

## Widom line and the liquid–liquid critical point for the TIP4P/2005 water model

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The Widom line and the liquid–liquid critical point of water in the deeply supercooled region are investigated via computer simulation of the TIP4P/2005 model. The Widom line has been calculated as the locus of compressibility maxima. It is quite close to the experimental homogeneous nucleation line and, in the region studied, it is almost parallel to the curve of temperatures of maximum density at fixed pressure. The critical temperature is determined by examining which isotherm has a region with flat slope. An interpolation in the Widom line gives the rest of the critical parameters. The computed critical parameters are  $T_c = 193$  K,  $p_c = 1350$  bar, and  $\rho_c = 1.012$  g/cm<sup>3</sup>. Given the performance of the model for the anomalous properties of water and for the properties of ice phases, the calculated critical parameters are probably close to those of real water. © 2010 American Institute of Physics. [doi:10.1063/1.3506860]

### I. INTRODUCTION

Despite being the most common liquid, water is atypical; the so-called water anomalies occur over a wide range of thermodynamic conditions. Those appearing at ambient conditions (such as the density maximum at atmospheric pressure) are known even outside the scientific community. With increasing pressure, the temperature of maximum density (TMD) is shifted to lower temperatures and, eventually, becomes smaller than the melting temperature. But density is not the only property showing an anomalous behavior in the supercooled regime. In fact, the discovery in the 1970s that several thermodynamic and transport properties of supercooled water exhibit a pronounced temperature dependence and appear to diverge slightly below the homogeneous nucleation temperature has inspired a large number of experimental and theoretical studies.<sup>1</sup> The appearance of polyamorphism, i.e., the existence of two different amorphous phases—high-density amorphous (HDA) and low-density amorphous (LDA) ice—was proven experimentally in the 1980s.<sup>2–4</sup> In 1992, from an analysis of computer simulation results, Poole *et al.* proposed the existence of a second critical point in the supercooled region of water.<sup>5</sup> Liquid–liquid immiscibility provides a convenient way to explain the appearance of polyamorphism. In fact, x-ray diffraction studies demonstrate that the intermediate states in the supercooled temperature range of water can be reconstructed as a linear combination of HDA and LDA ice, suggesting a first-order transition.<sup>6</sup>

Since the liquid–liquid transition would occur in a region which is difficult to access experimentally, the physical nature of the transition remains elusive. However, some experiments are consistent with—though do not prove—the coexistence of two different phases of (supercooled) liquid water.

A first-order transition between two liquids of different densities is consistent with experimental data for water.<sup>4,7–14</sup> However, there is a little agreement on the possible location of the liquid–liquid critical point (LLCP). Decompression experiments by Mishima and Stanley<sup>7</sup> suggest that it could be located around  $T = 220$  K and  $p = 1000$  atm. Recently, Fuentesvilla and Anisimov<sup>15</sup> have developed a scaled parametric equation of state to describe and predict thermodynamic properties of supercooled water. The scaled equation of state yields a similar critical temperature,  $T = 232$  K, but the critical pressure,  $p = 270$  atm is much lower than previous predictions. Some authors even suggest that the location of the LLCP lies in the negative pressure region.<sup>16,17</sup>

Confinement may provide an alternative way for testing the LLCP hypothesis for water because the presence of a solid interface severely distorts water's hydrogen bond network,<sup>18</sup> possibly inhibiting crystal nucleation.<sup>19</sup> A number of recent experiments of water in confined geometries (and protein hydration water as well) seem to confirm the LLCP.<sup>20–25</sup> However, another study puts some of this work into question.<sup>26</sup> Finally, it is worth noting that the existence of a liquid–liquid transition has been demonstrated experimentally for other systems, such as silicon,<sup>27</sup> selenium,<sup>28</sup> sulfur,<sup>29</sup> carbon,<sup>30,31</sup> phosphorus,<sup>32</sup> and triphenyl phosphite.<sup>33,34</sup>

The main body of support for the liquid–liquid immiscibility comes from computer simulation results. The existence of a second critical point has been demonstrated for a number of realistic water models<sup>5,16,35–43</sup> and other tetrahedrally coordinated liquids.<sup>44–47</sup> But the calculations with realistic models are computer intensive.<sup>42,43</sup> In an attempt to clarify the nature of the transition (and to speed up the calculations) simplified models have been introduced. Sometimes the simplified models try to mimic the main features of the water–water interaction, especially the orientational dependence associated with the hydrogen bond.<sup>48–52</sup> In other cases, the potential models have no orientational dependence.

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In particular, much work has been devoted to a class of models usually termed “core softened” or “ramp” potentials characterized by the presence of two repulsive length scales<sup>53–65</sup> These and other studies<sup>66</sup> have greatly contributed to the understanding of the general conditions for a liquid–liquid transition to occur and to its relation to the density anomalies. However, for certain properties, the models exhibit a quite different behavior from that of water.<sup>62,65</sup> For instance, the liquid–liquid coexistence line, unlike in tetrahedrally coordinated liquids, has a positive slope because the high density phase is more ordered than the low density one.<sup>59,67</sup> Thus, some care should be exercised in extrapolating the results for ramp models to the case of water. This is in strong contrast with the results for more or less realistic water models. In fact, up to now (to the best of our knowledge) all the studies with realistic water models predict the existence of a liquid–liquid transition. It seems then convenient to investigate this issue using a water model whose performance in accounting for the water properties is rather accurate so that the calculations with the model in regions of difficult experimental access can be considered trustworthy.

More than a decade after the proposal of the yet widely used water potential models such as SPC/E (Ref. 68) and TIP4P,<sup>69</sup> the present millennium has seen a clear upsurge in the field with the addition of new members to the TIPnP family, namely TIP5P,<sup>70</sup> TIP4P-Ew,<sup>71</sup> TIP4P/ice,<sup>72</sup> and TIP4P/2005.<sup>73</sup> This is probably a consequence of a fine tuning of the models produced by the inclusion of a wider set of target properties in the parametrization of the models. Among these, TIP4P/2005 probably gives the best agreement with experiment for a wide range of states and water properties.<sup>74</sup> Moreover, the model provides a quantitative account of many anomalous water properties, including not only the well known thermodynamic anomalies,<sup>75</sup> but also the dynamical ones.<sup>76</sup> Of particular relevance for the purposes of this work is the high quality of the predictions for the phase diagram of water both in the high temperature region<sup>77</sup> (vapor–liquid equilibria) and in the high density region<sup>73</sup> (ice–liquid and ice–ice equilibria). It is also noteworthy the excellent agreement of the TIP4P/2005 equation of state at low temperatures for the different ice polymorphs.<sup>73</sup> And finally, it is to be stressed that it reproduces with very high accuracy the ambient pressure isobar even in the supercooled region<sup>75</sup> (we will come back to this point later in this paper). In summary, the high quality of the predictions of TIP4P/2005 (including the region in which the liquid–liquid transition is expected) makes us confident on the reliability of the predicted results suggesting that they could be in close agreement with those that could eventually be found experimentally. Our goal will be to use the TIP4P/2005 model to investigate the possible existence of a liquid–liquid transition. We anticipate that the answer is positive and, thus, we also intend to provide the location of the second critical point as precisely as possible. Given the quality of the predictions of TIP4P/2005, we believe that the computed critical parameters are expected to be very close to the values for real water so this study may help in the search for the experimental confirmation of the existence and location of the hypothesized critical point.

In recent years, there has been increasing experimental activity trying to test the existence critical point in terms of a Widom line.<sup>15,25,67,78,79</sup> The Widom line is the locus of maximum correlation length emanating from a critical point. The first attempt of estimating the LLCPC through the line of maxima compressibility was done in 1997 for the ST2 and TIP4P models of water.<sup>35</sup> The study of the compressibility and other thermodynamic anomalies allows one to locate the Widom line with high precision at a moderate computer cost. But the Widom line can also be calculated from an analysis of other properties such as the specific heat,<sup>67,80,81</sup> excess entropy<sup>82</sup> or structural correlations.<sup>79,83,84</sup> A particular effort has been devoted to investigate the transport properties of water in the deeply supercooled region of water in confined geometries and to relate it to the existence of a Widom line (see Ref. 85 for a recent review on this topic). The Widom line is slightly dependent on the response function used for its calculation. But, since the Widom lines obtained using different properties must converge at the critical point, the computation of the LLCPC is independent of the property used in its determination. The main advantage of focusing on the Widom line is that it allows one to investigate the system (either experimentally or by computer simulation) *outside the critical region* which allows to trace quite simply the approach to the critical point. In this paper we will investigate the supercooled region of TIP4P/2005 in order to locate the Widom line and the LLCPC.

## II. SIMULATION DETAILS

All the simulations in this work have been done for a sample of 500 molecules in the isothermal–isobaric  $NpT$  ensemble using the molecular dynamics package GROMACS 4.0.<sup>86</sup> The time step was 2 fs. The Lennard-Jones potential has been switched from 8.5 Å up to a cutoff distance of 9.5 Å. Long range corrections were applied to the Lennard-Jones part of the potential (for both the energy and pressure). Ewald summations were used to deal with electrostatic contributions. The real part of the Coulombic potential is truncated at 9.5 Å. The Fourier component of the Ewald sums was evaluated by using the particle mesh Ewald (PME) method<sup>87</sup> using a grid spacing of 1 Å and a fourth degree polynomial for the interpolation. The simulation box is cubic throughout the whole simulation and the geometry of the water molecules is enforced using constraints.<sup>88</sup> Temperature has been set to the desired value with a Nosé–Hoover thermostat.<sup>89,90</sup> To keep the pressure constant, an isotropic Parrinello–Rahman barostat is used. The length of the simulations varies enormously from one point to another. Previous work indicated that 40 ns could be enough to obtain the isothermal compressibility at 1 bar in the vicinity of the melting point at ambient pressure. As one approaches the critical region longer runs are required in order to obtain smooth results for the density and isothermal compressibility also in the deeply supercooled region. Most of the runs of this work required around 200 ns of simulated time, with a longest run (for a state very close the critical point) of 800 ns. The total computer time of this work is estimated to be equivalent to 150 months in a single Opteron core.

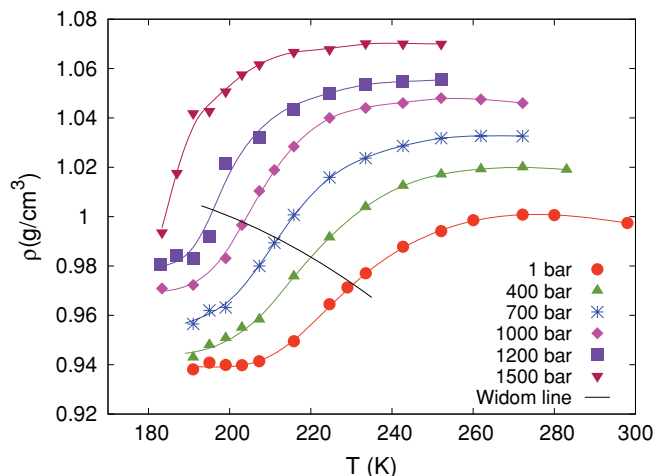


FIG. 1. Density as a function of temperature for different isobars. The full line crossing the isobars is the Widom line obtained using the isothermal compressibility data. The rest of the lines are a guide to the eye.

### III. WIDOM LINE

A recent investigation of the water anomalies using TIP4P/2005 has shown that the density at constant pressure shows (besides the well known maxima) an inflection point<sup>75</sup> at a temperature clearly below the melting point. Thus, the coefficient of thermal expansion exhibits a minimum in the supercooled region which may signal a point in the Widom line emanating from a critical point. Therefore, we decided to explore the isobars at higher pressures to confirm the expansivity minima and to trace out the corresponding Widom line. NpT simulations lasting 40 ns are long enough to provide a precise determination of the maximum in density at 1 bar, but longer runs (of the order of 100 ns) are required to obtain a smoothed curve in the region surrounding the inflection point. At the lower temperatures the density of the atmospheric isobar shows a region of flat slope or even a density minimum (Fig. 1). Runs lasting 200–300 ns were insufficient to establish without ambiguity the existence of a density minimum which has been found in lattice models of network forming fluids,<sup>91</sup> computer simulations of water<sup>40,62,65,84,92–94</sup> and experimental results for water in confined geometries.<sup>13</sup> In any case, it is clear that for temperatures below 205 K (at room pressure) the density does not decrease with temperature any more and the steep drop of density with temperature that occurs for temperatures below the TMD does not occur any longer. In this region, where the density curve is almost flat (or even increasing slightly as the temperature decreases) the water molecules are able to diffuse. Therefore, the existence of a flat region of densities (at room pressure) is a true equilibrium phenomena and should not be interpreted as any sign of glassy behavior. For temperatures below 190 K (at room pressure) the system becomes glassy but for the temperature range of 190–205 K (at room pressure) where the density curve is almost flat the molecules are able to diffuse and the runs are ergodic. The density of ice Ih at 200 K for the TIP4P/2005 is of about 0.93 g/cm<sup>3</sup> and increases as the temperature decreases. Would the density of water along the room pressure isobar decrease with temperature without

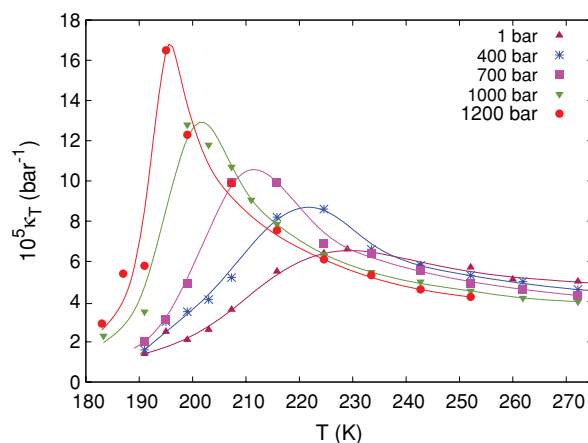


FIG. 2. Isothermal compressibility as a function of temperature along different isobars. Lines are a fit of the results using natural smoothing splines.

stopping and at a certain point it could become less dense than ice. Although we do not see any thermodynamic argument against that, it is obvious that this does not occur. At a certain temperature the density of water does not decrease with temperature any longer.

In Fig. 1 it can be seen that the general shape of the isobars follow similar trends as that of the ambient pressure isobar although the drop between the high and low density regions becomes increasingly sharper as the pressure increases. Despite that the density–temperature curves seem to be quite smooth, their shape makes difficult to fit them in an analytical function providing a precise location of the inflection point. From the volume fluctuations it is possible to obtain the isothermal compressibility,  $\kappa_T$ , in the same run used to obtain the density. The corresponding values of  $\kappa_T$  for each isobar are presented in Fig. 2. The curves exhibit a clear maximum, each of them providing a point of the Widom line. At higher pressures, the heights of the maxima increase and are shifted toward lower temperatures. This is a clear fingerprint of the approach to a critical point. The Widom line obtained from the  $\kappa_T$  maxima has been incorporated in Fig. 1. Visual inspection shows that the line approximately crosses the inflection points of the curves: indicating that Widom line computed from the maxima in the isothermal compressibility is roughly coincident with that which could be obtained from the minima in expansivity. In Fig. 3 we plot the Widom line in the  $p$ – $T$  plane together with the line of density maxima for TIP4P/2005. In the region studied both curves are almost parallel to each other, the difference between them being approximately 50 K. This is in accordance with the results for the mW water model.<sup>84</sup> We have also represented in the figure some experimental values of the density maxima. They are very close to the results for TIP4P/2005 which gives strong confidence in the predictions of the model.

At low temperatures the mobility of the molecules decreases. This could disable a correct sampling of the configurational space. We have therefore monitored the mean square displacement of the water molecules to be sure that a “glassy” state is not reached (notice that we do not refer here to the glass transition but to the minimum mobility conditions to ensure a proper sampling). In Fig. 3 we have also plotted the

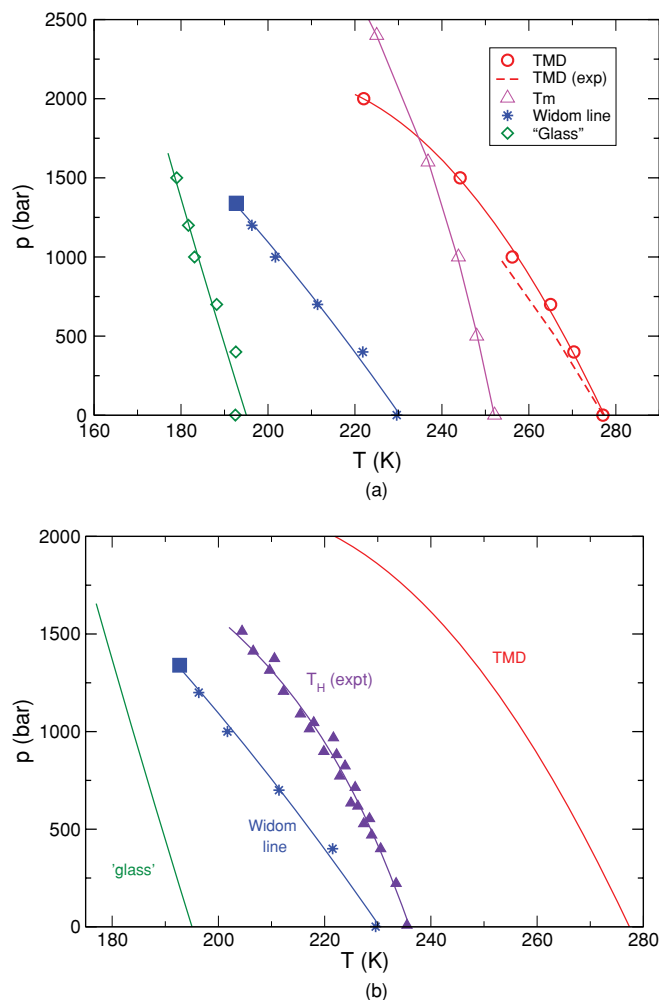


FIG. 3. (a) Upper panel: Widom line (stars) in the  $p$ - $T$  plane bracketed by the TMD line (circles) and the “glassy” line (diamonds; it is the locus of states for which the mean square displacement in 100 ns is  $8 \text{ \AA}^2$ ). The critical point is marked with a full box. Also shown are the computed melting temperatures of TIP4P/2005 and the experimental results for the TMD. (b) Lower panel: Widom line for the TIP4P/2005 water model and experimental homogeneous nucleation line. Also shown are the TMD and the “glassy” lines of TIP4P/2005.

line for which the mean square displacement in 100 ns is of the order of the (squared of the) molecular size. In particular, we have arbitrarily fixed such value to be  $8 \text{ \AA}^2$ . It can be seen that the Widom line lies beyond the line with possible sampling problems due to the reduced molecular mobility. Notice also that the chosen time (100 ns) is 2–4 times smaller than the time simulated for these states. However, the lack of mobility does limit the minimum temperature at which the calculations can be accurately performed at a given pressure. This is not important in general except for the investigation of the possible existence of a density minimum at low temperatures. Notice that if we would remove the point at the lowest temperature of the 1 bar curve in Fig. 1, the density would seem to exhibit a more or less defined minimum. Unfortunately, the point at lower temperature in the ambient pressure isobar is just in the limit of the “safe” sampling region, and the uncertainty in density is clearly larger than the precision required to analyze the existence of a density minimum. At higher pressures, the line which separates the “glassy” region

from the “equilibrium” one moves to lower temperatures. This can be easily understood since the pressure disrupts the hydrogen bond network, which helps the diffusion of the water molecules. Unfortunately, at increasing pressures, the region where the important drop in density occurs is also shifted toward lower temperatures and, finally, the region of possible density minimum is even less accessible.

In a couple of cases at 191 K we have observed a slow decrease in the density along the run with a simultaneous drop of the mean square displacement. The density finally reached a constant value close to that of ice suggesting the onset of nucleation events. However, a visual inspection of the final configuration did not reveal a crystal structure. Notice that, since our simulations did not allow the box shape to change, the appearance of ice could be frustrated. The crystallization of bulk water in simulation studies is rarely observed,<sup>95</sup> though the presence of interfaces greatly favors the process.<sup>96–98</sup> It is worth noting that in our simulation these events occurred at a temperature very close to the critical one. This is probably due to the increased fluctuations in the critical region.<sup>99</sup> A support of this interpretation is given in Fig. 3 (lower panel) which shows that the (experimental) homogeneous nucleation line lies quite close to the Widom line calculated in this work. The onset of crystallization in computer simulations of the supercooled region has also been reported for the TIP5P (Ref. 38) and mW models.<sup>100</sup> However, for TIP5P, the transformation required only 3 ns in some conditions whereas the time needed for TIP4P/2005 seems to be orders of magnitude larger. Further work is needed to clarify these issues.

#### IV. LOCUS OF THE CRITICAL POINT

As the pressure increases the Widom line approaches the critical point. But an analysis of the Widom line alone is not sufficient to locate the LLC. A procedure is needed to locate the critical point. To this end, different methods with varied degrees of sophistication have been used.<sup>5,40,43</sup> Notice that we had already a considerable amount of information on the equation of state of the model at low temperatures (see Fig. 1). Thus, we considered that in order to determine the critical point, the cheapest alternative in terms of computer time was to examine the shape of the pressure–density curves at constant temperature. The isotherm showing a flat region is the critical one. Additional points were then computed to define precisely the shape of the isotherms. The results are presented in Fig. 4. All the isotherms below 225 K show an inflection point which is almost coincident with the Widom line calculated in the previous section. Accordingly, the inflection point is shifted to higher pressures for decreasing temperatures while, as expected, the slope of the curves at the inflection point is reduced. For the isotherms below 200 K, runs of 300–500 ns are required to observe the results with a more or less smooth shape.

Although the 199 and 195 K isotherms show some signs of the vicinity to a critical point (a reduced slope at the inflection point), they are apparently supercritical (Fig. 4). It seems however that the 191 K isotherm is already below the critical temperature. At this temperature, two independent runs at 1400 bar using different initial configurations resulted in

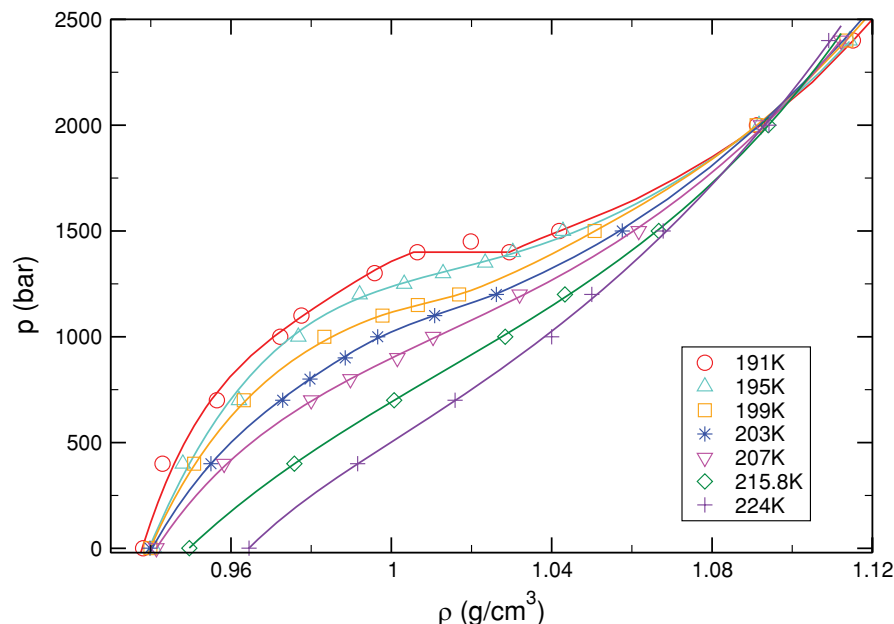


FIG. 4. Isotherms in the vicinity of the critical point. The results above 199 K have been fitted to a double exponential function. At the lower temperatures the fit was made in three stretches using a polynomial function in each of them.

different densities in runs of 400 ns each. It seems that each configuration stabilized as LDL and HDL, respectively, with no significant transitions between them. Curiously, a point at the same temperature but at 1450 bar showed clear signs of transitions between configurations with different densities. In this single case, the histogram of densities (Fig. 5) show two different peaks which, interestingly, correspond to approximately the same densities as those obtained in the runs at 1400 bar (1.000 and 1.029 g/cm<sup>3</sup>). Thus, this state lies within the coexistence region and, thus, 191 K corresponds to a subcritical isotherm. The critical temperature is then located between 191 and 195 K so we finally assign it the intermediate value  $T_c = 193$  K. Once the critical temperature is known,

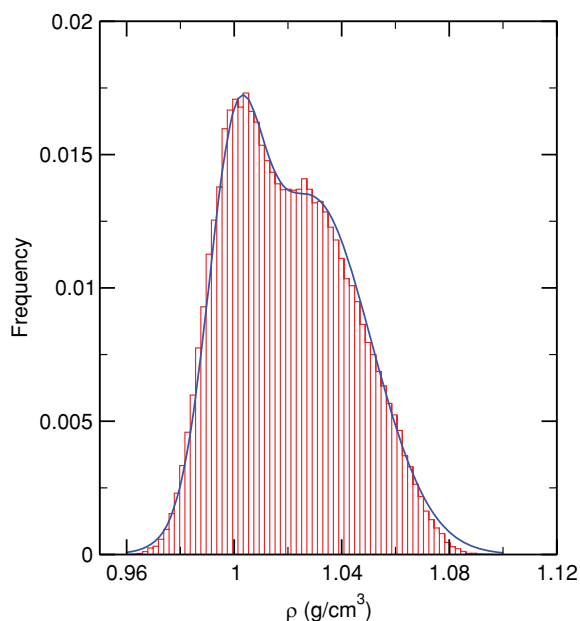


FIG. 5. Normalized frequency histogram of the densities for the state at  $T = 195$  K,  $p = 1450$  bar. The envelope is a double Gaussian fit of the results.

it is very easy to determine the rest of critical parameters. Figure 6 shows the Widom line in the  $p-\rho$  plane terminated at the critical temperature. An interpolation of the Widom line values gives  $p_c = 1350$  bar and  $\rho_c = 1.012$  g/cm<sup>3</sup>. The resulting critical parameters are noticeably close to the values obtained from quasielastic and inelastic neutron scattering of water confined in nanoporous silica matrices,<sup>21</sup> namely  $p_c = 1500$  bar and  $T_c = 200$  K.

## V. FINAL COMMENTS

In this work we have investigated the liquid-liquid immiscibility in the deeply supercooled region of water. We have shown that the TIP4P/2005 model exhibits a second critical point. This is in agreement with the results obtained for all the realistic models of water explored in the past. But the proposed values for the critical parameters differ considerably from one model to another.<sup>5,16,35,36,38,39,42</sup> We have reported that SPC/E and TIP5P fail in the prediction of the relative stability of ices. For three charged site models (SPC/E) this has been shown to be a consequence of a high dipole to quadrupole ratio.<sup>101,102</sup> It is likely that the failure of TIP5P has the same origin and, considering that the quadrupole moment of ST2 is very low,<sup>103,104</sup> one cannot expect that ST2 is able to account for the relative stability of ices. Besides, the melting temperature of three charged site models depends almost linearly on the quadrupole of the water molecule<sup>105</sup> which is the reason of the low melting temperatures obtained for SPC/E and TIP4P.<sup>106</sup> In summary, the location of the phase equilibria predicted by ST2, SPC/E, TIP4P, and TIP5P (especially when affecting ice-like structures) are probably quite different from the experimental ones. On the contrary, the very accurate overall performance of TIP4P/2005 and, especially, its ability to reproduce the experimental curve of density maxima at constant pressure (i.e., the TMD curve) strongly suggests that its predictions for the locus of the LLCP should be reasonable. Given the difficulties to

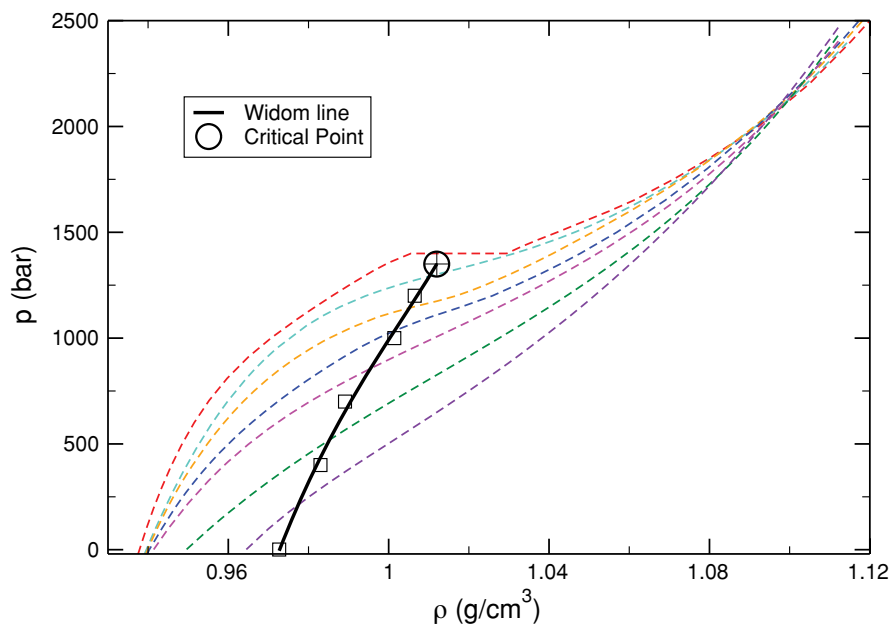


FIG. 6. Widom line (in the  $p$ - $\rho$  plane) ending at the critical point. Dashed lines are the isotherms already shown in Fig. 4.

obtain liquid water under the conditions expected for the second critical point, one has to resort to experiments in confined geometries. But confinement modifies the hydrogen bond structure. This is important to disable the nucleation and thus making possible the existence of a liquid well below the melting temperature. It has been reported that the hydrophilic confinement shifts the critical point of the liquid-liquid transition to a higher pressure.<sup>107</sup> In this way, it seems that the experimental (bulk) critical point should be somewhat lower than that determined in hydrophilic confinement. Our result for TIP4P/2005,  $p_c = 1350$  bar, fulfills this requirement since it is slightly below the experimental result,  $p_c = 1500$  bar, for water confined in silica matrices.<sup>25</sup>

We have found that, along the room pressure isobar, the density does not change much with temperature (or even increases slightly) below 205 K. With the accuracy of the current simulations we could not determine the minimum without ambiguity. In any case, there is a clear change in the way the density of supercooled water changes with temperature at about 205 K. We can state clearly that the density of water at this point stops decreasing when cooling (while the molecules are still diffusing so that this cannot be attributed to the appearance of glassy behavior). Therefore, it seems likely that the density of supercooled water will never become lower than that of ice Ih.

Another issue is the possibility of multiple liquid-liquid critical points. Evidence for multiple transitions have been reported for a number of systems closely related to water.<sup>41,61,93,108,109</sup> But these findings have been challenged by other studies.<sup>43,110,111</sup> In our study we have found a clear evidence for one liquid-liquid transition point. Of course, it remains to be seen what could happen in other thermodynamic regions not explored in this work.

As commented in the introduction, given the performance of the model for the anomalous properties of water and for the properties of ices, the calculated critical param-

eters are expected to be in close agreement with those of real water. Certainly, the finite size of the systems may have an effect on the final parameters. However, Poole *et al.* have shown no significant differences in the equation of state of ST2 water in the supercooled region for two system sizes made of 216 and 1728 water molecules, respectively.<sup>39</sup> It can also be argued that at low temperatures nuclear quantum effects may become significant. It is certainly true that nuclear quantum effects are important in water (even at room temperature) and its importance increases as the temperature decreases. For temperatures below 150 K classical simulations fail in describing the majority of the properties of water. However, we have found<sup>112</sup> that for temperatures above 150 K classical simulations with an effective potential that incorporates nuclear quantum effects through the potential parameters (i.e., TIP4P/2005) can describe quite well the equation of state of ices and water. In other words, although nuclear quantum effects in water are important, one may expect good predictions of the equation of state of water and ices for temperatures above 150 K provided that the water potential model was optimized to reproduce the experimental values in classical simulations. Since the equation of state determines the Widom line (i.e., the compressibility maxima or the thermal expansion coefficient minima), one can conclude that classical simulations can describe reasonably well the Widom line of real water (with a good potential model optimized for classical simulations).

In summary in this work we have determined the Widom line for the TIP4P/2005 model. The determination was possible because for this model (and for system size of 500 molecules) thermodynamic properties could be precisely determined in runs of less than a microsecond. The molecules were able to diffuse and it was possible to determine the properties of supercooled water rather accurately. Runs of the order of the microsecond were not sufficiently long to nucleate ice. Therefore, for this model and system size there is a window of time for which it is possible to

obtain equilibrium properties of the fluid without observing the nucleation of ice. We believe that the determination of the Widom line could be determined experimentally, although most likely one should be able to determine thermodynamic properties for a water sample of micrometer size and to be able to measure on a window time of the order of the microsecond. This is obviously quite challenging. On the other hand, if our simulations had lasted for seconds instead of microseconds then would have observed the “instantaneous” nucleation of ice in “just” a few seconds. Time and size increase the probability of ice nucleation, therefore the only way to avoid it is to decrease both.

## ACKNOWLEDGMENTS

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