Water's phase diagram: from classical thermodynamics to hydrogen-bond notion

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Hydrogen bond (O:H-O) relaxation in segmental length and its containing angle dictates respectively phase boundaries in water's phase diagram.

Abstract

This presentation features recent progress in understanding the phase diagram of water and ice from the perspective of hydrogen bond (O:H-O) cooperative relaxation with focus on how the segmental length and the containing angle of the O:H-O bond change with mechanical compression and thermal excitation. By interplaying theoretical predictions, numerical computations, and phonon spectrometrics, we firstly examined the O:H-O bond segmental length and phonon stiffness of: i) liquid water at 300 K and ice at 80 K as a function of pressure, ii) liquid water cooling from 350 K to 80 K under the ambient pressure, iii) mechanical freezing of the ambient water under compression up to 1.83 GPa, and, iv) liquid water heating from 253 to 753 K under 30 MPa pressure. Observations allow us to classify the $T_C(P)$ phase boundaries of water and ice into four types according to their slopes and then formulate them in terms of hydrogen bond relaxation in segmental length and containing angle. Observations reinforce the essentiality and effectiveness of hydrogen bond notion in dictating the unusual behavior of water and ice and clarify the bonding dynamics during phase transition, which is beyond the scope of classical thermodynamics.

Keywords: Water, ice, hydrogen bond, phase diagram, pressure, tempertaure

1 Introduction

Water is ubiquitously important to all lives and it is too strange, too anomalous, and too challenge. Understanding the anomalous behavior of water and ice remain incomprehensive despite extensive dedications in past decades. Alternative ways of thinking and approaching are indispensable though the classical thermodynamics and the contemporary quantum mechanics have contributed significantly. Consideration is necessary from the perspective of the asymmetrical, local, and short-range inter- and intra-molecular interactions within the hydrogen bond (O:H-O) and the involvement of Coulomb repulsion between electron pairs on oxygen ions [1].

Appendix shows the phase diagram of water and ice. Ice formed by water behaves strangely at lower temperatures and higher pressures. Water - H_2O - seems to be a simple molecule: two hydrogen atoms connected to a central oxygen atom in a V-shape. In everyday ice cooled from liquid water, which scientists call Ice Ih, the water molecules line up in a hexagonal pattern; this is why snowflakes all have six-sided patterns (The "h" stands for hexagonal). A variation called Ice Ic at lower temperatures, found in ice crystals floating high up in the atmosphere, forms cubic crystals, in fogs and clouds. The crystal structure of the ice is fairly loose — the reason that ice Ih is less dense than liquid water — and the O:H nonbonds between hydrogen atoms and other water molecules are longer and weaker than most atomic bonds.

At higher pressures, the usual hexagonal structure breaks down, and the bonds rearrange themselves in more compact, denser crystal structures, neatly labeled with Roman numerals: Ice II, Ice III, Ice IV and so on. Scientists have also discovered several forms of ice in which the water molecules are arranged randomly, as in glass. At a pressure of about 200 MPa, Ice Ih turns into a different type of crystalline ice, Ice II. Ice II does not occur naturally on Earth. Even at the bottom of the thickest portions of the Antarctic ice cap, the weight of three miles of ice pushes down at only one-quarter of the pressure necessary to make Ice II. But planetary scientists expect that Ice II, and possibly some other variations, like Ice VI (around 1 GPa $\sim 10^4$ atm pressure), exist inside icier bodies in the outer solar system, like the Jupiter moons Ganymede and Callisto.

With pressure high enough, the temperature need not even be cold for ice to form. Scientists considered what happens to tectonic plates after they are pushed back down into Earth's interior. At about 100 miles down, the temperature of these descending plates is 300 to 400 °C - well above the boiling point of water at the surface — but cool compared with that of surrounding rocks. The pressure of 2 GPa at this depth could be great enough to transform any water that was there into a solid phase known as Ice VII. No one knows whether ice can be found inside Earth, because no one has yet figured out a way to look 100 miles underground. Just as salt melts ice at the surface, other molecules mixing with the water could impede the freezing.

Ice also changes form with dropping temperatures. In hexagonal ice, the usual form, the oxygen atoms are fixed in position, but the O:H nonbonds between water molecules are continually breaking and reattaching, tens of thousands of times a second. At temperatures cold enough — below -200°C — the nonbonds freeze as well, and normal ice starts changing into Ice XI (orthorhombic structure). Astronomers were probably already looking at Ice XI on the surface of Pluto and on the moons of Neptune and Uranus. But instruments currently are not sensitive enough to distinguish the slight differences among the ices.

From ice XII to ice XVI, found just a decade ago are also with many new features. For instance [2], the cage-structured ice XVI has a density of $0.81\text{ g}\cdot\text{cm}^{-3}$ as the stable low-temperature phase of water at negative pressures (that is, under tension). This hollow hydrate structure exhibits cooling expansion below about 55 K, and that it is mechanically more stable and has at low temperatures larger lattice constants than the filled hydrate. When pressure is increased to 60 GPa, ice X phase forms with identical H-O and O:H length of $1.1\text{ \AA}$, corresponding to density of 1.84 times that of water at 4°C [3, 4].

Ice can turn to be partially ionic ($2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{\delta+}(\text{one lone pair}) + \text{HO}^{\delta-}(\delta = 0.62; \text{three lone pairs})$), which is realized by exchanging H with an electron at extremely high pressure (2 TPa) and high temperature (2000 K) [5]. The occurrence of this ionic phase follows the break-up of the typical O–H covalently bonded tetrahedrons in the hydrogen symmetric atomic phases and is originated from the volume reduction favorable for a denser structure packing.

The contribution to the lattice energy from the O:H intermolecular interaction increases and that from the intramolecular H-O bonding decreases when pressure is increased up to 2 GPa, as calculated using first principle and Quantum Monte Carlo calculations [6]. The elegantly used TIPnP (n varies from 1 to 5) model series and the TIP4Q/2005 modeled water ice but they exclude the possibility of bond relaxation and charge polarization. These rigid non-polarizable models can hardly reproduce the anomalies of water ice with high satisfaction [7, 8].

One often connects the structure and property Q of a substance directly to the external stimuli such as pressure, volume, entropy, and temperature $Q(PV, ST, \dots)$, which is exactly that the classical thermodynamics deals with large trunks. Such treatment employs concepts of entropy, enthalpy, Gibbs and Helmholtz free energy, and so on so forth with standard deviation δ depending on the sample size N in the form of $\sigma \propto N^{-1/2}$. This approach provides little information on how the chemical bond responds to external stimulus.

A number of formulae exists describing the $T_c(P)$ phase boundaries of water ice from the classical thermodynamic point of view, for the Liquid-Vapor phase transition. Unfortunately, few approaches are available for formulating the boundaries in general cases. For instances, Clausius–Clapeyron equation [9] describes water vapor under

typical atmospheric conditions (near standard temperature and pressure) and August-Roche-Magnus formula [10] approximates the temperature dependence of the saturation vapor pressure P_s :

$$\begin{cases} \frac{dP_s}{dT} = \frac{L_v(T)P_s}{R_v T^2} & (\text{Clausius - Clapeyron}) \\ P_s(T) = 6.1094 \exp\left(\frac{17.625T}{T + 243.04}\right) & (\text{August - Roche - Magnus}) \end{cases} \quad (1)$$

Where L_v is the specific latent heat of evaporation of water and R_v is the gas constant of vapor.

However, Pauling [11] indicated that the nature of the chemical bond bridges the structure and the property of a substance, and therefore, one can modulates the Q by relaxing the chemical bonds through controlling external stimuli such as pressure, temperature, coordination environment, chemical composition, electric and magnetic field [12]. The latter approach considers only the change of the order, length, and energy of interatomic bond under the quoted excitations. Pauling's premise challenges us to revisit the physical nature of a complex system by decomposing it into a simple representative of all bonds involved. Therefore, understanding how the water molecule works at transition from the perspective of O:H-O bond relaxation in segmental length, containing angle is important in understanding how water interacts with all the biological molecules in living organisms.

This presentation aims to accounting recent progress in due respect with focus on revisiting the T-P phase diagram of water and ice from the perspective of O:H-O bond cooperative relaxation under mechanical compression and thermal excitation. By interplaying with theoretical predictions, numerical computations, and phonon spectrometrics, we firstly examined the O:H-O bond segmental length and phonon stiffness of: i) liquid water at 300 K and ice at 80 K as a function of pressure, ii) liquid water cooling from 350 K to 80 K under the ambient pressure, iii) mechanical freezing of the ambient water under compression up to 1.83 GPa, and, iv) liquid water heating from 3253 to 753 K under 30 MPa pressure. Observations allow us to classify the $T_c(P)$ phase boundaries of water and ice into four types according to their slopes and then to formulate them in terms of hydrogen bond relaxation in segmental length and containing angle.

This exploration revealed the following: i) H-O bond elongation dictates the negatively-sloped $T_c(P)$ boundaries for the VII - VIII and the Liquid - Quasi-solid phase transition; ii) O:H nonbond contraction dominates the positively-sloped $T_c(P)$ profiles for the Liquid - Vapor phase transition; and, iii) O:H-O containing angle relaxation governs those of zero-sloped ($T_c = \text{constant}$ at the Ic - XI boundary) or infinitely-sloped ($P_c = \text{constant}$ at the (XII, XIII)-X boundary) $T_c(P)$ profiles. Numerical reproduction of the negatively-sloped $T_c(P)$ curves results in the H-O cohesive energy 3.97 eV for water and ice and duplication of the $T_c(P)$ boundary for Liquid-

Vapor transition turns out the pressure trend of the O:H length change. Raman examination revealed that the O:H and H-O contract simultaneously when turning the ambient water into ice VI by compression.

2. Principles: bond relaxation

2.1 Dimer bond: an isolated oscillator

Generally, one can focus on the representative bond that is an average of all in a substance from the perspective of Fourier transformation that correlated the distribution in real space and behavior in the energy or momentum domains. The length and energy of this representative bond determines the structural and performance of the substance [12].

Figure 1a shows a pairing potential $u(r)$ for the dimer bond in a regular substance, being taken as an isolated oscillator in the first order approximation. The coordinates (d, E_b) at equilibrium correspond to the length and energy of the bond for a single oscillator, which relax under an external stimulus, regardless of the shape of the particular $u(r)$. A Taylor series approximates the $u(r)$ as follows:

$$u(r) = \sum_n \frac{\partial^n u(r)}{n! \partial r^n} \bigg|_{r=d} x^n = E_b + \frac{\partial^2 u(r)}{2 \partial r^2} \bigg|_{r=d} x^2 + \frac{\partial^3 u(r)}{6 \partial r^3} \bigg|_{r=d} x^3 + 0(x^{n \geq 4}) \quad (2)$$

The zeroth differential is the bond energy at equilibrium E_b . Higher-order differentials corresponding to the harmonious and nonlinear vibrations determine the shape of the $u(r)$. The vibration amplitude x is 3% or less than atomic distance d of the substance at temperatures below melting. The second derivative defines the harmonious vibration frequency of the dimer with reduce mass, μ :

$$\begin{aligned} \frac{1}{2} \mu \omega^2 x^2 &= \frac{\partial^2 u(r)}{2 \partial r^2} \bigg|_{r=d_x} \propto \frac{E_x}{d_x^2} \\ \Rightarrow \omega_x^2 &\propto \frac{E_x}{\mu d_x^2} \end{aligned} \quad (3)$$

Generally, external stimuli, such as stressing and heating modulate the length $d(T, P)$ and energy $E(T, P)$ of the representative bond along a path function $f(T, P)$ [13]. For instance, compression stores energy into a substance by shortening and stiffening all bonds with possible plastic deformation when the compression is relieved. Tension does the opposite [14]. The following formulates bond relaxation in length and energy under stimuli P and T [12]:

$$\begin{cases} d(P, T) = d_b \left(1 + \int_{T_0}^T \alpha(t) dt \right) \left(1 - \int_{P_0}^P \beta(p) dp \right) \\ E(P, T) = E_b \left(1 - \frac{\int_{T_0}^T \eta(t) dt + \int_{V_0}^V p(v) dv}{E_b} \right) \end{cases}$$

(4)

where T_0 and P_0 are the ambient referential conditions. The $\alpha(t)$ is the thermal expansion coefficient.

$\beta = -\partial v / (\partial p)$ is the compressibility ($p < 0$, compressive stress) or extensibility ($p > 0$ tensile stress). The v is the volume of a bond (the product of length and its cross-sectional area). The $\eta(t)$ is the specific heat of the representative bond in Debye approximation. The Debye temperature Θ_D determines the rate of the $\eta(t)$ curve to its saturation. The integration of the $\eta(t)$ from 0 K to the T_m equals the bond energy under constant pressure [1].

Figure 1. (a) The long-range, mono-well potential for pairing atoms in a ‘normal’ substance [14] and (b) the asymmetrical, local, short-range, double-well potentials for the O:H-O bond pairing oscillators [15, 16]. Compression stores energy by shortening and stiffening the bond whereas tension does the opposite, along an $f(P, T)$ path in (a). Thermal expansion or cooling contraction also shift the potential coordinates (d , E) accordingly. O:H-O potentials include the O:H nonbond van der Waals like (vdW-like) interaction (maximal at $E_L \sim 0.25 \text{ eV}$, left-handed side), the H-O exchange interaction ($E_H \sim 4.0 \text{ eV}$, right-handed side), and the Coulomb repulsion (C-

repulsion) between electron pairs on oxygen ions [1]. Compression shortens the O:H nonbond and lengthens the H-O bond along the potential paths raising the O:H-O bond energy [17].

2.2 Hydrogen bond: a coupled oscillator pair

The hydrogen bond (O:H-O) between two oxygen ions is composed of the intramolecular H-O polar covalent bond and the intermolecular O:H nonbond interactions rather than either of them alone. Likewise, a O:H-O bond represents all interactions involved in water and ice, see Figure 1b, regardless of the geometrical configuration in water and ice. The O:H-O bond forms an oscillator pair coupled with Coulomb repulsion, whose segmental potentials and vibration frequencies follow the relationships [17]:

$$\begin{cases} u(r_L, r_H) = \sum_n \frac{1}{n!} \left[\left. \frac{\partial^n u_L(r)}{\partial r^n} \right|_{r=d_L} (\Delta r_L)^n + \left. \frac{\partial^n u_H(r)}{\partial r^n} \right|_{r=d_H} (\Delta r_H)^n + \left. \frac{\partial^n u_C(r)}{\partial r^n} \right|_{r=d_{O-O}} (r_L - r_H)^n \right] \\ \omega_x = 2\pi c \sqrt{\frac{k_x + k_C}{\mu_x}} \propto \sqrt{\frac{E_x}{\mu_x d_x^2}} \end{cases} \quad (5)$$

where c is the velocity of light traveling in vacuum. The k_x is the force constant, or the second derivative of the respective potential at equilibrium but the Coulomb potential is out of equilibrium. Subscript $x = H, L$, and C denotes the H-O bond, the O:H nonbond, and the O-O repulsion, respectively. The μ_x with $x = H$ and L represents the reduced mass for the H-O and the (H₂O):(H₂O) oscillator.

The combination of the short-range interactions, segmental disparity, and applied stimulus relaxes the O:H-O bond cooperatively. Oxygen ions always dislocate in the same direction but by different amounts along the O:H-O bond with H proton serving as the coordination origin [1]. The O:H contracts/elongates more than the H-O elongate/contracts. The segment becomes softer once it turns to be longer, and vice versa. The characteristic phonon frequency features the segmental stiffness. Table 1 tabulates the O:H-O bond cooperative relaxation dynamics in water ice under given stimuli of molecular undercoordination, mechanical compression, and thermal excitation in four regimes over full temperature range.

Table 1. Hydrogen bond relaxation under the stimuli of molecular undercoordination ($CN < 4$), cooling in the liquid, in the quasi-solid, and the solid phases (Ih, Ic, XI), and under compression.

Quantities	Bulk 4°C [18]	Skin (±15°C) [19]		CN < 4 [20]	Cooling in quasi- solid [21]	Cooling at T < 70 K [21]	Cooling in solid & liquid [21]	Compression (80 - 300 K) [3]
H-O length(Å)	1.0004	0.840	Δd_H	< 0		$\cong 0$	> 0	
H-O energy (eV)	3.97	4.66	ΔE_H	> 0		$\cong 0$	< 0	
O1s level shift (eV)	536.6	538.1	ΔE_{1s}			-		
H-O frequency(cm ⁻¹) (cm ⁻¹)	3200	3450	$\Delta \omega_H$			$\cong 0$		
Melting T _C (K)	273	315	ΔT_m	> 0	-	-		< 0
O:H length (Å)	1.6946	2.180	Δd_L	> 0		$\cong 0$	< 0	
Density(g·cm ⁻³)	1.0	0.75	$\Delta \rho$	< 0		< 0	> 0	
O:H energy (eV)	0.1	0.08	ΔE_L			$\cong 0$		
O:H frequency(cm ⁻¹)	220	75	$\Delta \omega_L$			$\cong 0$		
Freezing point T _N (K)	258 [21]	242 [22]	ΔT_N	< 0	-	-	-	> 0
∠O:H-O (°)	160	-	$\Delta \theta$	< 0	> 0	> 0	> 0; $\cong 0$	-

*Debye temperature and the characteristic phonon frequency is correlated by: $k\Theta_{Dx} \propto \hbar\omega_x$ ($x = L$ for O:H and $x = H$ for H-O), with k and $\hbar$ being Boltzmann and Plank constants.

With the aid of quantum calculations, Lagrangian oscillating mechanics and Fourier thermo-fluid transportation dynamics, and phonon spectrometrics, we have been able to consistently and quantitatively resolve quantitatively a few issues such as: 1) Mpemba effect – hot water freezes quicker than its cold [23], 2) supersolid skins for the slipperiness of ice and the hydrophobic and tough skin of water liquid [19], 3) ice expansion and mass density oscillation over full temperatures range [21], 4) anomalies of water molecules with fewer than four nearest neighbors in clusters and droplets[20], 5) Hofmeister effect – NaCl mediation of O-O repulsion [24], 6) density-geometry-dimension correlation of molecules packed in water and ice [18], 7) low compressibility and proton centralization of ice,[3] and, 7) mapping the local potential paths for the O:H-O bond relaxing with stimulus [17], etc. Progress made insofar has formed the subject of a recent treatise [1], which evidences the validity of this set of theoretical, numerical and experimental strategies in dealing with the physical behavior of water and ice.

3.1 Mechanical compression of ice

Molecular dynamics calculations [3] transformed the $V(P)$ profile [25] of ice into the $d_x(P)$ curves ($x = H$ for H-O bond shorted than 1.1 Å and $x = L$ for O:H nonbond longer than 1.1 Å) shown in Figure 2a. The extrapolated $d_x(P)$ curves meet at the point of proton centralization occurring in phase X at O-O distance of 2.20 Å under 59 GPa compression [26, 27], which clarifies that the $d_H = d_L$ in phase X [26] arises from the d_L contraction and d_H elongation instead of proton quantum transitional tunneling and that the extreme low compressibility of ice [28] results from the segmental length compensation under compression.

A combination of the O:H-O bond segmental length the measured phonon frequency [25] in Figure 2 confirms that compression shortens and stiffens the initially softer O:H nonbond and meanwhile lengthens and softens the initially stiffen H-O bond monotonically in ice. Measurements [29] (and see Figure 3) also revealed that the ω_H of the ambient water undergoes redshift before being crystalized.

Figure 2. O:H-O bond segmental (a) length and (b) phonon frequency cooperative relaxation of ice at 80 K and under compression, measured using synchrotron XRD and Raman spectroscopy for ice [25, 30]. Compression shortens the O:H nonbond ($d_L \sim 1.7$ Å) and stiffens its stretching vibration phonon ($\omega_L \sim 200$ cm^{-1}) but the H-O bond responds to compression oppositely ($d_H \sim 1.0$ Å, $\omega_H \sim 3000$ cm^{-1}). The $d_x - P$ curves in (a) meet at the point of proton centralization occurring in phase X at 2.20 Å under 59 GPa compression [26, 27]. Inset (a) illustrates the O:H-O bond relaxation under compression. Inset (b) the experimental set up of compression.

The following polynomials formulate the pressure (in GPa) dependence of the O:H-O bond segmental length (in Å) relaxation, see Figure 2b,

$$\begin{pmatrix} d_H / 0.975 \\ d_L / 1.768 \end{pmatrix} = 1 + \begin{pmatrix} 9.510 & 2.893 \\ -3.477 & -10.280 \end{pmatrix} \begin{pmatrix} 10^{-4} P^1 \\ 10^{-5} P^2 \end{pmatrix} \quad (6)$$

Taking the P as a hidden parameter, the $d_x/d_{x0} - P$ profiles give the size d_H , separation d_L , and density ρ of molecules packed in water and ice in the tetrahedrally coordinated yet fluctuating structure [18]:

$$\begin{cases} d_{OO} = d_L + d_H = 2.6950\rho^{-1/3} & (\text{Molecular separation}) \\ d_L = \frac{2d_{L0}}{1 + \exp[(d_H - d_{H0}) / 0.2428]}; & (d_{H0} = 1.0004, d_{L0} = 1.6946) \end{cases} \quad (7)$$

3.2 Mechanical freezing of ambient water

In order to examine the dynamics of O:H-O bond relaxation of ambient water under compression, we carried out Raman spectroscopic measurements. Figure 3 shows the pressure-dependent Raman spectra of 25°C deionized water in a diamond anvil cell. In the liquid regime, the ω_L trend is hardly resolved but the ω_H shift following the same trend as it is in ice despite the rate of shift. The Liquid-VI phase transition happens with an association of a sudden pressure drop from 1.35 to 0.86 GPa although the volume of the cell containing the water sample shrinks continually and gradually. At transition, a sudden blueshift occurs to both the ω_H and ω_L . The sharp features indicate ice formation. The blueshift of the ω_x indicates that both the O:H and H-O undergo contraction according to Figure 3. The ω_x shift in ice VI phase follows the same trend of that in ice VIII, see Figure 2b. The ω_H undergoes a redshift but ω_L a blueshift.

Assuming the volume of the diamond anvil cell remains unchanged, molecular separation will change approximately with $d_{OO} \propto P^{-1/3}$. Therefore, the d_{OO} changes from its liquid phase to ice VI phase by $(1.35/0.86)^{-1/3} \approx 0.86$, which means that the O-O separation shrinks spontaneously by 14%. The density increases by 57% upon solidification.

The sudden drop in pressure and the simultaneous blueshift of the ω_L and ω_H upon freezing indicates that both the O:H and H-O deformation dominates the boundary of Liquid-VI transition. The simultaneous O:H and H-O contraction suggests that the O-O Coulomb repulsion becomes weaker in the ice VI phase compared with liquid water.

Figure 3. Raman spectra of the mechanico-freezing of ambient deionized water (25 °C) reveals a sudden pressure drop from 1.35 to 0.86 GPa at freezing. The simultaneous ω_L and ω_H blueshift at transition indicates that the O:H nonbond and the H-O bond undergo contraction. In liquid and solid phase, the ω_x shift cooperatively at different shifting rates. Hatched vertical lines denote the ω_x of the skin (75 and 3450 cm^{-1}), bulk (< 300 and 3200 cm^{-1}) and the ω_H for bulk ice (3150 cm^{-1}). The skin feature at 3450 cm^{-1} persists throughout the applied pressures, which indicates that water contacts diamond hydrophobically.

3.3 Thermal excitation

Because of the segmental disparity, the O:H and H-O have their own specific heat $\eta_x(T/\Theta_{Dx})$ in Debye approximation. Therefore are two parameters characterizing the $\eta_x(T/\Theta_{Dx})$ curve. One is the Debye temperature Θ_{Dx} that determines the speed to reach $\eta_x(T/\Theta_{Dx})$ saturation. The Θ_{Dx} and the characteristic phonon frequency follow Einstein's relationship: $k\Theta_{Dx} = \hbar\omega_x$, where k is the Boltzmann's constant and $\hbar$ Plank's constant. The other is the integral of the $\eta_x(T/\Theta_{Dx})$ curve from 0 K to the melting point of the x segment, which is proportional to the cohesive energy E_x . Therefore, for water and ice, there are independent Θ_{Dx} and T_{mx} for each segment.

With the known $\Theta_{DL} = 198$ K, $E_L \approx 0.1$ eV and $E_H \approx 4.0$ eV and the characteristic $\omega_L \approx 200$ cm^{-1} and $\omega_H \approx 3200$ cm^{-1} [21], One can find the $\Theta_{DH} = \Theta_{DL}(\omega_H/\omega_L) \approx 3200$ K and arear integration ratio $I_H/I_L = 4.0/0.1 = 40$. A superposition of the $\eta_x(T/\Theta_{Dx})$ curves yields two intersecting temperatures that divide the full temperature range into four regimes of different η_L/η_H ratios, see Figure 4a, transiting at 273 K, 258 K (204 K for 1.4 nm droplet) and 70 K for bulk water. The transition temperatures are droplet size dependence because of the $\omega_x(\Theta_{Dx})$ response

to the molecular undercoordination. Molecules with fewer than four nearest neighbors as in the bulk are subject to H-O contraction and O:H elongation and the associated phonon stiffness relaxation [20].

Figure 4 A superposition of the specific heat $\eta_x(T)$ curves for the H-O bond ($x = H$) and O:H nonbond ($x = L$) yields (a) two intersecting temperatures that define four regimes of different η_L/η_H ratios over the full temperature range [21]. O:H-O bond (b) containing angle, (c) segmental length derived using eq (6) from measurement [31], and (d) phonon frequency relaxation under cooling excitation from liquid water to quansisolid (QS) quasi-solid, Ih, Ic and XI (orthorhombic structure) phases [21]. Arrows indicate the segment that follows regular rule of cooling contraction. At phase XI, neither segment contracts because of $\eta_x \approx 0$. The phase boundaries change with water droplet size. Pink color is for 1.4 nm sized droplet with low-temperature transition at 204 K [31] and grey for bulk transiting at 258 K [21]. Inset (b) illustrate O:H-O bond relaxation in the quasi-solid phase resulting in net O:H-O length gain, which makes ice float.. (b) Cooling stretches the angle θ in different regimes at different slopes [18].

Calculations of the O:H-O containing angle (θ), transformation of the measured density $\rho(T)$ profile [31] using eq (6) in (c), and Raman spectroscopy of phonons (d) show consistently four temperature regimes, which not only confirm the validity of the specific heat disparity of the O:H-O bond but also reveal the following:

- 1) The O:H-O containing angle θ remains constant in liquid because of the high fluctuating structures. Cooling stretching the θ in the quasisolid (QS) and solid phases at different slopes, which contribute positively to the O-O expansion in the QS phase but negatively to volume contraction in the Ic and Ih phases.
- 2) The segment of relatively lower η_x follows the regular rule of cooling contraction, which elongates the other segment through Coulomb repulsion. In the liquid and in the solid Ic and Ih phase, $\eta_L/\eta_H < 0$, the O:H contracts and the H-O expands at different rates.
- 3) In the QS phase, $\eta_L/\eta_H > 0$, situation reverses, the H-O contracts slightly but the O:H expands largely, which lengthens the O-O distance and lowers the mass density $\rho \propto (d_{O-O})^{-3}$, allowing ice to float. The QS phase boundary is water droplet size dependence
- 4) At the XI phase of very low temperatures, $\eta_x = 0$, neither segment undergoes length and frequency [32, 33] relaxation but the angle stretching results in volume cooling expansion [34] in extremely low temperatures like phase XI. The slight cooling volume expansion was further confirmed in [2] for the XVI phase of caged structures of ice.

The consistently cooperative relaxation of the segmental length and stiffness under compression and thermal excitation evidences the persistence of the Coulomb repulsion between electron pairs on oxygen ions. Such a Coulomb repulsion and O:H-O bond segmental disparity form the soul dictating its adaptivity, cooperativity, sensitivity, memory, and recoverability when subjected to stimuli such as mechanical compression, chemical contamination, molecular undercoordination, thermal excitation, and electric polarization [1], which has let to consistent resolution of the following mysteries of Mpemba paradox – hot water freezes quicker than its cold [23], floating of ice [21], regelation of ice – ice melts under pressure and freezes again when the pressure is relieved [3], slipperiness of ice [19], water's tough and hydrophobic skin [19], nanodroplet thermodynamics [20], Hofmeister effect [24], density-structure correlation [18], hydrogen bond potential paths [17], etc.

3.4 Thermal relaxation of H-O bond under 300 MPa pressure

According to the phase diagram in Appendix (Figure 7), water under 30 MPa pressure remains its liquid states in the temperature range from 253 to 753 K. Figure 5a shows the Raman spectra of the H-O stretching vibration, ω_L , of water under such conditions, as probed by Hu et al [35]. Initially, the spectra are dominated by both the 3200 cm^{-1} bulk mode and the 3450 cm^{-1} skin mode. The bulk mode corresponds to H-O length of 1.00 Å and O:H length of 1.68 Å while the skin mode to the H-O length of 0.95 Å and O:H length of 1.90 Å [19] because of molecular undercoordination induced H-O contraction and O:H elongation [20]. The presence of this skin mode in

the present case indicates that the water/cell contacting interface is hydrophobic. As temperature rises, the 3450 cm^{-1} mode shifts upward and increases its intensity rendering the intensity loss of the 3200 cm^{-1} mode. The significant blue shift of the 3450 cm^{-1} up to 3620 cm^{-1} indicates that the H-O bond becomes even shorter and stiffer, which is the same to liquid water heating under the ambient condition [36]. The ω_H for a monomer is 3650 cm^{-1} and for a dimer it is 3575 cm^{-1} . It can be seen that the liquid water under 30 MPa approach dimer at 673 K and monomer to 753 K.

Figure 5. Raman ω_H spectra of liquid water (a) under 30 MPa pressure as a function of temperature varying from 253 to 753 K and (b) Infrared absorption ω_H peak shift of liquid water under ambient pressure and turning to vapor phase (red circles) and Raman reflection ω_H peak shift of liquid water to superheated state (Reprinted with permission from [35, 36].)

4 Classification and formulation of water phase boundaries

4.1 $T_c(P)$ classification and formulation

The phase diagram of water and ice in Appendix (Figure 7) shows the following boundary $T_c(P)$ features according to their slopes:

$$T_C(P) = \begin{pmatrix} \delta(P_C) \\ Const \\ f_1(P) \\ f_2(P) \end{pmatrix} \Rightarrow \frac{dT_C(P)}{dP} = \begin{cases} \cong \infty & (X - XI, X - (VII, VIII), etc) \\ \cong 0 & (Ic - VI, XV - VI, etc) \\ > 0 & (Liquid - Vapour, Liquid - (III, IV, V, VII)) \\ < 0 & (VII - VIII, Ih - Liquid, etc) \end{cases} \quad (8)$$

$\delta(P_C)$ is a Kronig function. If $P = P_C$, $\delta(P_C) = 1$, else $\delta(P_C) = 0$, the critical P_C keeps constant irrespective of temperature. $Const$ indicates that T_C does not change with P . The $f_{1,2}(P)$ is a certain type of P dependent function but different slopes. The versatile $T_C(P)$ slopes represent different yet unclear dynamics of O:H-O bond relaxation at the phase boundaries.

For other ‘normal’ substance, the T_C is proportional to the atomic cohesive energy, $T_C \propto zE_z$, where z is the effective atomic CN and E_z is the cohesive energy of bond between the z -coordinated atoms [12, 37]. However, for water molecules, the T_C is proportional to the E_x because of the ‘isolation’ of the H_2O molecule by its surrounding lone pairs. The x needs to be certain.

Eq (3) yields the $T_C(P)$ profiles as a function of the segmental volume relaxation, $v_x = s_x d_x$ under compression with s_x being the cross-sectional area of the segment and assumed constant,

$$\frac{T_C(P)}{T_C(P_0)} = 1 - \frac{E_x(P)}{E_{x0}} = 1 - \frac{s_x \int_{P_0}^P p \frac{dd_x}{dp} dp}{E_{x0}} = \begin{cases} > 0 & (d_L) \\ < 0 & (d_H) \\ \cong 0 & (\theta) \\ \cong \infty & (\theta) \end{cases} \quad (9)$$

The E_{x0} is the segmental cohesive energy at the ambient standard conditions. Satisfying the slope criterion in eq (1), the dd_x/dp takes the opposite sign of the dT_C/dp . For the $dd_x/dp = 0$ or ∞ , $T_C(P)$ remains constant - neither segment undergoes length relaxation but the containing angle may vary. According to eq (5) and Figure 2b, compression shortens the d_L and lengthens the d_H . Therefore, d_H , d_L , and θ dominate the respective $T_C(P)$ profile, as indicated in eq (8). Therefore, the O:H-O length and angle relaxation dictates the $T_C(P)$ boundaries in the phase diagram of water and ice.

4.2 H-O bond dominance: $dT_C/dP < 0$

The $T_C(P)$ profiles for the Liquid-Ic and the ice VII-VIII phase transition epitomize the situation of negative slopes. With the known $d_x(P)$ relation in eq (5), the following proves that E_H relaxation dictates these $T_C(P)$,

$$\frac{T_c(P)}{T_c(P_0)} = 1 - \frac{s_H \int_{P_0}^P p \frac{dd_H}{dp} dp}{E_{H0}} < 1 \quad (10)$$

Reproduction of the measured $T_c(P)$ for the VII–VIII phase transition [38-40], and the $T_m(P)$ for ice melting (-22 °C at 210 MPa; +6.5 °C at -95 MPa) [41] requires that the integral must be positive, or the d_x decreases when the pressure is applied. Only the d_H in Eq. (5), meets this criterion. Therefore, the H-O bond dominates the T_m and the T_c , as shown in Figure 5. With the known $T_c(P)$ and the known $d_H(P)$ profiles one can determine the $E_{H0}(P_0 = 0.1 \text{ MPa})$, which specifies that the H-O bond elongation under compression results in the phase boundaries with $dT_c/dP < 0$.

Figure 6. Theoretical duplication of pressure dependence of the (a) $T_c(P)$ boundary for VII-VIII phase transition (scattered denote experimental results [38-40]) and boundary (b) between the liquid and the quasi-solid phase [41, 42] indicates that the H-O bond energy relaxation dictates these $T_m(P)$ of negative slopes.

Matching both the $T_m(P)$ and the $T_c(P)$ profiles yields an E_H value of 3.97 eV by taking the H atomic diameter of 0.106 nm as the H-O bond diameter [43]. This E_H value agrees with the energy of 4.66 eV for dissociating the HO bond of water molecules deposited on a TiO_2 substrate with less than a monolayer coverage, and 5.10 eV for dissociating water monomers in the gaseous phase [44]. Molecular undercoordination differentiates values of 5.10, 4.66 and 3.97 eV for the H-O bond in various coordination environments [20]. Reproduction of both the $T_c(P)$ for VII-VIII and $T_m(P)$ indicates that the $d_x(P)$ follows the same quantitative relationship given in Eq.(5) in the pressure and temperature ranges.

4.3 O:H nonbond dominance: $dT_c/dP > 0$

With the known $T_c(P)$ profiles of $dT_c/dP > 0$, one can clarify that such boundaries arise from O:H length depression and derive the $d_L(P)$ equation. A numerical fitting to the $T_c(P)$ profile for the Liquid-Vapor transition [45, 46], see Figure 6a, for instance, yields the following expression,

$$\frac{T_c(LnP)}{225.337} = 1 + 0.067757 \times \exp\left(\frac{LnP}{5.10507}\right) = 1 + A \exp\left(\frac{LnP}{B}\right) = 1 + AP^{\frac{1}{B}} \quad (11)$$

Equaling eqs (8) and (10),

$$AP^{\frac{1}{B}} = -D \int_{P_0}^P p \frac{dd_L}{dp} dp, \quad (12)$$

yields the pressure dependence of the O:H length,

$$d_L(P) = -\frac{A}{(B-1)D} \exp\left(\frac{-LnP}{1.2436}\right) = d_L(0.1MPa, 333K) \times P^{-0.80412} \quad (13)$$

Figure 6b plots the pressure trend of the O:H length at the Liquid-Vapor phase boundary obtained by taking the $d_L(0.1MPa, 333K)$ as unity of standard. Indeed, the slope of the $d_L(P)$ is negative. Likewise, one can obtain the pressure trend of the O:H distance implementing the same iteration for a specific phase boundary of $dT_c/dP > 0$.

Figure 7 (a) Fitting the $T_c(P)$ boundary for Liquid-Vapor phase transition (sourced from [45, 46] at different pressure ranges) with derivative of (b) the pressure trend of the $d_L(P)$ contraction in the Liquid-Vapor phase

boundary. Plotting in Ln scale is for reader's convenience. Two expressions in (a) provide best fit to the $T_C(P)$ for different temperature intervals.

4.4 O:H-O angle dominance: $dT_C/dP \approx 0$ or ∞

The phase boundaries of $dT_C/dP \approx 0$ or ∞ means that the T_C is bond energy independent. The O:H-O cooperative relaxation in length and energy does not contribute to such boundaries but bond angle relaxation changing the geometry configuration of ice.

$T_C(P) \approx 70$ K at the Ic-XI phase boundary is within the temperature regime where the specific heat $\eta_x \approx 0$ [21]. Neither the O:H nor the H-O bond is subject to length and energy relaxation but the O:H-O containing angle cooling stretching become dominance in the structure relaxation, as afore discussed, see Figure 4b and c [21].

The phase boundaries meet the criterion, $dT_C/dP \approx \infty$, at rather high pressures are insensitive to temperature, typically at boundaries of X-XI, X-(VII,VIII). The O:H and the H-O are identical in length of 0.11 Å in phase X [3]. Insignificant length relaxation happens to both segments at these boundaries but geometrical evolution because compression promotes yet heating demotes the proton centralization at the (VII, VIII)-X boundary [47-49]. Raman examination also confirmed that at the liquid-VI phase boundary, in Figure 3, both O:H and H-O undergo contraction, which indicates the solidification weakens the Coulomb repulsion between oxygen ions.

5 Outlook

Phase diagram of water and ice provides direct information of O:H-O bond relaxation along the boundaries of phase transition. Mechanical compression shortens and stiffens the O:H nonbond and lengthens and softens the H-O bond in most phases towards proton centralization. Thermal excitation changes the segmental length irregularly according to their relative specific heat. Reproduction of the negatively-sloped $T_C(P)$ profiles along the Liquid-Quasisolid and the VII-VIII boundaries confirmed that the H-O bond stretching dominate such boundaries with derivative of the E_{H0} energy of 3.97 eV. The O:H bond contraction dictate the positively-sloped boundaries, like Liquid-Vapor transition, giving rise to the pressure trend of O:H length relaxation. Neither O:H nor H-O relaxes in length and energy at boundaries of constant T_C or P but the angle is subject to variation, like the phase of IH-XI where the specific heat η_x approaches zero, and (VII, VIII)-X towards O:H and H-O length symmetrization. Raman examination varied that both O:H and H-O undergo contraction when turn liquid water to ice VI, which indicates the weakening of the Coulomb repulsion between oxygen ions in the ice VI phase. Providing deeper insight into the bond relaxation dynamics at phase transition, observations enrich substantially knowledge scoped beyond classical thermodynamics.

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Appendix: water's phase diagram

Figure 8. Phase diagram for water [45]. $dT_c/dP < 0$ at boundaries for II-V, Liquid-Ih, and VII-VIII transition

indicates that H-O bond elongation dominates. $dT_c/dP > 0$ at boundaries for Liquid-Vapor, Liquid-(V, VI, VII)

transition suggests that O:H nonbond contraction governs the $T_C(P)$ elevation. $dT_C/dP \approx \infty$ at the (VII, VIII)→X boundary occurring at 60 GPa corresponds to the O:H and H-O length symmetrization. Compression promotes yet heating demotes the proton centralization [47-49]. $dT_C/dP \approx 0$ at Ih-XI boundary in low temperatures ($\eta_x \approx 0$) indicates bond angle relaxation dominance with negligible change in the segmental lengths. (Reprinted with permission from [45, 48].)

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