Detection of Liquid-Liquid Phase Transitions in Supercooled Water by Computer Simulations of Various Water Models

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Polyamorphism is discussed for various one-component supercooled liquids. There are serious evidences from experiment and computer simulations for the occurrence of phase transitions between low-temperature amorphous phases. This suggests the existence of liquid-liquid critical points. The detection of all existing critical points (including hidden or metastable ones) is important for understanding the fluid properties in a wide thermodynamic range.
We studied liquid-liquid phase transitions in supercooled water by restricted ensemble MC simulations of the isotherms of homogeneous systems and by phase equilibria simulations in the Gibbs ensemble [1]. We report phase diagrams of five water models: ST2, ST2 with long-range corrections of the Coulombic interaction (ST2RF), SPCE,TIP4P and TIP5P. The number and location of the liquid-liquid phase transitions noticeably depend on the used water model.
All five models show multiple liquid-liquid phase separation in the supercooled region. Three distinct liquid-liquid phase transitions were found for the highly-structured ST2 water [1]. For this 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. Inclusion of a reaction field (ST2RF model) effectively strengthens the hydrogen bonding and shifts the first liquid-liquid critical point to positive pressures in agreement with theoretical predictions [2].
The less structured SPCE, TIP4P and TIP5P water models show liquid-liquid immiscibility regions at lower temperatures in comparison with the ST2 models. The first liquid-liquid phase transition is located entirely at negative pressures and has no triple point with the liquid-vapor phase transition down to 150 K. The second liquid-liquid phase transition is located at positive pressures in all models. Using the TIP5P water model (more structured than the SPCE model) indications for a re-entrant phase behavior are observed.
Estimations of the glass transition temperature show, that the observed critical points are located above this temperature for the ST2 models, whereas for the other models this may not be the case. We conclude, that real water may develop a multiple phase separation behavior in the supercooled region with a first critical point, probably, at negative pressures and above the glass transition temperature.
Further studies are necessary to clarify the nature, order parameter and universality class of the liquid-liquid critical points of one-component fluids.

References
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