Effects of Ion Sterics and Hydrodynamic Slip on Electrophoresis of a Colloidal Particle

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ADITYA KHAIR, TODD SQUIRES, Chemical Engineering, UC Santa Barbara — The classical theory of a spherical colloids’ electrophoretic mobility is founded on the Poisson-Nernst-Planck (PNP) equations and assumes the standard hydrodynamic no-slip boundary condition at the fluid/solid interface. In the (common) limit of thin double-layers, the mobility has long been known to exhibit a maximum at some zeta potential, then decrease and asymptote to a constant value. Dukhin, O’Brien, White and others showed this to result from the importance of excess ionic surface conductivity within the double-layer. The fundamental assumptions that underpin this result are, however, subject to challenge: in recent years, a finite liquid/solid slip has been measured over a variety of surfaces, and the PNP equations predict physically impossible ion concentrations precisely at the high zeta potentials where the mobility maximum occurs. Here, we discuss the dramatic effect that hydrodynamic slip and finite-ion-size steric effects in double-layers have upon the electrophoretic mobility of spherical colloids, and therefore upon the interpretation of electrophoretic mobility measurements.