P/2005			TIP5P		
	N	ρ	$\Delta U_{0~\rm K}$	N	ρ	$\Delta U_{0~{ m K}}$	N	ρ	$\Delta U_{0~{ m K}}$
XI	96	1.024		360	0.955		360	1.048	
ice i	96	0.970	+0.276	1024	0.894	+0.344	1024	0.984	+0.091
sI	46	0.904	+0.315	368	0.845	+0.283	368	0.920	+0.426
sII	136	0.893	+0.204	1088	0.832	+0.261	1088	0.911	+0.368
sH	34	0.871	+0.448	408	0.813	+0.356	408	0.888	+0.508

found experimentally to occur at about 70 K). When the pressure increases ice Ih transforms into ice II which is also in agreement with experiment. At negative pressures ice sII dominates the phase diagram and at even lower pressures, ice sH appears as the stable phase. This is consistent with the fact that the densities decrease in the order Ih, sII, sH. The phase diagram prediction of TIP4P/2005 is consistent with the transition points found from our calculations at 0 K. In fact, the coexistence pressures at 0 K estimated using the zero-order approximation (i.e., using the internal energies at 0 K and zero pressure) are presented in Fig. 5 as red circles and are consistent with those obtained from the Gibbs-Duhem simulations (that is to say the lines of the Gibbs-Duhem simulations tend to the red circles). The small discrepancy in the sII-sH transition pressure at 0 K from the zero-order approximation and from the Gibbs-Duhem is due to the fact that the zero-order approximation deteriorates slightly for large negative pressures. In any case the difference is small and falls within the error bars of our calculations. An interesting conclusion of the results of Fig. 5 is that for TIP4P/2005, ice i, ice i', and sI do no enter the phase diagram. In other words no pressure or temperature conditions exist at which these structures have the lowest chemical potential. However, whereas ice sI is only slightly less stable than sII, the differences between the chemical potentials of ices i and i' and that of sII are very large suggesting that these structures are much more unstable.

Different results are obtained if the TIP5P potential is employed instead of the TIP4P/2005. In particular ice II is the most stable phase at moderate temperature and low pressure while ice Ih only becomes stable at negative pressure. Furthermore, in agreement with our previous observations⁶⁷ on the sensitivity of the ice $XI \rightarrow Ih$ transition temperature on the potential, this transition temperature is shifted to a temperature of about 150 K. For TIP5P ice sII and sH appear at large negative pressures. The coexistence pressures, estimated using the zero-order approximation, are consistent with those obtained from the Gibbs-Duhem simulations, which gives us confidence in our results. A significant feature of the phase diagram of TIP5P is the appearance of ice i' as a stable thermodynamic phase. This was expected given our 0 K calculations, but it is clearly visible in the global phase diagram. Finally, the phase diagram of TIP5P illustrates some potential pitfalls that may be encountered in using this potential for nucleation studies—ices II, Ih, and i' all have very similar free energies. Hence, for temperatures below the melting point of the model, the phase nucleated from the fluid phase may not correspond to the most stable one from a thermodynamic point of view, but the one with the lowest activation energy barrier for nucleation. This may explain why Fennell and Gezelter obtained ice i from a nucleation study of the potential model SSD (Refs. 36–39) and demonstrates that further work is needed in order to understand the activation energies for nucleation of the various solid phases from liquid water.

Since the phase diagram predictions of TIP4P/2005 and TIP5P are different an obvious question is: which model provides a better description of real water? For positive values of the pressure we have shown recently that TIP4P/2005 provides a quite good description of the experimental phase diagram of water whereas TIP5P fails significantly. However, it is not immediately obvious what the situation is at negative pressure, especially given that no experimental results have been reported for the phase diagram at negative pressure. To gain further understanding of this issue we have performed DFT calculations at 0 K and zero pressure for these virtual ices. The energies of the various ices relative to that of ice XI are presented in Table III (notice again that we used the antiferroelectric structure of ice XI although it has been shown recently that the ferroelectric structure is slightly more stable). As can be seen from Table III, ice sII is the most stable phase after ice XI, in agreement with the predictions of TIP4P/2005 and in disagreement with the predictions of the TIP5P model. Furthermore, DFT predicts that ice i'has a large energy compared to ice XI, and so would not be expected to enter in the phase diagram, which again disagrees with the predictions of the TIP5P calculations. Hence, DFT calculations provide further support for the predictions of TIP4P/2005; namely, that ice Ih is converted to ice sII at moderate negative pressures and the ice i phase does not occur.

It is remarkable that the differences between the relative energies obtained from DFT differ only by at most ~0.09 kcal/mol from those obtained from TIP4P/2005. To obtain reliable phase diagram predictions from first principles, the errors should be of the order of ~0.1 kcal/mol, which illustrates the enormous challenge of determining the phase diagram of water from first principles. Concerning the densities, DFT predicts values which are closer to those obtained using the TIP5P potential, which suggests that common functionals can still be improved⁶⁸ as it well established that TIP5P overestimates the density of ice by approximately eight per cent. As an example of this overestimation, the experimental density of ice Ih at 0 K and 0 bar is 0.925 g/cm³. TIP4P/2005 predicts a density of about 0.955 in these conditions while DFT predicts a density of about 1.02 which is significantly larger than the experimental number. This deviation in density appears to arise from some systematic error in the energy functional and in fact by subtracting 0.07 g/cm³ from the DFT densities one get densities that are in reasonable agreement with those obtained from TIP4P/2005. An obvious conclusion from the results of this table is that at this point the TIP4P/2005 empirical model provides better estimates of the ice densities than DFT calculations. The inclusion of nuclear quantum effects⁶⁹⁻⁷¹ would improve the density predictions of both the DFT and TIP4P/2005 model since nuclear quantum effects tend to reduce the densities of ices compared to classical simulations. However, the reduction is expected^{/1} to be about 0.04 g/cm³ whereas the typical deviation between DFT and experimental is of about 0.10 g/cm³ indicating that besides incorporating nuclear quantum effects the functional used in the DFT calculations should be improved by, for example, considering hybrid and meta functionals and long range dispersion.

VI. CONCLUSIONS

In this work we have computed the phase diagram at negative pressures for two water potentials: TIP4P/2005 and TIP5P. Several virtual ices, with a density lower than that of ice Ih were considered. Free energy calculations, thermodynamic integration, and Gibbs–Duhem integration were used to obtain the phase diagram. As a test on the calculations of the phase diagrams, the properties of the ices at 0 K and zero pressure were obtained from NpT annealing simulations and transition pressures at 0 K were estimated using the zeroorder approximation. It has been shown that the transition pressures at 0 K obtained using the Gibbs–Duhem simulations are in agreement with those obtained from 0 K calculations, providing confidence in the reliability of our results.

For TIP4P/2005 it has been found that ices XI and Ih are the stable phases at room pressure, while ice II becomes stable at higher pressures. At negative pressures ice Ih is also stable, but transforms into sII and at even lower pressures into ice sH. By contrast, for TIP5P ice II is the stable phase at room pressure and moderate temperatures. At negative pressures one finds ice Ih, which transforms into ice XI at low temperatures. At large negative pressures one also finds sII and sH. Concerning the negative pressure region of the phase diagram the main difference between TIP4P/2005 and TIP5P is the appearance of ice i' as a stable phase for TIP5P. To clarify the situation we have performed DFT calculations for these virtual ices at 0 K and zero pressure. DFT significantly overestimates the densities of the ices but gives a relative ordering of the energies which is consistent with that found for TIP4P/2005 but not with TIP5P. Hence, in agreement with the predictions of the TIP4P/2005 model, DFT calculations suggest that the sequence of phases of water at negative pressures is ice Ih, sII, and sH and that ice i is metastable. In particular, both TIP4P/2005 and DFT predict guest-free sII to be more stable than ice i' despite ice i'

having a higher density than sII. The simulations on TIP5P have highlighted the care that must be taken with nucleation studies carried out with this potential. For this potential, at room pressure and temperature close to the melting point, there are multiple phases with very similar chemical potentials and so differences in the activation barriers may markedly affect the behavior observed.

Finally, an estimate of about 0.24 kcal/mol for the free energy difference between ice Ih and sI has been provided. This may be used in concert with the van der Waals Platteeuw theory to provide estimates of properties of gas hydrates (included phase equilibrium).

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