

Classical density functional theories of ionic solutions

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Most systems of biological and/or industrial interest contain charged species. The electrostatic coupling is often high (polyelectrolytes, proteins, ionic liquids etc.), in which case ion correlations are important. In this talk, I shall firstly describe how the Poisson-Boltzmann theory appears in a classical density functional approach, DFT. I will highlight its failures for highly coupled systems, and discuss various ways to (approximately) account for ion correlations, retaining the simple density functional description. Unfortunately, in most current DFT formulations, the range and strength of these correlations are determined by the hard core (Pauli) repulsion between the ions. This can actually lead rise to reasonable predictions, but only at very high salt concentrations (in which case the "Coulomb hole" happens to be similar to typical ion diameters). It is of course much more realistic, and relevant, to determine the ion correlations in terms of the electrostatics of the system. I will also discuss the possibility to treat freely mobile (unconnected) monovalent ions implicitly, using screened Coulomb interactions between the remaining explicit ions. This approach has proven useful to describe polyelectrolyte adsorption. We have recently made ellipsometry measurements, with data that are directly comparable with density functional predictions.