WATER, ION, AND GRAPHENE: AN ODYSSEY THROUGH THE MOLECULAR SIMULATIONS

Yanbin Wang

ABSTRACT

Water is known as the most common and complicated liquid on earth. Meanwhile, graphene, defined as single/few layer graphite, is the first member in the 2-dimensional materials family and has emerged as a magic material. Interactions between water and graphene generate many interesting phenomena and applications. This thesis focuses on applying molecular dynamics (MD) simulation method, a powerful computational tool, for investigating the graphene-water interactions associated with various energetic and environmental applications, ranging from the wettability modification, species adsorption, and nanofluidic transport to seawater desalination. A key component of one domain of applications involves a third component, namely salt ion. The critical factor for comprehending the influence of the salt ions is the manner in which they interact with the air-water and graphene-water). This thesis attempts that and discovers a fundamentally new way in which the behavior of ions with the air-water interfaces should be probed. In summary, therefore, the thesis becomes a computational odyssey exploring the mysteries cocooned in the interactions between water, graphene, and ions.

In Chapter 1, we introduce the motivation and methods and the overall structure of this thesis. Chapter 2, we focus on how MD simulations connect the statistical mechanics theory with the experimental observations. Chapter 3, I conduct MD simulations to reveal that the droplet spreading on a nanopillared graphene surface is driven by a pinned contact line and bending liquid-surface dynamics. In Chapter 4, I then look into the interaction between a water drop and a holey graphene membrane, which is prepared by removing carbon atoms in a circular shape and can serve as catalyst carriers. Simulation results show that holey graphene membrane enhances water accessible area as compared to non-holey graphite. As the carbon atoms around pores lose bonds and become chemically active, the edges get spontaneously terminated by air-borne hydrophobic or hydrophilic groups. Accordingly, chapter 5 studies the effect of various terminations on water-holey graphene interactions, showing that water flows faster and more thoroughly through the membrane with hydrophobic terminations, compared to that with hydrophilic terminations. We also investigate the stability of laminar stacking of nano-porous pristine graphene sheets in an aqueous environment. The system is prepared by immersing two single-layer graphene sheets into pure water and 1 M sodium chloride solution, and then a pressure gradient is applied across the graphene membrane. To quantitively evaluate the stable interlayer distance between two sheets, we use the interlayer distance as the reaction coordinate to generate a potential of mean force map by thermodynamic integration and umbrella sampling methods. The results indicate that the hydrophobic effect is dominating the graphene sheet interaction regardless of the presence of ion pairs or pressure gradients, which means that recombination of graphene sheets to graphite is not a rare event and pristine nano-porous graphene membrane is not stable in an aqueous environment. The result is supported by the experimental observation that graphene oxide membrane rather than pristine graphene membrane is more stable in water and more suitable for seawater desalination. In chapter 6, simulations describe the generation of enhanced water-graphene surface area during the water-holey-graphene interactions in presence of an applied time-varying force on the water drop. In chapter 7, we focus on the ion-water interaction at the water-air interface to fully understand the fluidic dynamics during any seawater desalination. Our research revisits the energetic change while ion approaches water-air interface and shows that the presence of ion at the interface

enhances capillary-wave fluctuation. The mechanism is that the ion at the interface generates atomic level deformation, and the system smoothens the energetically unfavorable deformation through rising capillary wave with the longest available wavelength. Consequently, the mixing entropy of the system capillary waves reduces and makes contributions to the overall system free energy.

Advisory Committee:

Associate Professor Siddhartha Das, Chair

Associate Professor Amir Riaz

Associate Professor Peter Chung

Associate Professor Yifei Mo

Minta Martin Professor Liangbing Hu, Dean's Representative