



2016 IUTAM Symposium on Nanoscale Physical Mechanics

## Supersolid skin mechanics of water and ice

Xi Zhang<sup>a</sup>, Yongli Huang<sup>b</sup>, Sanmei Wang<sup>b</sup>, Lei Li<sup>c</sup>, and Chang Q Sun<sup>a\*</sup>

<sup>a</sup>NOVITAS, School of EEE, Nanyang Technological University, Singapore 639798

<sup>b</sup>Key Laboratory of Low-dimensional Materials and Application Technology (MOE) and School of Materials Science and Engineering, Xiangtan University, Xiangtan, 411105, China

<sup>c</sup>Department of mechanical and electrical engineering, Yangtze Normal University, Chongqing 408100, China

---

### Abstract

Skins of water and ice perform anomalously in capacities of hydrophobicity, lubricity, mass density, thermal stability, viscoelasticity, and phonon frequency with yet little knowledge about the mechanism behind these anomalies. We present the recent progress in this regard from the perspective of molecular undercoordination induced O:H-O bond segmental cooperative relaxation and nonbonding electron polarization. The skin molecular undercoordination shortens the intramolecular H-O covalent bond spontaneously from 1.0 to 0.84 Å, while the Coulomb repulsion between oxygen anions lengthens the intermolecular O:H nonbond from 1.70 to 2.71 Å associated with strong polarization. The O:H-O resultant elongation depresses the mass density to 0.75 g/cm<sup>3</sup>; the polarization results the skin high stress, hydrophobicity, lubricity, viscoelasticity; the H-O contraction shifts its stretching vibration frequency from the bulk value of 3150 to 3450 cm<sup>-1</sup> at skin and to 3650 cm<sup>-1</sup> of vapor; the O:H elongation shifts its stretching mode from 210 of bulk to 180 cm<sup>-1</sup> at skin. Therefore, molecular undercoordination induced O:H-O bond relaxation and the associated polarization govern the performance of molecules at the skins of water and ice.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of organizing committee of Institute of the 2016 IUTAM Symposium on Nanoscale Physical Mechanics

*Keywords:* hydrogen bond; nonbonding electrons; polarization; bond relaxation; supersolidity; Raman shift; lubricity; hydrophobicity; Mpemba effect

---

\* Corresponding author.

E-mail address: [ecqsun@ntu.edu.sg](mailto:ecqsun@ntu.edu.sg)

## 1. Introduction

Skins of water and ice demonstrate interesting properties such as lubricity<sup>1,2</sup>, elasticity<sup>3</sup>, thermal stability<sup>4,5</sup>, and viscosity<sup>6</sup>, which cannot be observed at large trunk. For example, slipperiness of ice is one of the unanswered puzzles since Michael Faraday 1859<sup>7</sup>. Wisconsin featured the progress on ice surface lubricity in terms of melting induced by pressure<sup>8</sup>, frictional heating<sup>9</sup>, and a quasi-liquid layer existing at ice surface<sup>10</sup>. However, atomic force microscopy (AFM) results suggest that the skin layer is viscoelastic but not liquid-like from -10 to -30°C<sup>6</sup>. Sum-frequency generation spectroscopy (SFG) and molecular dynamics (MD) calculations suggested that the water molecules at surface are ordered “ice like” at room temperature<sup>11,12</sup>. Besides the flat surface, curved surface of nanodroplet and ultrathin water nanofilm also shows exotic properties, such as high surface tension<sup>13</sup>, thermal stability of highly curved nanodroplet<sup>14</sup>, increasing melting temperature<sup>15</sup>, solid-like molecular dynamics<sup>16</sup>, high elasticity and viscosity<sup>17</sup>. However, the principle behind those interesting properties is still unclear.

Surface termination makes water molecules undercoordinated (molecular coordination number  $z$  is smaller than 4) and bond-order deficient. Molecular under-coordination modulates the hydrogen bond network and induces the change of mechanical, electronic and thermal behavior of surface. For example, the undercoordinated covalent bond will contract spontaneously to lower the total energy<sup>18,19</sup>. The core electron energy level of atoms at surface will increase due to the enhancement of overlap integral. The O1s level energy is 536.6 eV in the bulk of water<sup>20</sup>, 538.1 eV in the surface of water, and 539.8 eV in gaseous molecules<sup>21</sup>. H-O vibrational frequency shifts from ~3200 cm<sup>-1</sup> for the bulk, to 3450 cm<sup>-1</sup> for the surfaces of water and ice<sup>3</sup> and to 3650 cm<sup>-1</sup> for gaseous molecules<sup>22-24</sup>. The thermal diffusion coefficient which correlated to density, thermal conductivity and specific heat of undercoordinated water will change due to the hydrogen bond network relaxation, modulating the thermal dynamics of Mpemba effect<sup>25-29</sup>.

Progresses have been made of various theoretical investigations on the unique properties of surface of water and ice. However, theoretical work has not provided guidance to experiments on the hydrogen bond mechanics of surface-terminated hydrogen-bond network. This work reviews recent progress in understanding the unique properties induced by molecular undercoordination at surface from the angle of O:H-O bond cooperative relaxation and polarization. The hydrogen bond mechanics of anharmonic oscillators was proposed under the stimulus of molecular undercoordination at skin (a thicker region than surface). Hence, the principle of exotic properties of ice and water skin was unveiled.

## 2. Principle

Hydrogen bond (O:H-O) is the basic unit of water and relaxes cooperatively under excitation. The O:H-O bond forms anharmonic, coupled, H-bridged oscillators with ultra-short interactions<sup>30,31</sup>, i.e. the weaker and longer O:H nonbond (denoted as L), the shorter and stronger O-H covalent bond (denoted as H) and the repulsive interaction between the bonding pair and lone pair (denoted as C). As shown in Figure 1, the two O atoms in a “O:H-O” bond always move in the same direction along the O:H-O bond by different amounts<sup>32</sup>.

As the effective coordination number ( $z$ ) decreases at skin (multi-layers of water molecules at surface) compared with full coordination of water molecules ( $z=4$ ) in bulk, the “O-H” will shrink spontaneously to release energy; while the “O:H” will extend due to the repulsion between the bonding pair and lone pair. The softer O:H ( $d_L$  length) bond always relaxes more in length than the stiffer H-O ( $d_H$ ) covalent bond does. As shown in Figure 1,  $x_i$  ( $i = L, H, \text{ and } C$ ) denotes the interionic distances (corresponding to the length of the springs) at equilibrium.

The Lagrangian motion equation for the O:H-O bond is given as<sup>33</sup>

$$\frac{d}{dt} \left( \frac{\partial L}{\partial (\dot{q}_i)} \right) - \frac{\partial L}{\partial q_i} = 0 \quad (1)$$

The Lagrangian  $L = T - V$  consists of the total kinetic energy  $T$  and the total potential energy  $V$ . The time-dependent generalized variables denote the displacements of  $x_L$  and  $x_H$ . The potential energy  $V$  is composed of four terms<sup>34</sup>: H, L, C and S for skin potential. A harmonic approximation of the potentials by omits the higher-order terms in their Taylor’s series.

Download English Version:

<https://daneshyari.com/en/article/5030619>

Download Persian Version:

<https://daneshyari.com/article/5030619>

[Daneshyari.com](https://daneshyari.com)