Nonlinear electrokinetic phenomena in the thin-double-layer limit

Ory Schnitzer

A solid brought in contact with an electrolyte solution spontaneously acquires surface charge. Coulombic attraction of the dissolved counter-ions to the surface triggers the formation of a screening diffuse layer. At equilibrium, the ionic densities in this layer are Boltzmann distributed, representing a balance between the electrostatic forces and the thermal agitation of the dissolved ions. The characteristic diffuse-layer width ("Debye length"), namely the length scale on which space-charge density attenuates towards the electroneutral bulk, is typically on the order of a few tens of nanometers. The term "electrokinetics" collectively refers to various non-equilibrium phenomena in which the mobile diffuse-layer ions are forced (say, by an externally applied electric field) to drift with respect to the bound surface charge. Although originating on the nanometric Debye scale, electrokinetic effects are characteristically manifested on much larger (micrometer) scales e.g. in the form of "electroosmotic" flow fields, or "electrophoretic" particle motion. Electrokinetic techniques constitute an essential tool in the study of colloidal systems: surface-charge densities are commonly estimated by correlating measured electrokinetic velocities. In recent years, moreover, emerging applications in microfluidic and Lab-on-a-chip devices have driven a surge in electrokinetic research. Indeed, electrokientics holds the promise of enabling automized manipulation of liquids, particles, and biological samples, without the use of moving parts.

Electrokinetic transport involves the coupling of ionic transport, electrostatics, hydrodynamics, and surface chemistry. The appropriate mathematical model is accordingly rather complicated, being comprised of a set of nonlinear partial differential equations, boundary conditions, and integral constraints. Moreover, direct numerical simulations are essentially impractical because of the inherent scale disparity associated with the smallness of the Debye length. Traditional theoretical studies are thus based upon various linearization schemes, entailing the assumptions of weak applied fields and weakly charged surfaces. These assumptions are seldom encountered in practice, especially in modern applications involving strong electric fields, new materials, and artificial configurations. In fact, experimentation under such conditions reveals a rich world of *nonlinear electrokinetic phenomena* still far from being well understood.

In this talk, I will present an alternative approximation path, where the inherent scale disparity is exploited via a systematic singular perturbation analysis in the limit where the dimensionless Debye length is small compared to the relevant dimensions of the system. We thus conceptually decompose the fluid domain into an approximately electroneutral bulk, and a diffuse (Debye) boundary layer. This result is a reduced macroscale model governing the electroneutral bulk where the diffuse-layer physics are represented by a set of effective boundary conditions; this model is not limited to weak fields or weakly charged surface and is amenable to various perturbation schemes and numerical computations. The usefulness of this approach will be demonstrated in the context of the fundamental problem of solid-particle electrophoresis. Notably, we find here a set of novel asymptotic approximations essentially covering the entire practical range of parameters. Time permitting, additional electrokinetic scenarios such as electrokinetic flows over free surfaces and nonlinear oscillations in electrochemical cells, will also be discussed.

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