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The Attribute of Water

Single Notion, Multiple Myths

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Nothing is softer or more flexible than water, yet nothing can resist it.

—Lao Tzu (571–470 B.C.)

If there is magic on this planet, it is contained in water.

—Loren Eiseley (1907–1977)

The great seal of truth is simplicity.

—Herman Boerhaave (1668–1738)

Simplicity is about subtracting the obvious, and adding the meaningful.

—John Maeda, *The Laws of Simplicity,* 2006

The nature of the chemical bond bridges the structures and properties of crystals and molecules.

—Linus Pauling, *The Nature of the Chemical Bond,* 1939

Bond and nonbond relaxation and the associated energetics, localization, entrapment, and polarization of electrons mediate the performance of substance accordingly.

—Chang Q. Sun, *Relaxation of the Chemical Bond,* 2014

O:H–bond segmental disparity and O–O repulsivity form the soul dictating the extraordinary adaptivity, coopera-tivity, recoverability, and sensitivity of water and ice

Dedicated to our beloved

Preface

Water is the source and central part of all life—without it, life cannot be sustained or evolve. Water is simple but magical, pure but elegant, perseverant but flexible. Water also symbolizes kindness, wisdom, wealth, and prosperity. Lao Tze, an ancient Chinese philosopher and thinker, wrote: *water represents the highest morality of human beings. It benefits all others, without expecting anything in return. It retains its ethical standard, but stays in where disdained* (上善若水, 利万物而不争。处众人之所恶, 故几于道).

Water is so magically sensitive to any perturbation of biological signals, radiations, and external constraints or stimuli that it lends itself to many romantic notions throughout history. Masaru Emoto described a variety of crystal patterns of ice grown from pure and polluted sources and influenced by emotions, thoughts, and voices in his book, *The Healing Power of Water*. James Brownridge dedicated himself for some 10 years to conducting over 20 experiments to identify the factors influencing the Mpemba effect, which describes the phenomenon where warmer water freezes more quickly than cold water, as first documented by Aristotle in 350 B.C. Gerald Pollack proposed *The Fourth Phase of Water* associated with the hydrophilic interface contact, which has explained numerous phenomena from the perspective of the exclusion zone of the layered, three-coordinated hydronium, H_3O^+, gel-like structure, capable of absorbing all types of energies, separating charges, and excluding microspores and organisms. Because of all these sensitive fascinations, water is described as having intelligence and spirit, and even as a messenger of God.

However, water is too strange, too anomalous, and too challenging, as noted by Philip Ball, a scientific writer and a former senior editor for *Nature*. Its versatile structural phases and strange behavior have fascinated inspiring minds such as Archimedes, Francis Bacon, René Descartes, Lord Kelvin, Isaac Newton, Siméon Denis Poisson, Thomas Young, Pierre-Simon Laplace, Carl Friedrich Gauss, Frantz Hofmeister, William Armstrong, Johann Gottlob Leidenfrost, Gilbert Newton Lewis, and Linus Pauling among many others. In 1611, Galileo Galilei and Ludovico delle Colombe ignited the debate on why ice floats, from the perspectives

of buoyant force, surface tension, and mass density. In 1859, Michael Faraday, James Thomson, and James Forbes started the debate on ice regelation—the behavior of ice melting under pressure and refreezing when the pressure is relieved. Michael Faraday, James Thomson, William Thomson (Lord Kelvin), and Willard Gibbs had been involved in exploring the slipperiness of ice since 1850, based on the concepts of quasi-liquid skin, pressure melting, and friction heating.

In the 125th anniversary special issue, *Science* magazine listed *The Structure of Water* as one of the 125 big questions to mankind. In 2012, the Royal Society of Chemistry organized a competition offering a £1,000 award to the participant, out of 22,000 entries, who could provide the best possible explanation for the Mpemba effect. The International Union of Pure and Applied Chemistry (IUPAC) gathered over 30 experts in Pisa in 2005 to form a task force to revise the definition of the hydrogen bond, and the agreed-upon result was published in 2011. To commemorate the 400th anniversary of the debate between Galileo and Colombe on the mystery of floating ice, twenty-five bright minds met in Florence, Italy, in July 2013, for a week, to discuss unanswered questions on water. However, fierce debates regarding the structure and anomalies of water are still ongoing, *converging* Mark Twain's (1835–1910) saying that *whiskey is for drinking; water is for fighting over*. The current status is that each of the various anomalies of water and ice is debated by multiple theories. It has been a long-standing dream of the scientific society to develop one notion that reconciles as many anomalies as possible.

Alternative ways of thinking and approaching are necessary to resolve the anomalies of water and ice. Turning our perspectives from classical thermodynamics to hydrogen bond (O:H–O) cooperativity, from single snapshots to statistical means, from surface to skin, and from spectroscopy to spectrometrics would be essentially helpful. In place of the conventional approach in terms of dipole–dipole interaction in the "dipole sea" of water, we have focused on the performance of a representative O:H–O bond for all as an asymmetrical oscillator pair with short-range interactions and O–O Coulomb coupling. This premise enables us to examine the consequence of the O:H–O cooperativity and polarizability on the detectable properties of water and ice.

An oxygen atom always tends to hybridize its *sp* orbits when interacting with atoms of any arbitrary electropositive elements and therefore a water molecule takes the tetrahedral configuration not only in the gaseous phase but also in solid at temperatures of only several Kelvins, although the O:H–O bond containing angle and its segmental lengths are subject to relaxation under perturbation.

Rather than the O:H nonbond or the H–O polar-covalent bond alone, the O:H–O bond integrates both the O:H intermolecular and the H–O intramolecular asymmetrical, ultra-short-range interactions and the Coulomb repulsion between electron pairs on adjacent oxygen. Being conventionally overlooked, the Coulomb repulsion between oxygen anions and the segmental disparity of the O:H–O bond form the soul dictating the extraordinary adaptivity, cooperativity, recoverability, and sensitivity of water and ice when responding to perturbation at any level.

The segmental disparity and the strong H–O bond allow for molecular flipping vibration, but unlikely the "proton tunneling transition" (Bernal-Fowler 1933) or

the "two-in two-out" proton frustration (Pauling 1935). Rather, the segmented O:H–O bond relaxes in a "master–slave" manner. One segment becomes stiffer if it turns to be shorter, and the other will become longer and softer. The O:H nonbond always relaxes more than the H–O bond. The flexible and polarizable O:H–O bond exists commonly to all phases irrespective of their geometries such as the superionic $OH_3^+:OH^-$ phase and the X phase of identical O:H and H–O distances. As uncovered by Yanming Ma at Jilin University, China, $(H_2O)_2$ only transits into the OH_3^+(hydronium):OH^- (hydroxide) configuration under 2 TPa pressure and 2000 K temperature. The O:H–O bonding premise is more comprehensively appealing than the convention of intermolecular dipole–dipole interactions, and it is also general to situations with a presence of electron lone pairs.

In dealing with the strongly correlated and fluctuating water system, one should be more focused on the statistical mean of the collection of all correlated parameters than on the instantaneous accuracy of a certain isolated quantity under a specific condition at a certain point of time. One has to keep in mind the meaningful parameters and disregard those such as the long-range interactions and nuclear quantum dynamics as the common background of all to derive a simple solution for the seemingly unrelated phenomena.

The specific heat disparity between the O:H nonbond and the H–O bond discriminates the thermal dynamics of water and ice in different temperature regimes, which defines a quasisolid phase where the negative thermal expansion occurs. The rule of global bond contraction between undercoordinated atoms also applies to water molecules at the skins of bulk water, hydration shells, droplets, bubbles, and hydrophobically encapsulated water. Molecular undercoordination not only disperses the quasisolid phase outwardly to lower the freezing temperature and raise the melting point but also creates a supersolid skin phase that is less dense, ice like, elastic, and hydrophobic.

An HX-type acid dissolves into the X^- anion and the H^+ that binds to an H_2O to form the hydronium H_3O^+ tetrahedron with one lone pair and the H_3O^+ interacts with one of its four neighbors through the O–H↔H–O anti-hydrogen bond (anti-HB). The H↔H serves as a point breaker of the entire HB network, making the bulk water "fragile". A YOH-type base dissolves into the Y^+ cation and the OH^- hydroxide with three lone pairs, and the HO^- interacts with one of its four neighbors through the O:↔:O super-HB that serves as a point compressor, elongating the H–O bond and releasing heat when reaction rakes place. The X^- and Y^+ solute ions create each an electric field to align, cluster, polarize, and stretch the H_2O molecules in the hydration shells. Electrification of H_2O molecular dipoles by the fields of artificially attached charge, or an externally applied potential will also align, stretch, and polarize the O:H–O bonds. Electrification of the O:H–O bond by opposite fields effects adversely than under either alone. The hydration shells of solute ions are essentially the same as the water skin exhibiting stronger supersolidity behavior. The macroscopic properties of water and ice depend discriminatively and functionally on the cooperative relaxation in length and energy of the segmented O:H–O bond and the associated polarization under excitation.

Phonon spectrometrics is a powerful tool that enables discovery of the molecular site, multifield driven O:H–O relaxation dynamics in terms of segmental lengths and stiffness, order of molecular fluctuation, and phonon abundance, which reveals sufficiently and exactly what is happening to water molecules of the same coordination environment under excitation. A combination of the micro-jet UPS and XPS collects molecular site-resolved information about electron polarization and the O 1s energy shift. Lagrangian mechanics is efficient in dealing with the O:H–O asymmetrical oscillator pair dynamics, which enables mapping the potential paths for the O:H–O bond at relaxation. Fourier thermo-fluid transport dynamics is essential for solving the heat conduction involved in the Mpemba paradox. The use of multiple strategies is necessary for unlocking the mysteries of water. Computations and spectrometrics serve as powerful tools for verifying the theoretical predictions that are key to solving the long-standing puzzles. These considerations have led to a set of experimental, numerical, and theoretical strategies that have enabled the presented efforts and progresses.

This volume deals with the scientific popularization, quantitative resolution, and insightful extension of the best known mysteries of water and ice. Consistent resolution to the noted mysteries verifies the validity of the O:H–O bond notion and the approaching strategies. This book also demonstrates how the segmented O:H–O bond responds adaptively and cooperatively to stimulus of chemical contamination, electrification, magnetization, mechanical compression, molecular undercoordination, thermal excitation, and their joint effect in a coordination-resolved manner, and how the bond relaxation changes the macroscopic properties of water and ice. This volume presents an effort to resolve, once and for all, the following systematic issues:

1. Crystallographic structure order (tetrahedrally-coordinated fluctuating monophase with a supersolid skin)
2. Density-geometry-size-separation correlation of molecules packed in water and ice
3. Bond-electron-phonon-property correlation of water and ice
4. Asymmetrical, short-range, and coupled potentials for the relaxed O:H–O bond
5. O:H–O bond relaxation kinetics crossing the phase diagram
6. Ice Regelation—compression lowers but tension raises the T_m (O:H–O bond recoverability and quasisolid-phase boundary dispersivity)
7. Pressure-induced O:H–O bond proton centralization (O:H compression and H–O elongation)
8. Ice floating (specific heat disparity defined quasisolid phase that undergoes cooling expansion)
9. Mass density thermal oscillation of water and ice and coordination-resolved liquid O:H–O bond thermal dynamics (specific heat ratio entitled master–slave manner relaxation at different temperatures)
10. Unusual thermodynamics of skins, hydration shells, free and confined nanodroplets and nanobubbles (H–O contraction elongates and polarizes the O:H nonbond)

11. Hydrophobicity and hydrophilicity transition (dipole creation and annihilation)
12. Superlubricity of ice and quantum friction (electrostatic repulsivity and O:H phononic elasticity)
13. Supersolid solute hydration shells (elastic, polarized, hydrophobic, less dense, and thermally more stable)
14. Quasisolid phase boundary dispersivity (phonon frequency relaxation modulates the Debye temperatures)
15. Hofmeister effect—ions modulation of surface tension and DNA solubility (O:H–O bond relaxation and polarization)
16. Molecular bonding in Lewis solutions of acids, bases, and adducts or salts (H↔H anti-HB pointer breaker in acid solutions, O:↔:O super-HB point compressor in base solutions, and solute ionic polarizer in adduct solutions)
17. Discrimination of acid and salt solutions in stress and solubility (ionic electrification and discriminative polarization)
18. Hofmeister solution thermal stability—critical pressures, temperatures, and durations for phase transition (O:H–O bond deformation by the coupled fields)
19. Armstrong water floating bridge (long-range ordered electrification disperses the quasisolid phase boundary)
20. Electromelting (artificial electrification effect on quasisolidity)
21. Magnetization and electromagnetic radiation—(moving dipoles—Lorentz field—current induction—antiferromagnetism)
22. Soil wetting by aqueous solutions (electric fields superposition)
23. Correlation of H–O phonon frequency, lifetime, self-diffusion, skin stress, and solution viscosity
24. Mpemba paradox—warm water freezes quickly (O:H–O bond memory and water skin supersolidity)
25. Molecular-site-resolved O:H–O bonding dynamics in terms of segmental stiffness, structure order, phonon abundance, etc.

Water forms such a strongly correlated and fluctuating system that not only involves asymmetrical, ultra-short-range, and coupling interactions but also responds sensitively to any perturbation or radiation in an ultra-long range manner under a domino-like effect.

Water is much more interesting but less complicated than many of us could ever imagine. Nothing is more fun than playing with water and ice from the perspective of predictive bond-electron-phonon-property collaborative relaxation. It is really an enjoyable and fascinating experience to tackle these anomalies. It is our obligation and great pleasure to share these discoveries and progress, although some formulations and solutions might be subject to further improvement and refinement. Corrections, critiques, and better solutions are welcome and furthermore, much appreciated.

We hope that this volume, though it contributes a tiny drop to the ocean of water knowledge, could inspire fresh ways of thinking and approaching and stimulate more interest and activities toward uncovering the mysteries of water and ice, especially in the contexts of water being embedded in or interacting with other

species. The strong correlation, fluctuation, localization, and polarization could be important ingredients in this understanding. Directing effort to interaction between water and soft matter and to water's role of messaging, regulating, repairing, and signaling in bioelectronics, food, drug, and life sciences could be even more challenging, fascinating, promising, and rewarding.

We express our sincere gratitude to friends and peers for their encouragement, invaluable input, and support, and to collaborators, particularly, research associates Dr. Xi Zhang, Dr. Yongli Huang, Dr. Zengsheng Ma, and Mr. Yong Zhou, for contributions. Last but not least, we thank our families, Mrs. Meng Chen, in particular, for assistance, patience, support, and understanding throughout this joyous and fruitful journey.

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Contents

About the Authors

Chang Q. Sun received his B.Sc. degree in 1982 from Wuhan University of Science and Technology and the M.Sc. degree in 1987 from Tianjin University, China, and served on its faculty until 1992. He earned his Ph.D. in Surface Physics at Murdoch University, Australia in 1996.

Dr. Sun has been working on the Coordination Bond and Electronic Engineering since 1990 with creation of the unique Bond Relaxation Theory that has enabled: (1) invention of the Coordination-Resolved Electron and Phonon Spectrometrics; (2) reconciliation of the behavior of bonds and electrons associated with undercoordinated atoms of defects, skins, nanostructures of various shapes, and heterocoordinated atoms in chemisorption and interfaces; (3) formulation of the atomistic, multifield solid mechanics; (4) correlation of bond relaxation and polarization to detectable quantities of aqueous and solid specimens; and (5) resolution of multiple mysteries of water and ice.

His contribution has been featured in two monographs, the present *The Attribute of Water* and the *Relaxation of the Chemical Bond* (Springer, 2014; Chinese edition published by High Education Press, Beijing, 2015), and multiple treatises published in *Friction* (2015), *Chemical Reviews* (2015; 2012), *Coordination Chemistry Reviews* (2015)*, Progress in Solid State Chemistry* (2015; 2007; 2006), *Surface Science Reports* (2013), *Progress in Materials Science* (2009; 2003), *Energy and Environment Science* (2011)*, Science China* (2012)*, Nanoscale* (2010), etc. Breakthroughs in water research have been featured by numerous media such as *Times, The Telegraph, Daily Mails, Physics Today, IOP News, Chemical World, Chem Views, Nature Chemistry*, *New Scientist,* etc.

Dr. Sun was conferred the First Laureate of the 25th Khwarizmi International Science Award in 2012 and the Inaugural Nanyang Award of Research in 2005, and finalist of Singapore Presidential/National Science Award in 2012 and 2003. He is currently on the Editorial Advisory Board of numerous scientific journals.

Yi Sun received her B.Sc. degree in Physics from University of Illinois at Urbana-Champaign (UIUC) in 2008, her M.A. in Economics and Ph.D. degree in Public Policy from the University of Chicago in 2016. Besides the current project, she has been devoted to the electron spectrometrics of binding energy shift of graphene, Ni/TiO_2, and Pt/CNT nanocrystals and interfaces and the superhydrophilicity, superfluidity, superlubricity, and supersolidity at the nanometric contacts from the perspective of undercoordination-induced quantum entrapment and polarization. She received the Commonwealth Edison/Bristow Award in Physics and was named a Chancellor's Scholar at UIUC in 2008.

Nomenclature

XPS	X-ray photoelectron spectroscopy
η	Viscosity
T_V/T_m	Evaporation/melting temperature
θ	Temperature
T_C	Critical temperature for phase transition except for evaporation
STM/S	Scanning tunneling microscopy/spectroscopy
SFG	Sum frequency generation
RPS	Residual phonon spectroscopy
RLS	Residual length spectroscopy
NTE	Negative thermal expansion
NEP	Nonbonding electron polarization
ρ	Mass density
H/LDL	High/low density liquid
FTIR	Fourier transformation infrared spectroscopy
E_x	O:H–O segmental cohesive energy
d_x	O:H–O segmental length
DOS	Density of states
CN(z)	Coordination number
BOLS	Bond order–length–strength correlation
η_X	Specific heat of the xth segment
ω_X	O:H–O segmental phonon frequency
τ_H	H–O phonon lifetime
ΔE_{1s}	O 1s core—level shift
Θ_{DX}	O:H–O segmental Debye temperature (x = L for O:H; x = H for H–O)
μ	Self-diffusivity
γ	Skin stress

Chapter 1
Wonders of Water

- *Water and ice respond to stimuli or perturbations unexpectedly with derivatives of numerous anomalies.*
- *One phenomenon is often associated with multiple debating theories but one principle should reconcile all observations.*
- *Clarification, correlation, formulation, and quantification of hydrogen bond (O:H–O) relaxation and polarization dynamics and its consequence on detectable properties should be the focus tracking forward.*
- *Focusing on the statistical mean of all the correlated parameters simultaneously is more reliably revealing than on the instantaneous accuracy of a parameter at a given time for the strongly correlated and fluctuating system.*

Abstract Water and ice perform differently from other usual substance when subject to tiny perturbation but most of its mysteries remain unresolved up to date despite extensive dedications made by generations. The aim of this volume is to show that alternative ways of thinking and approaching could be efficient to making substantial and systematic progress towards consistent understanding of the performance of water and ice and quantitative information on the hydrogen bond (O:H–O) bond relaxation and polarization dynamics under various perturbations, as well as their consequences on the detestable and correlated properties of water and ice.

1.1 Significance of Water and Ice

Water covers 70 % of Earth's surface, makes up 60 % of the human body, and forms 90 % of human blood composition. Besides the scientific significance in subject areas such as astrophysics, agriculture, biology, climate, environment, galaxy, geology, and living cells, water is of paramount importance to civilization, economics, diplomacy, history, military, politics, and international relations of a nation. As noted by Vladyslav Goncharuk [1], a colloid and water chemist and Academician of the National Academy of Sciences of Ukraine, in his monograph *Drinking Water*: The intellect of any nation is determined by the quality of its drinking water and the progress of a civilization depends on the level of water supply and sewage systems. Mastering sufficient water resources, a nation will be privileged in dealing with diplomacy and international affairs. In another word, water resource is related to the peace of the world.

Yet, each H_2O molecule of this common, seemingly simple substance—one oxygen atom bound to two hydrogen atoms with sp^3-hybridized directional orbits— holds an ocean of full mystery. Water is simple yet magic, pure yet elegant, perseverant yet flexible. Water also symbolizes kindness, wisdom, wealthy, and prosperity. According to Lao Tze (571–531 B.C., an Ancient Chinese Philosopher and Thinker), water represents the highest morality of human beings, which is beneficial for all kinds of things without expecting for any return. It retains its ethical standard yet stays in where disdained.

As the key component of water and biomolecules, the hydrogen bond (O:H–O) bond determines ubiquitously the unusual behavior of water and ice and other molecules containing simultaneously such bonding "–" and nonbonding ":" lone pair interactions. The electron lone pair associated with atoms of electronegative elements such as oxygen, nitrogen, and fluorine. The O:H–O bond and its polarizability give water with unique properties, accelerates or slows reactions, and holds together the three-dimensional configurations of deoxyribonucleic acid (DNA), proteins, and other supramolecules [2–4]. Given its importance in nature [5–16] and in geochemical sciences [17, 18], and its role in DNA and protein folding [2, 19–21], gene delivering [22–24], cell culturing [25], drug target binding [26], ion channel activating and deactivating [27], regulating, signaling, messaging, etc., water demonstrates extraordinary high degree of adaptivity, cooperativity, sensitivity, and recoverability with memory in responding to constraints or perturbations.

H_2O and the O:H–O bond between oxygen ions, being often confused with the H–O bond or the O:H nonbond, have been studied since the dawn of scientific thought. Approaches from the perspectives of classical thermodynamics and quantum mechanics have considerably advanced this subject field. Active areas regarding the intrinsic properties of water and ice include: (i) crystal structure optimization [28], phase formation and transition [29, 30]; (ii) reaction dynamics with other ingredients or at interfaces [31, 32]; (iii) O:H–O bond weak interactions [33, 34]; (iv) binding energy determination [35–41]; and, (v) phonon relaxation dynamics under various conditions [9, 32, 42–44].

Authoritative reviews and monographs on the advancement in this field have been focused on the following issues from various perspectives: phase and geometric structures [45–47], molecular clusters [48–51], ice nucleation and growth [16, 52], ice melting [53], slipperiness and friction of ice [54], and behavior of water ice subjected to positive pressure [55, 56] and negative pressure [48, 57]. Reviews have also covered topics on water surface charge density and polarization [58, 59], surface photoelectron emission [60, 61], phonon relaxation [18, 62, 63], water adsorption onto inorganic surfaces [64–68], imaging water molecules on different substrates [69], and ion effects on water properties and structures [70], among many other topics.

State-of-the-art probing techniques, such as neutron diffraction and X-ray diffraction (XRD) [71, 72], scanning tunneling microscopy/spectroscopy (STM/S) [73–75], O near k-edge X-ray absorption/emission fine structure spectroscopy (NEXFAS/NEXFES) [76, 77], microjet photoelectron emission spectroscopy (PES) [78], sum frequency generation (SFG) dielectric spectroscopy [59, 79], glancing-angle Raman spectroscopy [80, 81], etc., have propelled advancement in

studying the droplets, bubblers, surface, and interface of water and ice [63, 82] with or without acid and salt solutions [83].

However, water and ice are too strange, too anomalous, and too challenging [5, 84, 85]. Of particular interest to scientists is what happens at the interfaces where water meets air or other substances such as cells, proteins, micro channels, hydrophobic and hydrophilic skins of other solids. Much has been theorized and calculated, despite insufficient corroborating experimental confirmation. A series lectures by renown experts in the Enrico Fermi summer school "Water: fundamentals as the basis for understanding the environment and promoting technology" held in Varenna, Italy, in July 2013 has addressed the up to date knowledge about water on questions that remain unanswered about this molecule, and topics covered included: water in relation to other liquids, biological water, local environment of water protons, atmospheric water, amorphous solid phases of water, NMR studies of water, spectroscopic studies of water, the structure of liquid water, and supercooled water, among others. A four-week symposium on the theme of "Water—the Most Anomalous Liquid" was held during 13 October and 07 November 2014 in Nordita, Stockholm, Sweden, which brought together experimentalists and theoreticians in strong synergy to explore interpretations and to provide a strong basis for further advances towards a unified picture of water.

The current situation is that each of the various anomalies of water and ice is associated with multiple debating theories yet one simple notion that reconciles as many as possible anomalies is lacking. Progress is below expectation regarding the structure order, local potentials, O:H–O bond relaxation dynamics, acid-base-adduct solutions, and the charge behavior in the skin and in solutions. Little has yet been known about the mechanism behind the weird properties of water and ice demonstrated under perturbation by fields such as coordination reduction, chemical reaction, compression, electrification, magnetization, radiation, thermal excitation, etc. Property variations rarely follow the rules that govern the performance of other "normal" substance. The ways of charge induction and energy absorption, energy retention, energy conduction and dissipation remain challenge. Difficulties remain in accurately determining the three-dimensional coordination order and thermodynamic behavior [86].

Insights into the unusual behavior of water and ice is still far from systematic and consistent. For instance, one often confused either the intramolecular H–O interaction or the intermolecular $H_2O:H_2O$ interaction as the hydrogen bond, O:H–O, between water molecule or between oxygen ions. The coordination number (CN) of a water molecule varies from 2 to 5, depending on experimental conditions.

1.2 Phase Diagram

Water and ice has insofar formed 17 types of structures in the P-V phase diagram, see Fig. 1.1 [87]. A water molecule, H_2O, forms in a V shape: two hydrogen atoms connected to a central oxygen atom, but water molecules are socialized like they are in a concert—their mobility is temperature and impurity concentration dependent. The
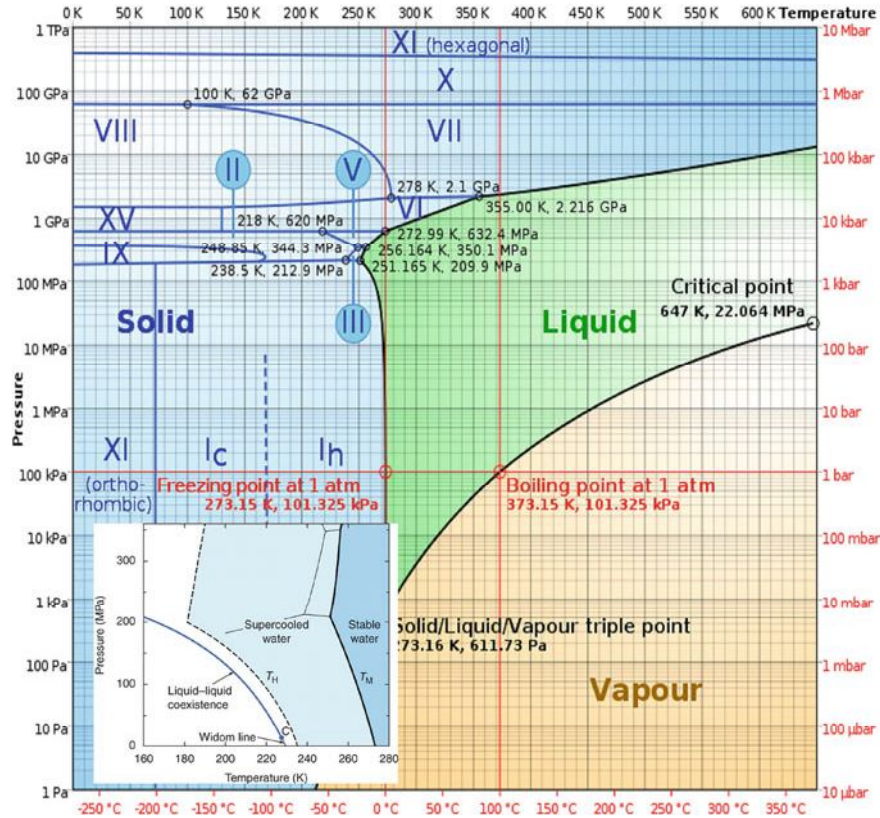
Fig. 1.1 Phase diagram for water ice [87]. The phase boundaries can be categorized according to their slopes: $dT_C/dP < 0$ for II–V, Liquid—I_h, and VII–VIII transition; $dT_C/dP > 0$ for Liquid–Vapor, Liquid—(V, VI, and VII) transition. $dT_C/dP \cong \infty$ at the (VII and VIII)—X boundary occurring at 60 GPa; $dT_C/dP \cong 0$ at I_h-XI boundary in low temperatures. (Reprinted with permission from [87, 89, 90].) The *inset* shows the supercooling behavior of emulsified liquid water. The homogeneous ice nucleation temperature (second critical pint T_H) varies with pressure. (Reprinted with permission from [91, 92].) (The *thick lines* show the Raman probing paths for the hydrogen bonding dynamics, which will addressed in Chap. 4, The inset shows the Non Man' Land region of quasisolidity (often called supercooled water))

H_2O: H_2O nonbond interaction in liquid is weaker than it is in solid; the O:H is even weakest in vapor. Classically, the concerted motion of water molecules is described by the interaction between molecular dipoles in a dipole sea, which overlooks the interaction between the intermolecular O:H nonbond and the intramolecular H–O bond. Coulomb repulsion between electron pairs on adjacent oxygen ions plays the key role in determining the concerted molecular association in water and ice [88].

Ice is the central to climate, geology, and life. Understanding its behavior is essential for predicting the future of our planet and unravelling the emergence of life in other planets of the Universe [93]. Water ice frosts planets, moons and comets in our Solar System. On Earth, white polar ice caps reflect up to 90 % of the

Sun's incoming radiation. On average, 7 % of the ocean's surface is frozen; sea ice alters ocean currents and limits the exchange of gases with seawater. Ice and snow coat 10 % of the land permanently and up to half of the Northern Hemisphere in midwinter. These blankets of frozen water insulate the ground and the oceans.

Ice clouds concentrate airborne chemicals and are sites for atmospheric chemistry. Above the poles, clouds of ice grains host ozone-depleting reactions, forming holes in the stratospheric ozone layer at high latitudes that expose millions of people to increased ultraviolet radiation. Chemical reactions in snow on the ground can produce ozone and other environmental pollutants. Organic toxins and mercury accumulate in snow can be released into rivers and oceans when the snow melts, where they enter the food web.

Ice behaves strangely at lower temperatures and higher pressures. In everyday ice cooled from liquid water, which scientists call Ice I_h, water molecules line up in a hexagonal pattern (the "h" stands for hexagonal); this is why snowflakes all have six-sided patterns. A variation called ice I_c 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 I_h is less dense than liquid water—and the O:H nonbonds between hydrogen atoms and other water molecules are longer and weaker than the H–O atomic bonds. The cubic ice can also form artificially in graphene nanocapilaries at room temperature [94]. The square ice I_c has a high packing density with a lattice constant of 0.283 nm and can assemble in bilayer and trilayer crystallites. Molecular dynamics (MD) simulations indicate that the square ice should be present inside hydrophobic nanochannels independently of the exact atomic nature of the channels.

At higher pressures, the usual hexagonal structure breaks down through bond angle and length relaxation [90], 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. There are also several forms of ice in which the water molecules are arranged randomly, as in glass. At a pressure of about 200 MPa, Ice I_h 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 expected 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 Calisto.

With pressure high enough, the temperature needs not even be low 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 300–400 °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 there into a solid phase known as Ice VII. Nobody knows whether ice can be found inside Earth, because no one has yet figured out a way to look 100 miles deep underground.

Just as salt melts ice at the surface, other molecules mixing could impede water freezing and ice melting. The critical temperatures for melting, freezing,

evaporating and dew forming from gaseous phase to liquid are tunable not only by tuning the pressure but also by adding chemical impurities or by varying the confinement conditions. Water molecules at the hydrophobic interface perform differently from those at the hydrophilic interfaces.

Ice also changes its form with dropping temperatures. In hexagonal ice, the usual form, the oxygen atoms are fixed in position, but the O:H nonbond between water molecules are continually breaking and reattaching, tens of thousands of times a second. At temperatures cold enough—below -200 °C both H–O bond and O:H nonbond freeze without relaxation but bond angle undergoes cooling stretching [95], 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.

From ice XII to ice XVI, found just a decade ago, are also furnished with many wired features. For instance, the cadge-structured ice XVI has a density of 0.81 g/cm^3 as the stable low-temperature phase of water at negative pressures (that is, under tension) [96]. Composed of undercoordinated molecules, this hollow hydrate structure exhibits cooling expansion at temperatures about and below 55 K. This phase, as shown in Fig. 1.2, is also 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 0.11 nm, reaching a density that is twice of ice I$_h$ [97, 98].

Ice can turn to be partially ionic: $2H_2O \rightarrow H_3O^{\delta+}:HO^{\delta-}$ ($\delta = 0.62$) by exchanging an H on a molecule with an electron on another at extremely high
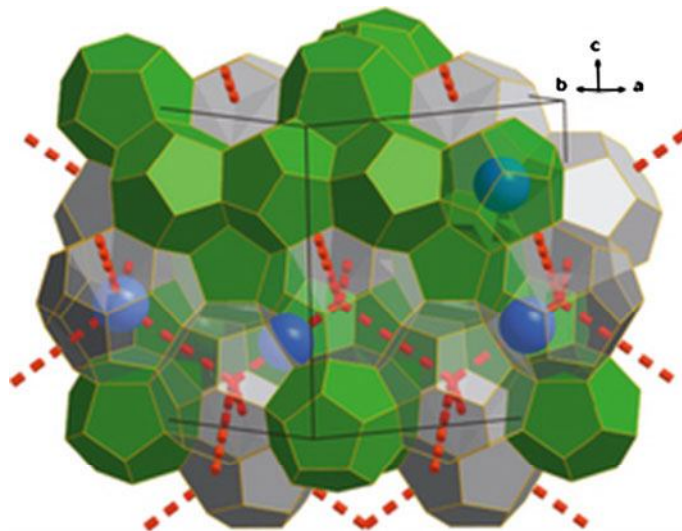
Fig. 1.2 Cage structures of the XVI phase. Ne atoms (in *blue*) can easily travel between large cages (in *grey*) passing through six-membered rings of water molecules (*red dashed lines*). Removal of Ne atoms from the small cages (in *green*) requires the presence of a water vacancy in one of the five-membered rings [99] (Reprinted with permission from [96].) (color online)

pressure (2 TPa) and high temperature (2000 K) [38], optimized using the package of crystal structure analysis by particle swarm optimization (CALYPSO) [100]. The $H_3O^{\delta+}$ likes an NH_3 molecule that has one electron lone pair. The $HO^{\delta-}$ likes a HF having three lone pairs Fig. 1.3 illustrates the crystal structure of $P2_1$ viewed along a axis. The large spheres represent the oxygen atoms whereas the small ones are for hydrogen atoms. The labelled H–O distances vary from site to site in the range of 0.902 and 1.182 Å under 2 TPa pressure. The occurrence of this partial ionic phase transition takes place by breaking up the typical O–H covalently bonded tetrahedrons in the hydrogen symmetric atomic phases.

In addition to the critical point for liquid-vapor phase transition, a second critical point exists [91, 101] for supercooling water, in the range of 145 K $< T_{c2} <$ 175 K range and $P_{c2} \approx$ 200 MPa pressure. This critical point, shown in Fig. 1.1 inset, was attributed to the homogeneous ice nucleation (T_H) or transition between the low-density and the high-density amorphous solid phase.

One may note that phase IV is absent in the phase diagram. Gerald Pollack [102], Professor of Biochemical Engineering at Washington University, suggests its presence at sites between water and hydrophilic interface. This phase is gel like, high density, positively charged OH_3^+ configuration), having the ability to exclude impurities and organisms.

In 2015, NASA announced the discovery of liquid water existence on Mars (see Fig. 1.4) as detected using infrared absorption spectroscopy with the characteristic phonon wave lengths of 1.4, 1.9 and 3.0 μm [103]. Spectrum analysis also found
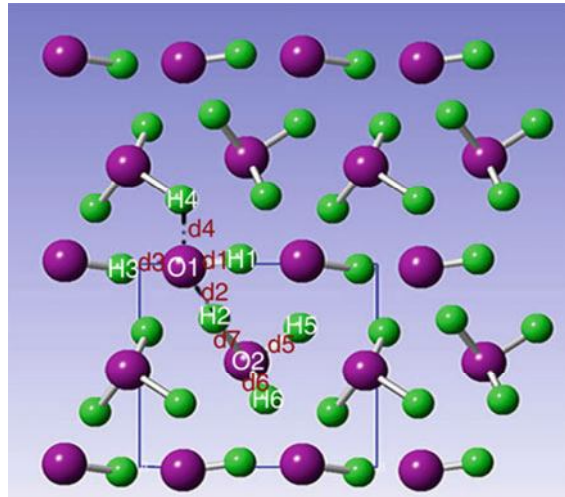
Fig. 1.3 $2H_2O$ transition into the superionic $H_3O^{\delta+}:HO^{\delta-}$ (δ = 0.62) under 2000 K temperatures and 2 TPa pressure. The *large spheres* represent the oxygen atoms whereas the *small ones* are for hydrogen atoms. The atoms and O–H distances are labelled in accordance (Reprinted with permission from [38]). The O:H–O bond remains but the $2H_2O$ evolves into respective NH_3 and HF like quasi-tetrahedron with different numbers of lone pairs
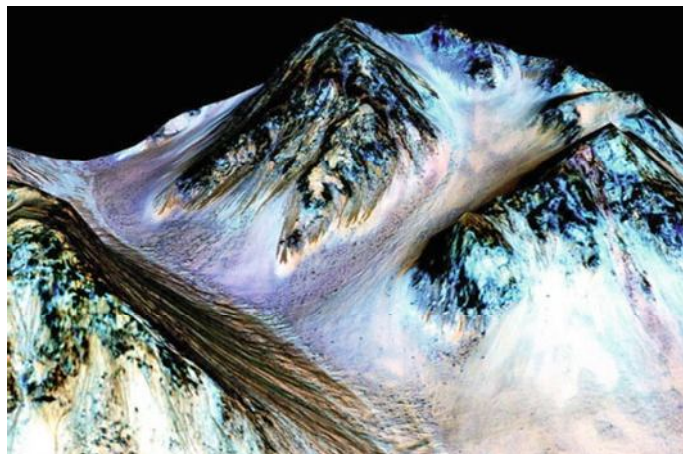
Fig. 1.4 This NASA photo, taken by an instrument aboard the agency's Mars Reconnaissance Orbiter, shows dark narrow 100 m long streaks on the surface of Mars that scientists believe were caused by flowing streams of salty water (by David Templeton/Pittsburgh Post-Gazette)

the water to be a brine containing forms of perchlorate, a chlorine salt. The average temperature is −33 °C. Normally, only exists ice under these conditions but it is possible for salted solution in the quasisolid phase—lower freezing temperature and higher viscosity from the quasisolid [88].

Yet the molecular mechanisms underlying these processes remain largely unknown [93]. It is essential to understand how chemical reactions proceed in ice and snow, and where they occur within the grain and crystal structure for building snow or ice-cloud modules for atmospheric and climate models or extrapolating laboratory studies to environmental conditions with enough confidence.

Sun et al. [95] shows that the superposition of the specific heat curves of the O:H nonbond and the H–O bond creates two intersecting temperatures that define the boundaries of the solid/quasisolid/liquid phases. The boundaries of this quasisolid phase correspond to temperatures of extreme densities, which are close to the critical temperatures for melting and freezing. In the quasisolid phase, the H–O bond undergoes cooling contraction and the O:H nonbond expansion resulting in low density of ice. Undercoordinated water molecules not only disperse the quasisolid phase but also create a supersolid phase presenting at sites of skins, defects, and the edge of the hydrogen bond networks. This elastic, less dense, polarized, thermally stable supersolid phase makes ice slippery and water's skin elastic, hydrophobic, and tough [104, 105].

The phase diagram of water and ice is very complicated with boundaries of versatile slopes. One often connects the structure and property Q(PV, ST, …) of a substance directly to the external stimuli such as pressure, volume, and temperature, which is exactly what the classical thermodynamics deals with for large trunks of regular substance. Such treatment employs concepts of entropy, enthalpy, Gibbs

and Helmholtz free energy, etc. These statistic quantities are associated with standard deviation δ depending on the sample size N in the form of $\sigma \propto N^{-1/2}$. This approach provides limited information on how the chemical bond responds to external stimulus in each phase and crossing the phase boundaries.

According to Pauling [106], the nature of the chemical bond bridges the structure and properties of crystals and molecules. Hence, formation and relaxation of the bond in angle and length and the associated energetics and dynamics of localization, entrapment, polarization, and transition of electrons mediate uniquely the structure and properties of a substance accordingly [107]. Therefore, the phase diagram is supposed to tell how the O:H–O bond relaxes over the entire phase map [90], as justified using phonon spectrometrics shortly.

1.3   Physical Anomalies

Water displays a surprising matrix of unusual properties. The origin of these anomalies is still a matter of debate, and so far a quantitative description of water's phase behavior starting from the molecular arrangements is still missing [108]. The following epitomizes some of the best-known mysteries desiring for consistent and quantitative resolution:

Stimulus	No.	Mysteries
Intrinsic attributes	1	Packing order [109]. Water ice exhibit 17 phases with uncertainty of molecular CN, O–O distance, and electronic configuration [109]
	2	Hydrogen bond [88]. Discrepancy and confusion exist in hydrogen bond definition: O:H–O bond between oxygen, intramolecular H–O polar covalent bond, and intermolecular O:H nonbond
	3	Local potentials [110]. Determination of the intra- and intermolecular potentials was not possible using the state-of-the-art methods of diffraction, electron and phonon spectroscopy
	4	Structures versus properties [88]. Factors control the structures and properties and their interdependence remain unclear
Mechanical compressuion/tension	5	Ice regelation [111]. Ice melts under compression and freezes again when the pressure is relieved. A 210 MPa pressure lowers the T_m from 273 to the limit of 251 K; a −95 MPa tension raises the T_m by 6.5 K; 18.84 MPa compression lowers the temperature of maximum density from 277 to 273 K; −180 MPa raises this temperature to 320 K
	6	Proton symmetrization [97]. Both O:H and H–O lengths become 0.11 nm at 60 GPa in phase X; salt addition lengthens the critical the O-O distance

(continued)

Stimulus	No.	Mysteries
	8	Phonon cooperative relaxation [112]. The low-frequency O:H phonon undergoes a redshift but the high-frequency H–O phonon undergoes a blue shift when the ice is compressed at $\leq$140 K up to a critical pressure $\sim$3.3 GPa and then the trends transit under high pressures
	9	Compressibility anomaly [84]. Water has a compressibility of 0.46 GPa^{-1} compared with 1.05 GPa^{-1} for CCl$_4$ at 25 °C. The compressibility having a maximum at temperature just below the minimum density and then drops with the rise of temperature up to a minimum centered at 46.5 °C [113]
Thermal excitation	10	Ice floating [95]. Oxygen and Argon shrink their volumes by 19 % of their liquid upon freezing. The density drops by 8 % when water turns to be ice. The lower density of ice makes ice float on water
	11	Density oscillation [95]. The density of water and ice oscillates over the full temperature range in four regimes. Cooling contraction occurs in the liquid and in the ice I$_h$ and I$_c$ phases but cooling expansion happens at transition from liquid to ice. The density remains almost constant in phase XI ($\leq$100 K)
	12	Second critical point [91, 101]. A second critical point exists, in addition to that for the normal liquid–vapor transition, in the 145 K $< T_{c2} <$ 175 K range and $P_{c2} \approx$ 200 MPa pressure
	13	Extraordinary specific heat [95]. Water has extraordinarily high specific heat that changes with temperature abnormally and disobeys Debye approximation. It takes a lot of energy to heat water (about ten times as much as the same mass of iron), and it must lose a lot of energy to cool down. So the vast bodies of water on earth help keep the earth's temperature fairly steady. On the other hand, land masses heat up and cool down more quickly. Different parts of the atmosphere are heated differently, which generates wind
	14	Temperature and pressure resolved refractive index [88]. The index rises from 1.33026 at −30 °C to a maximum value of 1.33434 at just below 0 °C before falling increasingly to 1.31854 at 100 °C. Compression raises but heating lowers the refractive index

(continued)

Stimulus	No.	Mysteries
Molecular undercoordination	15	Water's tough skin [114]. The surface tension of water is 72.75 mJ/m^2 compared with 26.6 mJ/m^2 for CCl_4 at 20 °C. The tension drops linearly with temperature
	16	Water skin density [105]. Classical thermodynamics predicts a denser skin but diffraction revealed a 5.9 % skin O–O elongation or 15.6 % density loss at 25 °C. In contrast, the skin O–O for liquid methanol contracts by 4.6 % associated with a 15 % density gain [115]
	17	Water skin refractive index [84]. The refractive index of water (measured at $\lambda = 589.2$ nm) skin is higher than it is in the bulk
	18	Droplet floating and dancing [88, 116]. Water droplet does not emerge immediately into the water but it dances continuously at the skin of the bulk for rounds
	19	Slipperiness of ice [117]. Ice skin is one of the slipperiest of ever known. The slipperiness of wet surfaces is greatest for hydrophilic/hydrophobic contact but least for hydrophilic/hydrophilic interaction [118]
	20	Supercooling and superheating [119, 120]. Water nanodroplets or bubbles undergo superheating at melting and supercooling at freezing, whose extent is droplet size dependence. A 1.2 nm sized droplet freezes at temperature below 172 K and the monolayer skin melts at 320 K
	21	Identical H–O phonon frequency for water and ice skin [105]. The skin of −20 °C ice shares an identical H–O frequency 3450 cm^{-1} with the skin of 25 °C water, in contrast to the bulk values of 3200(water)/3150(ice) cm^{-1} and 3650 cm^{-1} for the H_2O monomer in gaseous phase
Impurity and hetero-coordination	22	Isotope effect on phonon relaxation [88]. Deuterium ^2H replacement of H attenuates the intensity and redshifts the frequencies of all Raman phonons
	23	Superhydrophobicity, superfluidity, superlubricity, and supersolidity at contacting interface [121]
	24	Hydrophobicity/hydrophilicity transition [88, 102]. An air gap presents between water and hydrophobic contacts. The curved water skin is thermally more stable. Hydrophilic contact creates exclusion zone that is gel-like, separating charges, and excludes organisms and impurities. Water–protein interface exhibits two characteristic life times

(continued)

(continued)

Stimulus	No.	Mysteries
Aqueous and capacitor electrification	25	Hofmeister series [122, 123]. Anions and cations change the surface tension of the solution and the solubility of proteins in a sequential order of salts. Salts also modulate the critical temperatures for water phase transition and the gelation time of solutions
	26	Solute phase transition—critical pressures, temperatures, and gelation times [124, 125]. Charge addition and electric bias modulate the temperatures of ice melting and water freezing
	27	Armstrong effect—Water Bridge [126]. Water bridge can form across two beakers under 10^6 V/m field and sustain for hours under electric bias under the ambient temperature
Energy absorption, retention, transportation and dissipation	28	Mpemba paradox [127, 128]. Hotter water freezes faster than its cold, which is in counter-intuitive of Newton's law in thermal transportation
	29	Radiation absorption [129]. Water exchanges heat and gases with the environment and absorbs electromagnetic radiation and acoustic signals in a long-range manner
	30	Electromagnetic field modulated temperatures for melting and freezing [124, 130]. These critical temperatures vary with the intensity of the field. Superposition of fields generated by different sources may effect oppositely, such as solution Water Bridge [131] and soil wetting by aqueous solution [132]

Water is also a "universal solvent". Many minerals and vitamins can be transported throughout the body after being dissolved. Dissolved sodium and potassium ions are essential for nerve impulses. Water also dissolves gases, such as oxygen from the air, enabling water-living animals to use oxygen. Water, a major component of blood, also dissolves carbon dioxide, a waste product from energy production in all cells, and transports it to the lungs, where it can be breathed out. However, water is repelled by oily compounds, so our cells have membranes made of these. Many of our proteins have partly oily regions, and they tend to fold together, repelled by the surrounding water. This is partly responsible for the many and varied shapes of proteins. These shapes are essential for carrying out functions vital to life.

1.4   Challenges and Objectives

Philip Ball announced in 2014 in a special issue of the *Europe Physics Journal* [129]: No one really understands water. It's embarrassing to admit it, but the stuff that covers two-thirds of our planet is still a mystery. Worse, the more we look, the

more the problems accumulate: new techniques probing deeper into the molecular architecture of liquid water are throwing up more puzzles.

Although some of those puzzles—such as the tetrahedral coordination of a molecule in bulk water—seem now to be within reach of a resolution, other important questions, such as the nature of hydrophobic hydration and the existence of a second critical point in supercooled water [101], remain unanswered. More pertinent than the fact that some basic properties of water and hydration are still not understood, however, is the fact that many facets of water's behavior can now be seen to be inadequately accounted for by any picture that regards the liquid state as being the sum of its parts. That is to say, the phase, solvation and wetting behaviors of the liquid are not determined in a transparent way from the properties of the individual water molecules, but emerge from their collective interaction, over many length scales, in ways that can be highly contentious and context-dependent.

The difficulties in understanding liquid water are generally attributed to the cooperative hydrogen bonding, i.e., the binding energy of two H-bonded molecules is modified by the presence of a third molecule and nuclear quantum effects [133, 134]. Such effects occur because the proton is so light that classical mechanics can no longer adequately describe properties like spatial dispersion of the hydrogen positions, nuclear tunneling, zero-point energy and, naturally, quantization of nuclear motions.

According to Ball and Eshel [129], it is often insufficient to think only in terms of local interactions for understanding water's properties; one must take a systemic and holistic view, considering the ways in which water modifies its own tendencies in responding to its environment. Such a picture might be needed to explain multiple phenomena presented. We are at in the midst of a shift in our perception of water—a shift from the current molecular—level based approach (which focuses on the behavior of individual or small numbers of molecules) towards a new, systemic view of water. In this picture, water is perceived as an active substance that responds adaptively to external and internal constraints and signals. These responses can have profound effects on substances immersed in water, and in particular on the functioning of biological constituents, from molecules to living cells.

According to Pauling [106], the nature of the chemical bond bridges the structures and properties of crystals and molecules. Therefore, the interatomic bond and the performance of electrons are the starting point of consideration [107]. For other unusual substance, one bond represents all on average, but for water and ice, the represent hydrogen bond contains two parts—the O:H nonbond and the H–O polar-covalent bond. These two parts respond to perturbation cooperatively and differently associated with electron entrapment and polarization, which differs water and ice from other substance in physical properties.

Therefore, resolving mysteries of water ice regarding its structure order, O:H–O bond local potentials, and its physical anomalies and their interdependence under various stimuli is the key challenge. Bond relaxation in length and energy and the associated bonding charge entrapment and nonbonding electron polarization in the long-range responding to applied stimuli such as mechanical compression, molecular undercoordination (with fewer than four nearest neighbors as in the bulk),

thermal, electric, and magnetic excitation and radiation, for instance, all of which change the structure and property of a substance in the respective manner [107].

In modeling consideration, it is proper to formulate the intramolecular interaction and the intermolecular interaction dependently. Long-range responding to external stimulus is necessary because of the high sensitivity and fluctuation of water liquid. Examination of the statistical mean of all the correlated quantities with certain rules and multiple means is more realistic and meaningful than focusing on the instantaneous accuracy of a certain quantity at a point of time for a strongly correlated and fluctuating system. Modeling hypotheses and expectations, numerical calculations, and experimental measurements should be consistent and correlated in addressing the change of multiple properties for the highly correlated and fluctuating water. Alternative ways of thinking and multiple means of approaching are necessary to deal with these difficult issues effectively.

This volume aims to deal with the correlation between the anomalous behavior of water ice and the relaxation dynamics of the O:H–O bond under afore-mentioned stimuli from the perspective of hydrogen bond cooperative relaxation. Extending the Ice Rule of Bernal and Fowler [135] suggests a tetrahedral block that contains two H_2O molecules and four O:H–O bonds. This block unifies the length scale, geometric configuration, and mass density of molecular packing in water ice. This extension also clarifies the flexible and polarizable O:H–O bond that performs like a pair of asymmetric, coupled, H-bridged oscillator pair with ultra-short-range interactions and memory effect as well as extraordinary recoverability. Coulomb repulsion between electron pairs on adjacent oxygen anions and the disparity between the O:H and the H–O segments relax the O:H–O bond length and energy cooperatively when responds to perturbation.

The developed strategies have enabled clarification of origins of the following observations from the perspective of O:H–O segmental relaxation and associated bonding electron entrapment and nonbonding electron polarization:

(1) Pressure-induced proton centralization, ice regelation, and phase transition-temperature depression;
(2) Thermally-induced four-region oscillation of the mass density and the phonon frequency over the full temperature range;
(3) Molecular-undercoordination-induced supersolidity that is elastic, hydrophobic, thermally stable, with ultra-low density. The supersolid skin is responsible for the slipperiness of ice, the hydrophobicity and toughness of water skin, and the bi-phase structure of nanosized droplets and bubbles.
(4) Electrification of the O:H–O bond by the electric fields of solute point charge and a capacitor results in the Hofmeister series and the Armstrong water bridge.
(5) Magnetification of water dipoles by the Lorentz force: a magnetic field rotates the dipole at transitional motion and transits the rotating dipoles.
(6) O:H–O bond absorbs, retains, transmits, and dissipates all sorts of energy in a long-range manner with memory, which resolve the Mpemba paradox and the crystal pattern sensitivity of ice formation under perturbation.

However, there some limitations faced by conventional approaches. For instance, discriminating the cooperative relaxation of the O:H and the H–O segment is beyond the scope of neutron or X-ray diffraction that probes the O–O Radial Distribution Function (RDF) with structure factors. The relaxation of the stronger H–O bond dictates the electronic binding energy shift in all bands as the O:H energy is smaller than the tolerance level. The O K-edge absorption and emission spectroscopies collect information about the energy shift of the deeper O 1s core band and the upper valence band. The asymmetrical, ultra-short range interactions and the strong localization and polarization become dominance in quantum computations. London dispersion or the interaction between dipoles and the dipole-induced spontaneous dipoles also comes into play in determining the performance of water and ice.

Therefore, an interplay of density functional theory (DFT) and molecular dynamics (MD) calculations, Raman and IR phonon spectroscopy, XPS measurements has enabled clarification, correlation, formulation, and quantification of multiple best-known puzzles demonstrated by water ice. A Lagrangian solution has enabled mapping the landscape of the asymmetric potentials for the O:H–O bond at relaxation. The H–O bond relaxation shifts the melting point, O 1s binding energy, and high-frequency phonon whereas the O:H relaxation dominates polarization, viscoelasticity, and the O:H dissociation energy. Solving the Fourier thermal fluid transportation equation with adequate initial-and-boundary conditions would clarify the historical mystery of heating "emission–conduction–dissipation" in the Mpemba paradox. Attainments made in so far have thus verified our hypothesis and expectations consistently.

1.5   Scope of this Volume

This volume starts with a brief overview in Chap. 1 on the challenge, significance, and status in understanding the structure order, phase diagram, physical anomalies demonstrated by water and ice. Besides a brief introduction of the history background and the known structure models, Chap. 2 shows the essentiality of O sp^3-orobital hybridization that laid the foundation for the quasi-tetrahedron geometry for a water molecule interacting with hydrogen atoms through two bonding electron pairs and two nonbonding lone pairs. An extension of the quasi-tetrahedron geometry turns out an ideal tetrahedral block containing two H_2O molecules and four O:H–O bonds. This building block unifies the size, separation, structure order and mass density of molecules packed in water and ice.

Chapter 3 is focused on the flexibility and polarizability of the O:H–O bond that performs like an asymmetric, coupled, H-bridged oscillator pair with ultra-short-range interactions. The O:H–O bond disparity and the O–O Coulomb repulsion discriminate water and ice from other usual materials in responding to stimulus. The O:H–O bond responds to various stimuli cooperatively associated

with relaxation and polarization, which determines all detectable properties of water and ice including the phonon frequency, electron entrapment and polarization, reactivity, surface stress, solubility, thermal stability, viscoelasticity, etc.

Chapter 4 analyzes the phase diagram of water and ice from the perspective of O:H–O bond relaxation dynamics. The phase boundaries are categorized into four types according to their T_C−P_C slopes. Reproducing the negatively sloped boundaries for the Liquid-Quasisolid and VII/VIII boundaries confirmed that the H–O bond energy dictates theses transition, which results in the 3.97 eV H–O bond energy; reproduction of the liquid-vapor phase boundary turns out the pressure dependence of the O:H length. The XI–I_c phase boundary of constant T_C indicates that the O:H–O bond does not respond to thermal excitation and the VII/VIII–XI boundary of constant P_C suggests that the O:H and H–O segments relax identically under compression at this boundary. Seven paths of Raman probing confirmed the expected O:H–O bond relaxation dynamics crossing the phase diagram except for the "no man's land" regime that is subject to further verification.

Chapter 5 shows the mapping of the asymmetrical potential paths of the O:H–O bond at elongation and contraction, which further confirms the universality and adequateness of the O:H–O bond cooperativity notion. Lagrangian mechanics is hither to the most efficient means solving the O:H–O bond oscillator pair dynamics, which turns the known segmental length and vibration frequency into the respective force constant and cohesive energy, enabling the mapping of the potential paths.

Chapter 6 resolves the behavior of ice under compression, typically, the effect of regelation discovered by Michael Faraday in 1859. Compression shortens the O:H bond and stiffens its phonon while the H–O bond, as the slave, responds to compression oppositely, towards O:H–O length symmetrization. The softened H–O bond dictates the melting temperature of quasisolid ice so the regelation occurs. The resolution of regelation evidences the extraordinary recoverability of the O:H–O bond and the dispersivity of the quasisolid phase boundary.

Chapter 7 deals with O:H–O bond thermal relaxation over the full temperature range. Because of its disparity, each segment of the O:H–O bond has its own specific heat characterized by its Debye temperature and the thermal integral. The Debye temperature varies linearly with the characteristic phonon frequency and the integral is proportional to the segmental cohesive energy. The superposition of the specific heat curves defines two intersecting temperatures that divide the full temperature range into the liquid, quasisolid, solid I_{h+c}, and the XI phases with different specific heat ratios. The segment of relatively lower specific heat follows the regular rule of thermal expansion and the other part relaxes oppositely, so the mass density of water and ice oscillates over the full temperature range. This mechanism is completely different from the thermal expansion of other normal materials. The H–O cooling contraction and O:H expansion in the quasisolid phase elongate the O:H–O bond, which makes ice floats.

Chapter 8 resolves anomalies demonstrated by water molecules with fewer than four nearest neighbors presented in clusters, hydration shells, skins, and ultrathin

films. Particular attention is given on verifying the undercoordination induced supersolidity and quasisolid phase dispersivity. The supersolid skin that is elastic, hydrophobic, less dense, and thermally more stable lubricates ice and toughens water skin. The boundary dispersion of the quasisolid phase results in phenomena of "supercooling" at freezing and "supercooling" at melting of nanodroplets and nanobubbles.

Chapter 9 extends the skin supersolidity to the superlubricity of ice, dry and wet contacts, in terms of phononic elasticity and electrostatic repulsivity. The supersolidity depresses the O:H phonon frequency and enhance its vibrational magnitude, which ensures the phononic elasticity; the nonbonding electron polarization due to H–O contraction ensures the electrostatic repulsion at the contacting interface. The electrostatic repulsivity and phononic elasticity claim the responsibility for the superlubricity of ice, wet and dry contacts with involvement of polarized lone electrons or electron lone pairs.

Chapter 10 extends the supersolidity to liquid skin, which also applies to the superhydrophobicity for water droplet on solids, superfluidity for microchanels, and supersolidity for solid ^{4}He. The transition between superhydrophobicity and superhydrophilicity by UV radiation or plasma sputtering evidence the essentiality of the skin dipoles in the wetting/non-wetting transition, which also elaborates Wenzel-Cassie-Baster's notion for superhydrophobicity/superhydrophilicity enhancement by nanofabrication as the enhancement of energy quantum entrapment that raises the elasticity and the subjective polarization that enhances the repulsivity. Quantum entrapment dictates hydrophilicity but polarization dictates hydrophobicity.

Chapter 11 resolves the Mpemba paradox both experimentally and numerically, showing the essentiality of O:H–O bond memory and water skin supersolidity. Resolving the Fourier thermo-fluid dynamics revealed the essentiality of skin supersolidity that raises the local thermal conductivity favoing heat outward flow; experimental observations evidence the O:H–O bond memory that entitles the O:H–O bond emits energy at a rate proportional to its initial storage. The Mpemba effect only happens at the non-adiabatic source-drain interface in this "source-path-drain" cycling system, which is very sensitive to experimental conditions.

Chapter 12 deals with the O:H–O bond electrification by fields of solute ions in terms of molecular site, solute type, solute concentration, and temperature dependence of the O:H–O bond relaxation dynamics in aqueous solutions of salts, bases, and acids. Solute ions provide short-range electric fields that align, stretch, and polarize water molecular dipoles. Quantum fragilation due to the excessive H^+ on hydronium and quantum compression due to the additional lone pair on hydroxide formation resolve, respectively, the performance of acid and base solutions. Focus was given on the local bond stiffness, order of molecular fluctuation and the phonon abundance with multiple discoveries. For instance, electrification has the same effect of molecular undercoordination on relaxing and polarizing the O:H–O bond but the ionic effect proceeds throughout the solution. Molecules in the hydration shells are thermally more stable than those in the bulk or the H–O radical.

Chapter 13 discusses the interdependence of phonon frequencies, H–O phonon lifetime, solution viscosity, and skin stress, which forms the key component of

Hofmeister series—salt modulates the skin stress and the solubility of protein of the solution. The blueshift of the H–O phonon is associated with longer life, higher viscosity, and lower order of molecular fluctuation. Salts and bases raise but acids lower the skin stress of the solution.

Chapter 14 extends the salting effect to the conditions for phase transition of the solution—critical pressures, critical temperatures, and regelation times. Electrification stiffens the H-O phonon, lengthens the O:H-O bond, depresses the freezing temperature and elevates the melting point by dispersing the boundary of the quasisolid phase. High-pressure icing of the ambient solution conforms that compression recovers the deformed solvent O:H–O bond with excessive pressures transiting the solution into ice VI and then into ice VII. The additional pressure is solute concentration and type dependent, following the Hofmeister series. However, the NaI concentration increase has the same effect of heating on the phase transition under compression.

Chapter 15 extends the solute electrification to the long-range field of a capacitor with and without leaking and the combination of electric fields from different sources. The electrified quasisolidity and skin supersolidity enable the suspension of Armstrong's floating Water Bridge. Aqueous solutions can hardly form a Water Bridge because the cancellation of the electric fields of the solute ions and the capacitor. The cancellation effect of combined electric fields also promotes soil wetting by aqueous solution. O:H–O bond electrification by the opposite fields of the soil particles and the solutes reduces the viscosity of the solvent to an extent that is lower than it is under either field alone.

Chapter 16 deals with some miscellaneous issues on the basis of the established premises. These issues include the multiple field effects, droplet charging, energy exchange and absorption, and isotope effect on phonon relaxation, dielectric relaxation, negative thermal expansion, exclusion zone, magnetification, and the generality of the O:H–O bond in other lone-pair involved systems, etc.

Chapter 17 introduces strategies for probing and analyzing and their advantages and limitations. With the aid of X-ray and neutron diffractions, electron spectroscopies, quantum computations, phonon spectrometrics reveals the O:H–O bond relaxation dynamics in segmental length, energy, bond angle, H–O lifetime and viscosity, solubility, thermal stability, skin stress, of water and ice. This chapter also correlates these properties in terms of bond length, bond energy, and polarization.

This volume ends with Chap. 18 summarizing the gained understandings in terms of sixty laws for water and ice. Progresses evidence the efficiency and validity of ways of thinking, strategies of approaching, and the comprehensiveness of the present understandings—one notion for multiple myths.

In each chapter, we start with a digest of the challenge and clarification of a topic of specific concern, followed by historical background information for scientific popularization. We present then quantitative resolution based on experimental observations and numerical computations and followed by possible insight extension to related issues.

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