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SOME UNRESOLVED ISSUES WITH THE DLVO THEORY OF STABILITY OF CHARGED NANOPARTICLES

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The DLVO theory has been a “textbook” theory of colloidal stability for over 50 years; it adds repulsive electrostatic forces and attractive van der Waals forces (1). Here, we are concerned with the screened electrostatic forces only. We examine their theoretical foundation in the non-linear Poisson-Boltzmann equation (NLPB), whose inconsistencies are known but intractable to clarify; we argue that an electrostatically sound approach is required in order to make the most of the (well-worn) Poisson-Boltzmann paradigm.

We outline a linear electrostatic model - a “Maxwellian” model - in which charge densities and potentials are linearly related in every differential volume element, as required by the Poisson equation of classical Maxwellian electrostatics. The Maxwellian linearity leads to a system of contiguous linear Poisson-Boltzmann (PB) equations with free boundaries that demarcate co-ion exclusion regions at high potential surfaces (2, 3). At low potentials the system of Maxwellian PB equations folds into to a single PB equation with no co-ion exclusion boundaries (the Debye-Hückel model). These exclusion boundaries are not arbitrary but are obtained as free-boundary solutions of the contiguous PB equations. The positions of these boundaries represent “diffuse structure” of ionic distributions near charged surfaces. These boundaries also undergo “Cheshire cat” transitions, i.e. appear or disappear from charged surfaces at critical physicochemical conditions.

The Maxwellian model has been applied to data on swelling pressures of montmorillonite clays (4-7). Two general results have emerged and are of some interest. First, the greater dissociation of charged interfaces with increasing bulk ionic concentrations is described by the Lubetkin-Middleton-Ottewill (LMO) law. This law reduces to either 100% dissociated Gouy-Chapman model or to the undissociated Helmholtz model of charged interfaces. Some other results and applications are also discussed (8-11), particularly in relation to the organization of biomacromolecules in prokaryotic cells.

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