I-N Liquid-Liquid Phase Transition of Water and Its Potential Surface

Water in supercooled state exhibits many anomalous properties such as divergence of the thermodynamic response functions, liquid-liquid (amorphous-amorphous) transition. Recent computer simulation and theoretical model predict this kind of transition. In view of experimental aspect, it is hard to follow this transition since the area that the transition is expected to be observed in temperature-pressure diagram is inaccessible by experiment, called ‘no man’s land.’ Careful examination of the supercooled water show various kind of unique properties, in particular in configuration space.

I-N-1 The Melting Temperature of Proton-Disordered Hexagonal Ice: A Computer Simulation of TIP4P Model of Water

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[*J. Chem. Phys.* **112**, 8534 (2000).]

We report computer simulation results of free energies of proton-disordered hexagonal ice and liquid water at atmospheric pressure with TIP4P model of water. A new reference system is used to calculate the free energy of the ice phase. The melting point of proton-disordered hexagonal ice at atmospheric pressure is found to be T_m = 238 K. This result is consistent with a previous estimation, 230 K < T_m < 250 K, from molecular dynamic simulation of the surface melting of the proton-disordered hexagonal ice [G.-J. Kroes, *Surf. Sci.* **275**, 365 (1992)].

I-N-2 Hydrogen Bonds between Water Molecules: Thermal Expansivity of Ice and Water

TANAKA, Hideki

[*Phys. Chem. Chem. Phys.* **2**, 1595 (2000)]

The free energy components of two low pressure crystalline ices and an amorphous form of water are calculated over a wide range of temperatures. The Gibbs free energy at a given temperature is minimized with respect to volume of a system. This enables us to evaluate a thermal expansivity at fixed temperature and pressure from only intermolecular interaction potential. The negative thermal expansivity in low temperature is obtained for both crystalline ices and an amorphous form, which arises from the bending motion of hydrogen bonded molecules.

I-N-3 Potential Energy Surfaces of Supercooled Water: Intrabasin and Interbasin Structures Explored by Quenching, Normal Mode Excitation, and Basin Hopping

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[*J. Chem. Phys.* **113**, 11202 (2000)]

We investigate the potential energy surfaces of supercooled water; both intrabasin structures and distributions of the potential energy basins in configuration space by the steepest descent quenching and the normal mode excitation. The paths from liquid configurations to the corresponding local energy minima and the root mean square distance exhibit different characters below and above the temperature 213 K where the thermodynamics and structural properties change abruptly. The root mean square distance in the temperature range (298 K to 173 K) is larger than the corresponding harmonic oscillator system and it drastically increases above 223 K. Also increases the complexity along the steepest descent path by increasing the number of inflection points. In order to investigate the other potential energy basins distributed in the vicinity of the (central) basin that the molecular dynamics trajectory visits, the distributions of these basins are examined by the normal mode excitation. The number of distinct basins increases with increasing temperature in the same volume of configuration space. The minimum potential energy of the adjacent basin at low temperature is almost always higher than the minimum potential energy of the central basin while that of the adjacent basin at high temperature is comparable to the central basin. The locations of the other basin centers are mostly orthogonal to the normal mode excitation. The potential energy surfaces are also examined by the basin hopping technique to seek for lower energy configurations started with a random and high-energy molecular arrangement. It is found that energetically more stable molecules aggregate rather heterogeneously in the intermediate energy levels which are hardly observed in the simulation while the stable molecules distribute homogeneously in the lowest energy levels.

I-N-4 Molecular Dynamics Study of the Connectivity of Water Molecules in Supercooled States

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[*Mol. Liq.* in press]

We examine distributions of four-coordinated supercooled water molecules in two state points where the densities are considerably different from each other. It is found, although the coordination numbers are all four in local energy minimum structures free from thermal excitation, the magnitude of the connectivity of tetrahedrally coordinated molecules differs significantly between two supercooled states. We also investigate thermodynamic properties for liquids composed of two kinds of deformed water molecules having wider bond angles in order to compare the properties of those liquids with those of a realistic water model.

I-N-5 Ice Nanotube: What Does the Unit Cell Look Like?

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It is discovered that for an n-gonal ice nanotube built from stacking a single n-gonal ring of water, the unit cell consists of two stacked n-gonal rings. In one ring the O-H arms of water molecules line up clockwise whereas in the other ring the O-H arms line up counterclockwise. Among the n-gonal ice nanotubes examined, the pentagonal or hexagonal ice nanotube appears to be the most stable.

I-N-6 First-Order Transition in Confined Water between High Density Liquid and Low Density Amorphous Phases

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[*Nature* **406**, 564 (2000)]

Department of Chemistry and Center for Materials Analysis, University of Nebraska, Lincoln, Nebraska 68588, USA Supercooled water and amorphous ice continuously intrigue us withtheir rich metastable phase behaviour. In eighties, a high density amorphous to low density amorphous (HDA-LDA) solid-to-solid phase transition below 140 K was uncovered by Mishima and coworkers. In mid-nineties, a high density liquid to low density liquid (HDL-LDL) liquid-to-liquid phase transition was reported from computer simulations of supercooled water. Recently, a fragile-to-strong liquid transition was also proposed in supercooled water near 228 K, and was observed experimentally in supercooled bilayer water confined in-between hydrophilic slit pores. Here, we report molecular dynamics evidence suggesting a new type of first-order phase transition above the freezing temperature of bulk ice Ih at 0.1 MPa—a liquid-to-bilayer amorphous transition. This metastable phase transition appears uniquely when a two-layer water is confined in a hydrophobic slit pore at a width of less than one nanometer, that is, in a quasi-two-dimensional water. Some characteristics of this first-order transition resemble those found in tetrahedral substances such as liquid silicon, liquid carbon and liquid phosphorus.