Triple points and coexistence properties of the dense phases of water calculated using computer simulation†

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In recent years our group has performed a thorough study of the dense region of the phase diagram of water. In this paper we report the numerical results for the triple points and for the change in volume, Δv, and enthalpy, ΔH, along the coexistence lines involving liquid water and/or ices ih (hexagonal), II, III, V and VI for several simple water models. The predictions for Δv using the TIP4P/2005 model are in excellent agreement with the experimental values. As to ΔH for the same model, the computer simulation results are also satisfactory although there are small but significant differences between simulation and experiment.

I. Introduction

Water exhibits a rich variety of crystalline phases.[1] In fact, the phase diagram of water presents (at least) fifteen different solid phases[2–6] with the last ones discovered in recent years.[7–9] Despite the great number of studies of water and amorphous water by computer simulation,[10–18] the crystalline solids have received less attention. In recent years there is a clear increase in the interest to study solid phases of water by computer simulation[19–36] and in the determination of the relative stability of the different ices between them or with respect to the liquid.[19,37–52] Most of the studies have focused on the investigation of the melting temperature of hexagonal ice (Ih). For this reason, we undertook the task of calculating the complete phase diagram of water for two of the simplest and more popular water models: SPC/E,[53] and TIP4P.[54,55] As a result we were able to present the overall appearance of the dense region of the water phase for these models.[56] That work resulted in a number of important conclusions.

Firstly, it became apparent that the coexistence lines involving the liquid and any of the relatively low density ices (Ih, III, V, and VI) exhibited a reentrant behaviour. As the reentrants lie in the metastable region, this behaviour has not yet been seen in real experiments. The only experimental support comes from the fact that the liquid–ice Ih coexistence line has a negative slope (in the p-T plane) with the absolute value of the slope increasing with temperature. Because of this, the existence of the reentrant was already suggested some time ago[57] based exclusively on experimental results. Our results confirmed that, and thus, the part of the liquid-Ih line exhibiting a negative slope is simply the upper branch of the reentrant. Moreover, other ices also exhibited similar behaviour. Another important conclusion of our former work was that the phase diagram is a stringent test of water models. Although both models perform similarly for many liquid properties, their predicted phase diagrams are significantly different: that of TIP4P is in qualitative agreement with experiment while SPC/E shows significant departures. For SPC/E, ice II takes over most of the low to medium pressures range of the phase diagram so that ices Ih, III, and V become metastable phases.

This fact triggered new studies trying to explain the observed behaviour. The conclusions pointed towards the important effect of the quadrupolar interactions in water.[58–61] From a more practical point of view it was concluded that the superiority of TIP4P is a consequence of a more appropriate distribution of the charges, with the negative charge shifted from the oxygen atom.[56,58–60] It became clear that this information could be used to improve the water potential model and some effort was made in that direction. Two reparametrisations of TIP4P were proposed: TIP4P/Ice[62] and TIP4P/2005.[63] The first model was designed to reproduce the melting temperature of ice Ih while the second one was parametrised to produce a general purpose model for the condensed phases of water.

The interest of these studies eclipsed other questions involved in the phase diagram of water. But some properties fully deserve a report. The case of the enthalpy change at melting is paradigmatic, especially when compared with the importance attributed to the enthalpy of vaporisation which has been the basis (together with the density at ambient conditions) of most of the parametrisation schemes for water models. In fact, it seems interesting to investigate the change in the more relevant quantities (volume, entropy and enthalpy changes) along the coexistence lines. On the other hand, the great effort done in the calculation of the phase diagram of SPC/E and TIP4P (later extended to TIP4P/Ice and TIP4P/2005) may help other researchers to do similar work for other water models. The condition for this to be fulfilled is to make available the numerical values of the coexistence temperatures and pressures of the different coexisting phases and of thermodynamic quantities at the triple points. In this way, the aim of this work is twofold. Firstly, we want to provide the numerical values of the coexistence lines and triple points reported previously in a graphical manner. On the other hand, in this

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work we will analyse the changes in volume, entropy and enthalpy along the coexistence lines for the model (TIP4P/2005) that has provided a better overall agreement between simulation and experimental results.

II. Computational methods

The evaluation of the phase diagram of water is a rather involved task. For a review on this topic we refer the reader to ref. 64 but for completeness we give here a brief summary of methods employed. The number of molecules used were in the range 300–600. In all cases the LJ potential was truncated at 8.5 Å. Standard long range corrections to the LJ part of the potential were added (*i.e.*, $g(r) = 1$ beyond the cutoff). Note that this simple prescription (*i.e.* assuming $g(r) = 1$ beyond the cutoff) might introduce an error in the estimate of the long range correction, especially in solid phases (where $g(r)$ is not 1 even at large distances). The impact that this might have on the coexistence points is not easy to assess, as the effect is different for different phases and at different densities. By analyzing the internal energy of solid phases for different systems sizes we conclude that the use of the simple prescription $g(r) = 1$ to estimate the long range correction of the LJ part of the potential may introduce an error of about 1.5% in the determination of coexistence points, which is enough for the purposes of this work. The importance of an adequate treatment of the long range Coulombic forces when dealing with water simulations has been pointed out in recent studies.[65–68] In this work, the Ewald summation technique[69] has been employed for the calculation of the long range electrostatic forces. Isotropic NpT simulations were used for the liquid phase while anisotropic Monte Carlo simulations (Parrinello–Rahman like)[70,71] were used for the solid phases. A typical Monte Carlo NpT run involves about 30 000 cycles of equilibration and 70 000 cycles to obtain averages (defining a cycle as a trial move per particle plus a trial volume change).

We have used the free energy route combined with Gibbs–Duhem integration. The free energies for the solid phases have been evaluated using the Frenkel–Ladd method.[72] The combinatorial entropy due to proton disorder is accounted for as prescribed by Pauling[73] for completely disordered ices (Ih and VI). Initial proton disordered configurations were obtained by using the algorithm of Buch *et al.*[74] However, ices III and V are thought to be only partially disordered. In this case we used the combinatorial entropy calculated by means of an extension[75] of the ideas of Howe and Whitworth.[76] The residual free energy of the liquid was computed by following a thermodynamic path in which the charges are gradually switched off so that the water model transforms into a LJ model (for which the residual free energy is known[77]). Once an initial value was known for the free energy of the different phases, isobaric-isothermal (NpT) Monte Carlo simulations were performed to calculate the point at which the chemical potentials and pressures of the different pairs of phases cross providing a first value for the corresponding coexistence lines. These values are the starting points which allow to obtain the full equilibrium curves using the Gibbs–Duhem methodology[78] (which in essence consists in the integration of the Clapeyron equation along the coexistence using for ΔH and Δv the results obtained in the simulation runs).

The methodology described above was used to calculate the phase diagrams of SPC/E and TIP4P. As commented above, the procedure is rather cumbersome and has a relatively high computational cost. Soon after his proposal of the Gibbs–Duhem method, Kofke realized that the method could also be used in an extended way.[79,80] By writing the intermolecular potential as a function of a parameter λ, it is simple to show that (by an integration along λ) it is possible to determine the unknown coexistence point of a given potential model provided that the coexistence point for a different potential is known. We usually refer to this technique as Hamiltonian Gibbs–Duhem integration. The technique makes easier to evaluate the coexistence lines for any water model once they are known for a reference model. In this way, we were able to compute the melting temperatures of ice Ih for a number of models[81,82] from the value calculated using the free energy route for TIP4P. Another advantage of the Hamiltonian Gibbs–Duhem integration is that it allows a cross checking of the results obtained with free energy calculations. For instance, the ice Ih melting temperature of TIP4P has been evaluated with this technique starting at the known value for SPC/E.[81] The calculation differed from the free energy result by less than 1 K. The Hamiltonian Gibbs–Duhem integration has been used to calculate initial points on selected coexistence lines for the TIP4P/2005 and TIP4P/Ice water models from those previously known (through the free energy route) for TIP4P. The coexistence points obtained by the Hamiltonian Gibbs–Duhem integration are then the starting points to calculate the rest of the equilibrium curves of the other TIP4P-like models using the common Gibbs–Duhem integration.

It is perhaps interesting to note that the ice Ih melting temperatures of SPC/E, TIP4P, TIP4P/2005 and TIP4P/Ice have been checked by yet another independent procedure.[83] By putting in contact the liquid and the solid we were able to provide an independent test of the melting temperatures obtained *via* the procedures commented in the previous paragraphs. The differences between the melting temperatures calculated by means of the free energy-Gibbs Duhem route and the direct coexistence method were about 3 K for all the models investigated. We believe that this figure provides a reasonable estimate of the uncertainty of the melting temperatures we are reporting in this work.

The determination of the precise location and properties at the triple points poses a problem of consistency. As the free energy calculations leading to the three coexistence lines converging at a triple point are independent, and considering that the errors in the Monte Carlo simulations are intrinsically random, the simulations yield a triad of triple points instead of a single value. To illustrate this point we report in Fig. 1 the liquid–ice Ih, ice Ih-ice III and ice III-liquid (L-Ih-III) equilibrium curves converging at the liquid–ice Ih-ice III triple point for the TIP4P water model (in fact, this is simply an enlargement of a figure presented in our preliminary communication[56]). It can be seen that a shift of about 2 K in the curves for the liquid-Ih and liquid-III coexistence could make them pass through the same point in the Ih-III line. Thus, the uncertainty

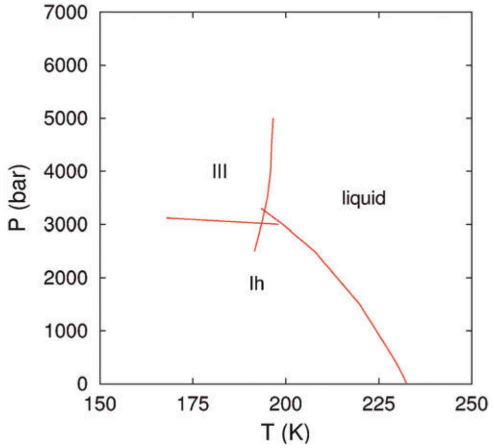

Fig. 1 Detail of the coexistence lines L-Ih, L-III and Ih-III for TIP4P showing the uncertainty in the location of the L-Ih-III triple point.

in the melting temperatures of ices Ih and III explain the observed behaviour. As the Ih-III coexistence line has an almost null slope the uncertainty is in this case perceived in the coexistence pressure. The uncertainty in the TIP4P L-Ih-III triple point pressure is around 150 bar. We have assigned the location of the L-Ih-III triple point for the TIP4P model as the barycentre of the triangle formed by the three converging coexistence lines. The barycentre has been roughly obtained by visual inspection using an enlarged plot of this region of the phase diagram. The problem found in the location of the triple point was avoided for less important triple points (particularly those not involving the liquid phase) of the TIP4P-like models because they were simply obtained by the intersection of only *two* equilibrium curves. The calculated triple points were then used as the starting points for the determination of the remaining coexistence lines.

The computation of the changes in volume and enthalpy are needed for the Gibbs–Duhem integration and these quantities have been obtained along the equilibrium curves. We used dual-processor computers so that the determination of the volume and enthalpy was performed in parallel for both phases. The calculation of the properties of the liquid phase give larger uncertainties and, thus, requires longer runs. We typically simulated 25 000 Monte Carlo cycles for liquid water and we adapted the number of cycles for the ices so that both phases at coexistence finish the calculation at the same time. The evaluation of the changes in volume and enthalpy at the triple points have been done in independent simulations. We have improved the statistics in this case by increasing the number of Monte Carlo cycles (typically using 160 000 cycles for liquid water).

III. Results

Table 1 gives the location of the triple points for several common water models. As mentioned in the introduction, the results for the SPC/E model are significantly different from experiment. Ice II is the stable phase at ambient pressure and ice Ih is the thermodynamically stable phase only at slightly negative pressures (below −60 bar) although the possibility of having ice Ih as an stable phase at positive pressures in the proximity of the melting point of the model can not be completely ruled out taking into account the uncertainty of our free energy calculations. For SPC/E, ices III and V are always metastable because of the greater stability of ice II and the range of appearance of ice VI in the phase diagram is severely reduced by ice II. On the contrary, the triple points of TIP4P, TIP4P/2005 and TIP4P/Ice are in qualitative agreement with the experimental ones indicating that the overall prediction of the phase diagram is quite satisfactory. Despite that, it can be seen in Table 1 that the triple points involving liquid water appear at lower temperatures than in the experiment. The best predictions are yielded by TIP4P/Ice (because it was specifically designed to reproduce the melting temperature of ice Ih) and the least satisfactory (within the TIP4P family of models) are those of TIP4P. As to the triple point pressures, these TIP4P-like models give, in general, satisfactory predictions (perhaps it is to be noticed that the estimates for the L-Ih-III and L-V-VI triple point pressures are somewhat high).

The numerical values of the coexistence points (as well as the densities and internal energies at coexistence) for TIP4P and SPC/E are given as ESI.† The coexistence points can be used as starting values for the determination of the phase diagram of other models using the Hamiltonian Gibbs–Duhem methodology just as it has been done in this work for the equilibrium curves for TIP4P/2005 and TIP4P/Ice (the coexistence lines for these models are also given as ESI†). Notice that the estimated uncertainty of the coexistence lines of TIP4P/2005 and TIP4P/Ice is larger than for TIP4P, SPC/E, since besides the uncertainty of the original reference model (TIP4P was used as a reference model) it incorporates the additional uncertainty introduced by the Hamiltonian Gibbs–Duhem methodology (thus for TIP4P/2005 and TIP4P/Ice the estimated uncertainty of the melting curves is of about 5 K, instead of the 3 K commented above for TIP4P and SPC/E).

The changes in volume and entropy at the triple points are compared to the experimental values in Table 2 for the TIP4P, TIP4P/2005 and TIP4P/Ice models. These TIP4P-like models

Table 1 Triple points of SPC/E, TIP4P, TIP4P/2005 and TIP4P/Ice models compared to the experimental results. The first value in each pair is the temperature (in K) and the second is the corresponding pressure (in bar)

Phases	SPC/E	TIP4P	TIP4P/2005	TIP4P/Ice	Expt.
L-Ih-III	—	(194.3, 3110)	(213.1, 3060)	(231.8, 2955)	(251.15, 2099)
L-Ih-II	(215, −60)	—	—	—	—
L-III-V	—	(196.6, 4000)	(215.3, 3690)	(232.6, 3270)	(256.15, 3501)
L-V-VI	—	(220.8, 8390)	(241.6, 8060)	(258.4, 7630)	(273.31, 6324)
Ih-II-III	—	(168.2, 3120)	(195.9, 3110)	(219.4, 2990)	(238.45, 2130)
II-III-V	—	(175.2, 4000)	(200.0, 3690)	(221.6, 3280)	(248.85, 3440)
L-II-VI	(228, 22030)	—	—	—	—

give quite good predictions. TIP4P/2005 gives a slightly better overall estimate of the volume change while TIP4P produces marginally better results for the changes in enthalpy.

Putting together the results shown in Tables 1 and 2, TIP4P/2005 and TIP4p/Ice provide better predictions for the phase diagram than TIP4P. Taking also into consideration the liquid–vapour equilibrium,[84,85] it is clear that, among TIP4P-like models, TIP4P/2005 provides the best description of the whole phase diagram of water (in fact, the statement almost certainly holds true not only for the comparison with the models considered in this work but also for any rigid water model). For this reason we present in Fig. 2 and 3 the changes in volume and enthalpy along the coexistence lines for the TIP4P/2005 model. For comparison we also show the plots for the corresponding experimental data. The model gives excellent predictions for all the 10 coexistence lines investigated. It predicts correctly not only the magnitude and sign of the volume changes but also the dependence of the change with temperature (notice that the slope of the curves for the model are very close to the experimental ones). As commented above, the uncertainties for the coexisting liquid densities are larger than those for the solid phases. We have then smoothed the results for the changes in volume for the Ih-L, V-L and VI-L equilibria. Given the similarity between experimental and simulation results, in the fit of the simulation results we have used the same functionality observed in the experiment so that the simulation data for the Ih-L and V-L curves have been linearised. The experimental data for the VI-L are clearly non-linear so we fitted the simulation results to a third order polynomial. The smoothed line shows a shape with a remarkable similarity with that of the experiment. Much more precise calculations would be needed to establish whether the model nicely accounts for the strange shape of the change of volume along the VI–L coexistence or it is simply an artifact of the smoothing procedure.

The agreement between the predictions of the model and experimental data is quite satisfactory for the enthalpy changes. The sign of the enthalpy change is predicted correctly in all cases. Besides the predictions from the model are in relatively good agreement with the experimental values. However, in most of the cases the TIP4P/2005 model underestimates the experimental values of the enthalpy changes. This is true for the three models, TIP4P, TIP4P/2005 and TIP4P/Ice (although the problem is more pronounced for TIP4P, being the difference with experiment somewhat smaller for the TIP4P/Ice). The melting enthalpy of ice Ih provides a good example. The experimental value is 1.44 kcal mol^{-1}. The predicted value is 1.05, 1.16 and 1.29 for TIP4P, TIP4P/2005

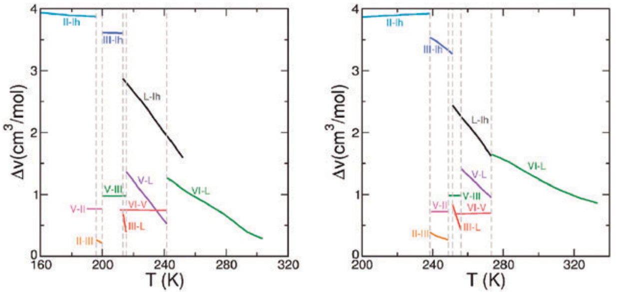

Fig. 2 Change of volume for the indicated coexistence lines. Left: TIP4P/2005; Right: experimental values as taken from Bridgmann.[3] Vertical lines indicate the temperature of the triple points.

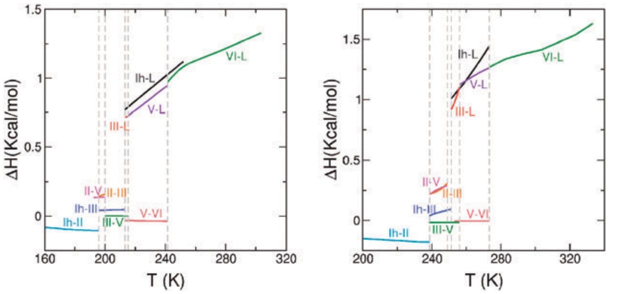

Fig. 3 Change of enthalpy for the indicated coexistence lines. Left: TIP4P/2005; Right: Experimental values as taken from Bridgmann.[3] Vertical lines indicate the temperature of the triple points.

Table 2 Volume (in cm^3 mol^{-1} K^{-1}) and entropy (in J mol^{-1} K^{-1}) changes at the calculated triple points of some water models compared to the corresponding experimental data taken from ref. 6. The last row shows the mean values of the (unsigned) deviations from the experimental results. Notice that in ref. 62, a misprint occurred in Table VI so that, for TIP4P/Ice, the entropy changes of the model and that of the experiment were exchanged (the volume changes of Table VI were correct)

	Transition		TIP4P		TIP4P/2005		TIP4P/Ice		Expt.	
Triple point	From	To	Δv	ΔS	Δv	ΔS	Δv	ΔS	Δv	ΔS
Liquid-Ih-III	L	Ih	2.81	−16.4	2.87	−15.0	3.10	−14.9	2.436	−16.8
	L	III	−0.63	−15.1	−0.72	−14.1	−0.59	−13.9	−0.839	−15.3
	Ih	III	−3.44	1.3	−3.59	0.9	−3.69	1.0	−3.275	1.6
Liquid-III-V	L	III	−0.21	−14.4	−0.38	−14.1	−0.52	−13.2	−0.416	−18.1
	L	V	−1.17	−14.3	−1.36	−14.1	−1.53	−13.1	−1.420	−18.3
	III	V	−0.96	0.1	−0.98	0.0	−1.01	0.1	−0.985	−0.3
Liquid-V-VI	L	V	−0.47	−16.1	−0.52	−16.4	−0.59	−15.7	−0.949	−19.3
	L	VI	−1.19	−16.2	−1.26	−17.0	−1.35	−16.2	−1.650	−19.4
	V	VI	−0.72	−0.1	−0.74	−0.6	−0.77	−0.5	−0.701	−0.1
Ih-II-III	Ih	II	−3.77	−1.8	−3.87	−2.2	−3.97	−2.1	−3.922	−3.2
	Ih	III	−3.49	1.3	−3.62	0.9	−3.71	1.0	−3.536	0.7
	II	III	0.28	3.1	0.26	3.1	0.26	3.2	0.387	3.9
II-III-V	II	III	0.22	3.1	0.21	3.1	0.24	3.1	0.261	5.1
	II	V	−0.74	3.2	−0.76	3.2	−0.78	3.2	−0.722	4.8
	III	V	−0.96	0.1	−0.97	0.0	−1.02	0.1	−0.984	−0.3
$\bar{d}$			0.17	1.4	0.15	1.6	0.18	1.8		

and TIP4P/Ice, respectively. Thus none of the models are able to quantitatively predict the melting enthalpy of ice Ih. TIP4P/2005 underestimates it by about 15% (notice that this is approximately the change of scale of the right and left hand plots of Fig. 3). At this point it is interesting to remind that TIP4P reproduces the experimental value of the vaporisation enthalpy of water, TIP4P/2005 overestimates the vaporisation enthalpy (although it is able to reproduce it when the polarisation correction first proposed by Berendsen's *et al.* is taken into account), and TIP4P/Ice overestimates significantly the vaporisation enthalpy of water (even after including the polarisation corrections). The fact that three models which such a different description of the vaporisation enthalpy, fail to describe the melting enthalpy means that to describe quantitatively the melting enthalpy of ice, new features should be incorporated in the model. It is likely that polarisability is the key ingredient required to improve the performance of the enthalpy changes of ices, but further work is required to confirm this point.

Another interesting observation is the slope with temperature of the transitions where ice III (and to less extent ice V) are involved. The slope seems to be more pronounced in experiment than in the model. It has been found experimentally that proton disorder in ices III and V is partial and changes with temperature.[86] We are not including this possibility within our calculations (that would required the incorporation of specific Monte Carlo moves that change the hydrogen bond connectivity). This partial ordering[87] may be affecting phase transitions[75] and enthalpy changes. Further work is needed to clarify this issue.

The coexistence data in the T-ρ plane obtained with the TIP4P/2005 model are presented in Fig. 4a (for a plot of the coexistence data in the *p*-T plane see ref. 63 and the preceding paper in this issue[88]). We have depicted the complete phase diagram except the low temperatures region (below 160 K) where quantum effects cannot be taken into account in our classical simulations.[89–91] Similarly to what happens for other projections of the coexistence data, the phase diagram of water in the T-ρ plane is quite different from that found for other ordinary substances. This is due to the fact that ice Ih has a lower density than its coexisting liquid. As a consequence the L-Ih lines drop as the temperature increases. The usual behaviour is recovered by the equilibrium curves of the liquid with the stable solids at higher densities and, thus, the liquid–solid envelope has a positive slope for ices III, V, and VI. Notice the unusual behavior of the more dense region of the liquid–VI coexistence line (at pressures over 25 000 bar) which shows the appearance of a reentrant.[56] The reentrant cannot be observed experimentally because the triple point L-VI-VII appears at lower temperatures than it does for the model. Thus, in the experiment, the reentrant would lie in a metastable region. Notice finally the range of existence of a recently reported plastic phase[88,92] at very high pressures (the coexistence data for the plastic phase have been taken from ref. 88).

The phase diagram has a remarkable complexity, especially in the vicinity of $\rho = 1.2$ g cm^{-3}. For this reason we have expanded the dense region in Fig. 4b. Even at this scale, it is difficult to detect the (small) range of existence (in both temperatures and densities) of ice III. Despite the fact that ice II has a relatively wide range of temperatures in which it is found as the thermodynamically stable phase, its density is always quite similar to its competitor ice III, so it also exhibits a narrow range of densities. Leaving aside "extreme" conditions (*i.e.*, low temperatures and pressures above 25 000 bar) the main difference between theory and experiment is a small shift of the whole diagram towards lower temperatures for TIP4P/2005 so this model may provide a quite realistic picture of the general appearance of the experimental phase diagram. The scarcity and discontinuity of experimental data make difficult to show the complete experimental phase diagram of water in the T-ρ plane. In fact, as far as we are aware, such a plot has not yet been depicted. Given the excellent predictions for the densities of the ices[62] and for the volume changes along the coexistence lines shown in this region, Fig. 4b provides a realistic picture of how the T-ρ projection of the experimental phase diagram should look like.

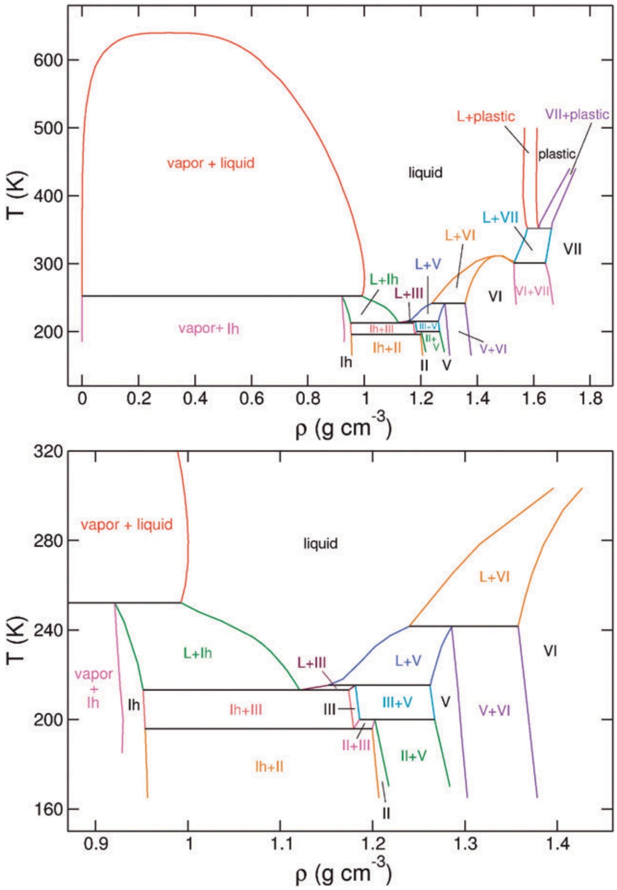

Fig. 4 Phase diagram of TIP4P/2005 water in the T-ρ plane. Top: the complete phase diagram (except the very low temperature and the extremely high pressure regions). Bottom: detail of the high density region.

IV. Conclusions

In this work we have checked the ability of simple rigid, nonpolarisable water models to account for the dense region of the phase diagram. We have shown that SPC/E does not predict the triple points appearing in the experiments. It is now known that the failure is due to the positioning of the negative charge at the oxygen atom in this model.[56,58–60] TIP4P-like models (which put the negative charge shifted around 0.15–0.16 Å from the oxygen) predict the same triple points as the experimental measurements. The predicted triple points appear at a somewhat higher pressures while the degree of accuracy for the temperatures depend on the particular model. The experimental triple point temperatures are quite well reproduced by TIP4P/Ice while they appear clearly shifted towards lower temperatures in TIP4P/2005 and, especially, TIP4P. Despite the differences in the location of the triple points, the three TIP4P-like models investigated in this work yield very similar results for the changes in volume and entropy at the triple points. Besides, these predictions are in acceptable agreement with the experimental data.

Taking also into consideration the liquid–vapour equilibrium,[84] TIP4P/2005 emerges as the model with the most accurate predictions among the models considered in this work (and, possibly, among all the rigid non-polarisable water models proposed up to now). We have, then, compared the predictions for the changes in volume and enthalpy for this model against the experimental data for the water coexistence curves. The agreement between simulation and experiment is excellent for the volume changes and quite acceptable for the enthalpy changes. Probably the polarisability should be included[93–97] into the model to describe quantitatively the melting enthalpy of ices.

Finally, we have plotted the T-ρ projection of the phase diagram for TIP4P/2005. Given the excellent predictions for the densities of the different phases and for the changes in volume along the coexistence curves this representation gives an idea of how the corresponding experimental should look like.

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