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Incorporation of the charge structure of water into electrostatics at the nanoscale

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Water mediated electrostatic interactions between charged macromolecules and ions are omnipresent in various nanoscale systems. From the charge selectivity of ionic channels in cells and artificial nanofiltration membranes to the energy storage ability of supercapacitors, these interactions are at the heart of many biological and industrial processes. An accurate formulation of electrostatics is thus necessary to understand the functioning of these systems, and also for the conception of new generation nanoscale devices with optimized efficiency. However, for several decades, the theoretical understanding of electrostatic interactions has been limited to dielectric continuum models such as the Poisson-Boltzmann (PB) formalism that bypass the charge structure of the water solvent. The talk will focus on newly developed theoretical approaches that aims at overcoming this limitation by incorporating the charge structure of solvent molecules into the current formulation of electrostatics.

In the first part of the talk, I will introduce the key electrostatic forces that are in play in nanoscale systems, and explain the modeling of these forces within the classical formulation of electrostatics. Then, I will outline the main drawbacks of the classical PB approach and present a more general dipolar PB (DPB) approach that considers the solvent molecules on the same footing as the ions [1,2]. Being a MF theory that models the solvent molecules as point dipoles, this extended approach neglects both electrostatic correlation effects and the non-local dielectric response of water. The remaining part of the talk will focus on improved formulations that overcome these two limitations.

The second part of the talk will be devoted to an extended DPB (EDPB) formalism, still based on the point dipole approximation, but able to account for electrostatic correlations beyond the MF level of approximation [3]. This new approach is particularly adequate for predicting the energy storage ability of carbon based supercapacitors, which are efficient nanoscale devices where electrostatic interactions bring the most important contribution to the structure of the double layer in the neighborhood of the electrode surface. I will show that unlike the PB and

DPB approaches that largely overestimate the experimental differential capacitance data, the EDPB formalism that can account for the surface polarization effects driven by electrostatic correlations exhibits a good agreement with experimental capacitance data of carbon based materials, thus correcting the predictions of the previous MF theories by one order of magnitude.

I will present in the third part of the talk a microscopic reformulation of non-local electrostatics that goes beyond the point-dipole approximation. By explicitly accounting for the discrete charge composition of solvent molecules, the microscopic polar liquid model embodies for the first time non-local electrostatic interactions at the molecular level of precision. I will show that unlike the previous DPB and EDPB formalisms that yields a local picture of solvent partition at charged surfaces, the new formalism is able to reproduce several characteristics of the interfacial non-local dielectric response behavior of water solvent revealed in Molecular Dynamics simulations [4] and Atomic Force experiments [5]. Within the same theoretical framework, I will discuss the hydration induced modification of the bare ionic polarizability, which is believed to be the most important ion specific effect on the interfacial behavior of inhomogeneous electroltyes. I will conclude by presenting a brief summary of open questions in the theoretical modeling of polar liquids.

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