Structure order, local potentials, and physical anomalous of water ice

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Synopsis

- **Hydrogen-bond (O:H-O) forms a pair of asymmetric, coupled, H-bridged oscillators with ultra-short-range interactions and memory.**
- **O:H-O bond cooperative relaxation and the associated binding electron entrapment and nonbonding electron polarization discriminate water and ice from other usual materials in the structure order and the physical anomalies.**
- **As a strongly correlated fluctuating system, water prefers the statistically mean of tetrahedrally-coordinated structure with a supersolid skin.**

Keywords: Water, hydrogen bond, phonon, pressure, temperature, skin, nanocluster, Mpemba paradox, Hofmeister series, Leidenfrost effect. Phase transition, supercooling, Coulomb Coupling, correlation and fluctuating

Contents

Abstract

This article deals with the geometric structure, local potentials, and physical anomalies demonstrated by water ice upon being cooled, compressed, and reduced number of neighbors. A "master-slave segmented H-bond (O:H-O)" forms a pair of asymmetric, coupled oscillators. The cooperativity of the H-bond in length and energy and the associated binding electron entrapment and nonbonding electron polarization dictate the unusual performance of water ice. This O:H-O bond notation allows specification of the short-range interactions and forces driving its cooperative relaxation. It has been revealed that: i) Compression shortens-and-stiffens the softer "O:H" bond and lengthens-and-softens the stiffer "H-O" covalent bond via the inter electron-pair repulsion, yielding the low compressibility, proton symmetrization, phase-transition temperature (T_C) depression, softer phonon (< 300 cm^{-1}) stiffening and stiffer phonon (> 3000 cm^{-1}) softening; ii) Molecular-undercoordination effects oppositely to compression due to the spontaneous contraction of the H-O covalent bond. This process results in a supersolid phase that undergoes molecular volume expansion, melting point (viscosity) elevation, binding energy entrapment, bonding charge densification, nonbonding lone electron polarization, stiffer phonon stiffening and softer phonon softening. The supersolidity of molecule clusters, surface skins, and ultrathin films of water makes them perform like ice and hydrophobic at the ambient temperature; iii) The disparity of the segmental specific heat discriminates the O:H from the H-O in responding to cooling, which shortens alternatively the segments in liquid, liquid-solid transition, solid, and at T < 80 K, resulting in four-region density and phonon-stiffness oscillation. The basic rule of sp^3-orbital hybridization of oxygen, detectable density, and the segmental length cooperativity have enabled solution to the discrepancies on the size, separation, structural order, and mass density of molecules packing in water and ice. Reconciling observations of O:H and H-O length symmetry under compression, O—O separation change at a surface and at cooling, solution clarifies: i) the preference of the fluctuated tetragonal structure of water, ii) the essence of inter electron-pair repulsion, and iii) the presence of the supersolid phase at regions consisting molecules with fewer than four neighbors. A combination of the Lagrangian mechanics of oscillator's vibration, molecular dynamics decomposition of volume evolution, and Raman spectroscopy of phonon relaxation has enabled probing of the asymmetric, local, short-range potentials pertaining to the H-bond. Numerical solution to the Fourier equation for the fluid thermodynamics with the skin supersolidity clarified the Mpemba paradox that arises intrinsically from O:H-O bond relaxation and happens only in the non-adiabatic ambient. O:H-O bond relaxation not only determines the manner of heat emission but also heat conduction. Heat emission proceeds at a rate depending on the initial energy storage and the skin supersolidity creates the gradients of density, specific heat and thermal conductivity.