Chemical physics of water

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There is hardly any aspect of our lives that is not profoundly influenced by water. From climate to commerce and agriculture to health, water shapes our physical environment, regulates the major energy exchanges that determine climate on Earth, and is the matrix that supports the physical and chemical processes of life as we know it (1). The chemistry and physics of water, which underlie all of its uses, its necessity for life, its effects on other molecules and on the environment, are very active areas of research at the present time. So, why is this? Surprisingly, there are major gaps in knowledge and understanding that persist despite this substance's ubiquity and central importance. This Special Feature on the Chemical Physics of Water contains 10 articles and aims to be a representative cross-section of current frontier research in this field. Articles include both Perspectives and original research contributions. The pioneering paper by Bernal and Fowler dealing with the chemical physics of water appeared in 1933 (2). It focused on understanding the anomalous properties of water and its ionic solutions from a molecular perspective, inspired by the newly minted quantum mechanical theory of electronic structure. Since that time, theory and computer simulation have become established as essential complements to laboratory experiments in unraveling the crucial role of water in an array of everyday processes and phenomena, spanning from the chemistry of life to the physics of wetting–dewetting transitions. The nature of intermolecular interactions in water remains a perennial topic of interest, with insightful articles appearing regularly (3, 4). Accordingly, this topic of research, although central to the chemical physics of water, has not been included in the present collection of articles.

Much of biology happens in an aqueous medium, and it is now widely accepted that water is an active participant in mediating and enabling biological function. However, important aspects of water's effect on the molecules of life remain poorly understood. The first article (5) in this collection is a Perspective by Philip Ball that discusses the special features of water that are key to its function in cell and molecular biology: a richness of roles that are a consequence of its status as a complex, structured liquid that is also a polar, protic, and amphoteric reagent.

Water's anomalous properties become increasingly pronounced in the supercooled regime, when the liquid is metastable with respect to crystallization. One possible explanation of this behavior involves the existence of a metastable liquid–liquid transition terminating at a critical point. This hypothesis has been the subject of vigorous debate among theoreticians, and its experimental verification or falsification underlies ongoing work by a number of leading groups. Implications include ice nucleation in the atmosphere and the nature of water in interstellar space. The second article (6) is a Perspective by Handle, Loerting, and Sciortino that provides a valuable overview of current knowledge and open questions in this very active area of water research.

The relationship between water structure and the kinetics and thermodynamics of self-assembly of complex hydrophobic surfaces is poorly understood. Implications include protein folding and the ultimate fate of apolar pollutants in water. The third article, by Xi et al. (7), deals with hydrophobicity of proteins and nanostructured solutes and how this is governed by topographical and chemical context.

Cells are micrometer-sized assembles of nature's nanoscale machines. Cell walls are composed of lipid bilayers with embedded membrane proteins. The interior of cells also contains encapsulated functional units, so the notion of buried interfaces is of paramount importance. Simpler models of the aforementioned biological constructs are provided by surfactant solutions. The fourth article in this collection is by Hensel et al. (8) and deals with the characterization of nanoemulsion surfaces in water–surfactant AOT systems.

The thermodynamic, transport, and structural properties of bulk water are affected in profound and incompletely understood ways by nanoscale confinement. Implications include energy storage, ice nucleation in clouds, desalination, and even replication of the influenza A virus inside infected cells. The fifth article in this collection, by Thomaston et al. (9), concerns the so-called M2 proton channel of the influenza A virus. The latter is in effect a proton

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injection machine that is responsible for acidifying flu virions that are inside infected cells, which in turn triggers replication of the virus. Thus, understanding the structure and function of this machine is vital to designing strategies to inhibit viral replication. The article by Thomaston et al. presents X-ray free-electron laser high-resolution structures of room temperature water networks, and insights into the proton conduction mechanism, occurring in the M2 channel.

The next pair of research articles (10, 11) deal with ions at aqueous interfaces. Major unanswered questions remain on the mechanism of selective ion adsorption at such interfaces, including, for example: What is the surface charge of neutral water droplets? There are important implications on an array of phenomena, ranging from ice nucleation at atmospherically relevant conditions to biological self-assembly and more. The sixth article, by Perrine et al. (10), deals with specific cation effects at aqueous solution–vapor interfaces as observed in experiments and complementary computer simulations. Importantly, this study identifies surfactant-like behavior of the lithium ion. The seventh article, by McCaffrey et al. (11), addresses ion adsorption to aqueous interfaces and it compares and contrasts the graphene/water and air/water interfaces.

The next three articles (12–14) deal with water at metal surfaces, catalysis in water, and water splitting, respectively. Understanding the behavior of water at catalytic (including metallic) surfaces is a central theme underlying much research on renewable sources of energy, including solar energy conversion by water splitting. The article by Kattirtzi, Limmer, and Willard (12) addresses the microscopic dynamics of charge separation at the aqueous electrochemical interfaces, a phenomenon that underpins many aspects of energy science. The article by Costentin and Nocera (13) deals with self-healing catalysis in water, and the Perspective by Rao and Dey (14) concerns solar thermochemical splitting of water to generate hydrogen.

Together, the 10 articles of this Special Feature highlight the diversity of contemporary topics in which water plays a critical role. Astonishingly, infection by the influenza virus (and hence the possibility of catastrophic pandemic flu) as well as the source of energy that could ensure the sustainability of life on planet Earth, both involve the disproportionation of water molecules. The topics presented herein touch on some of the grand challenges facing society today, and aim to convey to the reader the current excitement in this field.

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4 Chen M, et al. (2017) Ab initio theory and modeling of water. *Proc Natl Acad Sci USA* 114:10846–10851.

5 Ball P (2017) Water is an active matrix of life for cell and molecular biology. *Proc Natl Acad Sci USA* 114:13327–13335.

6 Handle PH, Loerting T, Sciortino F (2017) Supercooled and glassy water: Metastable liquid(s), amorphous solid(s), and a no-man's land. *Proc Natl Acad Sci USA* 114:13336–13344.

7 Xi E, et al. (2017) Hydrophobicity of proteins and nanostructured solutes is governed by topographical and chemical context. *Proc Natl Acad Sci USA* 114:13345–13350.

8 Hensel JK, et al. (2017) Molecular characterization of water and surfactant AOT at nanoemulsion surfaces. *Proc Natl Acad Sci USA* 114:13351–13356.

9 Thomaston JL, et al. (2017) XFEL structures of the influenza M2 proton channel: Room temperature water networks and insights into proton conduction. *Proc Natl Acad Sci USA* 114:13357–13362.

10 Perrine KA, et al. (2017) Specific cation effects at aqueous solution–vapor interfaces: Surfactant-like behavior of Li^+ revealed by experiments and simulations. *Proc Natl Acad Sci USA* 114:13363–13368.

11 McCaffrey DL, et al. (2017) Mechanism of ion adsorption to aqueous interfaces: Graphene/water vs. air/water. *Proc Natl Acad Sci USA* 114:13369–13373.

12 Kattirtzi JA, Limmer DT, Willard AP (2017) Microscopic dynamics of charge separation at the aqueous electrochemical interface. *Proc Natl Acad Sci USA* 114:13374–13379.

13 Costentin C, Nocera DG (2017) Self-healing catalysis in water. *Proc Natl Acad Sci USA* 114:13380–13384.

14 Rao CNR, Dey S (2017) Solar thermochemical splitting of water to generate hydrogen. *Proc Natl Acad Sci USA* 114:13385–13393.