

Towards a microscopic understanding of underscreening in concentrated electrolytes: Effects of confinement and composition fluctuations

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ABSTRACT

Electrostatic interactions play a critical role from biological systems to energy materials [1,2]. The classical Debye-Hückel and mean-field theories provide fundamental understandings of the screening of ionic interactions, but their applicability is limited only to dilute electrolytes [3,4]. Recent surface force measurement experiments [5,6] have challenged our current understanding of the screening phenomena: various concentrated electrolytes confined by mica surfaces show an unexpectedly long decay length of the force between surfaces (~ 10 nm), referred to as “underscreening”. Furthermore, they exhibit a universal cubic scaling relation of the decay length with ion size after properly normalizing both quantities with Debye screening length. Since the decay at large distance of the force between surfaces is expected to reflect the bulk correlation length of the liquid [6], several groups employed liquid-state theories or simulations to investigate bulk concentrated electrolytes. However, the anomalous underscreening found in the experiments is still puzzling, as bulk theories with the primitive model of electrolytes [7] and all-atom simulations [8,9] have only found underestimated exponents (1-2) instead of the cubic scaling exponent. A similar conclusion was obtained using classical Density Functional Theory for the primitive model [10] or all-atom simulations [11] to predict the decay of the ionic density profiles near an interface. This poster presents our current efforts to understand the microscopic origin of the long decay observed in surface force measurements with concentrated electrolytes, mainly focusing on the effects of confinement and interfaces. In our model Lennard-Jones electrolytes without composition fluctuations, we found the screening behaviors are similar in bulk and under confinement qualitatively and quantitatively, consistent with the previous theories. As a key component missing in previous simulations, including ours, confined electrolytes need to be modeled being in contact with the bulk reservoir so that their composition varies under different confinement while maintaining constant chemical potentials. Such grand-canonical simulations are computationally feasible via a hybrid non-equilibrium MD/MC method [12], which we have implemented in LAMMPS, a widely-used open-source simulator. With this method, we explore the effect of composition fluctuations on the underscreening in concentrated electrolytes, directly comparing the force profiles as a function of confinement. This work is a part of the SENSES (making Sense of Electrical Noise by Simulating Electrolyte Solutions) project [13], funded by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 863473).

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