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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 ($d_{OO}$) of molecules packing in water and ice in terms of statistic mean. This solution reconciles: i) the $d_{OO}$ 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 $\rho$ (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$_2$O) 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$_2$O molecule demonstrates high instantaneous asymmetry with coordination numbers varying from two22 to four or even greater23. The geometric structure of the weekly-ordered H$_2$O 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$^3$-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$^2$2p$^4$) catches two electrons from neighboring atoms such as hydrogen (H) and metals and then hybridizes its sp orbitals with tetrahedrally directional orbits26. In the case of H$_2$O, 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
The strong fluctuation proceeds more like the motion of a complex oscillator 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, coordination number reduction, and cooling. 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 the O:H interactions.

A molecular dynamics (MD) computation has enabled us to decompose the measured volume-pressure V(P) profile of compressed ice into the dH(P) and the dL(P) cooperative curves, see Figure 2. The dH(P) curves meet at dH = dL = 1.12 Å under ~59 GPa pressure of ice, which is exactly the measured proton symmetrization of hydrogen bond in ice.

This coincidence indicates that the MD derived dH(P) relation represents the true cooperativity of the dH and the dL bond relaxation. Plotting the dH(P) against the dL(P) yields immediately the (projection along the O-O) length cooperativity that is free from probing conditions or probing methods,

\[
\begin{align*}
\nu = \frac{2\nu + 3}{1 - 0.0055 \times \exp(dH/0.2428)}
\end{align*}
\]

The dH (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. Combining eqs (1) and (2), one is able to scale the size dH and the separation dOO of H2O molecules with the given packing order in Figure 1c and the measured density under various conditions. If the dOO or the dH 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) as input into the dOO 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. 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, which shifts the cross points of the two specific heat to temperatures outwardly away from that of the bulk (refer to Ref. 35). The dOO in a water droplet expands additionally in the skin region but one can only measure its average.
age	extsuperscript{26}. The \( d_{\text{OO}} \) values of 2.70 Å measured at 25°C and 2.71 Å at \(-16.8^\circ\text{C}\) 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 \( d_{\text{OO}} \), and the mass density \( \rho \) can be obtained by solving the equation with any one of these parameters as a known input,

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

Figure 3b shows the decomposition of the \( d_{\text{OO}} \) into the \( d_H \) of water and ice at cooling	extsuperscript{40,41}. The \( d_L(T) \) profiles follow the rules of O:H–O bond relaxation	extsuperscript{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 \( d_L \) relaxation confirms further that	extsuperscript{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 \( d_H \), molecular separation \( d_L \) (or \( d_{\text{OO}} \)), mass density \( \rho \), and structural order of: i) compressed ice	extsuperscript{26}, ii) cooling water and ice	extsuperscript{40,41}, and, iii) water surface and dimer	extsuperscript{0.19}. The \( d_{\text{OO}} \) of 1.0004 Å at unity density is within the measured values ranging from 0.970 to 1.001 Å	extsuperscript{21}. The \( d_{\text{OO}} \) values greater than the ideal value of 2.6950 Å at \( \rho = 1 \) (g·cm\(^{-3}\)) correspond to the supersolid phase (low-density, LDP) that exists indeed	extsuperscript{27–29} but only presents in the skins of water ice composed of molecules with fewer than four neighbors (Figure 4b)	extsuperscript{26}. Wilson et al	extsuperscript{19} have discovered that the surface \( d_{\text{OO}} \) expands by 5.9% from 2.801 to 2.965 Å at room temperature. If one considers the shortest distance of 2.70 Å	extsuperscript{10} and the longest 2.965 Å	extsuperscript{19} of measurements, the surface \( d_{\text{OO}} \) expands by up to 10%. Furthermore, the volume of water molecules confined in 5.1 and 2.8 nm TiO\(_2\) pores increase by 4 and 7.5%, respectively, with respect to that in the bulk	extsuperscript{43}. With a 5–10 Å thick air gap existing in between molecules and the hydrophobic surface	extsuperscript{44}, water molecules at the interface exhibit skin vibration attributes	extsuperscript{3400 cm\(^{-1}\)} compared to that of 3200 cm\(^{-1}\) for the bulk water. The separation \( d_{\text{OO}} = 2.980 \) 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 \( d_{\text{OO}} \) expansion and polarization because of the inter electron-pair repulsion	extsuperscript{26}. The least density of ice is 0.92, which corresponds to \( d_{\text{OO}} = 2.695(0.92)^{-1/3} = 2.7710 \) Å. However, the density of the supersolid phase is \( \rho = (2.695/2.965)^{3} = 0.7509 \) 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
optical reflection measurements of water and ice, all the reported data for the skin are reasonably correct.

The molecular separation $d_{OO} = d_{HH} + d_{HL}$ grows and molecular size $d_{HL}$ shrinks simultaneously at the skins because of the molecular undercoordination. The H-O bond contraction follows Goldschmidt-Pauling’s rule of “atomic coordination number-radius” correlation. The $d_{OO}$ 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 with densely entrapped bonding electrons. 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, these 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 Rue, the $d_{HL}$ and $d_{HH}$ cooperativity, the solution has reconciled measurements of hydrogen-bond length symmetrization of ice under compression, $d_{OO}$ relaxation of water and ice at cooling, and $d_{OO}$ 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 $d_{HH}$ 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 undercoordination and the inter-electron-pair repulsion pertaining to the O:H-O bond.

Methods

The MD calculations were performed using ForceIt’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 the research and prepared figures. Y.Z., J.Z. and WZ. involved in explanations. C.S. wrote the manuscript. All authors reviewed the manuscript.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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