

MOLECULAR MODELING OF MATERIALS AND THEIR AQUEOUS INTERFACES FOR GEOCHEMICAL AND ENVIRONMENTAL APPLICATIONS

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Molecular-level understanding of mineral-water interfaces is extremely important for many geochemical, environmental, and technological problems, such as geological carbon sequestration, nuclear waste disposal in geological formations, heterogeneous catalysis, etc. Experimental nanoscale studies of such systems are not always feasible, and their results often require considerable interpretation in the efforts to extract quantitative surface-specific and confinement-specific information from the measurements. Molecular computer simulations significantly complement such efforts by providing invaluable atomic scale background understanding of the specific effects of mineral substrate structure and composition on the structure, dynamics and reactivity of interfacial and nano-confined aqueous phase.

Based on the successful development and implementation of the CLAYFF force field (Cygan et al., 2004), we have in recent years performed a series of molecular dynamics simulations of aqueous interfaces with several representative inorganic and organic nanoporous materials (Kalinichev et al., 2002, 2007, 2010, 2013; Morrow et al., 2013; Wang et al., 2004, 2006, 2009) in order to better understand and quantify the effects of the substrate composition and structure on the properties of interfacial and nano-confined aqueous fluids. Individual H₂O molecules and hydrated ions at interfaces simultaneously participate in several dynamic processes, which can be characterized by different, but equally important time- and length- scales. The first molecular layer of interfacial water at all substrates is often highly ordered, indicating reduced translational and orientational mobility of the H₂O molecules. However, this ordering cannot be simply described as “ice-like”, but rather resembles the behavior of supercooled water or amorphous ice, although with significant substrate-specific variations. These simulations results help to interpret on the fundamental molecular scale the experimental observations for the same systems from NMR, IR, X-ray, and neutron scattering, and other experimental techniques.

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