Microscopic Physics of Electrical Double Layers

by

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The electrical double layer exists at the phase boundaries of electrolyte solutions, where oppositely charged counterions from solution preferentially accumulate to screen interfacial surface charges. Due to the ubiquity of electrolytes, the electrical double layer plays a central role in many fields in science and engineering, including colloid science, electrochemistry, biology, and membrane science. Across these fields, mathematical models of the double layer have been used to analyze and predict the behavior of electrochemical interfaces in contact with electrolyte solutions. Even so, the standard continuum approaches and assumptions that are applied usually fail to describe the microscopic arrangement and structuring of ions and solvent in the electrical double layer, limiting their predictive power.

In this thesis, I develop mathematical models to predict the microscopic structure of ionic solutions at charged interfaces, relevant for a wide set of problems including membrane transport, electrochemical capacitors, ionic liquid electrolytes, bioseparations, electrowetting, cement cohesion, and general colloidal stability. The continuum mathematical models I derive for the electrical double layer capture electrostatic correlations in electrolytes containing multivalent ions, the molecular-level layered structures in ionic liquids and concentrated electrolytes, interfacial orientational ordering of common polar liquids such as water, and the effects of electrolyte confinement in pores down to the nanoscale. These effects are not captured in applications of standard continuum theories for dilute electrolyte solutions, but are essential in accurately describing the equilibrium and nonequilibrium properties of electrolytes at charged interfaces. The key feature of the theories explored in this thesis is the inclusion of microscopic physics using formulations of nonlocal electrostatics, which encode additional microscopic length scales of discrete molecules, ions, and cofinement geometry into the continuum theory.

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