

Abstract submitted to ELKIN06 on December 31, 2005

## **A Theory of Electrokinetics at Highly Charged Surfaces**

Martin Z. Bazant<sup>1, 2</sup>, M. Sabri Kilic<sup>1</sup>, and Armand Ajdari<sup>3</sup>

It is well known that the classical Poisson-Nernst-Planck equations of electrokinetics predict nonsense for zeta potentials only a few times the thermal voltage ( $> 0.1$  Volt), namely ion densities exceeding the physical limit, especially for large or multivalent ions at high ionic strength. In the traditional context of colloids, such “large” zeta potentials are uncommon (at least, near equilibrium), but in electro-microfluidics it is common to apply a volt or more across the double layer, to increase the flow rate. Even at lower operating voltages, it is clear that the standard model of a “dilute solution” must break down near the surface. A tell-tale sign is the as-yet unexplained, universal decay of nonlinear electrokinetic flow with increasing concentration (above 10 mM) and possible flow reversal at large voltage (where electrochemical reactions may also play a role). Here, we propose a mathematical model of first-kind electrokinetics at highly charged surfaces which takes into account (i) steric effects, through the modified Poisson-Boltzmann equation of Borukhov et al. (1997), and (ii) a generic picture of the viscoelectric effect. We derive slip formulae for electro-osmosis and diffusio-osmosis, which correct the classical theories of Smoluchoski and Deryagin, respectively, for flow saturation at highly charged surfaces. The theory predicts some interesting new phenomena, such as the induced-charge electrokinetic motion of an uncharged, ideally polarizable metal sphere in a uniform electric field, when the electrolyte is asymmetric. A complete treatment of this and other problems in nonlinear electrokinetics, however, also requires generalizing Dukhin’s theory of surface conduction and accounting for salt adsorption in the double layer.

---

<sup>1</sup> Department of Mathematics, Massachusetts Institute of Technology, Cambridge, MA 02139.

<sup>2</sup> Institute for Soldier Nanotechnologies, 500 Technology Square, Cambridge, MA 01239.

<sup>3</sup> Laboratoire de Physico-Chimie, UMR ESPCI-CNRS 7083, 10, rue Vauquelin, F-75005 Paris, France.