

# Vapor-liquid equilibria from the triple point up to the critical point for the new generation of TIP4P-like models: TIP4P/Ew, TIP4P/2005, and TIP4P/ice

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The vapor-liquid equilibria of three recently proposed water models have been computed using Gibbs-Duhem simulations. These models are TIP4P/Ew, TIP4P/2005, and TIP4P/ice and can be considered as modified versions of the TIP4P model. By design TIP4P reproduces the vaporization enthalpy of water at room temperature, whereas TIP4P/Ew and TIP4P/2005 match the temperature of maximum density and TIP4P/ice the melting temperature of water. Recently, the melting point for each of these models has been computed, making it possible for the first time to compute the complete vapor-liquid equilibria curve from the triple point to the critical point. From the coexistence results at high temperature, it is possible to estimate the critical properties of these models. None of them is capable of reproducing accurately the critical pressure or the vapor pressures and densities. Additionally, in the cases of TIP4P and TIP4P/ice the critical temperatures are too low and too high, respectively, compared to the experimental value. However, models accounting for the density maximum of water, such as TIP4P/Ew and TIP4P/2005 provide a better estimate of the critical temperature. In particular, TIP4P/2005 provides a critical temperature just 7 K below the experimental result as well as an extraordinarily good description of the liquid densities from the triple point to the critical point. All TIP4P-like models present a ratio of the triple point temperature to the critical point temperature of about 0.39, compared with the experimental value of 0.42. As is the case for any effective potential neglecting many body forces, TIP4P/2005 fails in describing simultaneously the vapor and the liquid phases of water. However, it can be considered as one of the best effective potentials of water for describing condensed phases, both liquid and solid. In fact, it provides a completely coherent view of the phase diagram of water including fluid-solid, solid-solid, and vapor-liquid equilibria. © 2006 American Institute of Physics. [DOI: 10.1063/1.2215612]

## I. INTRODUCTION

Since the pioneering work of Barker and Watts<sup>1</sup> and Rahman and Stillinger,<sup>2</sup> the interest in simulating water and aqueous systems has increased steadily. Although a large number of potential models have been proposed for water, suggesting that none is completely satisfactory, some of them are more popular than others, indicating that they are not all equivalent.<sup>3,4</sup> Three of the most popular models are the simple rigid nonpolarizable TIP4P,<sup>5</sup> extended simple point charge (SPC/E),<sup>6</sup> and TIP5P (Ref. 7) models. All of these are computationally cheap, with a Lennard-Jones (LJ) site located on the oxygen and partial positive charges located on the hydrogen atoms. In TIP4P the negative charge is located along the bisector of the H–O–H bond, with the parameters of the potential chosen to match the experimental density and vaporization enthalpy of liquid water. In the SPC/E model

the negative charge is located on the oxygen atom, with the potential parameters fitted to reproduce the density of liquid water and the diffusion coefficient. However, and this is an important remark, the SPC/E model does not reproduce the vaporization enthalpy of real water unless an extra term, called the polarization energy, is added. In TIP5P the negative charges are located on the “lone pair” electrons, with the potential parameters chosen to account for the same properties as TIP4P as well as the temperature of maximum density at room pressure.

In the last 15 years the ability to compute phase equilibria for water models has opened new questions as to the ability of models to describe the phase diagram of water. For this reason the vapor-liquid equilibrium has been computed<sup>8–14</sup> for different water models. However, it is only recently that fluid-solid equilibrium has been considered<sup>15–19</sup> and only in the last two years that the goal of determining the complete phase diagram for these models has been undertaken. In fact, one of the main findings of our recent

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work<sup>20–22</sup> is that only TIP4P is able to describe qualitatively the phase diagram of water [for instance, ice II and not ice  $I_h$  is the stable phase at melting for SPC/E and TIP5P (Ref. 23)]. However, TIP4P has too low melting point,<sup>17,18,23</sup> critical point,<sup>10</sup> and temperature of maximum density (TMD),<sup>24,25</sup> and it was evident that the model could be improved. It was also clear that the idea of the self-polarization term (essential in the determination of parameters of the SPC/E model) could also be used in a modified TIP4P model and that the ability to reproduce the TMD of real water (as TIP5P) is an attractive feature. In the last two years two models have been proposed by two different groups that have essentially followed this route to develop an improved water potential. These are the TIP4P/Ew (Ref. 26) and the TIP4P/2005 potentials.<sup>27</sup> While keeping the charge distribution of TIP4P—first proposed by Bernal and Fowler<sup>28</sup>—to provide a reasonable phase diagram prediction, the parameters are chosen to reproduce the TMD and vaporization enthalpy of real water by including a self-polarization term. In addition to this, both models were designed to be used with a proper treatment of the Coulombic forces<sup>29,30</sup> (say, Ewald sums or reaction field). The main difference between these two models is the precise location of the negative charge. We have recently shown<sup>24</sup> that the difference between the temperature of maximum density and the melting temperature is about 25 K (at  $p=1$  bar) for TIP4P-like models, whereas for real water this difference is approximately 4 K (also at  $p=1$  bar). Thus it is impossible for TIP4P-like models to match simultaneously the temperature of melting and the temperature of the maximum density. Since TIP4P/Ew and TIP4P/2005 models reproduce the TMD, we found it useful to develop a model matching the melting temperature of real water, namely, TIP4P/ice.<sup>31</sup> It seems of interest to determine the vapor-liquid equilibria of these models (taking into account that fluid-solid and solid-solid is already known), and since for these models the triple point is now available, it is possible for the first time to determine the complete vapor-liquid equilibria curve (from the triple point up to the critical temperature).

## II. METHODOLOGY

In this work the Gibbs-Duhem methodology (i.e., the integration of the Clapeyron equation) first proposed by Kofke will be used to determine the vapor-liquid coexistence curve from an initial coexistence point.<sup>32–37</sup> The Gibbs-Duhem integration is basically an integration of the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}. \quad (1)$$

The vapor pressure changes several orders of magnitude along the coexistence curve. Its logarithm is a smooth function when plotted as a function of the inverse of the temperature. For this reason it is more convenient to integrate the following modified form:<sup>32</sup>

$$\frac{d \ln p}{d\beta} = - \frac{\Delta H}{p\beta\Delta V}, \quad (2)$$

with  $\beta=1/kT$ . For the integration of Eq. (2) we shall use a fourth order Runge-Kutta algorithm.<sup>38</sup>

The number of molecules used to describe the vapor or the liquid phases is 360. *NPT* runs in cubic simulation boxes were used to obtain the properties of both phases. The number of cycles used to integrate the Clapeyron equation is about 20 000 per state (in a fourth order Runge-Kutta algorithm four runs are performed from one temperature to the next so that so that the number of cycles generated between two consecutive temperatures is about 80 000). We define a cycle as a trial movement per particle (translation or rotation) plus a trial volume change. Consecutive temperatures used for the integration of the Clapeyron equation differ typically by about 10–20 K. Ewald sums were used to deal with electrostatics. The Coulombic interaction in real space and the LJ potential were truncated at about 0.9 times the value of the half of the simulation box length. Long range corrections to the LJ contribution were included. We started the Gibbs-Duhem integration at  $T=450$  K (a temperature intermediate between the critical temperature and the triple point temperature of these models). In one run, the vapor pressure curve was determined from  $T=450$  K up to the triple point temperature. We should mention here that the use of the Gibbs-Duhem integration is particularly useful to obtain the coexistence at very low temperatures (i.e., those of the triple point temperature of the model) since it does not require particle insertion. Notice that the use of the Gibbs ensemble methodology<sup>39,40</sup> would have become terribly expensive at low temperatures where the insertion of a water molecule in the liquid phase becomes difficult. The same is true for histogram reweighting techniques<sup>41</sup> that could not be used at the temperatures of the triple point of the model. Since in this work we pretend to calculate for the first time the complete coexistence curve of the model (from the triple point up to the critical point), the choice of the Gibbs-Duhem integration seems a reasonable choice. Notice that the Gibbs-Duhem technique was used previously by Yezdimer and Cummings<sup>42</sup> for a polarizable model of water. A second Gibbs-Duhem run was performed from  $T=450$  K up to a temperature about 5% below the critical temperature. We found empirically that the last temperature at which the Gibbs-Duhem technique can be used successfully is that at which the density of the liquid is smaller than  $0.57 \text{ g/cm}^3$  or that of the vapor higher than about  $0.10 \text{ g/cm}^3$ . This occurs at a temperature about 5% below the critical temperature. Once the Gibbs-Duhem runs are finished, we have values of the vapor pressure of the model from the triple point up to about  $0.95T_c$ . From the Gibbs-Duhem runs values of the densities and enthalpies of the two coexistence densities are also available. However, in order to obtain more precise values of the coexistence properties long *NPT* runs (between 100 000 and 1 000 000 cycles) were performed for each temperature at the coexistence pressure.

The Gibbs-Duhem methodology requires the knowledge of an initial coexistence point (i.e., the vapor pressure for a certain temperature). We choose  $T=450$  K as the initial tem-

perature of the Gibbs-Duhem runs. Therefore a procedure to determine the vapor pressure at this temperature for each model is needed. We have used Hamiltonian Gibbs-Duhem integration.<sup>23,32,34</sup> In this methodology, it is possible to determine, for a fixed temperature, the coexistence pressure of a certain model of water starting from the coexistence pressure of another model of water.<sup>23</sup> In a previous work we applied this methodology to the fluid-solid equilibria to determine the melting point of several models of water.<sup>23</sup> The results obtained in this way were in good agreement with those obtained from direct fluid-solid coexistence simulations.<sup>43</sup> A similar approach was used by Sturgeon and Laird to determine the melting point of a model of aluminium.<sup>44</sup> In this work we apply the methodology to the vapor-liquid equilibria. For the TIP4P model, the vapor-liquid equilibria have been determined by Lisal *et al.*<sup>10</sup> by using the Gibbs ensemble methodology. They have reported the coexistence pressure of the TIP4P model at  $T=450$  K to be  $p=11.36$  bars. These authors used reaction field for the electrostatics so that long range Coulombic forces were properly taken into account. Starting from this value we used Hamiltonian Gibbs-Duhem integration to determine the vapor pressure at this temperature for TIP4P/2005, TIP4P/ice, and TIP4P/Ew models. Details about the implementation of the technique can be found elsewhere.<sup>23</sup> In this work four values of the coupling parameter were used to connect the TIP4P model with the model of interest. This methodology was checked in two different ways. Firstly, we were able to reproduce the reported values of the vapor pressure at  $T=450$  K for the SPC/E (Refs. 8 and 9) and TIP5P models.<sup>11</sup> Secondly, we performed some simulations with direct coexistence between the fluid and the vapor. The simulations with direct vapor-liquid coexistence were performed with GROMACS (Version 3.3).<sup>45</sup> In this case the simulation box had typical dimensions of  $30 \times 30 \times 100 \text{ \AA}^3$ . In the central part of the simulation box a slab of 1024 water molecules was located. After an equilibration run of 200 ps, a long simulation of 2 ns was performed to obtain thermodynamic averages. The time step was 1 fs. The molecular dynamics simulations were performed in the  $NVT$  ensemble by using a Nose Hoover thermostat<sup>46,47</sup> with a relaxation time of 2 ps. These simulations allowed us to determine the vapor pressure directly since this is nothing but the component of the pressure tensor perpendicular to the interface. In this direct coexistence simulations the potential was truncated at 12  $\text{\AA}$ , and particle mesh Ewald (PME) methodology<sup>48</sup> was used to deal with long range Coulombic forces.

### III. RESULTS

In Table I results for the coexistence pressure at  $T=450$  K for TIP4P, TIP4P/Ice,<sup>31</sup> TIP4P/Ew,<sup>26</sup> and TIP4P/2005 (Ref. 27) are presented. Let us start by discussing the results for the TIP4P model. For the TIP4P model the coexistence pressure obtained from direct coexistence simulations agrees quite well with that obtained by Lisal *et al.* from Gibbs ensemble simulations.<sup>10</sup> This indicates clearly that the vapor pressure for the TIP4P model at  $T=450$  K reported by Lisal *et al.* can be used with confidence as the

TABLE I. Vapor-liquid equilibria at  $T=450$  K as obtained from Hamiltonian Gibbs-Duhem integration and from direct vapor-liquid interface simulations. Densities of the liquid  $\rho_l$  and of the gas  $\rho_g$  are given in  $\text{g/cm}^3$ . The vapor pressure of the TIP4P model as obtained from Gibbs ensemble simulations by Lisal *et al.* (Ref. 10) are also given.

Model	Technique	$T/\text{K}$	$p/\text{bar}$	$\rho_l$	$\rho_g$
TIP4P	Gibbs ensemble	450	13.33	0.831	$7.7E-3$
TIP4P	Interface	450	13.61	0.824	$7.8E-3$
TIP4P/2005	Hamiltonian	450	4.46	0.883	$2.34E-03$
TIP4P/2005	Interface	450	4.52	0.879	$2.42E-03$
TIP4P/Ew	Hamiltonian	450	5.47	0.871	$2.94E-3$
TIP4P/Ew	Interface	450	5.64	0.866	$3.15E-3$
TIP4P/ice	Hamiltonian	450	1.51	0.913	$7.63E-4$
TIP4P/ice	Interface	450	1.16	0.910	$8.1E-4$

initial state needed in Hamiltonian Gibbs-Duhem integration. In Table I the vapor pressures obtained for TIP4P/ice, TIP4P/Ew, and TIP4P/2005 as obtained from Hamiltonian Gibbs-Duhem integration and from direct simulations are presented. The agreement is quite satisfactory. This consistency provides further evidence of the correctness of the methodology used in this work. We believe that the results obtained from Hamiltonian Gibbs-Duhem integration should be preferred to those obtained from direct coexistence. The reason is that whereas it is possible to incorporate properly long range correction to the LJ contribution in the Hamiltonian Gibbs-Duhem methodology it is not possible to do the same for the direct coexistence technique.<sup>49,50</sup> The results obtained for the direct coexistence technique correspond in principle to the results of a truncated potential, whereas those of the Hamiltonian Gibbs-Duhem integration correspond to those of a system where the long range contribution has been included. In any case, since the value of the cutoff used in the direct coexistence simulations was large ( $r_c=12 \text{ \AA}$ ), differences are expected to be small. The only difference between both methodologies is that liquid densities obtained from direct interface simulations are slightly lower (by about 0.5%) than those obtained from Hamiltonian Gibbs-Duhem integration, and this is probably due to the cutoff.

Tables II–IV present the coexistence curves for the TIP4P/2005, and TIP4P/Ew, and TIP4P/ice, respectively. For the TIP4P/2005 model the estimated uncertainty of the density has been included. The range of temperatures varies from the triple point temperature up to about 95% of the critical temperature. For real water the difference between the melting point and triple point temperatures is about 0.01 K,<sup>51</sup> the melting temperature being  $T_m=273.15$  K and the triple point temperature being  $T_t=273.16$ . We shall assume that for the different models of water of this work the difference between the melting point and triple point temperatures is also quite small. In this way the values reported in our previous work for the melting temperature of the different water models would be taken here as the value of the triple point temperature. Notice that since the vapor pressure at the triple point is essentially zero, the difference between the melting temperature and the triple point temperature can be given approximately as the inverse of the slope of the melting curve at the melting point [i.e.,  $1/(dp/dT)$ ]. Values

TABLE II. Vapor-liquid equilibria for the TIP4P/2005 model as obtained from Gibbs-Duhem simulations. Densities are given in  $\text{g}/\text{cm}^3$ . Figures in parentheses indicate the estimated uncertainty. The lowest temperature of the table corresponds to that of the triple point.

$T/K$	$p/\text{bar}$	$\rho_l$	$\rho_g$
620	117.0	0.561(7)	$10.3(3)E-2$
610	100.4	0.598(7)	$7.44(15)E-2$
600	86.26	0.629(6)	$5.93(13)E-2$
590	73.85	0.650(4)	$4.63(8)E-2$
570	53.45	0.703(4)	$3.16(5)E-2$
550	38.01	0.741(3)	$2.13(3)E-2$
530	26.45	0.775(2)	$1.415(11)E-2$
510	17.89	0.807(2)	$9.35(7)E-3$
490	11.71	0.835(2)	$6.09(5)E-3$
470	7.39	0.861(2)	$3.85(2)E-3$
450	4.46	0.883(2)	$2.342(10)E-3$
430	2.55	0.905(2)	$1.379(7)E-3$
410	1.37	0.923(2)	$7.59(3)E-4$
390	0.689	0.943(2)	$3.966(11)E-4$
370	0.316	0.9585(10)	$1.891(4)E-4$
350	0.131	0.9713(12)	$8.23(2)E-5$
330	$4.78E-2$	0.9841(13)	$3.166(9)E-5$
310	$1.50E-2$	0.9932(14)	$1.055(3)E-5$
300	$7.78E-3$	0.9965(14)	$5.642(5)E-6$
290	$3.87E-3$	0.9990(14)	$2.900(6)E-6$
270	$7.94E-4$	0.9999(18)	$6.358(10)E-7$
252.1	$1.51E-4$	0.9924(25)	$1.300(11)E-7$

of this slope for several water models have been reported elsewhere,<sup>23,27</sup> illustrating that differences between the melting point and triple point temperatures are for many water models smaller than 0.01 K. A first interesting point emerges from the results of Tables II–IV. The vapor pressure at the

TABLE III. Vapor-liquid equilibria for the TIP4P-Ew as obtained from the Gibbs-Duhem simulations of this work. Densities are given in  $\text{g}/\text{cm}^3$ . The lowest temperature of the table corresponds to that of the triple point of the model.

$T/K$	$p/\text{bar}$	$\rho_l$	$\rho_g$
600	99.97	0.571	$8.0E-2$
590	85.69	0.602	$6.43E-2$
580	73.4	0.639	$5.09E-2$
570	62.55	0.664	$4.06E-2$
550	44.62	0.714	$2.68E-2$
530	31.20	0.752	$1.79E-2$
510	21.27	0.784	$1.18E-2$
490	14.05	0.817	$7.49E-3$
470	8.96	0.846	$4.78E-3$
450	5.47	0.871	$2.94E-3$
430	3.17	0.895	$1.71E-3$
410	1.73	0.915	$9.60E-4$
390	0.885	0.935	$5.10E-4$
370	0.415	0.954	$2.506E-4$
350	0.176	0.969	$1.11E-4$
330	$6.60E-2$	0.981	$4.39E-5$
300	$1.13E-02$	0.994	$8.201E-06$
280	$2.71E-03$	1.000	$2.108E-06$
260	$5.09E-04$	0.998	$4.255E-07$
245.5	$1.23E-04$	0.992	$1.087E-07$

TABLE IV. Vapor-liquid equilibria for the TIP4P/ice as obtained from the Gibbs-Duhem simulations of this work. Densities are given in  $\text{g}/\text{cm}^3$ . The lowest temperature of the table corresponds to that of the triple point of the model.

$T/K$	$p/\text{bar}$	$\rho_l$	$\rho_g$
680	126.6	0.565	0.101
670	110.26	0.593	0.078
660	95.72	0.619	0.062
650	83.30	0.643	0.0481
630	62.43	0.687	0.0345
610	45.99	0.723	0.0238
590	33.27	0.759	0.0165
570	23.58	0.785	0.0113
550	16.32	0.811	0.00777
530	10.97	0.836	0.00519
510	7.13	0.859	0.00341
490	4.46	0.877	$2.145E-3$
470	2.66	0.898	$1.305E-3$
450	1.515	0.913	$7.63E-4$
430	0.811	0.930	$4.23E-4$
410	0.404	0.945	$2.191E-4$
390	0.1859	0.958	$1.048E-4$
370	$7.74E-2$	0.971	$4.574E-5$
350	$2.866E-2$	0.981	$1.788E-5$
330	$9.23E-3$	0.987	$6.086E-6$
300	$1.210E-3$	0.993	$8.765E-7$
280	$2.36E-4$	0.992	$1.831E-7$
272.2	$1.156E-4$	0.985	$9.26E-8$

triple point for the three models of water considered in this work (TIP4P/2005, TIP4P/Ew, and TIP4P/ice) is quite similar. In fact, the vapor pressure at the triple point for TIP4P/2005 and TIP4P/Ew is  $1.5 \times 10^{-4}$  and  $1.2 \times 10^{-4}$  bar, respectively (see Tables II and III). For TIP4P/ice (see Table IV) the pressure at the triple point is  $1.2 \times 10^{-4}$  bar. Therefore, TIP4P models seem to have a vapor pressure at the triple point of about  $1.3 \times 10^{-4}$  bar. This is roughly 50 times smaller than the experimental vapor pressure of water at the triple point,  $6 \times 10^{-3}$  bar. Notice that the vapor pressures at the triple point have not been estimated from extrapolation to low temperatures. They have been obtained directly from the Gibbs-Duhem simulations. Since the vapor pressure appears in a logarithmic form in Eq. (2), this equation can be integrated easily even at low temperatures.

Let us now determine the critical properties. For this purpose we closely follow the treatment of Guissani and Guillot.<sup>52</sup> By using the Wegner expansion<sup>53,54</sup> the difference between the density of the liquid and the gas densities along the coexistence curve can be written as

$$\rho_l - \rho_g = A_0 |\tau|^{\beta_c} + A_1 |\tau|^{\beta_c + \Delta} + A_2 |\tau|^{\beta_c + 2\Delta} + A_3 |\tau|^{\beta_c + 3\Delta}, \quad (3)$$

where  $\tau = 1 - T/T_c$ ,  $\beta_c = 0.325$ , and  $\Delta = 0.5$ . In the same way the sum of the liquid and gas densities can be written as

$$\rho_l + \rho_g = 2\rho_c + D_{1-\alpha} |\tau|^{1-\alpha} + D_1 |\tau|. \quad (4)$$

The first equation contains the scaling law and scaling corrections to the difference between liquid and vapor densities. The second equation contains the law of rectilinear diameters<sup>55,56</sup> plus an additional term with the limiting be-

havior in the proximities of the critical point. We shall use the two previous equations to describe the coexistence densities of the gas and the liquid phases at high temperatures. The total number of parameters in these equations is 8 ( $A_0$ ,  $A_1$ ,  $A_2$ ,  $A_3$ ,  $T_c$ ,  $\rho_c$ ,  $D_{(1-\alpha)}$ , and  $D_1$ ). We refer the reader to the excellent discussion of Guissani and Guillot concerning the use of these two equations to describe the vapor-liquid envelope of water.<sup>52</sup> Let us just mention here that these equations have two important merits. The first one is that they are able to describe the coexistence densities (vapor and liquid) of real water in a broad temperature range (from 450 K up to the critical point). Secondly these equations describe successfully the deviations from the law of rectilinear diameters that occur for real water at high temperatures. It has been noted by several authors that the diameters of the coexistence densities (the average density of the liquid and vapor phase at coexistence) are not linear at high temperatures but present at a certain curvature.<sup>9,42,52</sup> To determine the critical temperature and density we typically used 11 liquid densities and 11 vapor densities (10 for TIP4P/Ew) from  $T=450$  K (510 K for TIP4P/ice) up to the last upper temperature where we could implement successfully the Gibbs-Duhem integration. These figures represent approximately a range of temperatures between 70% and 95% of the critical temperature of the model. In addition to these data the densities of the vapor at room temperature and at the normal boiling point were also included in the fit. With these data we obtained the eight parameters of the fit. There is an indirect way of checking that the numerical analysis performed to determine the critical properties is reliable. One can use the experimental coexistence densities (liquid and vapor) at the same selected temperatures (say, 11 temperatures between 70% and 95% of the critical temperature of real water) and perform the same fit as the one used for the simulation results. Then, one may check whether the experimental critical point (temperature and density) is reproduced. We have found that this is indeed the case. The error is about 1 K for the critical temperature and  $0.003 \text{ g/cm}^3$  for the critical density. The reproducibility of the experimental vapor-liquid envelope gives us confidence in the methodology used to determine the critical temperature and density. We should mention that the law of rectilinear diameters and the critical scaling for the difference of densities failed to provide satisfactory estimates of the actual values for the critical properties of real water when using the experimental values of the coexistence densities in the mentioned range of temperatures  $0.70-0.95T_c$ .

For the calculation of the vapor pressure we fitted our simulation results to Antoine's law:<sup>56</sup>

$$\ln(p) = A + \frac{B}{T + C}. \quad (5)$$

The critical pressure was estimated by replacing the estimated critical temperature in the fit of the vapor pressure. In Table V the critical properties of the different models as obtained from the previous analysis are reported. In Table VI the values of  $A$ ,  $B$ , and  $C$  of Eq. (5) describing the vapor pressures of the TIP4P models are presented. TIP4P/2005 predicts quite well the critical temperature being just 7 K below the experimental value. The same is true for

TABLE V. Critical properties of TIP4P/2005, TIP4P/Ew, and TIP4P/ice as obtained in this work. The critical densities are reported in  $\text{g/cm}^3$ . The normal boiling point ( $p=1$  bar) as obtained in this work,  $T_b$ , is also given. Melting temperatures of the different models,  $T_m$ , were taken from our previous work (Ref. 23 and 27). Critical properties are labeled with the subscript  $c$ . The properties for the TIP4P model were taken from Lisal *et al.* (Ref. 10) (critical density obtained in this case from the law of rectilinear diameters).

Model	$T_c/K$	$p_c/\text{bar}$	$\rho_c$	$T_m/K$	$T_b/K$	$T_m/T_c$
Experiment	647.1	220.64	0.322	273.15	373.15	0.422
TIP4P/2005	640	146	0.31	252.5	401	0.394
TIP4P/Ew	628	141	0.29	245.5	394	0.390
TIP4P/ice	705	163	0.31	272.2	437	0.389
TIP4P	588	149	0.315	232.5	364.4	0.394

TIP4P/Ew although in this case the deviation with experiment is slightly higher (19 K). The TIP4P/ice model overestimates significantly the critical temperature. It should be mentioned that our estimates of the critical temperatures for TIP4P-Ew and TIP4P/ice are in good agreement with a recent estimate of Baranyai *et al.*<sup>57</sup> For the critical densities the predictions of the three models are reasonably good. In the three cases these are slightly lower than the experimental value. Concerning the critical pressure, the three models underestimate its value. When compared to the critical properties of the original TIP4P model it can be seen that TIP4P-Ew and TIP4P/2005 provide a significant improvement in the estimates of the critical properties of water. The only nonpolarizable model yielding estimates of the critical properties of similar quality to those of TIP4P/2005 is SPC/E. Thus, the inclusion of the self-correction term improves significantly the prediction of the critical properties, regardless of the precise geometry of the model (TIP4P or SPC/E type).

In Table V the melting point of these models,  $T_m$ , and the ratio  $T_m/T_c$  are also given. For the original TIP4P model this ratio adopts the value of 0.394. For the TIP4P-Ew and TIP4P-2005 this ratio takes the values of 0.390 and 0.394, respectively. This suggests that there is a corresponding state law for the TIP4P family of potentials. For these systems the liquid range as given by  $T_m/T_c$  is about 0.39. For real water this ratio is 0.42. The agreement is reasonable and better than for the rest of the water models. In fact, the value of this ratio is about 0.33 for SPC models (SPC and SPC/E) and about 0.51 for TIP5P models.<sup>23</sup> Notice that the value of the ratio  $T_m/T_c$  is strongly affected by the geometry of the molecule

TABLE VI. Vapor pressure of TIP4P/2005, TIP4P/Ew, and TIP4P/ice as given by Antoine's equation [Eq. (5)]. The vapor pressure is given in bars, the temperature in kelvin. The parameters of the fit [Eq. (5)]— $A$ ,  $B$ , and  $C$ —obtained by fitting the vapor pressures from  $T=300$  K up to the proximities of the critical point are given. The fit should not be used outside the range of the fit.

Model	$A$	$B$	$C$
TIP4P/2005	12.46120	-4476.552	-41.49840
TIP4P/Ew	12.39495	-4368.127	-41.27812
TIP4P/ice	12.55820	-4931.839	-44.01296

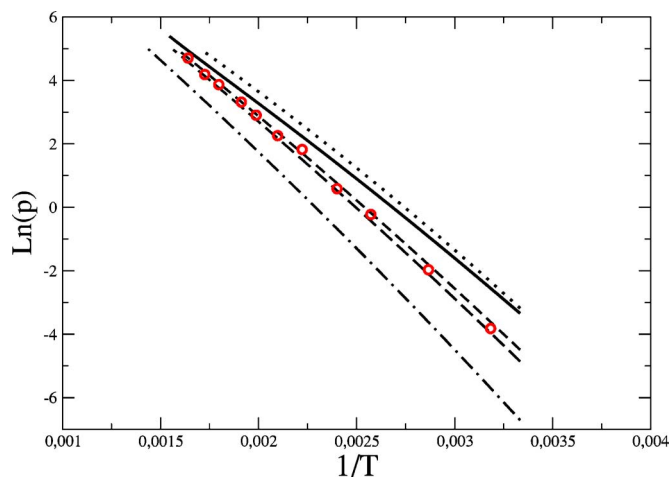


FIG. 1. Vapor pressure of TIP4P models and comparison with experiment. The vapor pressure is presented from 300 K up to the critical point of the model. Experiment: solid line, TIP4P/2005: long dashed line, TIP4P/Ew: short dashed line, TIP4P: dotted line, and TIP4P/ice: dashed dotted line. Open circles: vapor pressure of the SPC/E model. Pressures in bars, temperatures are given in kelvin.

and by the charge distribution.<sup>58,59</sup> It is also possible to estimate the boiling point of these models by replacing the normal pressure ( $p=1$  bar) in Antoine's equation and solving for the corresponding temperature. In this way the boiling temperature has been determined for TIP4P-Ew, TIP4P/2005, and TIP4P/ice. The values are  $T=394$  K,  $T=401$  K, and  $T=437$  K, respectively. For TIP4P-Ew the boiling temperature has been estimated recently<sup>60</sup> by Horn *et al.* as  $T=392(2)$  K. Thus the value obtained in this work is in quite good agreement with this previous estimate.<sup>60</sup> Notice that the TIP4P/Ew, TIP4P/2005, and TIP4P/ice models overestimate the boiling temperature of water, and this is in contrast with TIP4P that underestimates it (the boiling point is 364 K for the original TIP4P). This is because the vapor pressures of TIP4P-Ew, TIP4P/2005, and TIP4P/ice are lower than the experimental value, whereas TIP4P yields higher vapor pressures. This is more clearly seen in Fig. 1 where the vapor pressure curve of water for these models is presented. Results of the vapor pressure for the SPC/E model are also included in Fig. 1. Not surprisingly, the vapor pressure curves of TIP4P/Ew, TIP4P/2005, and SPC/E are quite similar. Models with a built-in self-polarization correction term to reproduce the experimental vaporization enthalpy yield similar vapor pressures. The vaporization enthalpy can be obtained from the internal energy values reported in Table

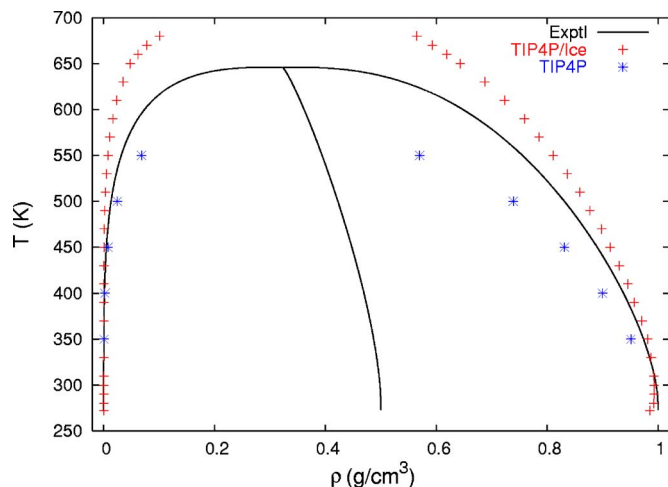


FIG. 2. Coexistence densities of the vapor-liquid equilibria as obtained in this work for TIP4P/ice compared with TIP4P (taken from Ref. 10) and experimental results (Refs. 61 and 62). Asterisks: TIP4P; plus: TIP4P/ice; solid line: experiment.

VII and from the coexistence densities and pressures presented in Tables II–IV. The original TIP4P model matches the vaporization enthalpy at room temperature and pressure (by design), whereas the other models tend to give too high values. Guillot has shown that there is a correlation between the vaporization enthalpy and the critical temperature.<sup>3</sup> The larger the vaporization enthalpy, the larger the critical temperature. The results of this work for the critical temperature of the TIP4P models can be rationalized in terms of this correlation.

In Fig. 2 the coexistence densities of TIP4P and TIP4P/Ice are presented. Both models fail in describing the coexistence densities of real water.<sup>61,62</sup> Figure 3 displays the coexistence densities for TIP4P-Ew and TIP4P/2005. These two models nicely reproduce the orthobaric densities at low temperatures. This is not a surprise. Due to the low value of the compressibility of water, it is obvious that a model describing correctly the density of liquid water at normal pressure in a broad temperature range will also describe successfully the orthobaric densities at low temperatures (where vapor pressure is quite small). It is interesting to stress that a model describing correctly the value and location of the maximum in the density of water—and also the thermal expansion coefficient—will describe correctly the densities along the normal pressure isobar. For this reason it is likely that it will provide a good description of the orthobaric densities and,

TABLE VII. Residual internal energies of the liquid  $U_l$  and gas phase  $U_g$  along the coexistence line for TIP4P/ice, TIP4P/2005, and TIP4P/Ew. Reported values are in kcal/mol.

	TIP4P/ice		TIP4P/2005		TIP4P/Ew	
$T$	$U_l$	$U_g$	$U_l$	$U_g$	$U_l$	$U_g$
590	-8.77	-1.23	-7.05	-1.89	-6.64	-2.41
550	-9.36	-0.80	-7.79	-1.32	-7.44	-1.63
450	-10.75	-0.21	-9.27	-0.34	-8.96	-0.44
390	-11.54	-0.06	-10.10	-0.14	-9.78	-0.15
350	-12.15	-0.02	-10.66	-0.09	-10.34	-0.08
300	-12.90	-0.01	-11.40	-0.01	-11.06	-0.01

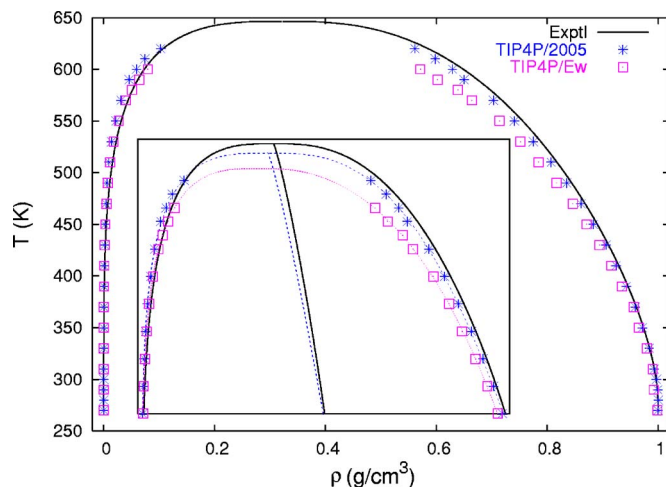


FIG. 3. Coexistence densities of the vapor-liquid equilibria as obtained in this work for TIP4P/2005 (asterisks) and TIP4P/Ew (squares) compared to experimental results (solid line). The inset represents the region used in the fit to calculate the critical point (the dashed and dotted lines are the fitted values for TIP4P/2005 and TIP4P/Ew, respectively).

probably, of the critical temperature of water. In other words, a precise description of the density of water along the  $p = 1$  bar is an important first step to predict the orthobaric densities and the critical temperature. It is also clear that, within the TIP4P geometry, the only way to achieve this goal is to include the self-polarization term in the fitting procedure. Any attempt to reproduce the vaporization enthalpy of water without including this correction (as it is the case for the original TIP4P, TIP5P, and SPC) cannot reproduce the high temperature region of the vapor-liquid equilibria. In summary, the relative success of TIP4P/Ew and TIP4P/2005 in describing the vapor-liquid envelope arises from the acknowledgment of two features shown by their competitor models SPC/E and TIP5P. The TIP5P model illustrates the fact that fitting the TMD is a good idea for obtaining water models. The TIP5P model was able to reproduce the TMD of real water when used with a simple spherical cutoff. Unfortunately when Coulombic forces were considered more carefully the TMD was shifted by about 7 K to higher temperatures<sup>11,24</sup> although this problem can be easily solved by a minor change of the potential parameters as illustrated by Rick when proposing the TIP5P-Ew model.<sup>63</sup> SPC/E shows that the inclusion of the self-polarization term is also a good idea. Our recent studies on melting points and TMD of TIP4P models clearly indicated that the only way a TIP4P model could reproduce the TMD of real water is by including the SPC/E self-energy term. Thus, in our view the new generation of TIP4P models benefits from the ideas introduced by the developers of SPC/E and TIP5P.

As regards the high temperature regime it can be seen how TIP4P/Ew and TIP4P/2005 do a nice job and that TIP4P/2005 follow the experimental liquid densities up to the proximities of the critical point. Concerning the vapor, it can be stated that neither TIP4P-Ew nor TIP4P/2005 describes accurately the properties of the vapor. The inclusion of the polarization term in the description of the vaporization enthalpy implies that the chemical potential of the liquid is too low so that vapor pressures and coexistence vapor den-

sities tend also to be too low, as was already shown in Fig. 1. In this respect TIP4P/Ew and TIP4P/2005 behave as SPC/E which is not surprising since the potential parameters were obtained in the same spirit. In our opinion TIP4P/2005 improves greatly the description of the liquid and solid phases of water, providing even a reliable estimate of the critical temperature and orthobaric densities, but cannot make a miracle describing properly also the properties of the gas phase. In this respect it is neither better nor worse than their predecessors. Unless many body forces (i.e., three body dispersion forces of the Axilrod Teller type and, especially, polarization contributions) are included, one cannot simultaneously describe the vapor and dense phases. Notice that this is true not only for water but also for a system as simple as Ar. The existence of a polarization contribution makes the problem more evident, but it is not unique of water. In our opinion the only way to improve the predictions of the properties for which the models are not successful (vapor pressures and vaporization enthalpies) is to include many body forces.<sup>64</sup> However, it is clear that TIP4P/Ew and TIP4P/2005 offer an overall improvement in the description of the condensed phases of water. In particular, the TIP4P/2005 provides an excellent description of the phase diagram of water and of the equation of state of the different ices, with a melting point for ice  $I_h$  just 20 K below the experimental value. It also reproduces nicely the TMD, the curvature of the normal pressure isobar (i.e., a good value of the thermal expansion coefficient), the diffusion coefficient, and the equation of state for pressures up to 40 000 bars. This work shows that the predictions for the critical temperature, density, and orthobaric densities are also excellent. In summary, TIP4P/2005 is a good effective potential for dense phases of water, but since it does not incorporate many body forces (i.e., polarization or dispersion three body forces) it cannot describe accurately neither vapor pressures, nor virial coefficients, nor vaporization enthalpies. This is the price to pay for the use of effective pair potentials neglecting many body effects.

Let us finish by presenting the vapor-liquid and vapor-solid equilibria for the TIP4P/2005 model in the temperature density plane. This is done in Fig. 4. At the triple point the density of the solid (ice  $I_h$ ) is smaller than that of the liquid. At temperatures above the triple point temperature the solid formed upon compression is not ice  $I_h$  but one of the other polymorph of water. At temperatures below the triple point temperature the vapor condenses into ice  $I_h$ , which by compression melts into a more dense liquid. When this liquid is further compressed, it freezes into another polymorph (ices III or V depending on the thermodynamic conditions). The range of densities in which ice  $I_h$  is stable is quite narrow, as it can be seen in Fig. 2. This kind of behavior was already found in a primitive model of water.<sup>65,66</sup> The limiting line on the left hand side of the ice  $I_h$  inland represents the ice densities along the sublimation line. Since the vapor pressure is quite low, the coexistence densities along the sublimation line can be obtained approximately by performing  $NPT$  runs at zero pressure. The limiting line on the right hand side of the ice  $I_h$  inland corresponds to the coexistence densities along the melting line of ice  $I_h$ , which were obtained in our

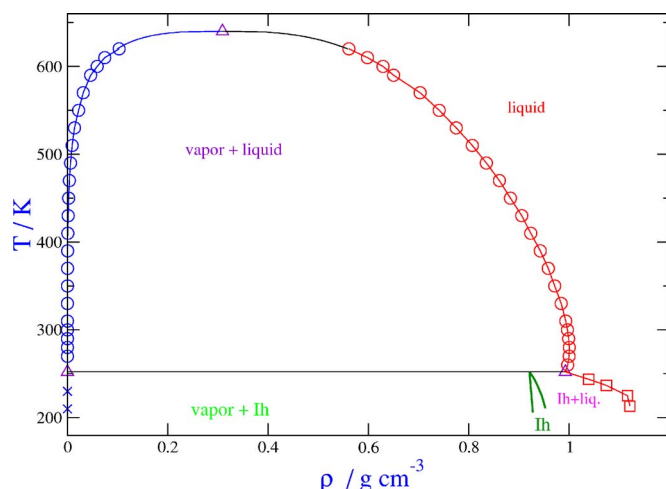


FIG. 4. Phase diagram in the  $T$ - $\rho$  representation for the TIP4P/2005 model. Notice the presence of an island of ice  $I_h$  at temperatures below the triple point.

previous work.<sup>27</sup> To the best of our knowledge it is the first time that the vapor-liquid and fluid-solid coexistence curves are presented in a  $T$ - $\rho$  plot for a water model.

#### IV. CONCLUSIONS

In this paper the vapor-liquid equilibria of recently proposed models which can be considered as variations of the TIP4P model have been computed. Starting from the known vapor pressure of the TIP4P at the  $T=450$  K model and applying Hamiltonian Gibbs-Duhem integration, the vapor pressures of the TIP4P/2005, TIP4P/Ew, and TIP4P/ice have been determined. The obtained coexistence pressures were in good agreement with those obtained from direct simulations of the vapor-liquid interface at the same temperature. Once the vapor pressure at  $T=450$  K was calculated, Gibbs-Duhem integration was used to determine the vapor-liquid coexistence curve from the triple point up to about 0.95 the critical temperature. In this way the vapor pressure of the models was determined in the complete liquid regime. The use of the Gibbs-Duhem integration (which does not require insertions) allowed us to study this broad range of temperatures. After the coexistence pressures are calculated, we performed relatively long simulations to precisely determine the coexistence properties. From the coexistence densities at high temperatures (i.e., those above 450–500 K) the critical properties of TIP4P/2005, TIP4P/Ice, and TIP4P/Ew models were determined. The critical temperature is too low for the original TIP4P and too high for the TIP4P/ice. The predicted TIP4P/Ew critical temperature is much better, and that of TIP4P/2005 is in excellent agreement with experiment (being the deviation of just 7 K). The orthobaric densities predicted by the TIP4P/2005 are also in excellent agreement with experiment. Concerning the vapor properties, it can be stated that none of the models predicted quantitatively neither the vapor pressures, the vapor densities, nor the critical pressure. In our view, this illustrates that within the TIP4P family it is not possible to describe satisfactorily the vapor and the liquid branches simultaneously. Good effective liquid potentials cannot describe correctly the vapor branch. Many

body forces are responsible for this limitation, which applies not only to the complex water, but also to the simpler Ar. It should probably be recognized that in water the problem becomes more evident since, in addition to the three body dispersive forces, there is also the important contribution of polarization, which is also a many body effect. In our view, the TIP4P/2005 is a good potential model for the liquid and represents what probably may be expected from a rigid non-polarizable model. It is likely that the only possible way to improve the model in a significant way is to include the polarizability.

For the TIP4P models it has been found that the vapor pressure at the triple point is relatively constant for all the models and amounts to about  $1.3 \times 10^{-4}$  bar. It was also found that the critical pressure of all these models is relatively constant and amounts to about 150 bars. For TIP4P-like models the ratio between the triple and the critical temperatures is of about 0.39 which is in relatively good agreement with the experimental value of 0.42. In other words, TIP4P-like models do follow a law of corresponding states. It is also obvious that it is not possible for the TIP4P family to fit simultaneously the triple point temperature and the critical temperature. In any case, the error of the TIP4P/2005 is not too high, being just 20 K too low for the triple point temperature and 7 K too low for the critical point temperature. Notice that for the TIP4P family the TMD occurs at about 23 K above the triple point temperature.<sup>24</sup> For this reason the TIP4P/2005 reproduces nicely the TMD of real water. Any attempt to improve the predictions for the triple point and critical point temperatures would spoil the good agreement found for the TMD. In summary, all together, it looks a good idea to use the TIP4P geometry (it provides a good phase diagram prediction) by finding the parameters to reproduce the TMD (as was done when TIP5P was proposed) and including the polarization contribution when trying to match the experimental value of the vaporization enthalpy (as was done in the proposal of SPC/E). When this is done, there emerges a model like TIP4P/2005 which can be considered a good effective pair potential for the condensed phases of water but which fails (as expected) to describe the properties of the vapor phase.

#### ACKNOWLEDGMENTS

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