Thermodynamics and structure of TIP4P/Ice supercooled water

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The existence of the liquid-liquid critical point (LLCP) [1] of water has been a long-discussed problem and the arguments that speak in favor of its existence are usually based on simulation data analysis. Standard ways to describe structural changes of the simulated system, like pair correlation function or the structure factor, have been proved to be not sensitive enough to describe the liquid-liquid transition. Therefore, a number of so-called local structure parameters were defined to identify structural changes around individual molecules. Most of these parameters were defined ad-hoc do describe only a specific level of structural order and thus results of certain parameters may be in contradiction with each other. They also very often depend on an ambiguous criterion like hydrogen bond or nearest neighbors definition [2]. Recently there was an attempt to overcome these criterion definitions by employing parameters based on properties of Delaunay triangulation applied to water molecules rather than investigate molecules themselves [3]. These parameters exhibit significant structural changes in the supercooled area but their physical explanation is problematic.
Thermodynamic and structural properties of TIP4P/ice [4] water have been studied in detail in the region of the expected occurrence of the second critical point. Various structure order parameters along with the Delaunay tessellation and density histogram have been used with a focus on their ability and mutual consistency to provide the necessary information. Whereas density histograms clearly show the bimodal distribution corresponding to the coexistence of two metastable density states, most of the standard structural parameters provided only information about the increase in the level of molecular order with lowered temperature. Only the parameter called the local structure index and parameters based on the Delaunay tesselation provided information consistent with the density histogram. The bimodality in these parameters has been connected to the anomalous behavior of the isothermal compressibility which increases in the supercooled region gaining the λ-shape form which a sign of the presence of the critical point.

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FIGURES

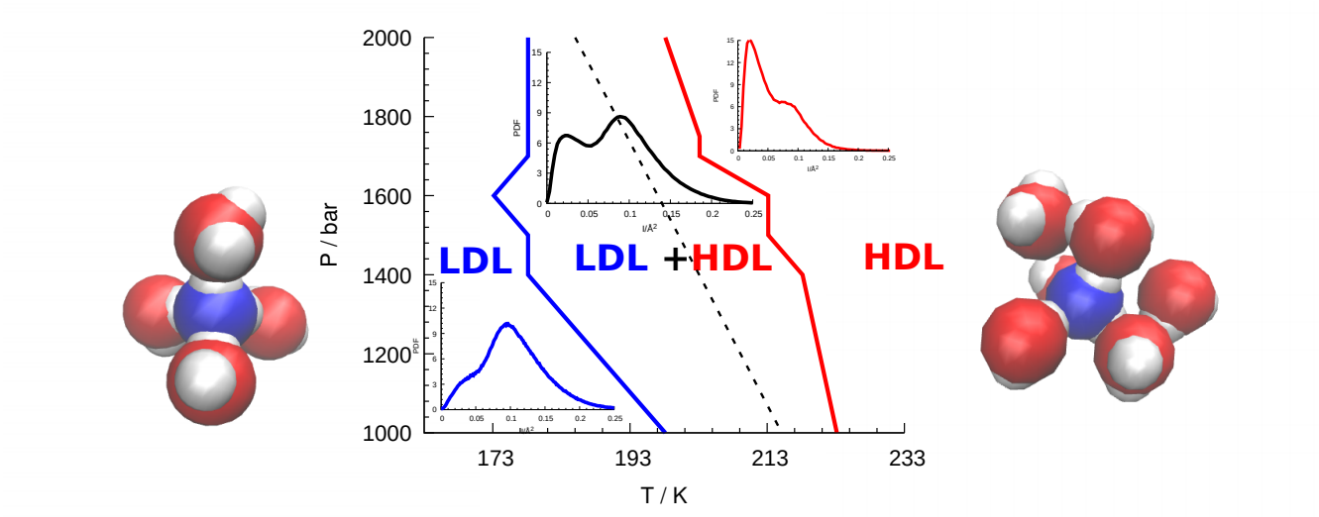

Figure 1: Illustration of changes in the structure of supercooled water at various thermodynamic conditions. Typical behavior of the local structural index is shown for each area..