28e Nonlinear Screening Theory for Charged Colloids

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Suspensions of highly charged colloids are multicomponent systems that consist of mesoscopic colloidal particles in a medium composed of co- and counterions and a molecular solvent. Many equilibrium aspects of these systems have long been understood on the basis of the DLVO theory, which predicts effective screened-Coulomb interactions ~exp(-kr)/r between pairs of colloidal particles at separation r, with k the inverse Debye length of the suspending medium. We rederive the DLVO theory by integrating out the solvent and the microscopic ions in the partition function of the system, and show that the linear screening theory that underlies the DLVO theory breaks down at extremely low concentrations of salt (small k), and for high colloidal charges: nonpairwise interactions become relevant because of the long Debye length, and the colloidal charge must be renormalized due to counterion condensation effects. These nonlinear screening effects turn out to have pronounced effects on the thermodynamics and the phase behavior of the suspension, which we calculate and compare with experimental observations. If time permits I will also discuss some recent progress on colloidal sedimentation (which involves spontaneous macroscopic electrostatic fields driven by the ionic entropy), as well as colloidal crystals in mixtures of oppositely charged particles (which have been observed experimentally and can be explained largely by the DLVO theory).