A Discrete Ion Stochastic Continuum Overdamped Solvent Algorithm for Modeling Electrolytes

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In this talk we present a methodology for the mesoscale simulation of strong electrolytes. This is an extension of the Fluctuating Immersed Boundary (FIB) approach that treats a solute as discrete Lagrangian particles that interact with Eulerian hydrodynamic and electrostatic fields. In both cases the Immersed Boundary (IB) method of Peskin is used for particle-field coupling. Hydrodynamic interactions are taken to be overdamped, with thermal noise incorporated using the fluctuating Stokes equation, including a “dry diffusion” Brownian motion to account for scales not resolved by the coarse-grained model of the solvent. A combination of mid-point time stepping, a “random finite difference” term in the hydrodynamic equation, and the explicit inclusion of a stochastic drift correction in the “dry diffusion” ensures fluctuation dissipation balance is satisfied and the system is reversible with respect to the Gibbs-Boltzmann distribution. Long range electrostatic interactions are computed by solving the Poisson equation, with short range corrections included using a novel immersed-boundary variant of the classical Particle-Particle Particle-Mesh (P3M) technique. Also included is a short range repulsive force based on the Weeks-Chandler-Andersen (WCA) potential. The new methodology is validated by comparison to Debye-Hückel theory for ion-ion pair correlation functions, Debye-Hückel-Onsager theory for conductivity (including the Wien effect for strong electric fields), and by comparison to molecular dynamics for electro-osmotic flows. In each case good agreement is observed, provided that hydrodynamic interactions at the typical ion-ion separation are resolved by the fluid grid.