

**HYDRATION AND ASSEMBLY AT INTERFACES:  
THERMODYNAMIC, STRUCTURAL AND KINETIC STUDIES**

By

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## ABSTRACT

Many experimental and theoretical studies over the past few decades have shown that the aqueous environment is important for biological structure, stability and function and these are connected to the properties of vicinal water and are influenced by water-mediated interactions. Various water-mediated interactions such as hydrophobic, electrostatics drive these processes. Out of these, characterization of hydrophobic interactions at the molecular level has gained substantial importance. A significant theoretical framework exists in literature for hydration and association of small hydrophobic solutes in various aqueous solutions, however, a molecular level understanding of hydration of interfaces is still lacking. The primary goal of this thesis is to understand and characterize hydrophobicity in various aqueous interfacial systems using the tools of computer simulations guided by physics and statistical mechanics.

Hydrophobicity is often characterized macroscopically by the droplet contact angle. Its molecular signatures have, however, remained elusive. Our results on hydration of realistic surfaces with a wide range of chemistries from hydrophobic ( $-\text{CF}_3$ ,  $-\text{CH}_3$ ) to hydrophilic ( $-\text{OH}$ ,  $-\text{CONH}_2$ ) show that the water density near weakly attractive hydrophobic surfaces (e.g.,  $-\text{CF}_3$ ) can be bulk-like or larger, and provides a poor quantification of surface hydrophobicity. In contrast, density fluctuations in their vicinity are enhanced and water-water correlations display characteristics similar to those near a vapor-liquid interface. Hydrophilic surfaces suppress density fluctuations and reduce the water-water correlation length in their vicinity. The normalized density fluctuations, probability of cavity formation, or the free energy of binding of hydrophobic solutes to interfaces correlate quantitatively with the macroscopic wetting properties and serve as excellent signatures of hydrophobicity. Our results suggest a potentially robust approach for characterizing hydrophobicity of more complex and heterogeneous surfaces of proteins and biomolecules, and other nanoscopic objects.

Vapor-liquid interface is characterized by long range correlations. We show that these long-range correlations are very sensitive to surface-fluid attractions and quench rapidly with increasing strength of attraction with the surface. Partially wetting surfaces,

thus, have only molecular-scale “short-range” correlations and these “short-range” correlations contain information about surface solvophobicity. These results are qualitatively same for for two completely different fluids (Lennard Jones and water) at very different state points suggesting that the underlying physics of these correlations is universal.

Additives and co-solutes are often present in aqueous solutions for various biophysical phenomena, therefore characterizing hydrophobicity or hydrophobic interactions in such systems is necessary to understand its consequences on stability and function of biomolecules. To this end, we carefully examine the effect of addition of Guanidinium chloride and other salts on hydrophobic interactions. A multi-parametric study in temperature, size and solute-solution attractions domain highlight how the balance between various interactions is altered and provide important insights into their effect on stability of biomolecules in these solutions. Kinetics of hydrophobic collapse is intricately linked to the conformational thermodynamics and dynamics of the solvent in these solutions and considerably slows down in Guanidinium solutions. Our work here provides a conceptual framework to understand thermodynamics, structure and dynamics of other complex biological self-assembly in these solutions.