

UCLA

Department of Chemistry & Biochemistry

SCOTT LECTURE

Prof. John D. Weeks

Department of Chemistry and Biochemistry

University of Maryland



presenting

Solvation, Structure, and Simulations of Systems with Strong Coulomb Interactions: The Long and Short of It

Coulomb interactions present major challenges to theory and computer simulations not only because of their characteristic long range but also because they can be very strong at short distances and compete efficiently with the other strong molecular core interactions. We describe a general theoretical approach for classical molecular models by exactly separating the point charge Coulomb interaction into a slowly-varying long-ranged component that arises from a rigid Gaussian charge distribution with width σ , and the remainder, which is short ranged and can be added to the other short-ranged core interactions. When σ is properly chosen, we show that one can account very accurately for the locally averaged effects of the long-ranged components in terms of an effective single particle potential, or "local molecular field" (LMF), making consistent use of a simple mean field approximation. The general theory is a mapping that relates the properties of a nonuniform system with long ranged intermolecular interactions in a given external field (arising, e.g., from charged solutes or walls) to those of a simpler "mimic system" with short-ranged intermolecular interactions but in an effective or restructured LMF field. Characteristic phenomena in strongly coupled ionic solutions such as ion pairing or the effective attraction between like charged objects induced by multivalent counterions are quantitatively captured in the simpler mimic system.

These ideas prove particularly useful in understanding properties of classical water models such as the extended simple point charge (SPC/E) model. We divide the potential of the SPC/E water model into short and long ranged parts. The short ranged parts define a minimal reference network model that captures very well the structure of the local hydrogen bond network in bulk water while ignoring effects of the remaining long ranged interactions. This deconstruction can provide insight into the different roles that the local hydrogen bond network, dispersion forces, and long ranged dipolar interactions play in determining a variety of solvation and dielectric properties of water. We use these short ranged models along with LMF theory to quantify the influence of these interactions on the structure of hydrophobic interfaces and the crossover from small to large scale hydration behavior in the solvation of hydrophobic solutes of varying sizes.

Monday, January 13, 2014
4:00 P.M.
2033 Young Hall

Reception
5:15 P.M.
3037 Young Hall

Contact: Carol Canedo at x64956 or carol@chem.ucla.edu for more information