New Perspectives on Electrokinetics

(Tutorial #8)

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We treat the Poisson-Nernst-Planck (PNP) equations as the basis for a consistent framework of the electrokinetic (EK) effects. The static limit of the PNP equations is shown to be the charge-conserving Poisson-Boltzmann (CCPB) equation, with guaranteed charge neutrality within the computational domain. We propose a surface potential trap model [1] that attributes an energy cost to the interfacial charge dissociation. In conjunction with the CCPB, the surface potential trap can effect a surface-specific adsorbed charge layer. By defining a chemical potential that arises from the charge neutrality constraint, a re-formulated CCPB can be reduced to the form of the Poisson-Boltzmann (PB) equation, whose prediction of the Debye screening layer profile is in excellent agreement with that of the PB equation when the channel width is much larger than the Debye length. However, important differences emerge when the channel width is small so that the Debye screening layers from the opposite sides of the channel overlap with each other. In particular, the theory automatically yields a variation of that is generally known as the "charge regulation" behavior, attendant with predictions of force variation as a function of nanoscale separation between two charged surfaces that is in good agreement with the experiments, with no adjustable or additional parameters. We give a generalized definition of the potential that reflects the strength of the EK effect; its variations with the concentration of surface specific and non-specific salt ions are shown to be in good agreement with the experiments. To delineate the behavior of the electro-osmotic (EO) effect, the coupled PNP and Navier-Stokes equations are solved numerically under an applied electric field tangential to the fluid-solid interface. The EO effect is shown to exhibit intrinsic time dependence that is non-inertial in its origin. Under a step function applied electric field, a pulse of fluid flow is followed by relaxation to a new ion distribution, owing to the diffusive counter current. We have numerically evaluated the Onsager coefficients associated with the EO effect, L21, and its reverse streaming potential (SP) effect, L12, and show L12=L21 in accordance with the Onsager relation. We conclude by noting some of the challenges ahead.

*Work done in collaboration with Li Wan, Shixin Xu, Maijia Liao, and Chun Liu

[1] Li Wan, Shixin Xu, Maijia Liao, Chun Liu, Ping Sheng, " *Electric Double Layer and Electrokinetics: A Surface Potential Trap Model,"* Physical Review X, to appear