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Ion Correlations at an Electrified Liquid/Liquid Interface NOUAMANE LAANAIT, MIROSLAV MIHAYLOV, BINYANG HOU, HAO YU, University of Illinois at Chicago, PETR VANYSEK, Northern Illinois University, BINHUA LIN, MATI MERON, CARS, University of Chicago, ILAN BENJAMIN, University of California at Santa Cruz, MARK SCHLOSSMAN, University of Illinois at Chicago — Ion correlations have been suggested as the underlying mechanism of a number of counterintuitive phenomena such as like-charge attraction. Here we present the first molecular-level tests of density profiles predicted by an ion correlations model. Synchrotron x-ray reflectivity reveals ion condensation at the liquid/liquid interface, when polarized with an electric field.[1] Tuning the density of this ionic layer allows for a detailed study of ion correlations as a function of the Coulomb coupling strength in the system. We propose a parameter-free density functional theory that describes ion-ion correlations within a weighted density approximation and explicitly treats ion-solvent effects through a solvent interaction potential simulated by molecular dynamics. Agreement with the x-ray reflectivity and the interfacial excess charge is found over the entire experimental range of ion-ion correlation energies up to nearly 4 k_BT. These results suggest that ion correlations in the electrical double layer can be accurately described by mapping to a simple Coulomb system, in this case a one-component plasma.

[1] N. Laanait et al. J. Chem. Phys., **132**, 171101, 2010

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