Electrostatics beyond Poisson-Boltzmann: Effects of Self-Energy

Zhen-Gang Wang
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

Ions are essential in physical chemistry, colloidal science, electrochemistry, biology and many other areas of science and engineering. While their role is commonly described in terms of screening and translational entropy, many phenomena, ranging from some classical experimental observations made many decades ago to some new systems of current interest, cannot be explained, even qualitatively, by these concepts. A key effect that is often ignored or inadequately treated in the main literature on electrolytes and polyelectrolytes is the self-energy of the ions. In this talk, I will discuss several self-energy effects in macromolecular and interfacial systems. First, we show that the preferential solvation energy of the ions provides a significant driving force for phase separation. This concept is used to develop a theory to explain the dramatic shift in the order-disorder transition temperature in PEO-PS diblock copolymers upon the addition of salt. Second, we show that the dielectric contrast between the polymer backbone and the solvent significantly affects the conformation and charge condensation in dilute polyelectrolyte solutions. Third, we show that the image force has qualitative effects on the double layer structure and forces, such as like charge attraction and charge inversion. Finally we present a simple theory for treating charge correlation effects in polyelectrolyte solutions that self-consistently account for the conformation changes of the polyelectrolyte chains.