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.

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