

Multiscale Modeling of Electronic Polarization Effects in Interfacial Thermodynamics and Nanoscale Transport Phenomena

by

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Abstract

Molecular simulations, along with the tools of statistical mechanics, can provide essential mechanistic insights about the thermodynamic and transport properties of electrolytes at solid/water interfaces, which has broad applications in several scientific disciplines ranging from membrane science to biophysics and electrochemistry. At any solid/water interface, water being a polar solvent and salt ions being charged species, can exert strong electric fields which can in turn result in a significant electronic polarization of the solid. However, a fundamental understanding of the role of electronic polarization effects on interfacial thermodynamics and nanoscale transport has been largely lacking. In this thesis, a multiscale approach involving quantum chemical and classical molecular dynamics (MD) simulations is advanced to investigate the role of polarization effects, first at planar solid/water interfaces, and subsequently under nanoscale confinement, using 2D and 1D graphitic nanomaterials as model systems.

First, I investigated the nature of the intermolecular interactions of water with graphene, the two-dimensional analog of bulk graphite, utilizing quantum chemical simulations carried out using the symmetry-adapted perturbation theory (SAPT). The SAPT simulations are utilized to develop an all-atomistic polarizable force field to model the graphene-water interactions, and carry out MD simulations to investigate the role of electronic polarization effects on the contact angle of water on graphite (multilayer graphene). To this end, an extended dynamical approach based on the classical Drude oscillator model is used, where every carbon atom in graphene is partitioned into a Drude particle (DP, representing the carbon electron cloud) and a Drude core (DC, representing the carbon nucleus), which are connected by a harmonic spring, while the electrostatic interactions between the DCs and the DPs are modeled using a dipole field tensor. It is shown that the graphene-water polarization interactions have a significant impact on the interfacial entropy of water compared to the graphene-water dispersion interactions. This physical phenomenon is shown to contribute to a significant underprediction of the water contact angle if the graphene-water polarization energy is instead modeled implicitly using a pair-wise additive potential, such as the Lennard-Jones potential. Therefore, this study highlights the need to self-consistently model the graphene-water polarization interactions in MD simulations of wetting phenomena.

Second, I extended the theoretical framework to investigate the thermodynamics of salt ion adsorption at the graphene/water interface by modeling salt ions from the Hofmeister series, including validating my theoretical findings with experimental data. It is shown that the graphene-ion and graphene-water interactions are coupled via the electric fields which the salt ions and the

water molecules exert at the graphene/water interface. While the graphene-ion polarization energy is found to be significantly large in vacuum, this polarization energy is shown to be nearly nullified in the presence of water molecules at the graphene/water interface (more than 85% screening). Finally, for all the salt ions investigated, the ion adsorption behavior is found to be governed by a water-mediated molecular mechanism involving an interplay between the ion-water and water-water interactions, which is also shown to broadly apply to all solid/water interfaces.

Third, the modeling tools developed to model electronic polarization effects at planar solid/water interfaces are extended to study the behavior of pure water and electrolytes under nanoscale confinement. To this end, I investigated the thermodynamic and transport properties of water molecules confined inside carbon nanotubes (CNTs) of different diameters, ranging from 0.8 nm, where there is space for only a single file of water, to 2.3 nm diameter, where a bulk-like phase of water can be clearly identified near the CNT center. By carrying out MD simulations of water confined inside CNTs, it is shown that electronic polarization effects can yield a pronounced change in the friction coefficient of water. An anomalous maximum in the friction coefficient is also reported for CNTs with diameter close to 1.02 nm, which is attributed to the formation of a hollow shell-like configuration of water molecules with enhanced water density and structuring. Finally, I investigated the free energy barrier as well as the single file diffusive and electrophoretic transport of potassium (K^+) ions through a 0.8 nm diameter CNT, in collaboration with researchers from the Lawrence Livermore National Laboratory (LLNL). By calculating the diffusion coefficient of K^+ ions confined inside the CNT, I show that the diffusion of K^+ ions in the presence of the single file water chain is extremely slow, with the diffusion coefficient being at least three orders of magnitude smaller than the bulk diffusion coefficient. On the other hand, it is shown that the single file water chain disintegrates in the presence of external electric fields, such that the K^+ ions translocate through the CNT in the form of ion-water clusters at significantly larger velocities. This fundamentally different molecular mechanism of diffusive versus electrophoretic ion transport is ultimately shown to result in a breakdown of the Nernst–Einstein relationship in close agreement with concurrent experimental measurements by collaborators from LLNL.

In conclusion, this thesis aims at bridging the significant length and timescales associated with modeling electronic polarization at the atomistic level all the way to the determination of macroscopic properties (e.g., free energy of ion adsorption, ion diffusion coefficient) which are measurable experimentally. By investigating the wetting of graphitic surfaces, the thermodynamics of salt ion adsorption, and the confined water and salt ion transport through CNTs, this thesis also underscores the broad relevance of electronic polarization effects in interfacial phenomena.

Thesis Supervisor: Professor Daniel Blankschtein

Title: Herman P. Meissner (1929) Professor of Chemical Engineering