Tunable soft structure in charged fluids confined by dielectric interfaces

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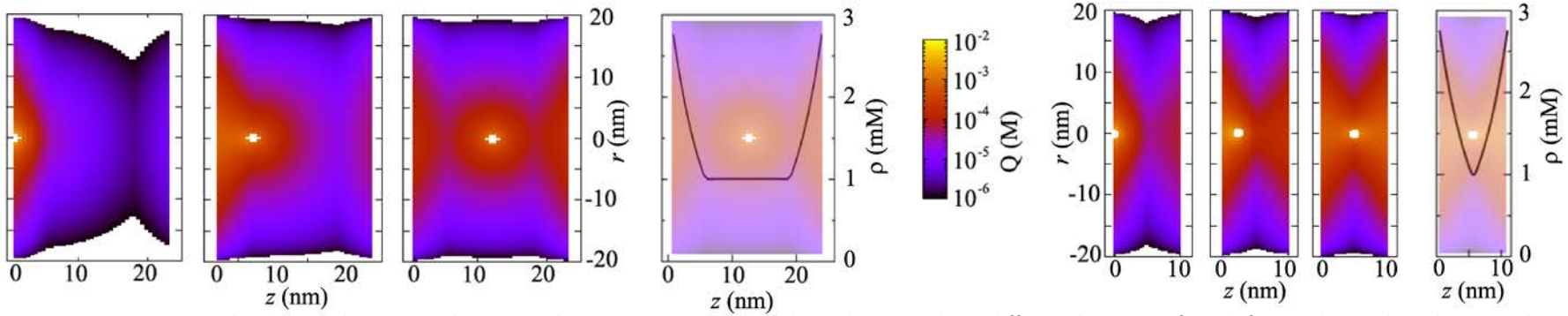
Fluids of charged particles act as the supporting medium for chemical reactions and physical, dynamical, and biological processes. The local structure in an electrolytic background is deformed by micro- and nanoscopic polarizable objects. Vice versa, the forces between the objects are regulated by the cohesive properties of the background. We study here the range and strength of these forces and the microscopic origin from which they emerge. We study the soft structure in primitive model electrolytes calculated by an accurate and rigorous liquid-state theory known as the AHNC.



The anisotropic screening cloud around a monovalent anion between two adsorbing boundaries at three different locations, from left to right, in the adsorption layer, near the adsorption layer, and between the walls is shown. The colors indicate the mean total charge around an anion located at the center of the white area. The mean density of ions displays an increase near the boundaries caused by the short-range attraction of the boundary. Although the adsorption is relatively weak (driven by a potential difference of −1 k_BT*), it is clearly visible that the adsorbed layers contain a large fraction of the screening ions and that the ions within the adsorbed layer correlate visibly with the ions in the other layer, especially at smaller separations (2 Debye lengths for the four left figures and 0.8 Debye length for the four right figures.*

- We describe several distinct ion-induced forces in aqueous solutions of monovalent ions at salt concentrations ranging roughly between 0.01 and 1 M that are expected to compete for dominance with the well-known screened Coulomb forces.
- We introduce the concept of soft structure to connect the induced forces to the local microscopic structure in the ionic fluid and visualize the deformation of the local environment around the ions near several types of boundaries that are neutral, adsorbing, charged, polarizable, or a combination of these properties. The considered forces cannot be found by well-known (practical) mean-field theories and are relevant for neutral solutes or solutes close to an isoelectric point as well.
- We aim to provide an intuitively appealing overview to aid and enhance predictability and control in experiments. The results from the AHNC may provide guidance for the development of simple scaling laws, potentially efficient and practical DFTs, and coarse-grained simulation methods to overcome the disparate length, time, and energy scales that characterize nanomaterials and biological matter.

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