

Multiple Critical Points of Supercooled Water

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We determined liquid-liquid and liquid-vapor coexistence regions of various water models by restricted ensemble MC simulations of the isotherms of uniform density systems and by phase equilibria simulations in the Gibbs ensemble. All studied water models show multiple liquid-liquid phase transitions in the region of the supercooled liquid. Three distinct liquid-liquid phase transitions were found for the ST2 water model. The lowest density liquid-liquid transition meets the liquid-vapor phase transition at a triple point and ends in a metastable critical point at negative pressure. The second and third liquid-liquid phase transitions are located at positive pressures. TIP4P, TIP5P and SPCE water models show two liquid-liquid phase transitions: the first one is found at negative pressures, while the second one is located at positive pressures. Addition of a reaction field to the original ST2 model essentially decreases the liquid density in comparison with real water. As a result the two liquid-liquid phase transitions appear at positive pressures only. For real water we may expect multiple liquid-liquid phase transitions with critical point of the first liquid-liquid phase transition at negative pressure.

1. Introduction

The presence of a critical point determines the properties of a fluid in a wide range of thermodynamical conditions. The anomalous properties of liquid water could be explained by the influence of a distant liquid-liquid critical point located in the supercooled region [1]. The existence of various amorphous ices and their mutual transformation via first order phase transitions [2,3] supports this hypothesis. From computer simulations evidences for a liquid-liquid phase transition at positive pressures were obtained for the ST2 water model with reaction field [1,4-9] and the TIP5P water model [10]. Additionally, simulations of low-temperature TIP4P water indicated the existence of a liquid-liquid critical point [5,7,11], probably at negative pressures [11]. The existence of a liquid-liquid phase transition in real water and in various water models is still an area of debates.

In this paper we present computer simulation studies of liquid-liquid phase transitions in various water models. The possible location of liquid-liquid critical points in real water is inferred.

2. Simulation Methods

The coexistence of different states of supercooled water was studied by Monte Carlo (MC) simulations of isotherms in the density fluctuation restricted ensemble [12] and by MC simulations in the Gibbs ensemble [13].

In the restricted NPT ensemble the cubic simulation box with 513 molecules was divided into 27 equally sized cubic subcells which contain an equal number of molecules. The number of molecules in the subcells was kept unchanged in the course of the simulations. This inhibits phase separation in the simulation box and allows a controlled extension of the isotherms into the region of metastability. Typically up to 2×10^5 molecular moves per molecule were done in the course of a MC simulation run. Isotherms were studied at temperatures $T \geq 150$ K.

Liquid-liquid coexistence was also studied by MC simulations in the Gibbs ensemble, using up to 1000 molecules. Due to the extremely low acceptance probability of molecular transfers between two dense liquid phases these simulations were restricted to $T \geq 260$ K and $\rho < 1.3$ g/cm³. The liquid-vapor coexistence curves of water were simulated at $T \geq 75$ K, using up to 600 molecules.

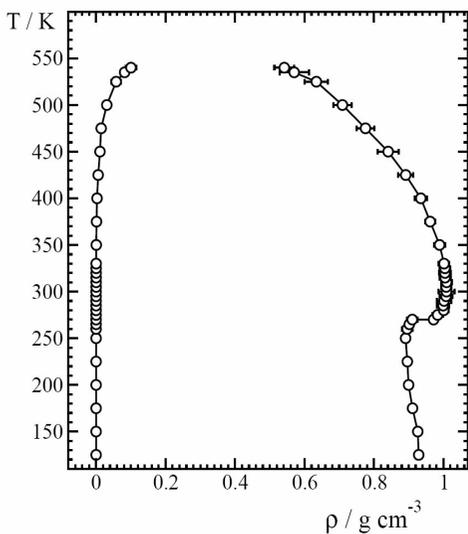


Fig. 1. Liquid-vapor coexistence curve of ST2 water.

ST2 [14], TIP4P [15], TIP5P [16] and SPCE [17] water models were used in our studies. In all cases a simple spherical cutoff of the intermolecular interactions at 9 Å was used. In accord with the original parametrization of these models [14-17], no long-range corrections for the Coulombic interaction were included. Additionally, we used the ST2 water model including a reaction field to account for the long-range Coulombic interaction (ST2* water model hereafter), which was already intensively studied in the supercooled region [1,4-9].

3. Results and Discussion

The liquid-vapor coexistence curves of the ST2 and TIP4P/TIP5P water models, obtained by simulations in the Gibbs ensemble, are shown in Figs. 1 and 2, respectively. A sharp jump of the liquid branch of the coexistence curve of the ST2 water model is observed at $T = 270$ K (Fig. 1). This break directly evidences a liquid-liquid phase transition, and moreover a triple point at which the water vapor coexists with two liquid phases of different densities [18]. The liquid branch of the coexistence curve of TIP4P water (Fig. 2) does not show such a break and changes continuously with temperature. Also the TIP5P (Fig. 2) and SPCE water models show a behavior quite similar to the TIP4P model.

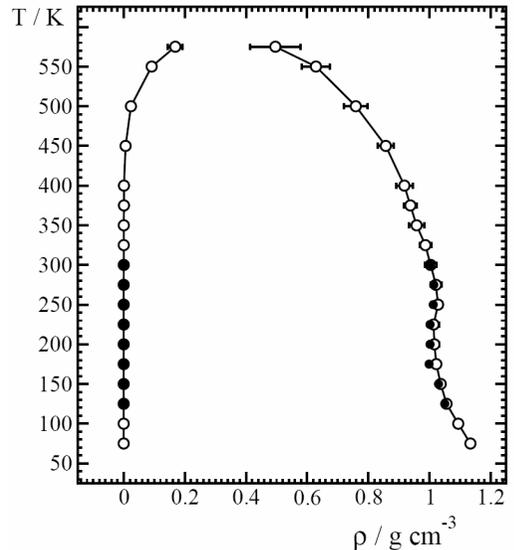


Fig. 2. Liquid-vapor coexistence curve of TIP4P (open symbols) and TIP5P water (closed symbols).

All these water models (ST2, TIP4P, TIP5P and SPCE) pass at saturated vapor pressure a liquid water density maximum of about 1 g/cm^3 . Addition of long-range corrections for the Coulombic interactions in these water models, which were parameterized for simple spherical cut-off, ultimately decreases the density of the liquid water. This effect is especially pronounced in the case of the ST2 water model, where the density decreases from 1.0 to 0.93 g/cm^3 due to the use of a reaction field [1,4-9]. In such a modified ST2 model (ST2*) the liquid density also varies continuously along the coexistence curve, in contrast to the original ST2 model.

A direct equilibrium between two liquid phases was obtained for the ST2 model at temperatures $T = 270$ and 260 K by using Gibbs ensemble simulations [18]. The densities of the coexisting liquid phases at $T = 270$ K are in good agreement with the values, obtained from the liquid-vapor coexistence curve (Figs. 1 and 4). Additionally, the simulations in the Gibbs ensemble show a second liquid-liquid coexistence in the density interval between about 1.02 and 1.12 g/cm^3 (Fig. 4). At $T < 260$ K a direct equilibration of two dense liquid phases is practically unachievable. Therefore, to locate liquid-liquid coexistence at lower temperatures and higher densities we used simulations of isotherms in a restricted *NPT*

ensemble, comparable to the one used by Hansen and Verlet [12].

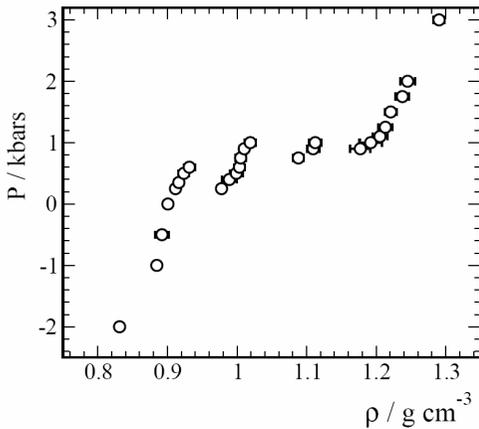


Fig. 3. Isotherm ($T = 235$ K) of supercooled ST2 water.

The isotherms of the ST2 water model at $T = 260$ and 275 K confirmed the existence of two liquid-liquid phase transitions. The densities of the coexisting liquid phases of the first (lowest density) phase transition, obtained from the simulated isotherm at $T = 275$ K are in good agreement with the densities, obtained from the Gibbs ensemble simulations of the liquid-vapor and the liquid-liquid coexistence curves at $T = 270$ K. It is important, that the first liquid-liquid phase transition at $T = 275$ K is located at negative pressures ($P \approx -200$ bar). Thus, the critical point of this transition is located at *negative* pressures. Restricted *NPT* ensemble simulations of the liquid spinodal of the liquid-vapor coexistence curve [18] evidence, that the first liquid-liquid critical point is located in a thermodynamic state, which is metastable with respect to evaporation. At $T < 270$ K the lowest density liquid-liquid phase transition occurs at positive pressures. This means, that with decreasing temperature the saturated liquid water approaches a liquid-liquid spinodal. For the ST2 model the liquid-vapor coexistence curve crosses the liquid-liquid spinodal just below 270 K. Taking into account the temperature shift of the density maximum of the ST2 model with respect to real water, this singular temperature may be estimated for real water as ~ 240 K. This value is close to the experimentally estimated temperature of a thermodynamic singularity of water at about 228 K [19].

The $T = 235$ K isotherm evidences three liquid-liquid phase transitions of the ST2 water model (Fig. 3). The third phase transition appears in the density interval between about 1.10 and 1.20 g/cm^3 . The location of the three liquid-liquid two-phase regions with respect to the liquid-vapor coexistence curve is shown in Fig. 4. Note, that the densities of the four phases of supercooled water, obtained in our simulations (see Figs. 3 and 4), correlate with the available experimental densities of amorphous forms of water at $T = 77$ K and $P = 0$ (shifted to slightly higher densities due to the lower temperatures): low-density amorphous ice [2] ($\rho \approx 0.94$ g/cm^3); hyperquenched amorphous water [20] ($\rho \approx 1.04$ g/cm^3); high-density amorphous ice [1,21] ($\rho \approx 1.17 - 1.19$ g/cm^3 , $\rho \approx 1.14 - 1.15$ g/cm^3); very-high-density amorphous ice [21] ($\rho \approx 1.25 - 1.26$ g/cm^3).

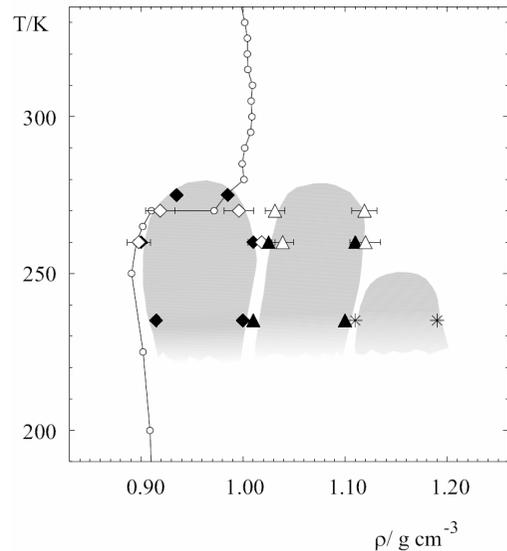


Fig. 4. Liquid-liquid and liquid-vapor coexistence regions of ST2 water. Open symbols – from Gibbs ensemble simulations. Closed symbols – from restricted *NPT* ensemble simulations. Circles – liquid branch of the liquid-vapor coexistence. Diamonds – first liquid-liquid transition. Triangles – second liquid-liquid transition. Stars – third liquid-liquid transition. Shaded areas show a rough estimate of the liquid-liquid two-phase region.

The different liquid phases of one-component fluids should contain different concentrations of molecules with specific local ordering. To clarify

the local structures, which are associated with the observed liquid-liquid phase transitions of the ST2 water, we used a recently observed relation between phase transitions and percolation transitions [22]. We found, that tetrahedrally ordered water molecules with exactly 4 neighbors in the first coordination shell are the percolating structural units, which are linked with the first liquid-liquid transition. The corresponding structural units which are responsible for the highest density transition are water molecules with any number of neighbors, but a tetrahedral order of the four nearest.

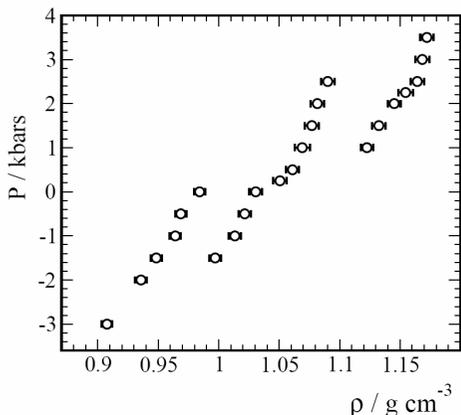


Fig. 5. Isotherm ($T = 175$ K) of supercooled TIP4P water model.

Simulations of the isotherms in the restricted NPT ensemble allowed also the location of the liquid-liquid phase transitions in other water models. As an example, we present in Fig. 5 the isotherm $T = 175$ K of TIP4P water. Quite similar isotherms were obtained for the TIP5P and SPCE water models. In all three cases there are two liquid-liquid phase transitions: the first one is located at negative pressures, while the second one is situated at positive pressures. We should mention, that in the case of TIP5P water a third (probably reentrant) liquid-liquid phase transition could be noticed at $T = 175$ K. The first liquid-liquid phase transition in these three models is located at negative pressures in a wide temperature range. In contrast to the ST2 model, a triple point is not observed even at extremely low temperatures (see Fig. 2). Note also, that in TIP4P, TIP5P and SPCE water the critical temperature of the second liquid-liquid phase transition is always close to or higher

than the critical temperature of the first liquid-liquid phase transition.

The modified ST2* water model significantly overestimates the structuring of real water. This results in a noticeably lowered liquid density at ambient conditions. From low-temperature isotherms we found two liquid-liquid phase transitions of ST2* water, both at positive pressures. The location of the first phase transition with a critical temperature of about 260 K agrees well with the previous results for the same water model [1,4-9]. The shift of the first liquid-liquid critical point from negative to positive pressures, when using the more structured ST2* instead of the original ST2 model, is in good qualitative agreement with the results, obtained for the extended van der Waals model with incorporated hydrogen bonds [23]. The second liquid-liquid phase transition appears below ~ 235 K in the density interval from about 1.05 to 1.15 g/cm^3 .

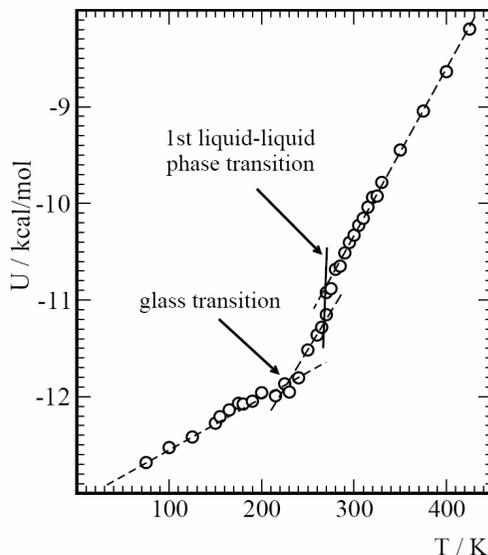


Fig. 6. Temperature dependence of the average potential energy per water molecule along the liquid branch of the ST2 liquid-vapor coexistence line.

At very low temperatures the liquid phases transform into glassy phases. We estimated the temperature T_g of the glass transition for some studied models by analyzing the temperature dependence of the potential energy along the liquid-vapor coexistence curve. For the ST2 model T_g at P

≈ 0 is about 225 K (see Fig. 6) and so, all three observed phase transitions are above T_g . For the TIP4P model the estimated value of T_g is about 180 K, which is close to the critical temperatures of both liquid-liquid phase transitions. A similar relation is observed for the SPCE water model, where T_g is about 188 K [24]. Due to the non-monotonous variation of the water mobility with density, it is difficult to predict the evolution of T_g with pressure. Therefore, we can not exclude, that all simulated phase transitions are liquid-liquid transitions indeed.

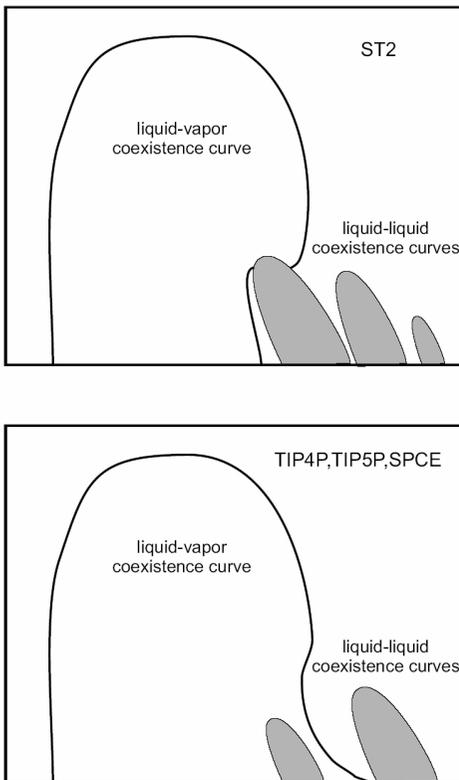


Fig. 7. Schematic representation of the location of the liquid-liquid coexistence curves relative to the liquid-vapor coexistence curve for various water models.

Summarizing, the most popular water models show two categories of phase diagrams (Fig. 7). The key difference between these two diagrams is the existence of a triple point of liquid-vapor and first liquid-liquid phase transitions for the ST2

model. The crossing of the liquid-vapor and the liquid-liquid coexistence curves could explain the anomalous behavior of various properties of liquid water at low temperature along the saturation line. To decide, which of the presented phase diagrams (Fig. 7) is closer to real water, further studies are necessary. In particular, water models which are appropriate for the description of the properties of real water at supercooled temperatures should be able to reproduce the phase diagram of the crystalline ices.

4. Conclusions

Computer simulations of various water models show the existence of at least two liquid-liquid phase transitions in the supercooled region. For water models, which provide a liquid water density maximum of about 1 g/cm^3 at ambient conditions, the critical point of the first liquid-liquid phase transition is located at negative pressures. Therefore, the first liquid-liquid critical point of real water should be expected at negative pressures.

Acknowledgements

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