Water at functional interfaces

Shekhar Garde and Mark L. Schlossman, Guest Editors

Water is, perhaps, the most important material known to humankind—fascinating even in its pure state for the range of anomalous properties it displays. There has been an increasing realization that understanding the behavior of water at interfaces—from those of small solutes to biomolecules and polymers to inorganic materials and metals—holds the key to understanding disparate phenomena, from self-assembly, biofouling, and catalysis to corrosion. In this issue of *MRS Bulletin,* we highlight recent advances in understanding the molecular behavior of water near a range of interfaces of interest to the broader materials community.

Introduction

That water is a solvent medium, described simply as a continuum dielectric medium, is an old perspective. The molecular nature of water, its asymmetric charge distribution, its geometry, and the resultant tetrahedral hydrogen-bonding network together contribute to the fascinating behavior of water in its pure state, as well as in solution and near various complex interfaces.[1,2] Numerous fundamental questions persist in our understanding of molecular-scale interactions of water with interfaces and their consequences for natural and synthetic systems.[3] These include the following: How do the structure and dynamics of water respond to the chemical and topographical context provided by solutes, biomolecules, and organic/inorganic materials? For example, biomolecular surfaces illustrate a complex patterning of hydrophilic and hydrophobic regions whose importance is far from fully understood. What are the consequences of the altered structure and dynamics of water on water-mediated interactions and assembly? For instance, assembly of solutes in an aqueous environment often requires removal (i.e., desolvation) of hydrated water molecules prior to solute aggregation. Recent computer simulations demonstrate that barriers to desolvation are lowered near hydrophobic interfaces, providing for preferential solute aggregation at the interface (**Figure 1**). Finally, what are the implications of water structure and dynamics for interfacial reactions and catalysis? As an example, preferential interactions of ions with water

interfaces influence molecular conformations that ultimately determine molecular reactivity (**Figure 2**). Given that interfaces are the most important motif in bio- and nanotechnologies, answering the previous questions is central to many applications. To this end, a deeper understanding is emerging from a combination of state-of-the-art experiments and theory as well as molecular modeling and simulations.

Articles in this issue

Stable and transient hydrogen-bonding interactions between water molecules and the molecular and particulate solutes that are usually present in aqueous media have numerous consequences for assembly and reactions within the aqueous environment. Although many experimental techniques can probe the macroscopic consequences of this underlying molecular structure and dynamics, only a few can reveal these effects on a molecular length scale.[4] These techniques include high-resolution scattering of x-rays and neutrons, specialized spectroscopy techniques, and scanning probe microscopies. In their article in this issue, Fenter and Lee review x-ray scattering studies of water ordering at solid surfaces, focusing on the angstrom-scale organization of water molecules at mineral–water and graphene–water interfaces as well as the effects of adsorbed ions on this organization. They quantify the hydration of surfaces with different characteristics, including those that are charged, uncharged, reactive, and ionic.

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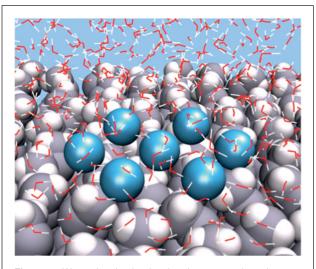
Figure 1. Water desolvation barriers between solutes in bulk water are reduced near hydrophobic surfaces, leading to preferential assembly at the surface. Reprinted with permission from Reference 11. © 2013 American Chemical Society.

Strong hydrogen–bonding interactions in water coupled with specific interactions with hydrophilic, hydrophobic, or ionic interfaces lead to the organization of water molecules both perpendicular and parallel to the surface, with a specific structure determined by the surface characteristics. This information along with details of hydration of charged/ionic surfaces forms the basis for understanding the reactivity and chemical interactions of these surfaces.

It is interesting to note that the data from Fenter and Lee's experiments do not display dramatic dewetting near a hydrophobic graphene–water interface; instead, layering of water is observed extending out to about 1 nm from the surface, qualitatively consistent with the latest simulation data and theoretical understanding of the hydration of extended hydrophobic surfaces. The availability of such experimental data on several interfaces should be of tremendous interest to the molecular

modeling and simulations community to test their methods, models, and force fields.

In this issue, Striolo reviews computational studies of interfacial water at solid surfaces, including predictions of hydrogen–bonding networks that result from the specific geometry and chemistry of surface adsorption sites. Comparisons between computations and experiments such as those presented by Fenter and Lee clarify our understanding of the time-averaged molecular structures that result from the interactions of water with real surfaces. Dynamic properties of water near surfaces are also influenced by the structure of interfacial water. Such effects include variations in diffusion within and perpendicular to the surface, as well as dynamic fluctuations that vary with the chemical and physical nature of the surface. As discussed by Striolo, these structural and dynamical features of interfacial water influence the self-assembly of surfactants, proteins, and nanometer-sized particles in aqueous environments.

In the midst of self-assembly, as the surfaces of a nanoparticle and protein approach each other, regions of water confined on the nanometer scale are created and possibly stabilized or destroyed as self-assembly proceeds. The behavior of nano-confined water plays a role in the fate of this self-assembly process and has consequences for the development of nanotechnology in many areas. The choice of ligand that forms a corona about the metal core of a nanoparticle determines its interactions with water, subsequently affecting its interactions with proteins. In their article in this issue, Moyano et al. review studies in which the charge and hydrophobicity of nanoparticle surfaces were selectively varied to alter the nanoparticle–protein interaction. Isothermal titration calorimetry provides insights into the thermodynamic role of water in this interaction. For some applications, it is just as important to ensure that proteins do not bind to nanoparticles as it is to ensure that they do bind for other applications. Moyano et al. discuss both cases, providing routes to the development of technologies in the areas of sensing, nanocomposite biomaterials, and protein delivery that benefit from protein binding to nanoparticles, as well as stealthy nanoparticles that avoid interactions with proteins to address critical challenges in medical nanotechnology. Fundamental knowledge emerging from such studies could be combined with the engineering of proteins to design new protein–nanoparticle systems for bionanotechnology applications.

Naturally abundant clay materials consist of layered particulates. Water in the interlayers and in interparticulate nanopores influences important functions of clay, including its ability to contain and filter environmental pollutants. Water molecules confined in tight spaces and nanopores are subject to the interactions imposed by solid surfaces described in the articles by Fenter and Lee and by Striolo, but

Figure 2. Molecular dynamics simulations of short peptides, with neutral (left) and charged end-groups (right), illustrate conformational changes that result from preferential ion–ion interactions near a water liquid–vapor interface. Amino (N) and carboxyl (C) termini of the peptides are marked in the figure. The peptides are amphiphilic because the hydrophobic leucine (L) groups prefer to position themselves near the vapor phase. Charged groups of the $^+GL_5G^-$ peptide submerge into the water, thereby pulling the peptide to the liquid side of the interface. The yellow mesh illustrates the Willard-Chandler instantaneous interface. Reprinted with permission from Reference 12. © 2014 PNAS.

also to the additional constraint of a second, neighboring surface. Rotenberg describes the results of computer simulations and experimental studies on the swelling of clays by interlayer water, as well as the distribution and transport of water and ions in clay nanopores.

Chemical heterogeneity is characteristic of naturally occurring surfaces and may play a decisive role in their functionality. In the case of biological surfaces, such as those of proteins, or geological surfaces, such as the clays discussed by Rotenberg, the heterogeneity occurs on the atomic scale. Although it is possible to characterize the hydrophilic or hydrophobic properties of heterogeneous surfaces by experimental techniques that average over large areas of the surface, important aspects of site-specific behavior are lost in such characterizations. For biomolecules, hydropathy scales are frequently used to characterize the local hydrophobicity of their surfaces. These scales, however, do not account for chemical and topographical context provided by the protein surface, and are, therefore, not predictive. Recent theoretical considerations and simulation studies suggest that quantifying the behavior of water in the vicinity of the proteins—specifically, local water density fluctuations and related measures—provides the solution to this challenging problem.[5–7] Density fluctuations are enhanced near large hydrophobic patches and quenched near hydrophilic or ionic patches.[5,8] Naturally, one expects the local dynamics of water also to be related to such context-dependent measures. Song et al. discuss an experimental approach, namely, Overhauser dynamic nuclear polarization (ODNP), that can quantify site-specific dynamics of water molecules and relate these dynamics to the context-dependent hydrophobicity/hydrophilicity of the underlying protein surface. They point out synergies involved in such interactions; for example, sulfonic acid groups and fluorinated polymer surfaces in a Nafion fuel cell membrane fulfill complementary roles of retaining water to allow it to swell, yet limiting water binding to allow for transport.

The consequences of water ordering and dynamics near solid surfaces on molecular length scales lead to surface-tension and wetting-driven phenomena on larger length scales. As one example of the latest advances in this area, in their article in this issue, Park and Lee describe the directed assembly of colloidal particles with complex geometries and surface chemistries. This article illustrates opportunities for self-assembly and interfacial interactions that go beyond the already fruitful studies of spherical nanometer- and micrometer-sized particles with uniform chemical compositions. Particles with anisotropic shapes and anisotropic surface chemistries, often referred to as Janus particles, provide for novel and controllable particle orientations at liquid interfaces. In addition to the electrostatic interparticle interactions that arise at the liquid–liquid interface between polar and nonpolar fluids, the subsequent influence of anisotropic particles on the nearby shape of the liquid interface also plays a role in tuning the interparticle interactions at the interface. Park and Lee demonstrate that these features can be used to generate complex, hierarchical structures of Janus particles in liquids. An enhanced understanding of water interactions at heterogeneous surfaces, combined with the design of particles with such surfaces, should lead to the ability to target and design specific hierarchical structures.

Conclusions

As the materials community looks to the future with a focus on learning from nature and incorporating elements of biological principles into materials design, it is clear that water will become an increasingly important "material." Although frequently characterized as a continuum dielectric in the past, it is now understood that the role of water goes beyond that of a solvation medium. Instead, the structure of water—its molecular packing, orientation, and organization, as well as its electronic structure—becomes central to understanding water-mediated interactions. Given the ubiquity of interfaces, this issue of *MRS Bulletin* addresses questions of how the structure and dynamics of water respond to the chemical and topographical context provided by the interface,[9,10] how these phenomena can be investigated by experiment as well as by theory and simulations, and what their implications are for self-assembly.

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