SAND2011-8811C

11th Meeting of the American Physical Society,
Division of Fluid Dynamics,
Baltimore, MD

Examining Permittivity Effects in Electric Double Layers using Molecular Dynamics and Atomistic-to-Continuum Modeling

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November 22, 2011

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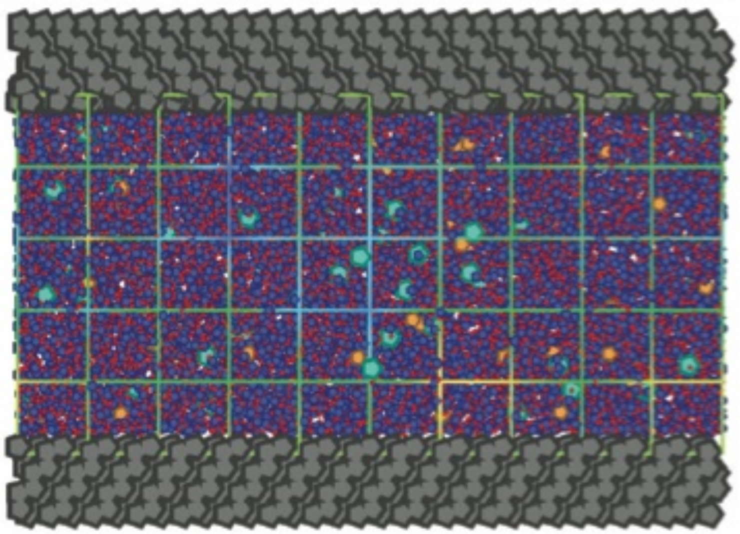
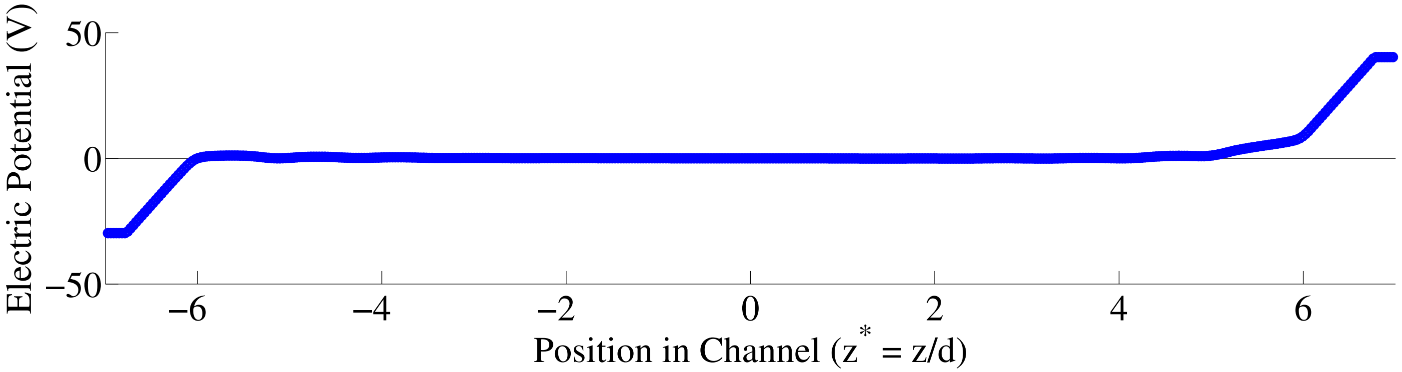
Motivation: Atomic Simulations of Electric Double Layers



Nanochannel simulation of salt water forms EDL, (Templeton et al. *2011)*



Asymmetric potential drop implies counter-ion dependent capacitances

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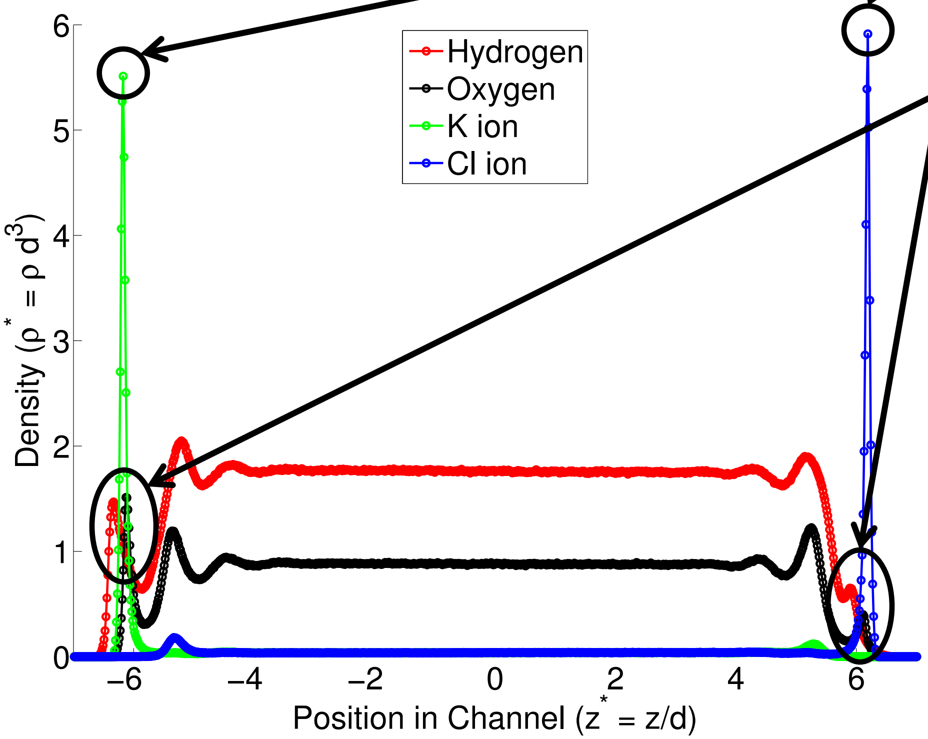
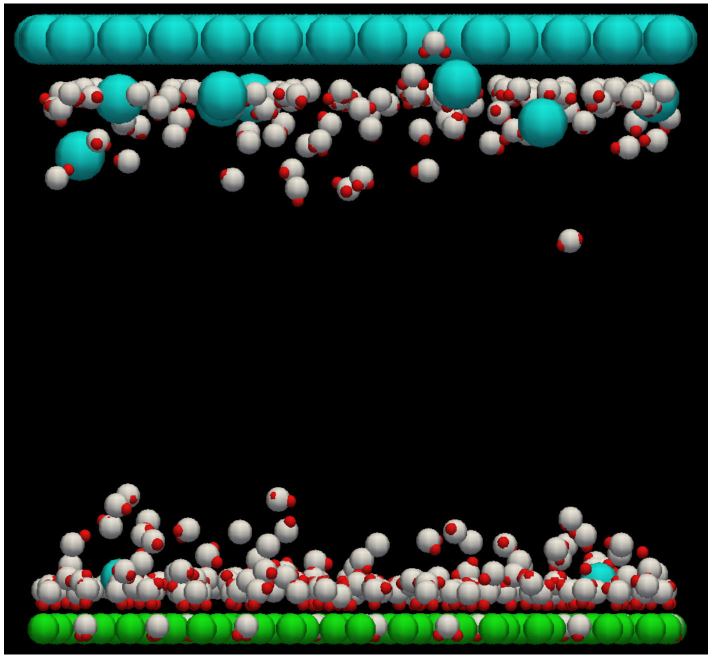
Motivation: Understand Dielectric Structure of EDL

Same amount of charge stored in each EDL

Different near-wall water density



Species' Densities in MD Nanochannel



***Goal**: quantify this picture*

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Multiscale Theory: Electric Potential

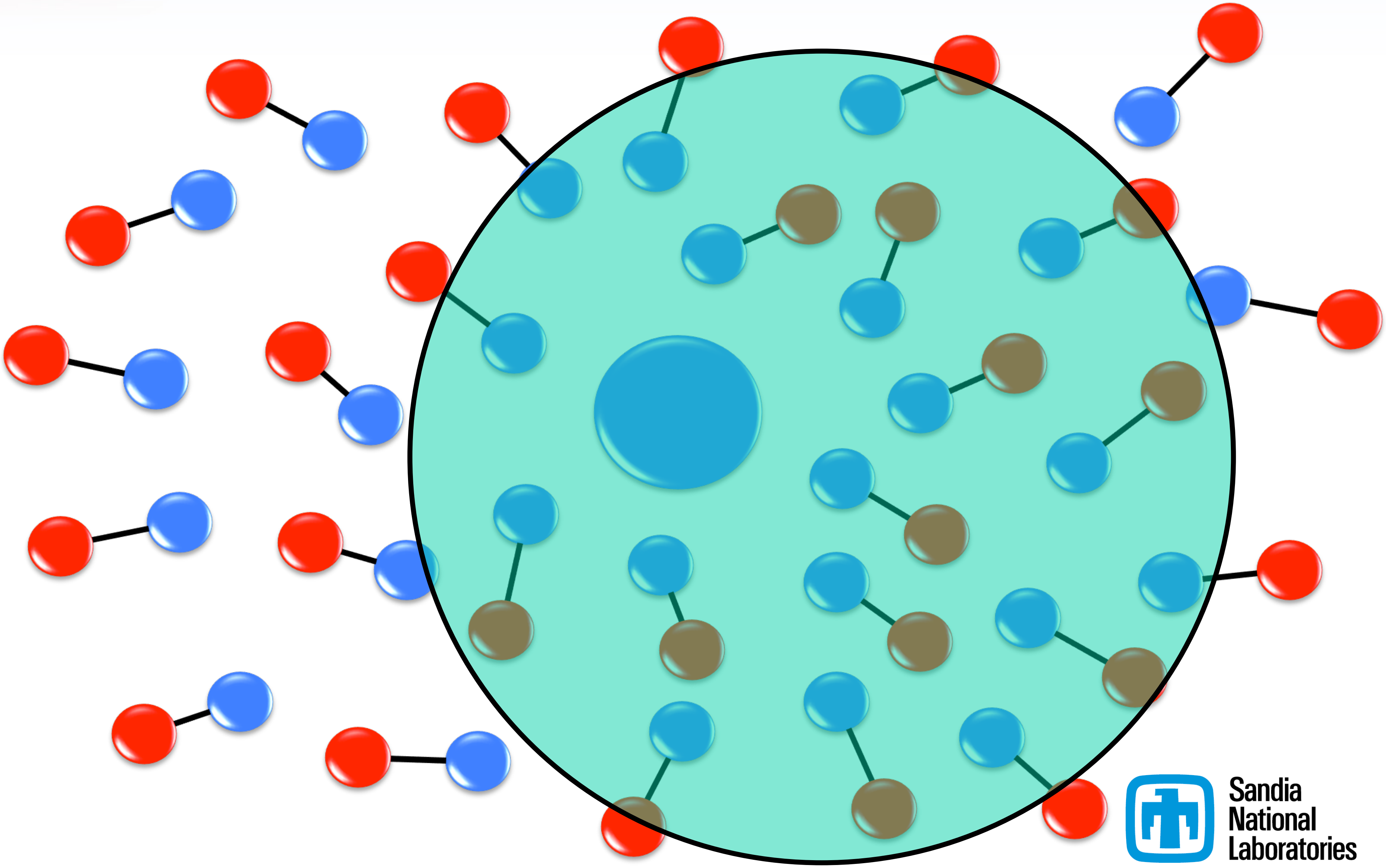
"True" Poisson equation governing the electric potential at fine scales

$$\epsilon_0 \nabla \cdot \mathbf{e}\left(\mathbf{x}\right) = \varrho\left(\mathbf{x}\right)$$

Charge density arises from discrete charges at atom locations

$$\varrho(\mathbf{x}) = \sum_{i=1}^{N_f} q_i \delta\left(\mathbf{x} - \mathbf{x}_i\right) + \sum_{n=1}^{N_M} \sum_{i=1}^{N_n} q_i^n \delta\left(\mathbf{x} - \mathbf{x}_i^n\right)$$

Coarse-Graining Illustration



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Compare with the coarse scale electric potential

$$\mathbf{E}\left(\mathbf{x}\right) \equiv \int_\Omega \mathbf{e}\left(x'\right) \psi\left(\mathbf{x} - \mathbf{x}'\right) d\mathbf{x}'$$

Where the coarse-grained charge density is

$$\rho\left(\mathbf{x}\right) = \sum_{i=1}^{N_f} q_i \psi\left(\mathbf{x} - \mathbf{x}_i\right) + \sum_{n=1}^{N_M} \sum_{i=1}^{N_n} q_i^n \psi\left(\mathbf{x} - \mathbf{x}_n - \mathbf{x}_i^n\right)$$

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Multiscale Theory: Mathematical Construction

To recover our normal notions of electric fields in a medium, expand the charge density using Taylor series expansion

$$\rho\left(\mathbf{x}\right) = \sum_{i=1}^{N_f} q_i \psi_i + \sum_{n=1}^{N_M} q_n \psi_n + \frac{\partial}{\partial \mathbf{x}} \cdot \left(- \sum_{n=1}^{N_m} \sum_{i=1}^{N_n} q_i^n \mathbf{x}_i^n \psi_n + \sum_{i=1}^{N_n} q_i^n \mathbf{x}_i^n \otimes \mathbf{x}_i^n \cdot \frac{\partial}{\partial \mathbf{x}} \psi_n - \ldots \right)$$

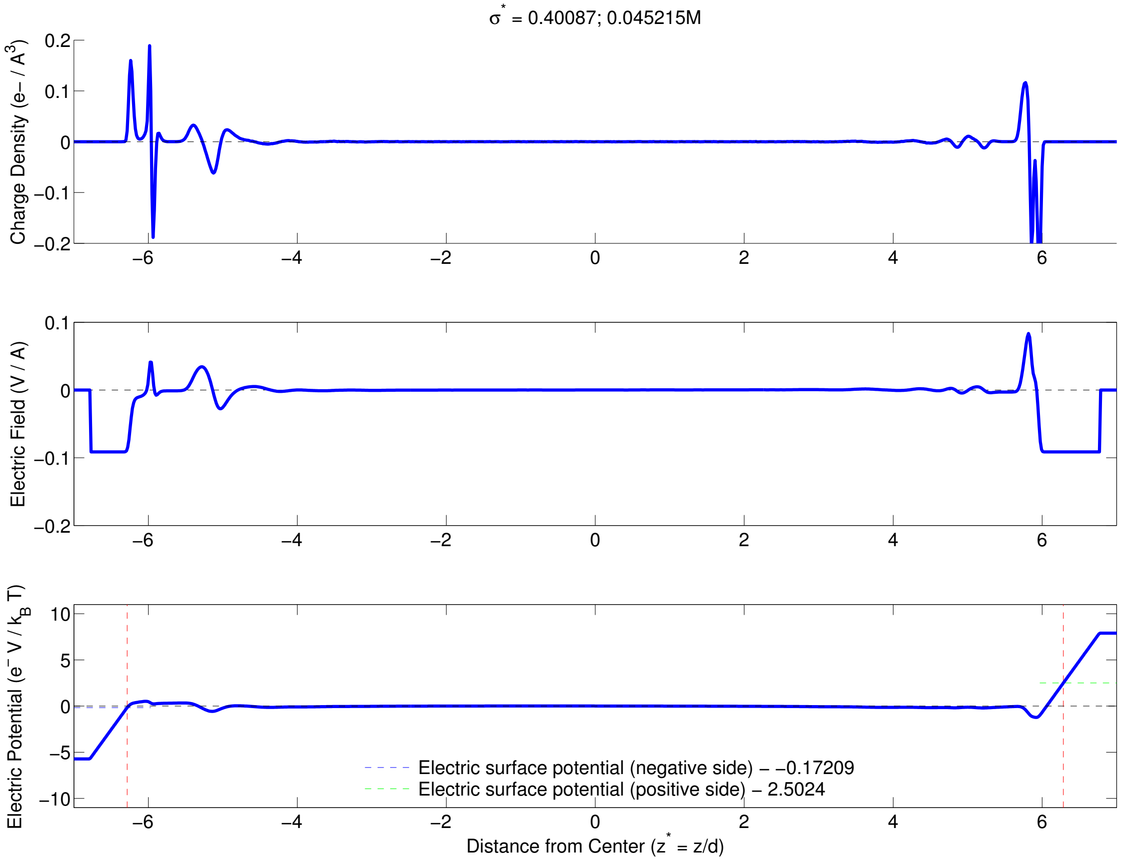
Gives rise to the normal coarse electric potential equation

$$\nabla \cdot \mathbf{D}\left(\mathbf{x}\right) = \sum_{i=1}^{N_f} q_i \psi_i + \sum_{n=1}^{N_M} q_n \psi_n$$

The electric displacement vector is

$$\mathbf{D}\left(\mathbf{x}\right) = \epsilon_0 \mathbf{E}\left(\mathbf{x}\right) + \sum_{n=1}^{N_m} \mathbf{p}_n \psi_n - \frac{1}{2!} \frac{\partial}{\partial \mathbf{x}} \cdot \left(\sum_{n=1}^{N_m} \mathbf{q}_n \psi_n \right) + \ldots$$

Application: EDLs in Nanochannels



Different Polarization accounts for different potential difference

Conclusions & Future Work

We can understand species-dependent differences in EDL properties based on the size of ions and electrical moments of solvent molecules

- Changes can impact applications in electro-osmosis and energy storage

We have developed a post-processing capability in the MD code LAMMPS (http://lammps.sandia.gov) to apply these methods to small molecules

Future work will include this capability in numerical calculations involving atomic interactions with electric fields

- Concentration/field varying permittivity to standard MD EDL simulations
- Dynamic permittivity calculation for use with MD electric field solvers
    - Including error analysis
- Performance improvements in MD electric field solvers by splitting dipole, quadrupole, etc., moments from free charges
- Interplay of coarse-graining functions with desired molecular properties