Size, separation, structural order, and mass density of molecules packing in water and ice

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The structural symmetry and molecular separation in water and ice remain uncertain. We present herewith a solution to unifying the density, the structure order and symmetry, the size (H-O length $d_H$), and the separation ($d_{OO}$ or the O:H length $d_L$) of molecules packing in water and ice in terms of statistic mean. This solution reconciles: i) the $d_L$ and the $d_H$ symmetrization of the O:H-O bond in compressed ice, ii) the $d_{OO}$ relaxation of cooling water and ice and, iii) the $d_{OO}$ expansion of a dimer and between molecules at water surface. With any one of the $d_{OO}$, the density $r(g/cm^3)$, the $d_L$, and the $d_H$, as a known input, one can resolve the rest quantities using this solution that is probing conditions or methods independent. We clarified that: i) liquid water prefers statistically the mono-phase of tetrahedrally-coordinated structure with fluctuation, ii) the low-density phase (supersolid phase as it is strongly polarized with even lower density) exists only in regions consisting molecules with fewer than four neighbors and, iii) repulsion between electron pairs on adjacent oxygen atoms dictates the cooperative relaxation of the segmented O:H-O bond, which is responsible for the performance of water and ice.

Water and ice has attracted much attention because of its anomalies pertaining to issues from galaxy to geology, astrophysics, biology, climate, and to our daily lives1–7. However, the structure order, the geometric symmetry, the size and the separation between molecules packing in water and ice ($H_2O$) and their correlation remain yet highly disputed, independent issues despite decades-long intensive investigation. For instances, the separation between adjacent oxygen atoms ($d_{OO}$) was measured to vary from 2.70 to 3.00 Å8–20 and the molecular size (the H-O bond length $d_H$) changes from 0.970 to 1.001 Å21. A $H_2O$ molecule demonstrates high instantaneous asymmetry with coordination numbers varying from two22 to four or even greater23. The geometric structure of the weekly-ordered $H_2O$ liquid was interpreted in terms of either the monomial-phase of tetrahedrally-coordinated structures with thermal fluctuation2,24–26 or the mixed-phase of low- and high-density fragmentation27–29. However, uncertainties in these seemingly independent issues determine jointly the density of water and ice that is macroscopically detectable but the correlation among these quantities is often ignored in consideration. This fact serves as one essential constraint for the solution to the uniqueness of structure order and molecular separation, in terms of statistic expectation, that water molecules prefer. Therefore, these structural and dimensional discrepancies can be resolved simultaneously based on the framework reported in this Letter without needing any assumption or approximation.

Results
Firstly, the sp$^1$-orbital hybridization is the unique choice of oxygen upon reacting with atoms of relatively lower electronegativity, irrespective of the structural phase30. As shown in Figure 1a, an oxygen atom ($2s^22p^4$) catches two electrons from neighboring atoms such as hydrogen (H) and metals and then hybridizes its sp orbitals with tetrahedrally directional orbits26. In the case of $H_2O$, one O forms two intramolecular H-O bonds with shared electron pairs and $\sim 4.0$ eV binding energy32 and fills up the rest two orbits with its nonbonding electron lone pairs “:” to form the intermolecular O:H non-covalent bonds of $< 0.1$ eV binding energy33. The inhomogeneous
distribution of charge and energy around the central oxygen atom entitles a H$_2$O molecule only C$_v$2 group symmetry except for the rotation and vibration of the molecule. Therefore, an oxygen atom always tends to find four neighbors to form a stable tetrahedron but the nonequivalent bond angles (\(\angle \text{H-O-H} < 104.5^\circ\) and \(\angle \text{H:O:H} > 109.5^\circ\)) and the repulsion between electron pairs on oxygen\[^{26,32}\] refrain the steady tetrahedron from being formed in the liquid phase. The strong fluctuation proceeds more like the motion of a complex pendulum surrounded by four non-bonding lone pairs, because of the O:H bond switching on and off restlessly in a period of sub-picosecond\[^{2,25,28,29}\]. Therefore, it would be more realistic and meaningful to consider the statistic expectation of the coordination number, the structure order, and the molecular separation in all phases at question for a long time span rather than seeking for the instant-aneous accuracy of a certain independent quantity by taking the snapshot at a quick flash\[^{25}\] for the highly correlated and fluctuating O:H-O bond.

Finally, the O:H-O bond, in Figure 1d, consists of the longer-and-softer part of the O:H van der Waals bond (d$_{v}$) and the shorter-and-stiffer part of the H-O polar-covalent bond (d$_{d}$) rather than either of them alone. The O:H-O bond approximates a pair of asymmetric and H-bridged oscillators coupled by Coulomb-repulsion, whose relaxation in length and energy and the associated local charge distribution determine the anomalies of water ice under various stimuli such as compression\[^{32}\], coordination number reduction\[^{26}\], and cooling\[^{15,38}\]. Under excitation, oxygen atoms dislocate along the O:H-O bond in the same direction but by different amounts with H atom as the coordination origin. The O:H-O interaction in Figure 1d holds statistically true in any phase including amorphous despite the strong fluctuations whose extent is subject to the thermal conditions due to the switching on and off of the O:H interactions.

A molecular dynamics (MD) computation has enabled us to decompose the measured volume-pressure V(P) profile of compressed ice\[^{36,37}\] into the d$_{d}(P)$ and the d$_{v}(P)$ cooperative curves\[^{32}\], see Figure 2. The d$_{v}(P)$ curves meet at d$_{v} = d_{d} = 1.12$ Å under ~59 GPa pressure of ice, which is exactly the measured proton symmetry metatization of hydrogen bond in ice\[^{18,39}\]. This coincidence indicates that the MD derived d$_{v}(P)$ relation represents the true cooperativity of the d$_{v}$ and the d$_{d}$ bond relaxation. Plotting the d$_{v}(P)$ against the d$_{d}(P)$ yields immediately the (projection along the O—O) length cooperativity that is free from probing conditions or probing methods,

\[
\begin{align*}
\frac{d_{v}}{d_{d}} &= \sqrt{\frac{3a}{2}} = 2.6950\rho^{-1/3} \\
\sqrt{2a} &= 4.4001\rho^{-1/3}
\end{align*}
\]

(1)

The d$_{v}$ (x = L and H) value approaches the true bond length with ~1.5% deviation (1—cos(10°) = 0.015) as the O:H-O angle remains 160° in liquid and greater in solid\[^{33}\]. Combining eqs (1) and (2), one is able to scale the size d$_{v}$ and the separation d$_{OO}$ of H$_2$O molecules with the given packing order in Figure 1c and the measured density under various conditions. If the d$_{OO}$ or the d$_{v}$ matches those of direct measurement, the structure order in Figure 1c and eqs (1) and (2) are justified true and unique.

Using eq 1, one can convert, as shown Figure 3a for instance, the measured density p(T) profiles of water droplets of different sizes (1.4 and 4.4 nm)\[^{30,41}\] as input into the d$_{OO}$ as an output for water at different temperatures. The density transition points change with water droplet size. For droplet of 1.4 nm, the transition is at 205 K, it is at 242 K for 4.4 nm droplet and 258 K for the bulk water\[^{42}\]. The droplet size discriminated density transition arises from the specific heat disparity of the O:H- and the H-O within the O:H-O bond. As the droplet size is reduced, the H-O bond becomes shorter and stiffer yet the O:H bond the otherwise\[^{23}\], which shifts the cross points of the two specific heat to temperatures outwardly away from that of the bulk (refer to Ref. 35). The d$_{OO}$ in a water droplet expands additionally in the skin region\[^{42}\] but one can only measure its aver-
The d_{OO} values of 2.70 Å measured at 25°C and 2.71 Å at −16.8°C match exactly the conversion of 2.6950 Å that is a projection along the O−O at 4°C. This consistency justifies sufficiently that both eq 1 and the packing order in Figure 1c describe the true situations in both water and ice. Furthermore, the data reported in Ref. 10 is essentially accurate and correct.

Discussion

The non-covalent bond length d_{L}, molecular size d_{H}, molecular separation d_{OO}, and the mass density ρ can be obtained by solving the equation with any one of these parameters as a known input,

\[ d_L = \frac{-2.5621 \times [1 - 0.0055 \times \exp((d_{OO} - d_L)/0.2428)]}{0}. \]

Figure 3b shows the decomposition of the d_{OO} into the d_{H} of water and ice at cooling 40,41. The d_{H}(T) profiles follow the rules of O:H−O bond relaxation 26,32,35: i) both oxygen atoms dislocate in the same direction (see inset) along the O:H−O bond by different amounts with respect to the H atom; ii) the longer-and-softer O:H part always relaxes more than the shorter-and-stiffer H−O part does. The cooperativity of the d_{H} relaxation confirms further that 35: i) cooling contraction happens only to the O:H bond in the solid (T < 205 K (Data 1) or 241 K (Data 2)) and in the liquid phase (T > 277 K), which lengthens the H−O bond slightly by inter-electron-pair repulsion, resulting volume contraction; ii) in the freezing transition phase, the process of length relaxation reverses, leading to the O−O length gain and volume expansion at freezing.

Figure 4 shows the solution consistency to the measured molecular size d_{L}, molecular separation d_{H} (or d_{OO}), mass density ρ, and structural order of: i) compressed ice 26, ii) cooling water and ice 40,41, and, iii) water surface and dimer 10,19. The d_{H} of 1.0004 Å at unity density is within the measured values ranging from 0.970 to 1.001 Å. The d_{OO} values greater than the ideal value of 2.6950 Å at ρ = 1 (g·cm⁻³) correspond to the supersolid phase (low-density, LDP) that exists indeed 27–29 but only presents in the skins of water ice composed of molecules with fewer than four neighbors (Figure 4b) 26.

Wilson et al 19 have discovered that the surface d_{OO} expands by 5.9% from 2.801 to 2.965 Å at room temperature. If one considers the shortest distance of 2.70 Å 10 and the longest 2.965 Å 19 of measurements, the surface d_{OO} expands by up to 10%. Furthermore, the volume of water molecules confined in 5.1 and 2.8 nm TiO₂ pores increase by 4 and 7.5%, respectively, with respect to that in the bulk 43. With a 5–10 Å thick air gap existing in between molecules and the hydrophobic surface 44, water molecules at the interface exhibit skin vibration attributes 45 of 3400 cm⁻¹ compared to that of 3200 cm⁻¹ for the bulk water. The separation d_{OO} = 2.980 Å for a dimer is even greater.

In these supersolid regions, molecular under-coordination shortens the d_{H} and lengthens the d_{L}, resulting in d_{OO} expansion and polarization because of the inter electron-pair repulsion 26. The least density of ice is 0.92, which corresponds to d_{OO} = 2.695(0.92)¹⁷⁻¹ = 2.7710 Å. However, the density of the supersolid phase is ρ = (2.695/2.965)² = 0.7509 g·cm⁻³, which is far lower than the least density of the bulk ice or the maximal density of water (0.75/0.92/1.0), according to eq 1. Considering the limitation of penetration depth in the

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**Figure 2** | (a) MD calculation reproduction of the V(P) profile of ice 36 with derivatives of the O−H and H−O lengths meeting at \( d_{H} = d_{L} = 1.12 \ \text{Å} \) under 58.6 GPa compression, which agrees with the measurements of \( d_{H} = d_{L} = 1.12 \ \text{Å} \) at 59 GPa 38,39.

**Figure 3** | (a) The d_{OO} ∼ ρ(T) profiles (eq 1) of water droplets of different sizes (1.4 and 4.4 nm) 40,41 match the d_{OO} values measured at 25°C and −16.8°C (Figure S1 and S2 of Supporting Information) 36. (b) The d_{H} and the d_{L} (eq 2) agrees with results of MD calculations 35. Inset (b) illustrates the cooperative relaxation of the segmented O:H−O bond. One part becomes longer; the other part will be shorter by different amounts due to the inter-electron pair repulsion.

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The size, separation, structural order, and mass density of water and ice. We may conclude: thus resolved the seemingly independent geometry and dimension coordination. The H-O bond contraction follows Goldschmidt-Pauling’s rule of "atomic coordination number-radius" correlation; the dOO expansion results from the Coulomb repulsion between electron pairs on adjacent oxygen atoms. The skin region, consisting molecules with fewer than four neighbors, forms such an amazing supersolid phase that possesses the attributes of low-density, high elasticity, polarized, dielectric instability, thermally stable, and hydrophobic. The timescale for hydrogen-bond switching dynamics at the surface is about three times slower than that in the bulk because of the strong polarization and high viscosity.

The findings apply to any situations including solid-liquid (water-ice) interface skin as only mass and volume are involved. At the water-hydrophobic surface of different materials, this findings are only valid to the water skin that forms the low-density supersolid state of polarized, depleted, elastic, and thermally stable. An air gap of 0.5 ~ 1.0 nm thick presents between the superhydrophobic substrate and water.

The straightforward yet simple solution presented herewith has thus resolved the seemingly independent geometry and dimension uncertainties of water and ice. We may conclude:

(i) One should focus on the statistic mean of all the factors and their cooperativity involved rather than the instantaneous accuracy of the individual parameter once at a point of time for the strongly fluctuated water system.

(ii) The size, separation, structural order, and mass density of molecules packing in water and ice are correlated, which is independent of the structural phases of water and ice or the probing conditions.

(iii) Constrained by the Ice Rule, the dH and dL cooperativity, the solution has reconciled measurements of hydrogen-bond length symmetrization of ice under compression, dOO relaxation of water and ice at cooling, and dOO expansion of a water dimer and molecules at water surface.

(iv) With any one of the molecular separation, mass density, O:H bond length, and H-O distance as a known input, one can determine using this solution unambiguously the rest three parameters and their change with external conditions such as pressure, temperature, and coordination environment.

(v) The tetrahedrally-coordinated structure could be the unique choice of water and ice despite fluctuations in the dL and the O:H-O angle due to the non-equivalent H:O:H and H-O:H bond angles and the inter-electron-pair repulsion.

(vi) The supersolid (low-density) phase indeed exists but only in regions consisting water molecules with fewer than four neighbors. The supersolid phase forms because of the Goldschmidt-Pauling’s rule of H-O bond contraction due to molecular under-coordination and the inter-electron-pair repulsion pertaining to the O:H-O bond.

Methods

The MD calculations were performed using Forcei’s package with ab initio optimized forcefield Compass27. The Compass27 has been widely used in dealing with the electronic structures and the hydrogen bond network of water and amorphous ices as well as water chains in hydrophobic crystal channels.

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Author contributions
X.Z. and Y.H. contribute equally in computations. Z.M. and W.L. initiated the topic of this work. All authors contributed to the data analysis, writing of the manuscript. All authors reviewed the manuscript.

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