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Electrokinetics of Correlated Electrolytes and Ionic Liquids BRIAN STOREY, Olin College, MARTIN BAZANT, MIT — Perhaps the most basic assumption of classical electrokinetic theory is the mean-field approximation, where the each ion feels only the electric field produced by the mean charge density (via Poisson's equation) rather than the fluctuating Coulomb forces with individual neighbors. Here, we present a simple continuum model for electrostatic correlations between finite-sized ions, which leads to a 4th order modified Poisson equation, convenient for the analysis of electrokinetic phenomena. When the mean-field approximation breaks down, e.g. due to large ion concentrations, large ion valences, and/or nanoscale confinement, the zeta potential loses its significance, and the model predicts that electro-osmotic flows are typically reduced - or even reversed - by correlation effects, compared to the prediction of the Helmholtz-Smoluchowski formula. This may help to explain the over-prediction of induced-charge electro-osmotic flows by classical models. An interesting limit of the model describes electro-osmosis in solvent-free ionic liquids and molten salts, which may be important in energy storage and electroactuation applications.

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