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Electrical Double Layers: Predicting Overcharging and Layering of Ions using Continuum Models  ANKUR GUPTA, ANANTH GOVIND RAJAN, EMILY CARTER, HOWARD STONE, Princeton University — Electrical double layers (EDLs) form the basis for several phenomena such as electrophoresis, supercapacitor charging and discharging, and desalination. However, existing continuum models for the EDL are unable to predict experimentally-observed phenomena such as ion layering and EDL overcharging. To overcome these limitations, atomistic methods like classical density functional theory and molecular dynamics simulations have been employed to elucidate the nanoscale structure of EDLs. In this work, we bridge the gap between the continuum and atomistic approaches by proposing a modified continuum model. Our model predicts a near-wall stratified structure in EDLs wherein the cations and anions are arranged in layers, even in the dilute limit. Furthermore, we predict that for trivalent ions, the double layer can locally possess a net charge larger than the surface, a phenomenon commonly known as overcharging. Our model does not require any fitting parameters or additional boundary conditions, and only depends on the ion properties. Since our approach is at the continuum scale, we envision that it can be readily extended to out-of-equilibrium systems such as electrophoresis and dynamics of supercapacitors.