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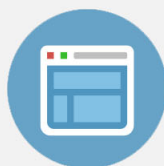
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Determining the phase diagram of water from direct coexistence simulations: The phase diagram of the TIP4P/2005 model revisited

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Direct coexistence simulations between the fluid and solid phases are performed for several ices. For ices I_h and VII it has already been shown that the methodology is successful and the melting point is in agreement with that obtained from free energy calculations. In this work the methodology is applied to ices II, III, V, and VI. The lengths of the direct coexistence runs for the high pressure polymorphs are not too long and last less than 20 ns for all ices except for ice II where longer runs (of about 150 ns) are needed. For ices II, V, and VI the results obtained are completely consistent with those obtained from free energy calculations. However, for ice III it is found that the melting point from direct coexistence simulations is higher than that obtained from free energy calculations, the difference being greater than the statistical error. Since ice III presents partial proton orientational disorder, the departure is attributed to differences in the partial proton order in the water model with respect to that found in the experiment. The phase diagram of the TIP4P/2005 model is recalculated using the melting points obtained from direct coexistence simulations. The new phase diagram is similar to the previous one except for the coexistence lines where ice III is involved. The range of stability of ice III on the p-T plot of the phase diagram increases significantly. It is seen that the model qualitatively describes the phase diagram of water. In this work it is shown that the complete phase diagram of water including ices I_h , II, III, V, VI, VII, and the fluid phase can be obtained from direct coexistence simulations without the need of free energy calculations. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4824627>]

I. INTRODUCTION

Simulation studies of water have been an important area of research since the pioneering works of Barker and Watts¹ and Rahman and Stillinger.² The description of the phase diagram represents a way to test the ability of water potential models.^{3–7} New models were developed with an improved description of the phase diagram of water and of the maximum in the density of liquid water (TIP4P/Ice,⁸ TIP4P-Ew,⁹ and TIP4P/2005¹⁰). The phase diagram has been evaluated for a number of water models using both classical simulations^{11–14} and simulations including nuclear quantum effects.^{14–16}

The methodology employed to determine the phase diagram for simulation is often based on the calculation of an initial point for each coexistence line followed by Gibbs Duhem integration¹⁷ to trace the rest of the coexistence line. At coexistence, the chemical potential of water in both phases (at a certain temperature and pressure) becomes identical. For the fluid phase it is relatively simple to determine the chemical potential. However, the calculation of the chemical potential of the solid phases requires special techniques such as the Einstein crystal method¹⁸ proposed by Frenkel and Ladd or its variant Einstein molecule method^{19,20} proposed by Vega and Noya. Until recently, solid free energy calculations were performed with home-made programs but it has been shown^{21,22}

that the calculations can indeed be performed with free molecular dynamic packages such as GROMACS.²³

Ices can be divided into three families: ices in which the protons are orientationally ordered (ices II, VIII, IX, XI, XIII, XIV, and XV), ices with full proton disorder (I_h , VI, and VII), and ices with partial proton disorder (III and V). For the first two types the evaluation of the free energy of the solid phase is rather trivial. For proton ordered ices, it suffices to compute the free energy of the solid configuration. When the system presents total proton disorder, one can take a representative configuration and add the Pauling entropy contribution²⁴ which accounts for the number of possible configurations compatible with the Bernal-Fowler rules.^{25–27} However, when there is partial proton disorder (III and V) things are more difficult. The approach we have used in the past has been to take a representative configuration of ices III and/or V, calculating its free energy by the Einstein crystal/molecule method, and then adding a modified Pauling entropy²⁸ (accounting for the fact that the proton disorder is only partial). But the choice of a “representative” configuration of a partially disordered ice is not a trivial task since the energy of different configurations varies significantly.^{29,30}

Another way to calculate the melting point of a solid is to use direct coexistence simulations. In the direct coexistence technique, the two phases of interest (typically a solid and a fluid phase) are put in contact within the same simulation box. Although it can be implemented in different ways, a possibility is to fix the pressure of interest and to perform simulations

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at different temperatures to obtain the equilibrium melting temperature. The procedure was first proposed by Ladd and Woodcock^{31,32} in the 1970s and is steadily becoming more popular, especially after the works of Morris and Song³³ and Fernandez *et al.*³⁴ The direct coexistence method has been successful in determining the melting point of ice I_h for common water models,^{34–38} with predictions in good agreement with those obtained from free energy calculations.³⁴ The same approach was applied^{39,40} to other simple ice structures related to cubic ice Ic (i.e., VII and the plastic crystal phase). The technique also allows to determine the mechanism and growth rate of ice I_h.^{41–46} Besides, it has been applied to a number of substances including hydrates,⁴⁷ methanol,⁴⁸ or patchy colloids.⁴⁹

To be of practical use, the direct coexistence method requires that the melting/freezing occurs on time scales below the microsecond. An interesting issue is whether the technique could also be useful in the investigation of more complex water polymorphs as it is the case of ices II, III, V, and VI. This is one of the goals of this work. We will show that the melting point obtained from direct coexistence simulations of ices II, V, and VI is identical to that obtained from free energy calculations of the TIP4P/2005 water model. However, for ice III, the melting point evaluated using the direct coexistence technique is about 25 K higher than that obtained from free energy calculations, thus increasing significantly its stability region. As discussed later in the manuscript, this is due to the differences in the experimental and simulated proton partial ordering of ice III. We shall also revisit the phase diagram of TIP4P/2005 from the melting points obtained from direct coexistence simulations. Although the stability range of ice III is larger than that found in experiment, TIP4P/2005 still provides a reasonable description of the water phase diagram (we only take into consideration the experimentally stable ices I_h, II, III, V, and VI). In summary, it will be shown that direct coexistence simulations (along with Gibbs Duhem integration) suffice to determine the phase diagram of water. An important conclusion of the study is that direct coexistence simulation results do not seem to be strongly affected by the proton ordering used in the initial configuration. This is not the case of free energy calculations for which the proton ordering is fixed in the input configuration. The problem is that one cannot take for granted that the proton ordering found in experiments is identical to that found for the model.

II. METHODOLOGY

Solid phases studied in this work are ices II, III, V, and VI. Ice II is proton ordered, ices III and V are partial proton disordered phases, and VI shows full proton disorder. For the proton disordered solid phases, we used the algorithm of Buch *et al.*⁵⁰ to generate a starting configuration that satisfies the Bernal-Fowler rules with a dipolar moment close to zero.²⁵ For ice II, the initial configuration is obtained directly from crystallographic coordinates. Although ice II has a rhombohedral unit cell, we use an equivalent orthorhombic cell in order to work with a more simple simulation box.²² The number of molecules in the solid phase must be an integer multiple of the number of molecules in the unit cell of the corresponding

TABLE I. Number of water molecules (N) and box size of the different systems studied in this work.

System	N	Box size (Å ³)
Ice VI-liquid	1440	18×18×95
Ice V-liquid	1008	21×23×50
Ice III-liquid	1296	20×20×75
Ice II-liquid	1296	26×23×58

ice polymorph. Table I shows the number of molecules and box size for the systems studied. The number of molecules is always above 1000. With this system size the magnitude of finite size effects is rather small.³⁴ The initial configuration is obtained by putting together a slab of the solid and a slab of the fluid, and removing possible overlaps at the interface. Thus, at the beginning of the runs approximately half of the molecules are solid and half fluid.

We performed *NpT* molecular dynamics simulations at different temperatures and pressures using the molecular dynamics package GROMACS (v4.5.5)²³ with a time-step of 1 fs. The temperature was fixed using a velocity rescaling thermostat^{51,52} with a relaxation time of 1 ps. To keep the pressure constant, a Parrinello-Rahman barostat^{53,54} was used. The relaxation time of the barostat was 1 ps. The three different sides of the simulation box were allowed to fluctuate independently to allow changes in the shape of the solid region and to avoid the existence of stress in the solid. The typical length of the simulations was about 10–20 ns (except for the system formed by ice II and liquid water). The geometry of the water molecules was enforced using constraints.⁵⁵ The Lennard-Jones part of the potential was truncated at 8.5 Å. Ewald sums were used to deal with the electrostatic interactions. The real part of the Coulombic potential was also truncated at 8.5 Å. The Fourier part of the Ewald sums was evaluated using the particle mesh Ewald (PME) method.⁵⁶ We used an interpolating fourth order polynomial together with a 0.1 nm grid.

To determine the equilibrium temperature between the solid phase and fluid phases at a given pressure we proceed as follows. Simulations at several temperatures are performed at the pressure of interest. The time evolution of the energy is followed. When the temperature is above the melting temperature of the model the solid phase melts until, eventually, the system transforms completely into a fluid phase. This transformation is reflected in a steady increase of the potential energy of the system. If the temperature is below the melting point, the fluid phase freezes and the entire system will become solid. In this case the potential energy of the system will decrease with time. We estimate the melting temperature at the pressure of interest as the average of the lowest temperature for which the solid phase melts and the highest temperature for which the fluid phase freezes. By following this procedure we determine an initial coexistence point (i.e., a temperature and pressure where both phases are in equilibrium). Once an initial coexistence point is obtained for a certain solid-liquid transition one can trace the entire coexistence line by using the Gibbs-Duhem¹⁷ integration method proposed by Kofke. Basically the Gibbs Duhem integration

method consists in integrating numerically the Clapeyron equation, by determining the enthalpy and volume difference between the two coexistence phases from NpT simulations. In this work we use a fourth-order Runge-Kutta integration to integrate the Clapeyron equation.

To describe the water interactions we use TIP4P/2005,¹⁰ a rigid and nonpolarizable model proposed by our research group. The model provides a reasonable description of many water properties both in the liquid^{13,57–59} and solid states.^{10,60,61} In fact, it has demonstrated a better overall performance than other common rigid, non-polarizable models.⁶²

III. RESULTS

The direct coexistence method has proved to be quite successful in determining the I_h -liquid coexistence. In fact, in a previous work³⁴ we have shown that the melting point obtained from direct coexistence simulations at room pressure was in very good agreement with that obtained from direct coexistence simulations. The same was found by other authors.⁶³ But the structure of ice I_h is quite simple, all the molecules are connected in a tetrahedral network. Other solid water polymorphs are much more complex and it remains to be seen if the direct coexistence method is able to yield satisfactory results for them. Table II presents the melting temperatures T_m of the different ices studied in this work modeled with the TIP4P/2005 model.

We start by commenting the results for the ice VI-liquid equilibrium at a pressure of 12 000 bar. The time evolution of the energy of this system is shown in Fig. 1. From this plot one can estimate the equilibrium melting temperature of ice VI at 12 000 bar to occur at 267 K. The typical time to freeze the liquid slab is of about 15 ns. It has been reported³⁴ that the freezing of water into ice I_h also required times of about 10 ns. Thus, there is not much difference between the ice growth rates for ices VI and I_h . This is interesting since ice VI is a much more complex structure than ice I_h . Ice VI consists of two inter-penetrated (but not interconnected) sub-lattices, the molecules of each sub-lattice being connected by hydrogens bonds. Besides, in ice VI, not all molecules are topologically equivalent while all the molecules are topologically equivalent in ice I_h . This difference in the complexity of the structure is not reflected in the crystal growth rates. In a previous work, we reported the equilibrium temperature between ice VI-liquid at 12 000 bar using free energy calculations. The value obtained was 267 K. The good agreement obtained between these two different techniques gives confidence in

TABLE II. Melting temperatures as obtained from free energy (FE) calculations and from direct coexistence (DC) simulations of this work.

Phases	p (bar)	T_m (FE)/K	T_m (DC)/K
Ice VI-liquid	12000	267(5)	267(2)
Ice V-liquid	7000	238(5)	241(3)
Ice III-liquid	3500	215(5)	240(4)
Ice II-liquid	2900	215(5)	215(4)
Ice I_h -liquid	1	252(5)	249(3)

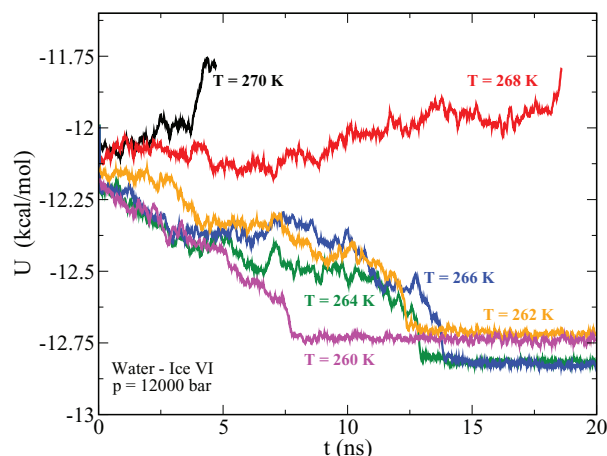


FIG. 1. Evolution of the potential energy as a function of time along NpT runs at 12 000 bar for the system ice VI-liquid water using the TIP4P/2005 model.

the accuracy of the calculated melting temperature also for structurally complex ice polymorphs.

Let us now consider the results for ice V-liquid water. We have determined the equilibrium temperature at 7000 bar. The features are similar to those discussed for ice VI (the time evolution of the energy of the system is given in the supplementary material⁶⁴). The kinetics is even faster than for ice VI, since in less than 6 ns it is possible either to melt or to freeze the entire sample. However, it should be taken into account that the length of the simulation box (L_z) for ice VI is almost twice that of ice V. Since the initial configuration is approximately half liquid and half solid, for a proper comparison between the growth rates of both ices, one should multiply the results obtained for ice V by a factor of two. When this is done one finds that the growth rates of ices VI and V are rather similar. Once again the complexity of the solid structure (ice V has several types of topologically non-equivalent water molecules) is not reflected on the kinetics. From the evolution of the energy with time, one may estimate the melting temperature of ice V to be 241(3) K at 7000 bar. This is in very good agreement with the value obtained from free energy calculations, namely 238(5) K. It is interesting to point out that a certain amount of partial proton ordering has been found in experiments with ice V. However, our results with TIP4P/2005 indicate that the degree of proton partial ordering of ice V is very small. Thus, assuming full proton disorder for this model seems to be a quite reasonable approximation.

As for ice III-liquid water, direct coexistence simulations were performed at a pressure of 3500 bar. Results are presented in Fig. 2. The melting of ice III occurs rather quickly for temperatures above 243 K. Freezing is found for temperatures below 237 K. This is also confirmed from the snapshots of the initial and final configurations. Snapshots of the initial and final configurations at two different temperatures (above and below the melting point) for ices III, V, and VI are given in the supplementary material.⁶⁴ The growth rate of ice III is slightly slower than that found for ices VI and V: it takes about 20 ns to freeze the entire system at 237 K. From the results presented here we conclude that the melting point at 3500 bar is around 240 K. Free energy calculations yield a

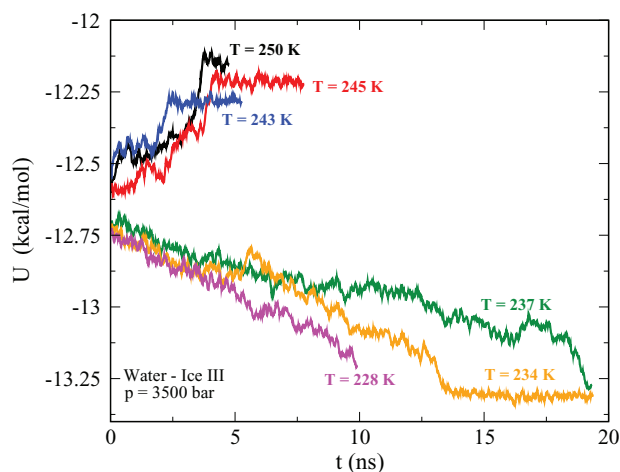


FIG. 2. Evolution of the potential energy as a function of time along NpT runs at 3500 bar for the system ice III-liquid water using the TIP4P/2005 model.

melting point of 215(5) K at this pressure. It is clear that both results are not in agreement, the difference being of about 25 K, clearly greater than the error bar. What is the origin of the discrepancy? Which of the two estimates is the correct one? Ice III is a proton disordered phase. However, it does not present complete but only partial proton disorder. There is a way to indicate the degree of proton disorder through the parameters α and β which measure the occupancy of certain lattice positions by the hydrogens (see Table IV of Ref. 65 or Fig. 4 of Ref. 28 for a description of the hydrogen positions labeled as α and β). When the proton disorder is complete, $\alpha = 0.5$ and $\beta = 0.5$. When the proton disorder is not complete these parameters differ from 0.5. Experimentally, Finney and co-workers⁶⁵ found $\alpha = 0.35$ and $\beta = 0.52$. It is important to point out that for ice III deviations of α and/or β from 0.5 (the value found when the proton disorder is complete) do not imply the existence of net polarization in the solid. Ice III is a non-ferroelectric solid even though experimentally it has only partial proton disorder. In our determination of the phase diagram of TIP4P/2005¹⁰ we imposed the experimental values of α and β to generate a proton disordered configuration. The free energy of this configuration was obtained from free energy calculations by using the Einstein crystal method. After that, we added an estimation of the Pauling-like entropy for a system with partial proton disorder.²⁸ The disagreement between the melting points obtained via free energy calculations and direct coexistence simulations seems to indicate that the assumption that the values of α and β for the model are the same as the experimental ones may be incorrect. There are now several indications supporting this assertion.

The relaxation time for proton disorder is of the order of microseconds at room temperature,⁶⁶ beyond the time scale affordable in computer simulations. Thus, computer simulations do not allow the entire rearrangement of the hydrogen bonding network unless special moves (sampling the proton order) are introduced. The use of this type of moves was initiated by Rahman and Stillinger⁶⁷ and further improved by Rick and Haymet.^{68–70} Recently, we introduced^{29,71,72} this type of moves in a paper aimed at computing the dielectric

constant of ices. We found that the values of α and β in ice III for TIP4P/2005 were $\alpha = 0.5$ and $\beta = 0.25$, different from those found in experiment. This is also reflected in the internal energy. In fact, at 243 K and 2800 bar, using the experimental populations for α and β , the residual internal energy was found to be about 0.22 kcal/mol⁷³ higher than the one obtained when introducing the Rick-Haymet moves.²⁹ Therefore, using the experimental values of α and β for TIP4P/2005 significantly decreases the stability of ice III. We should have used the values of α and β corresponding to the model rather than the experimental ones. However, the latter values have only been reported in 2011,²⁹ so they were unknown in 2005.¹⁰

We have still a second evidence. In this work we have performed direct coexistence runs using different initial proton disordered configurations of ice III. Independent of the α and β values in the starting configuration, we found that the melting point was always close to 240 K. The fact that the equilibrium temperature in direct coexistence simulations is not too sensitive to the details of the proton disorder of the ice III slab is interesting. It means that the ice III growing from the melt adopts the correct proton ordering regardless of the proton ordering of the initial slab. Thus, the system uses the solid slab as an initial template but generates the correct proton ordering when growing. Therefore, the melting point obtained from direct coexistence simulations for ice III is more reliable than that obtained previously from free energy calculations where an incorrect proton ordering was used for the model. This represents a clear advantage of direct coexistence simulations with respect to free energy calculations. One neither needs to know in advance the degree of partial proton ordering nor needs to evaluate a modified Pauling-like entropy for a system with partial ordering.

Notice that ice III is a special case within the solid phases of water. For the rest of ices, the internal energy and the free energy change very little with the details of the proton disorder. In fact, the assumption of full proton disorder for ices I_h, VI, and VII seems to be fully justified. For ice V at 5300 bar and 243 K the internal energy did not change so dramatically when using the experimental values of proton ordering or those obtained after introducing Rick and Haymet moves (the energy was found to be about 0.06 kcal/mol^{29,73} lower when using the Rick and Haymet moves). This is about one fourth of the change found for ice III. Thus, the effect is much smaller for ice V than for ice III. Therefore, the message is that ice III must be treated with care when computing the phase diagram of water as pointed out by Ramirez *et al.*³⁰ Direct coexistence simulations provide a robust way of bypassing the tricky issue of the partial proton disorder.

The change in the melting point of ice III certainly affects the appearance of the phase diagram so that it is necessary to recalculate it. We performed Gibbs Duhem integration for the ice I_h-liquid, ice VI-liquid, ice V-liquid, and ice III-liquid coexistence curves (for the Gibbs Duhem runs involving ice III we used a configuration with an internal energy located in the center of the energy distribution shown in Fig. 2 of Ref. 29). The I_h-liquid line meets the ice III-liquid line at the fluid-I_h-III triple point. It is interesting to note that, from this point, one can start a Gibbs Duhem run to compute the I_h-III coexistence

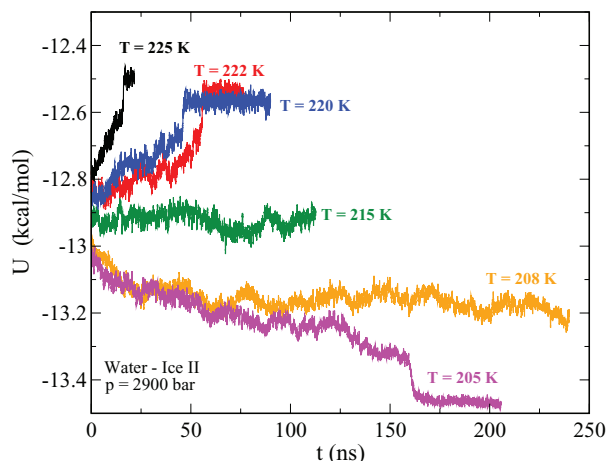


FIG. 3. Evolution of the potential energy as a function of time along NpT runs at 2900 bar for the system ice II-liquid water using the TIP4P/2005 model.

line. Similarly the III-liquid coexistence curve intersects the V-liquid coexistence line at the III-V-liquid triple point. From this triple point one can proceed with Gibbs Duhem runs to determine the III-V coexistence curve. The V-VI-liquid triple point can be analogously located from which the V-VI coexistence line can be obtained. By proceeding in this way it is possible to determine a large portion of the phase diagram including solid-solid transitions.

The coexistence lines of liquid water with ices I_h , III, V, and VI lie in the stable region of the phase diagram. This is not the case of the ice II-liquid coexistence. However, some other coexistence curves involving ice II (I_h -II, II-III, II-VI, and II-V) do appear in the experimental phase diagram. In order to complete the calculation of the water phase diagram from direct coexistence simulations it is necessary to determine at least one point of some of these solid-solid coexistence lines. This calculation is a harsh test of the possibilities of the direct coexistence method. A triple point involving ice II must be computed. We have shown in previous paragraphs how can this be done. For instance, the liquid- I_h -II triple point may be obtained as the intersection of the liquid- I_h and liquid-II curves. But it remains to be demonstrated that direct coexistence is feasible for the calculation of the melting point of a metastable (and proton ordered) ice. To check if this is true we have performed direct coexistence simulations for the II-liquid equilibrium at 2900 bar. The results of the runs for ice II are shown in Fig. 3. Although much longer runs than for the other ices are required (about 100 ns or more), the method is able to provide an estimate of the melting curve of ice II, about 215 K. Likely, the low melting temperature of ice II is responsible for the slower dynamics of crystal growth. The calculated melting temperature may be compared with that from free energy calculations. This value has not yet been reported but previous work⁷⁴ enables one to easily obtain the location of the liquid- I_h -II triple point. We need only to extend the I_h -II coexistence line until it crosses the I_h -liquid water equilibrium. Both curves intersect at about 2900 bar and 215 K. Thus, we find again an excellent agreement between the free energy results and direct coexistence simulations.

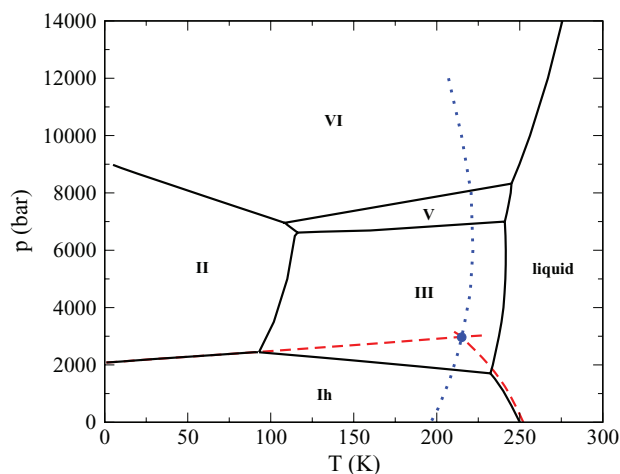


FIG. 4. Phase diagram for the TIP4P/2005 water model as obtained from direct coexistence simulations (black solid lines). The red dashed lines are the I_h -II and I_h -liquid lines as determined from free energy and Gibbs Duhem calculations in our previous work. The blue dotted line is the melting line of ice II obtained from Gibbs Duhem integration after determining an initial point (circle) at 2900 bar from direct coexistence simulations.

Once the melting point of ice II at 2900 bar is known (by two routes) one can use Gibbs Duhem integration to calculate the II-water coexistence line. The melting point of ice II at 1 bar is about 195 K (i.e., more than 50 degrees below that of ice I_h). Thus, ice I_h is the stable solid phase of TIP4P/2005 at room pressure. Moreover, at higher pressures, the melting curve of ice II also appears at a temperature below that of other polymorphs. Thus, the melting of ice II is metastable at any pressure (see Fig. 4). The knowledge of the liquid- I_h -II triple point allows one to trace the I_h -II equilibrium until the curve intersects the I_h -III coexistence line at the I_h -II-III triple point. Similarly, the II-III, II-V, and II-VI coexistence curves may be determined. The resulting phase diagram for TIP4P/2005 water model as obtained from direct coexistence simulations is presented in Fig. 4.

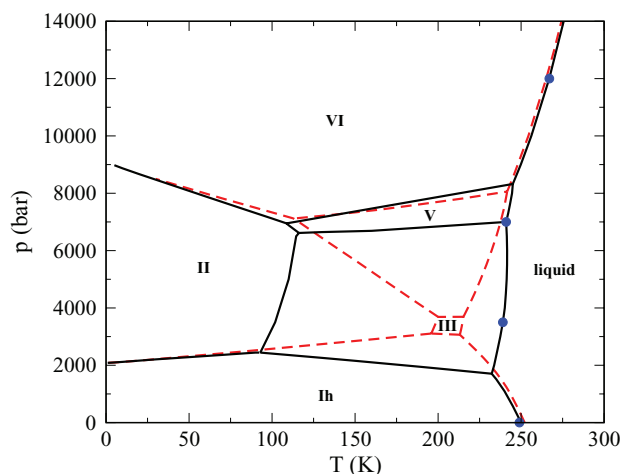


FIG. 5. Phase diagram for the TIP4P/2005 water model as obtained in this work (full lines) compared with that of Ref. 10 obtained from free energy calculations (dashed lines). The blue circles are results from direct coexistence simulations from this work.

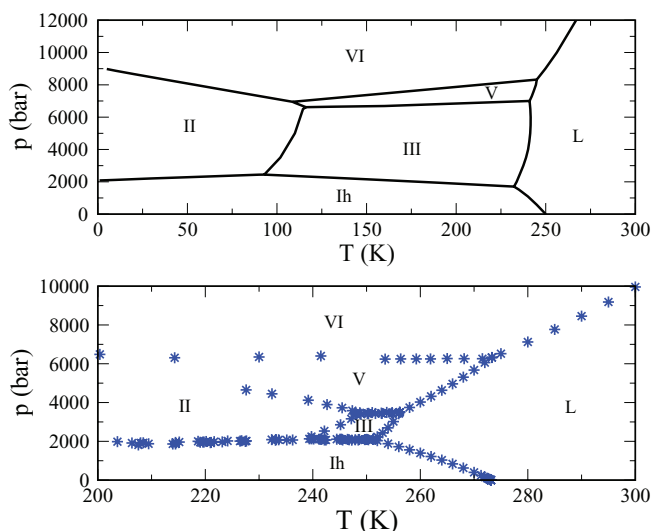


FIG. 6. Phase diagram for the TIP4P/2005 water model (top) compared with the experimental phase diagram (bottom).

Fig. 5 shows the phase diagram of TIP4P/2005 from this work compared to that obtained in our previous work.¹⁰ The coexistence lines not involving ice III are essentially the same as those reported in Ref. 10. Thus, VI-liquid, V-liquid, I_h -liquid, V-VI, II-VI, and II-V are hardly affected by the revision. However, the range of temperatures and pressures where ice III is stable has increased significantly. Now ice III occupies a larger part of the phase diagram of water. This is in line with the results of Habershon and Manolopoulos⁷⁵ and Ramirez *et al.*³⁰ who found a larger stability region for ice III for another TIP4P-like model (q-TIP4P/f).¹⁵ It seems that for TIP4P/2005 (and probably for other TIP4P models as TIP4P,⁷⁶ TIP4P-Ew,⁹ or TIP4P/Ice⁸) we underestimated the stability of ice III which should occupy a larger portion of the phase diagram than previously assumed. Whether this is true also for other charge geometries (SPC/E, TIP5P) is an issue that deserves a further study. The comparison with respect to experiment is shown in Fig. 6. Although the region of stability of ice V is underestimated and that of ice III is overestimated, the prediction of TIP4P/2005 is still qualitatively correct. It is interesting to note that we have recently shown that the introduction of nuclear quantum effects significantly increases the stability of ice II, thus reducing that of ice III.¹⁴ It seems that to understand the small range of existence of ice III on the experimental phase diagram it is important to deal not only with the partial proton disorder but also with the effect of nuclear quantum effects.

IV. CONCLUSIONS

In this work we have shown that direct coexistence simulations can be applied successfully to determine the melting point of the high pressure polymorphs of water. Since the intersection of the melting curves of two different polymorphs provides a triple point, solid-solid lines can also be computed with the method in combination with Gibbs-Duhem integration. Thus, direct coexistence allows one to determine the whole phase diagram of a substance. The method has been ap-

plied here to ices II, V, and VI obtaining good agreement with the results obtained from free energy calculations. In previous work, it has been shown that the technique also works for ices I_h and VII so that both methodologies are in agreement. However, it is found that the results for ice III differ. An analysis of the results seems to indicate that the effect of the partial proton disorder is significant for this polymorph. In fact, Monte Carlo simulations of TIP4P/2005 with special moves to better sample the hydrogen bond network showed that the equilibrium values of α and β are different from those found experimentally. Since we used the experimental parameters defining the proton ordering, our previous free energy calculations were not correct for ice III. On the other hand, we have found that, when using direct coexistence simulations, the resulting melting temperature is not significantly affected by the particular proton ordered introduced on the solid slab of the initial configuration. It seems that the initial slab is used as a template for the growth of ice.

We have recomputed the phase diagram of the TIP4P/2005 using the correct melting temperature of ice III. The range of stability of ice III increases significantly with respect to our previous work. However, the experimental phase diagram of water is still described qualitatively. The impact on our recent work¹⁴ on TIP4PQ/2005¹⁶ will be much smaller (ice III will occupy a slightly larger portion on the phase diagram) since we used for TIP4PQ/2005 a configuration with an internal energy located in the center of the energy distribution shown in Fig. 2 of Ref. 29 (rather than a configuration with the experimental values of α and β), and the Pauling entropy.¹⁴

The results presented here also present other interesting possibilities for studies of fluid-solid equilibrium. For instance, determining the fluid-solid interfacial free energy for high pressure polymorphs would be an interesting topic to consider.^{77,78} Rozmanov and Kusalik⁷⁹ and Weiss *et al.*⁴⁵ have determined that the growth rate of ice I_h is maximum at temperatures about 15 K below the melting point. The results obtained in this work illustrate that the growth rate can also be determined for high pressure polymorphs of water. Whether such maximum in the growth rate also exists for other polymorphs is an interesting question. Finally, let us mention that the growth rate of ice I_h is quite anisotropic and its magnitude depends on the plane of the solid exposed to the fluid phase.^{46,80} For ice I_h the fastest growth is obtained when exposing the prismatic secondary plane. For direct coexistence simulations it is convenient to choose a plane for the solid-liquid interface for which the dynamics is fast since the coexistence temperature does not depend on the plane, and one would like to have fast relaxation (growth/melt) of the interface. The same is likely to be true for other polymorphs. We have not studied here the anisotropy of ice growth (a topic of interest for future studies⁸¹) but we have shown that there is at least a plane for the selected ices for which the ice growth proceeds at a reasonable speed. As to whether the finding of this work can be extended to other substances remains to be tested. The methodology will work as far as the dynamics of the fluid/solid interface (melt/growth) occurs on a time scale affordable by current computers (i.e., below the microsecond regime). If this is not the case the technique in principle should work, but the computer time may exceed current

capacities. Free energy calculations are not affected by these kinetic factors. However, it should be pointed out that, although the Einstein crystal methodology can be easily implemented for systems with complete order or complete disorder, it is not yet entirely clear how to implement it for systems where the disorder is partial. Ice III (and, to a less extent, ice V) are two examples of solids where there is partial proton disorder. The fcc solid phase of the restricted primitive model which shows partial substitutional ordering of the particles is another example.^{82,83} It would be of interest in the future to establish a rigorous procedure to evaluate the free energy of these type of solids.

Note added in proof. After this study was completed we were made aware of two interesting papers relevant to the content of this paper. Wang *et al.*⁸⁴ have shown that direct coexistence simulations of the ice-water interface can also be successfully applied to calculate the phase diagram for polarizable models of water. On the other hand, Ramirez *et al.*⁸⁵ have suggested that other ices not considered in this work (as for instance ices IX and XII) could become more stable at certain thermodynamic conditions than the polymorphs considered here.

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- ¹J. A. Barker and R. O. Watts, *Chem. Phys. Lett.* **3**, 144 (1969).
- ²A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **55**, 3336 (1971).
- ³See <http://www.lsbu.ac.uk/water/> for information about water properties.
- ⁴E. Whalley, *J. Chem. Phys.* **81**, 4087 (1984).
- ⁵M. D. Morse and S. A. Rice, *J. Chem. Phys.* **76**, 650 (1982).
- ⁶E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, *Phys. Rev. Lett.* **92**, 255701 (2004).
- ⁷E. Sanz, C. Vega, J. L. F. Abascal, and L. G. MacDowell, *J. Chem. Phys.* **121**, 1165 (2004).
- ⁸J. L. F. Abascal, E. Sanz, R. G. Fernández, and C. Vega, *J. Chem. Phys.* **122**, 234511 (2005).
- ⁹H. W. Horn, W. C. Swope, J. W. Pitera, J. D. Madura, T. J. Dick, G. L. Hura, and T. Head-Gordon, *J. Chem. Phys.* **120**, 9665 (2004).
- ¹⁰J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005).
- ¹¹C. Vega, E. Sanz, J. L. F. Abascal, and E. Noya, *J. Phys.: Condens. Matter* **20**, 153101 (2008).
- ¹²C. Vega, J. Abascal, E. Sanz, L. MacDowell, and C. McBride, *J. Phys.: Condens. Matter* **17**, S3283 (2005).
- ¹³C. Vega, J. L. F. Abascal, M. M. Conde, and J. L. Aragonés, *Faraday Discuss.* **141**, 251 (2009).
- ¹⁴C. McBride, E. G. Noya, J. L. Aragonés, M. M. Conde, and C. Vega, *Phys. Chem. Chem. Phys.* **14**, 10140 (2012).
- ¹⁵S. Habershon, T. E. Markland, and D. E. Manolopoulos, *J. Chem. Phys.* **131**, 024501 (2009).
- ¹⁶C. McBride, C. Vega, E. G. Noya, R. Ramírez, and L. M. Sesé, *J. Chem. Phys.* **131**, 024506 (2009).
- ¹⁷D. A. Kofke, *J. Chem. Phys.* **98**, 4149 (1993).
- ¹⁸D. Frenkel and A. J. C. Ladd, *J. Chem. Phys.* **81**, 3188 (1984).
- ¹⁹C. Vega and E. G. Noya, *J. Chem. Phys.* **127**, 154113 (2007).
- ²⁰E. G. Noya, M. M. Conde, and C. Vega, *J. Chem. Phys.* **129**, 104704 (2008).
- ²¹J. L. Aragonés, C. Valeriani, and C. Vega, *J. Chem. Phys.* **137**, 146101 (2012).
- ²²J. L. Aragonés, E. G. Noya, C. Valeriani, and C. Vega, *J. Chem. Phys.* **139**, 034104 (2013).
- ²³D. van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, and H. J. C. Berendsen, *J. Comput. Chem.* **26**, 1701 (2005).
- ²⁴L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
- ²⁵J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).
- ²⁶V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford University Press, 1999).
- ²⁷J. L. Finney, *J. Mol. Liq.* **90**, 303 (2001).
- ²⁸L. G. MacDowell, E. Sanz, C. Vega, and J. L. F. Abascal, *J. Chem. Phys.* **121**, 10145 (2004).
- ²⁹J. L. Aragonés, L. G. MacDowell, and C. Vega, *J. Phys. Chem. A* **115**, 5745 (2011).
- ³⁰R. Ramirez, N. Neuerburg, M. V. F. Sierra, and C. P. Herrero, *J. Chem. Phys.* **137**, 044502 (2012).
- ³¹A. J. C. Ladd and L. Woodcock, *Chem. Phys. Lett.* **51**, 155 (1977).
- ³²A. J. C. Ladd and L. Woodcock, *Mol. Phys.* **36**, 611 (1978).
- ³³J. R. Morris and X. Song, *J. Chem. Phys.* **116**, 9352 (2002).
- ³⁴R. G. Fernández, J. L. F. Abascal, and C. Vega, *J. Chem. Phys.* **124**, 144506 (2006).
- ³⁵O. A. Karim, P. A. Kay, and A. D. J. Haymet, *J. Chem. Phys.* **92**, 4634 (1990).
- ³⁶T. Bryk and A. D. J. Haymet, *J. Chem. Phys.* **117**, 10258 (2002).
- ³⁷M. A. Carignano, P. B. Shepson, and I. Szleifer, *Mol. Phys.* **103**, 2957 (2005).
- ³⁸J. L. F. Abascal, R. García Fernández, C. Vega, and M. A. Carignano, *J. Chem. Phys.* **125**, 166101 (2006).
- ³⁹E. Schwegler, M. Sharma, F. Gygi, and G. Galli, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 14779 (2008).
- ⁴⁰J. L. Aragonés, M. M. Conde, E. G. Noya, and C. Vega, *Phys. Chem. Chem. Phys.* **11**, 543 (2009).
- ⁴¹H. Nada and Y. Furukawa, *J. Cryst. Growth* **169**, 587 (1996).
- ⁴²T. Bryk and A. Haymet, *Mol. Simul.* **30**, 131 (2004).
- ⁴³H. Nada, J. P. van der Eerden, and Y. Furukawa, *J. Cryst. Growth* **266**, 297 (2004).
- ⁴⁴M. A. Carignano, *J. Phys. Chem. C* **111**, 501 (2007).
- ⁴⁵V. C. Weiss, M. Rullich, C. Kholer, and T. Frauenheim, *J. Chem. Phys.* **135**, 034701 (2011).
- ⁴⁶D. Rozmanov and P. G. Kusalik, *J. Chem. Phys.* **137**, 094702 (2012).
- ⁴⁷J. Vatamanu and P. G. Kusalik, *J. Phys. Chem. B* **110**, 15896 (2006).
- ⁴⁸D. Gonzalez Salgado and C. Vega, *J. Chem. Phys.* **132**, 094505 (2010).
- ⁴⁹E. G. Noya, C. Vega, J. P. K. Doye, and A. A. Louis, *J. Chem. Phys.* **132**, 234511 (2010).
- ⁵⁰V. Buch, P. Sandler, and J. Sadlej, *J. Phys. Chem. B* **102**, 8641 (1998).
- ⁵¹G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).
- ⁵²G. Bussi, T. Zykova-Timan, and M. Parrinello, *J. Chem. Phys.* **130**, 074101 (2009).
- ⁵³M. Parrinello and A. Rahman, *J. Appl. Phys.* **52**, 7182 (1981).
- ⁵⁴S. Nosé and M. L. Klein, *Mol. Phys.* **50**, 1055 (1983).
- ⁵⁵B. Hess, H. Bekker, H. J. C. Berendsen, and J. G. E. M. Fraaije, *J. Comput. Chem.* **18**, 1463 (1997).
- ⁵⁶U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, *J. Chem. Phys.* **103**, 8577 (1995).
- ⁵⁷C. Vega and E. de Miguel, *J. Chem. Phys.* **126**, 154707 (2007).
- ⁵⁸C. Vega, J. L. F. Abascal, and I. Nezbeda, *J. Chem. Phys.* **125**, 034503 (2006).
- ⁵⁹M. A. Gonzalez and J. L. F. Abascal, *J. Chem. Phys.* **132**, 096101 (2010).
- ⁶⁰J. L. F. Abascal and C. Vega, *Phys. Rev. Lett.* **98**, 237801 (2007).
- ⁶¹M. M. Conde, C. Vega, and A. Patrykiewicz, *J. Chem. Phys.* **129**, 014702 (2008).
- ⁶²C. Vega and J. L. F. Abascal, *Phys. Chem. Chem. Phys.* **13**, 19663 (2011).
- ⁶³M. S. G. Rauland and P. G. Kusalik, *J. Chem. Phys.* **134**, 014710 (2011).
- ⁶⁴See supplementary material at <http://dx.doi.org/10.1063/1.4824627> for initial and final configurations (at two temperatures) for the direct coexistence runs of ices VI, V, and III and for the time evolution of the energy in the runs of the ice V-liquid interface.
- ⁶⁵C. Lobban, J. L. Finney, and W. F. Kuhs, *J. Chem. Phys.* **112**, 7169 (2000).
- ⁶⁶R. K. Chan, D. W. Davidson, and E. Whalley, *J. Chem. Phys.* **43**, 2376 (1965).
- ⁶⁷A. Rahman and F. H. Stillinger, *J. Chem. Phys.* **57**, 4009 (1972).
- ⁶⁸S. W. Rick and A. D. J. Haymet, *J. Chem. Phys.* **118**, 9291 (2003).
- ⁶⁹S. W. Rick, *J. Chem. Phys.* **122**, 094504 (2005).
- ⁷⁰S. W. Rick and D. Freeman, *J. Chem. Phys.* **132**, 054509 (2010).
- ⁷¹L. G. MacDowell and C. Vega, *J. Phys. Chem. B* **114**, 6089 (2010).
- ⁷²J. L. Aragonés, L. G. MacDowell, J. I. Siepmann, and C. Vega, *Phys. Rev. Lett.* **107**, 155702 (2011).

- ⁷³E. G. Noya, C. Menduina, J. L. Aragones, and C. Vega, *J. Phys. Chem. C* **111**, 15877 (2007).
- ⁷⁴J. L. F. Abascal, E. Sanz, and C. Vega, *Phys. Chem. Chem. Phys.* **11**, 556 (2009).
- ⁷⁵S. Habershon and D. E. Manolopoulos, *Phys. Chem. Chem. Phys.* **13**, 19714 (2011).
- ⁷⁶W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.* **79**, 926 (1983).
- ⁷⁷R. Handel, R. L. Davidchack, J. Anwar, and A. Brukhno, *Phys. Rev. Lett.* **100**, 036104 (2008).
- ⁷⁸R. L. Davidchack, R. Handel, J. Anwar, and A. V. Brukhno, *J. Chem. Theory Comput.* **8**, 2383 (2012).
- ⁷⁹D. Rozmanov and P. G. Kusalik, *Phys. Chem. Chem. Phys.* **14**, 13010 (2012).
- ⁸⁰H. Nada and Y. Furukawa, *J. Cryst. Growth* **283**, 242 (2005).
- ⁸¹J. Anwar and D. Zahn, *Angew. Chem., Int. Ed.* **50**, 1996 (2011).
- ⁸²C. Vega, J. L. F. Abascal, C. McBride, and F. Bresme, *J. Chem. Phys.* **119**, 964 (2003).
- ⁸³B. Smit, K. Esselink, and D. Frenkel, *Mol. Phys.* **87**, 159 (1996).
- ⁸⁴L.-P. Wang, T. Head-Gordon, J. W. Ponder, P. Ren, J. D. Chodera, P. K. Eastman, T. J. Martinez, and V. S. Pande, *J. Phys. Chem. B* **117**, 9956 (2013).
- ⁸⁵R. Ramirez, N. Neuerburg, and C. P. Herrero, *J. Chem. Phys.* **139**, 084503 (2013).