THERMODYNAMIC FORMULATION OF CHARGED LIQUIDS BASED ON THE ASYMMETRIC TREATMENT OF DISTINCT IONIC INTERACTION RANGES

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ABSTRACT

The accurate characterization of ion correlations in charged solutions is critical for the control of various biophysical and industrial processes ranging from ion transport through plasma membranes to water purification and desalination procedures. The theoretical tools enabling the comprehension of these systems is based on the the Debye-Hückel (DH) theory suffering from major limitations [1]. Namely, the validity of the DH formalism neglecting the ionic hard-core (HC) size and including exclusively electrostatic weak-coupling-level ion correlations is limited to the characterization of monovalent salts at dilute concentrations.

In this talk, I will present an ion size-augmented self-consistent DH (SCDH) theory of bulk electrolytes exploiting the asymmetric incorporation of the short- and long-range ion interactions via their virial and cumulant-level treatment, respectively [2,3]. The underlying variational splitting of the distinct interaction ranges enables the accurate prediction of ionic activity coefficients, internal energies, osmotic pressures, and radial distribution functions up to molar salt concentrations. Via comparison with simulations and experimental data, I will show that the SCDH formalism can also reproduce accurately the underscreening and overscreening effects occurring in monovalent and multivalent electrolytes. The analytical transparency of the SCDH theory enables the detailed characterization of the ionic association mechanism behind these effects in terms of the close competition between repulsive HC and attractive charge correlations.

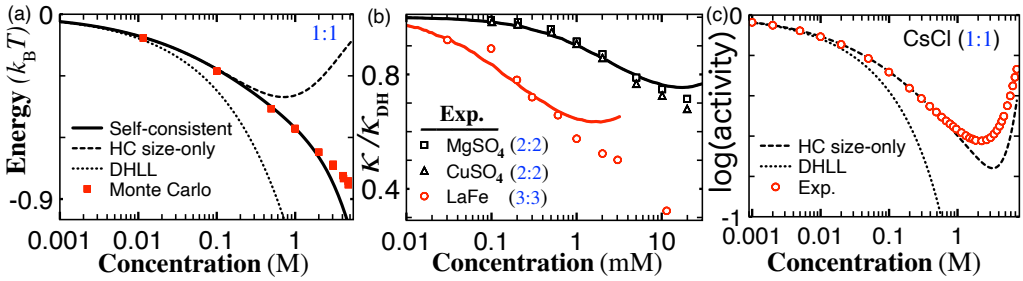

Figure 1: a) Internal energy, (b) reduced screening parameter, and (c) ionic activity.

Keywords: Thermodynamics of electrolytes, charge correlations, hard-core interactions, ion size

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