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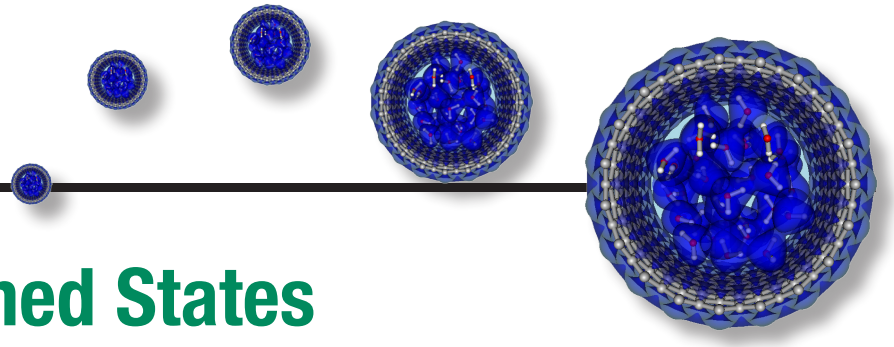

Water in Confined States

Collaborators at UC Davis, Lawrence Livermore National Laboratory, and UC Berkeley are defining a computational paradigm to simulate water at the nanoscale that can be applied to problems in both materials science (e.g., water in zeolites) and biology (e.g., water in contact with amino-acids and proteins). In 2007, the group determined the effect of the surface electronic structure on the properties of water confined states by prototypical hydrophobic substrates.

In the last decade, water in confined environments (Figure 1) has attracted considerable attention due to its relevance to many systems in several diverse fields of science, including biology, nanofluidic devices, inorganic materials, and geology. For example, in cell membranes, key phenomena taking place in aqueous solutions occur in confined geometry: proteins such as acquaporins are believed to transport water in a very fast way due to the presence of a channel in their secondary structure, where water is confined. In the field of material science, confined water is found in clays and cements but also in zeolites that are characterized by the presence of cylindrical pores with diameters as small as 7 Å. Zeolites have been widely investigated for their catalytic activity, and changes in the solvation properties of water molecules are expected to influence the thermodynamic equilibrium of solvent- driven reactions. Yet it is poorly understood how chemical reactivity is influenced under confinement.

An important general question on confined water concerns the influence of the confining medium and, in particular, the impact of the hydrophobic (hydrophilic) character of the confining surface on the structural, electronic, and dynamical properties of the liquid. Does a confined phase of water exist

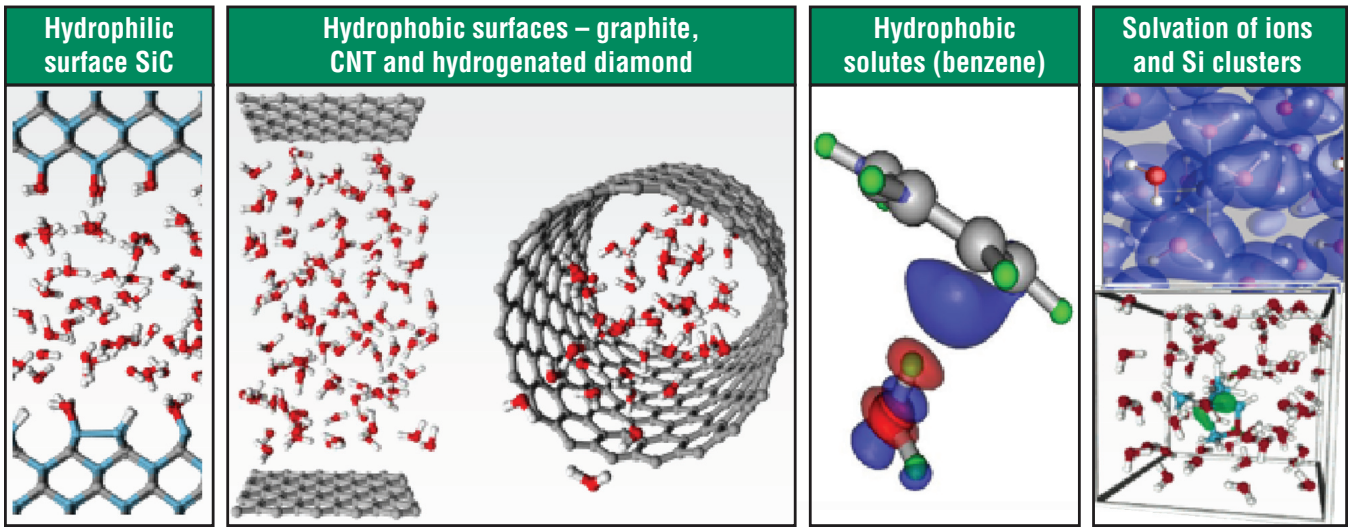

Figure 1. Examples of the various water confinement configurations.

that is independent of confining surfaces, or does the presence of an interface represent the dominant influence on the properties of the nanoscale liquid?

Experimentally, structural properties of water confined by both hydrophilic and hydrophobic media have been mostly studied by means of X-ray and neutron diffraction techniques, which give access to pair correlation functions. Interpreting experimental results on confined water has proven rather difficult in many instances, and firm conclusions based only on experimental observations are sometimes hard to draw. For this reason, atomistic simulations are often performed in parallel with experiments. Atomistic simulations represent a unique and powerful tool to describe, in a microscopically detailed way, changes in hydrogen bond patterns, molecular preferential orientation, and translational and rotational dynamics. Simulations can be employed to obtain low energy structures, or to calculate, through molecular dynamics (MD), statistical ensemble averages and thermodynamic quantities, and to extract quantities directly comparable to experiments (e.g., pair correlation functions, infrared spectra, bond lifetimes, etc.).

In 2007, the research team determined the effect of the surface electronic structure on the properties of water in confined states of graphene (a single planar sheet of bonded carbon atoms) and carbon nanotubes. These results would not have been possible without an INCITE allocation, which the team used to run calculations on IBM Blue Gene/L supercomputers at the Argonne Leadership Computing Facility and IBM's T.J. Watson Research Laboratory. Research conclusions stemmed from the results of several different sustained runs carried out over a number of months.

Next, the researchers will complete *ab-initio* simulations of ions in confined water, in particular, alkali and halogen ions in water confined in carbon nanotubes. They will also begin calculations of Raman spectra of water, in addition to infrared spectra simulations, as well as calculations of water confined by substrates with electronic properties different from those of graphite and nanotubes. Electric field calculations will use a new version of Qbox optimized to compute localized Wannier functions (i.e., quantities needed to do calculations in electric fields). Tests of the new version of the code are under way.

The Argonne Leadership Computing Facility and the INCITE program directly support the primary mission of DOE's Office of Advanced Scientific Computing Research to discover, develop, and deploy computational and networking tools that enable researchers in the scientific disciplines to analyze, model, simulate, and predict complex phenomena.

Recent Publications

1. M. Allesch, F. Lightstone, E. Schwegler, and G. Galli, "First principles and classical molecular dynamics simulations of solvated benzene," *J. Chem. Phys., 2007* (accepted).
2. M. Sharma, E. Schwegler, D. Donadio, and G. Galli, "Probing water in confined media: infrared spectra" (submitted).
3. G. Cicero, J. Grossman, E. Schwegler, F. Gygi, and G. Galli, "Enhanced diffusion and resilient hydrogen bonding of water in confined media" (submitted).

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