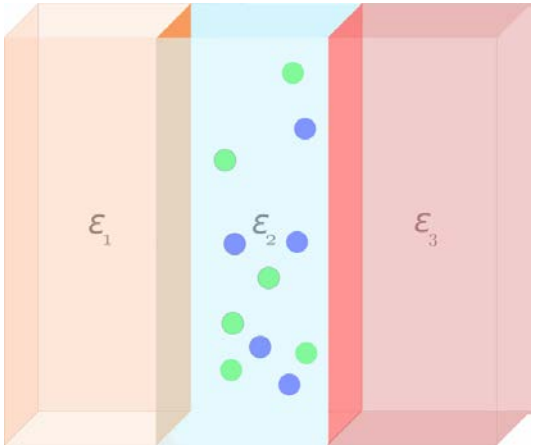
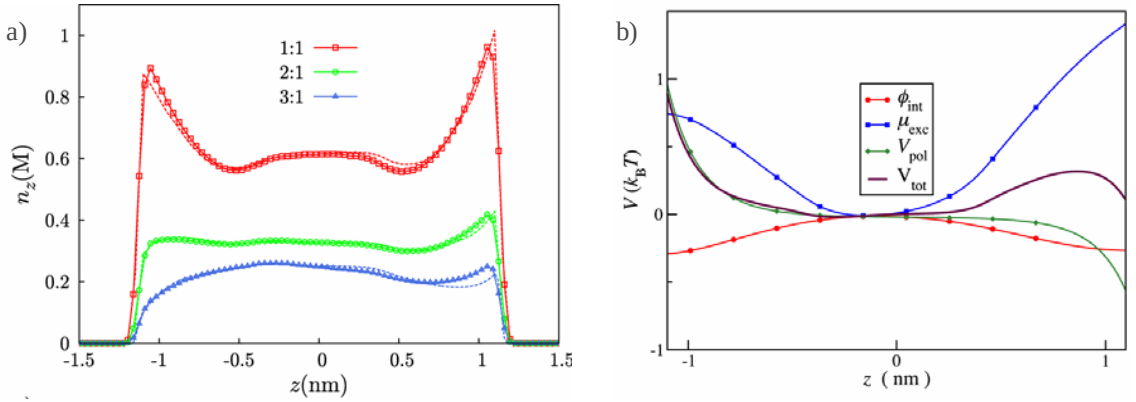
Ionic Structure in Liquids Confined by Dielectric Interfaces

Yufei Jing, Vikram Jadhao, Jos W. Zwanikken and Monica Olvera de la Cruz

We compute the ionic structure in a model system of electrolyte confined by two planar dielectric interfaces using molecular dynamics (MD) simulations and liquid state theory. We explore the effects of high electrolyte concentrations, multivalent ions, dielectric contrasts, and external electric field on the ionic distributions. We observe the presence of non-monotonic ionic density profiles leading to a layered structure in the fluid which is attributed to the competition between electrostatic and steric (entropic) interactions. We find that thermal forces that arise from symmetry breaking at the interfaces can have a profound effect on the ionic structure and can oftentimes overwhelm the influence of the dielectric discontinuity. The combined effect of ionic correlations and inhomogeneous dielectric permittivity significantly changes the character of the effective interaction between the two interfaces.





a) Density n_z of positive ions for a c_n = 0.5M electrolyte confined within two polarizable planar interfaces with dielectric 20|80|160. Symbols correspond to MD results and dashed lines to AHNC calculations. b) The corresponding potentials acting on the trivalent ions are shown separately, calculated y the AHNC

J. Chem. Phys. 143, 194508 (2015); DOI: 10.1063/1.4935704

DDR&E and AFOSR under Award No. FA9550-10-1-0167; NSF Grant No. DMR-1309027.