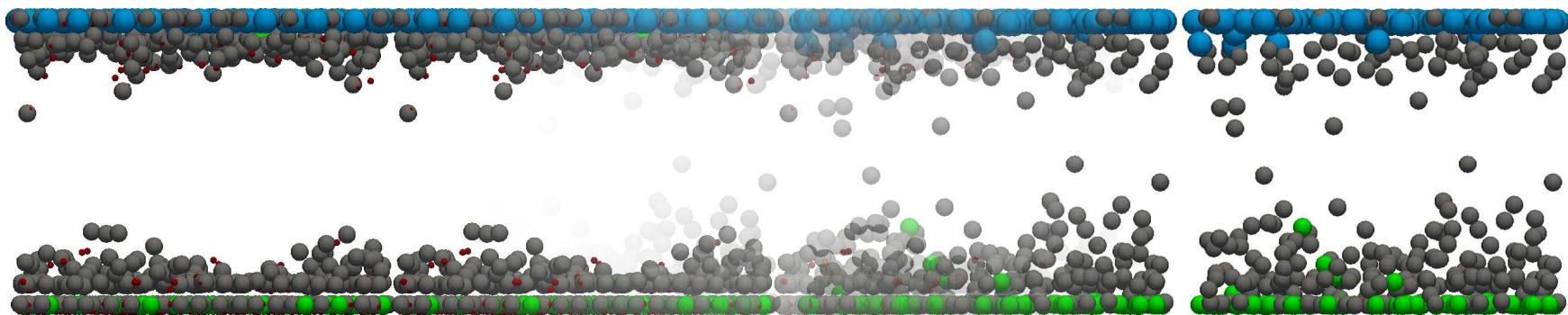
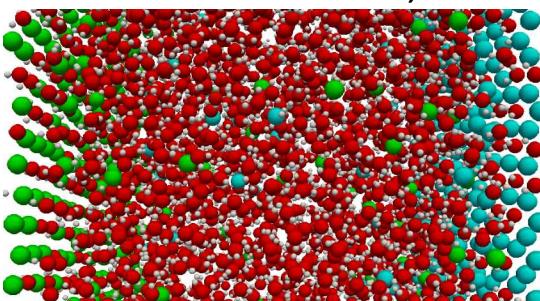
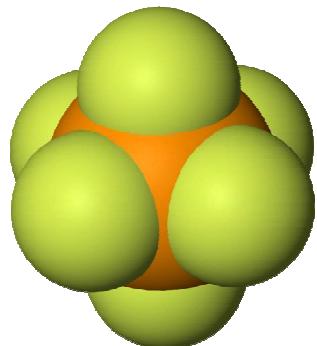


Exceptional service in the national interest



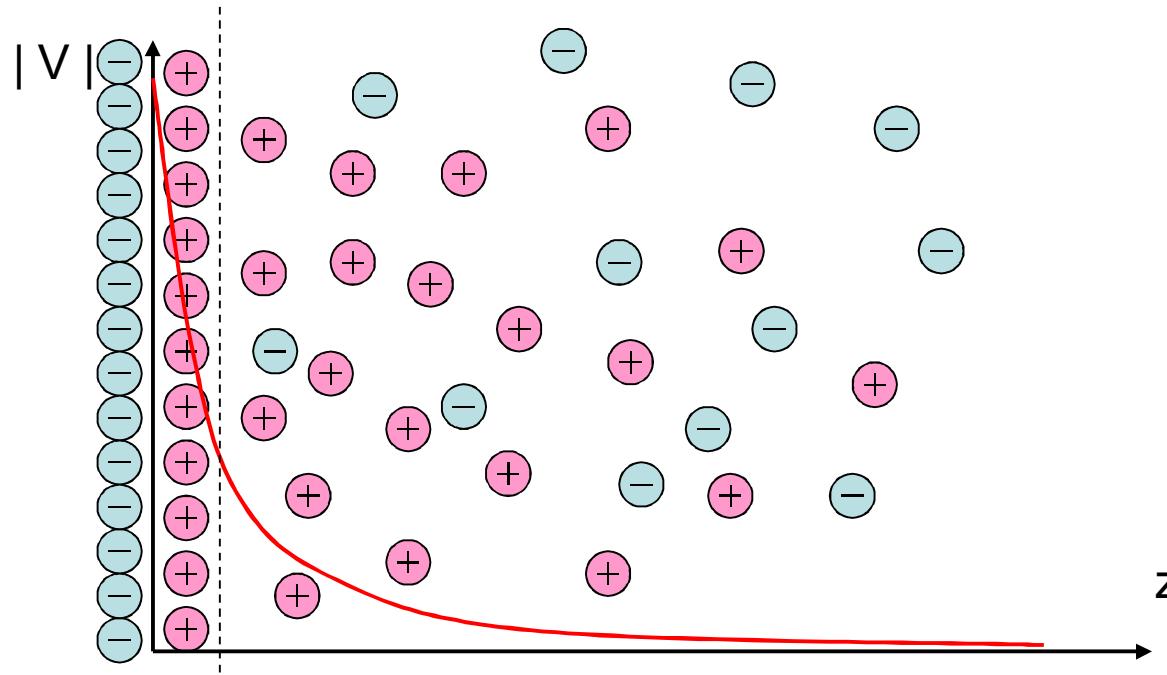
Atomistic Effects in Electric Double Layers at High Voltages



Jonathan W. Lee, Jeremy A. Templeton, Kranthi K. Mandadapu,
Ali Mani, and Jonathan A. Zimmerman

Tuesday, July 23, 2013
Raleigh, NC

Electric Double Layer



Classical Poisson-Boltzmann (PB) Theory

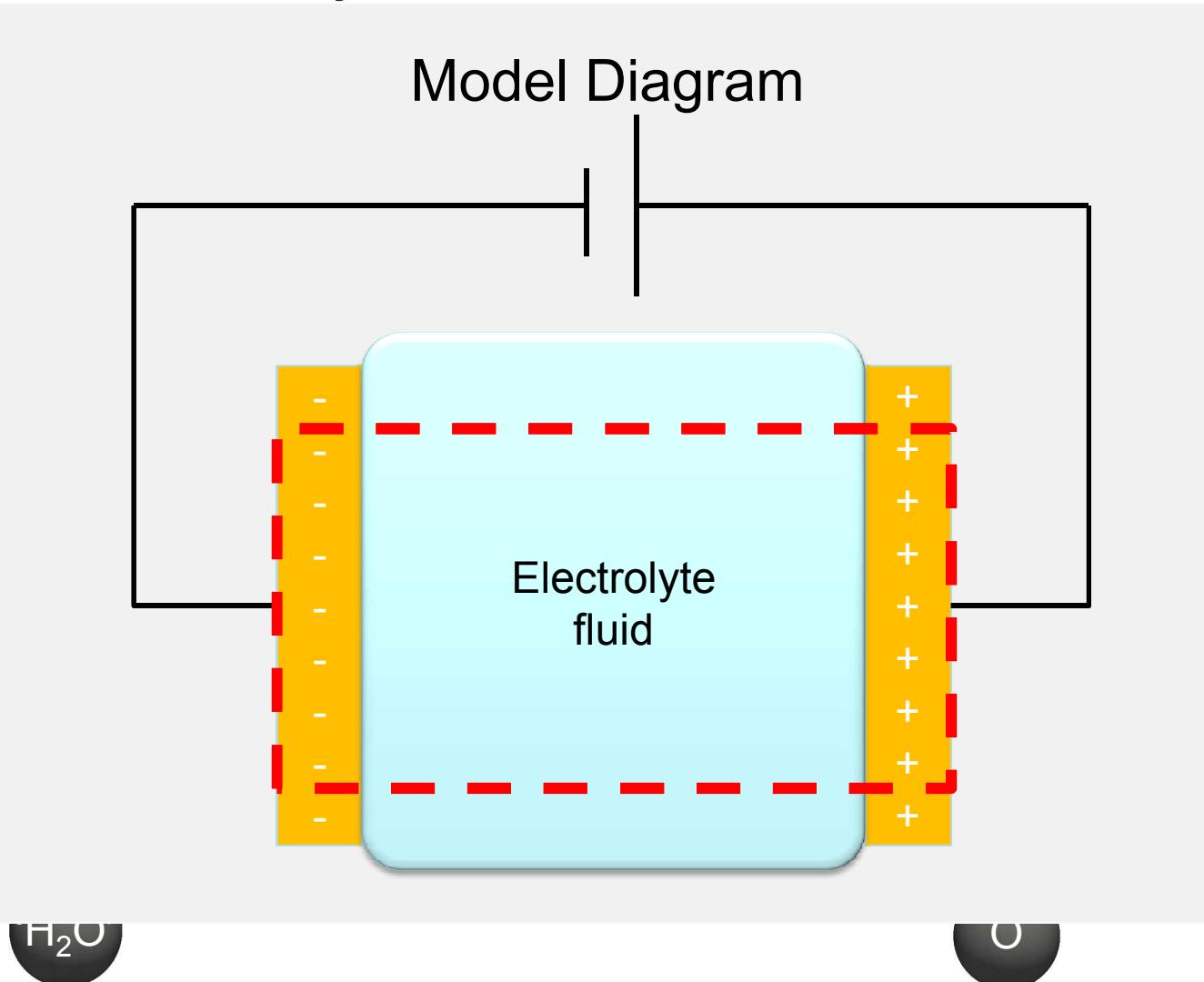
- Ion concentration follows Boltzmann distribution
- Electric Potential changes monotonically towards bulk
- How does EDL change with model fidelity and more realistic materials?

Molecular Dynamics Models

Primitive

- + are
- Nor
- rep
- Diel

Model Diagram

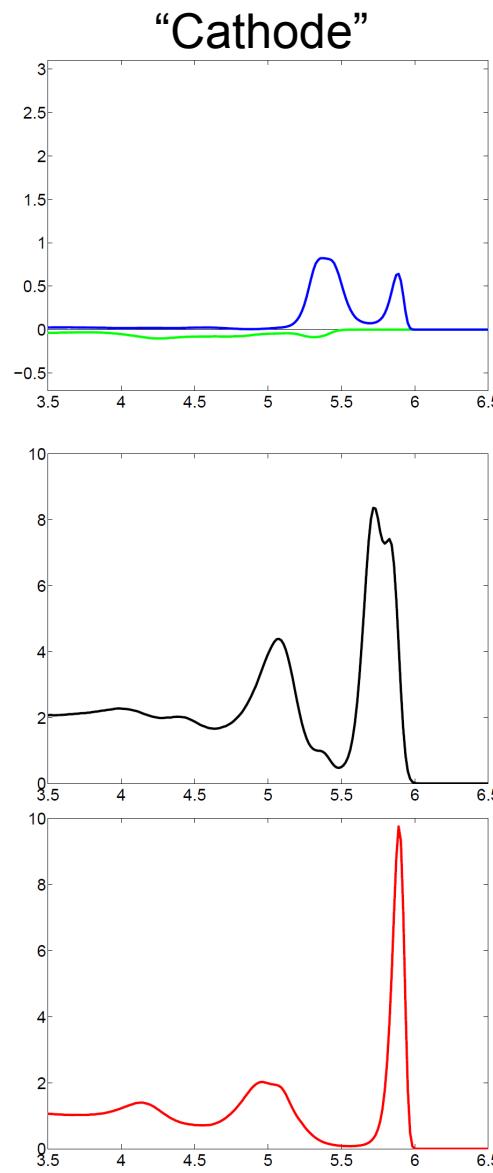
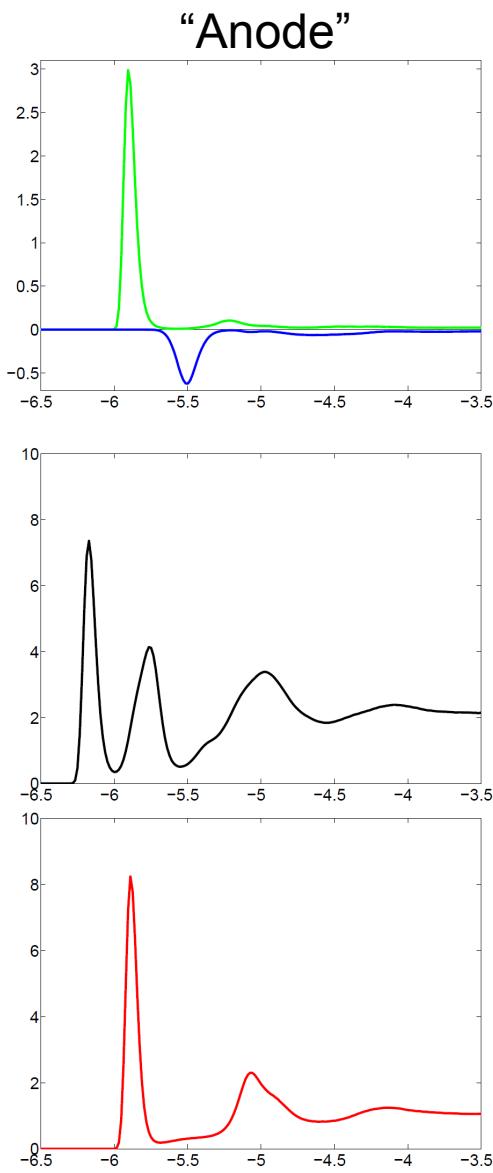


Density Profiles

Ion Densities

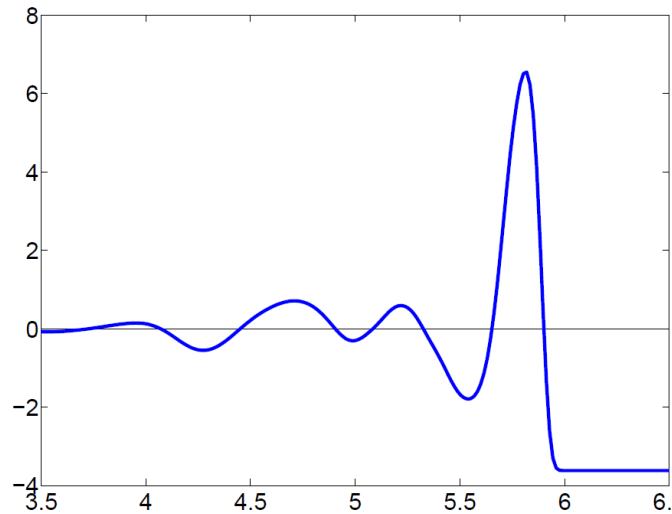
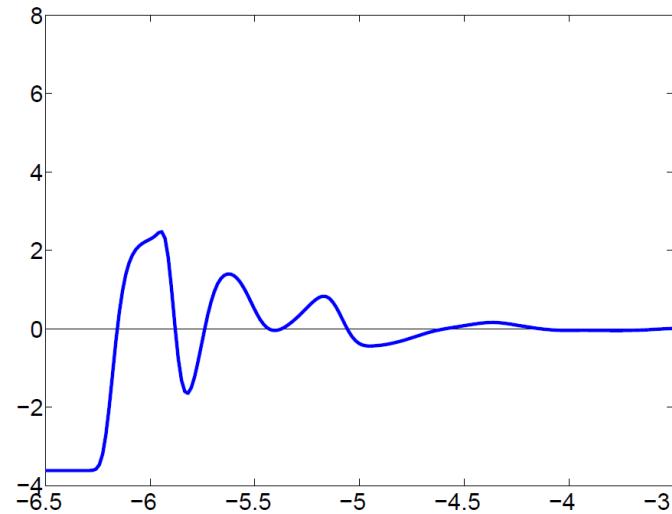
Hydrogen Densities

Oxygen Densities

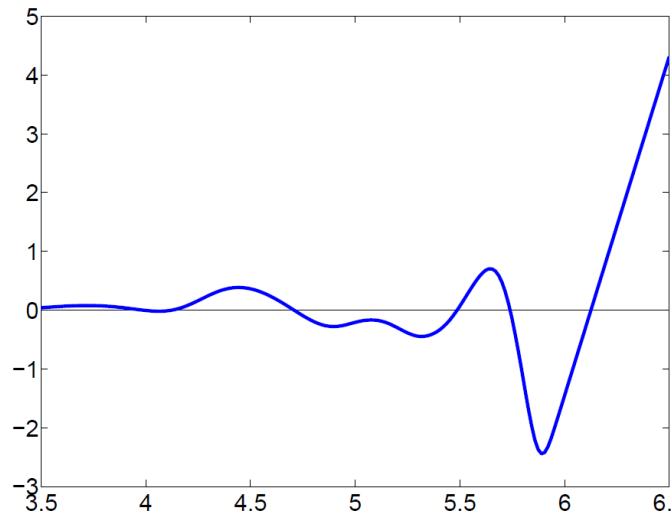
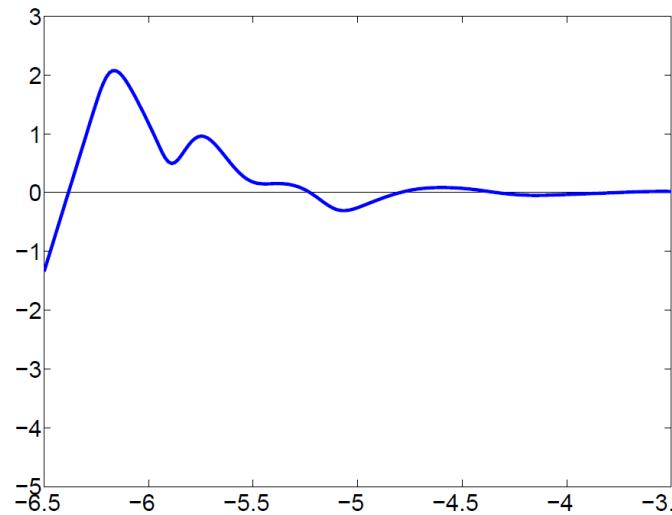


E-Fields & E-Potentials

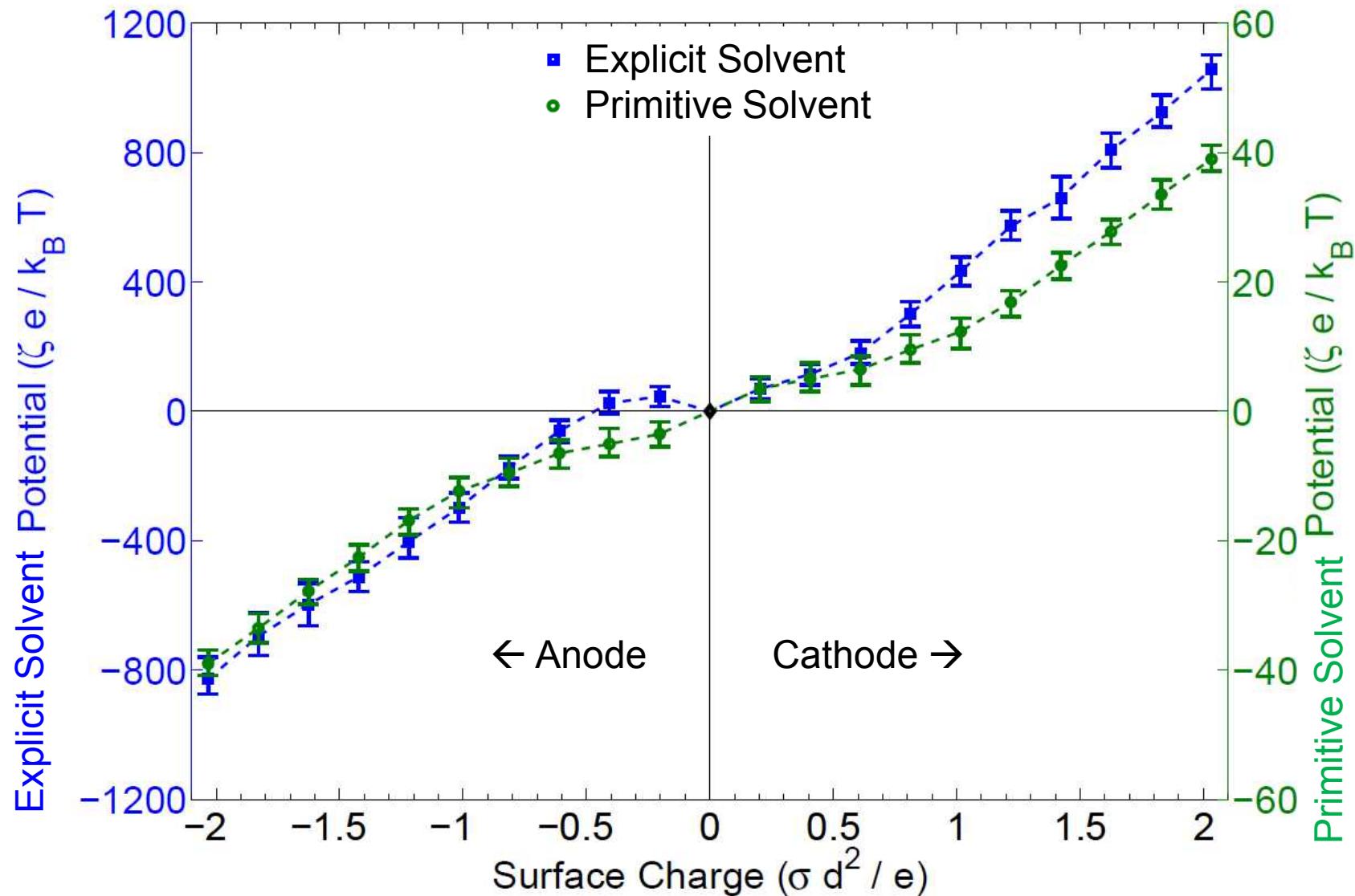
Electric
Field



Electric
Potential

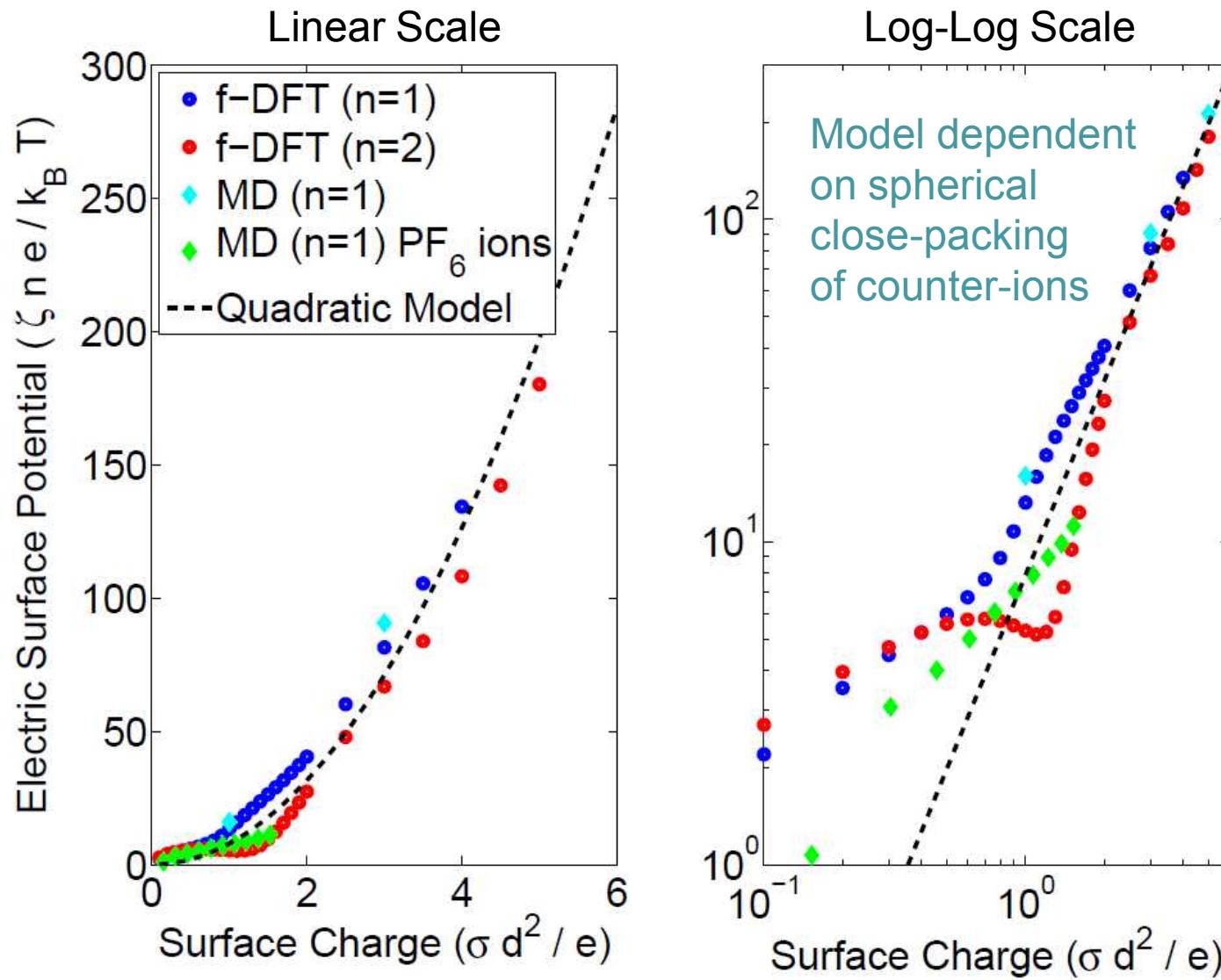


Bare Wall Potential Comparison



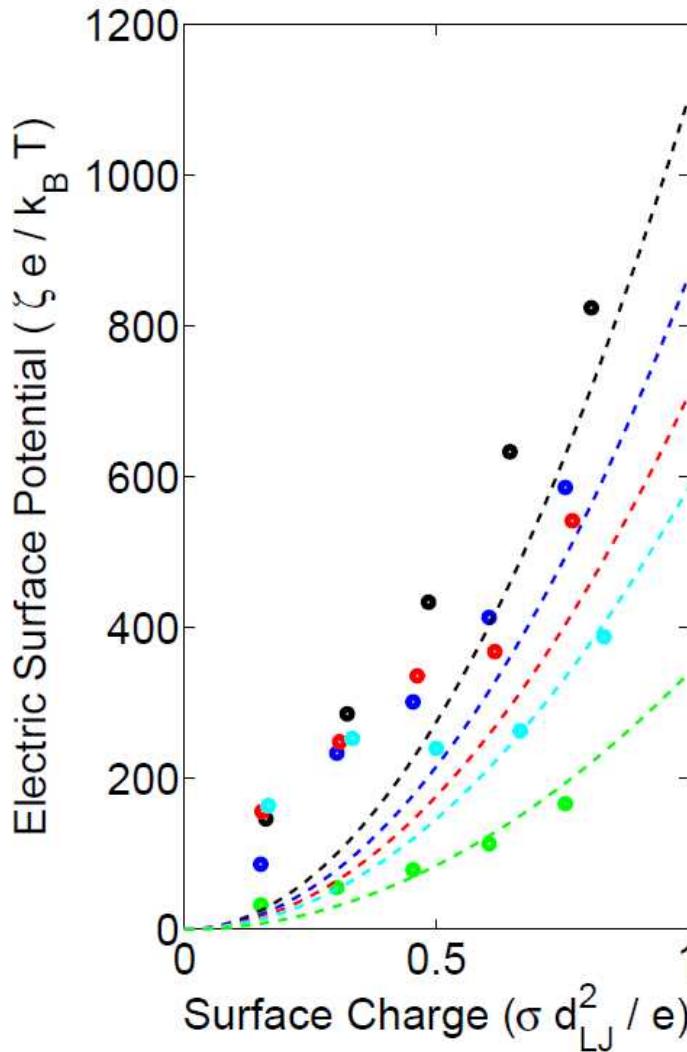
High Charge Asymptotic Limit

(primitive solvent model only)



Structured Surface Effects

(e.g., explicit water solvent with KCl at cathode)



Surface lattice perturbs capacitance

- ion packing reduced
- solvent permittivity altered?

- (100) FCC Gold, $f \sim 0.23$
- (100) FCC Copper, $f \sim 0.29$
- Graphite, $f \sim 0.36$
- (111) Silicon, $f \sim 0.43$
- LJ Wall, $f \sim 0.74$

Asymptotic model captures magnitude

- packing fractions from geometric calculations
- magnitude scaled for primitive vs explicit solvent difference

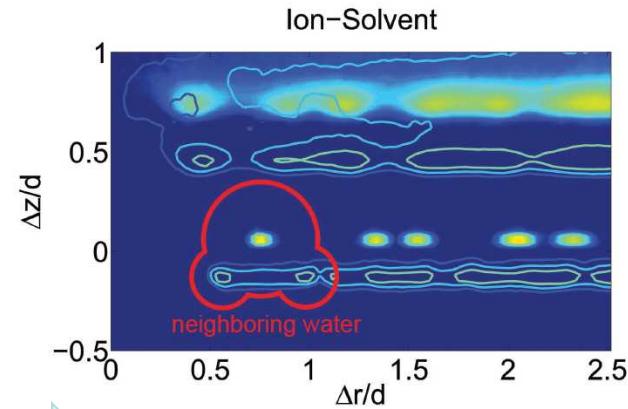
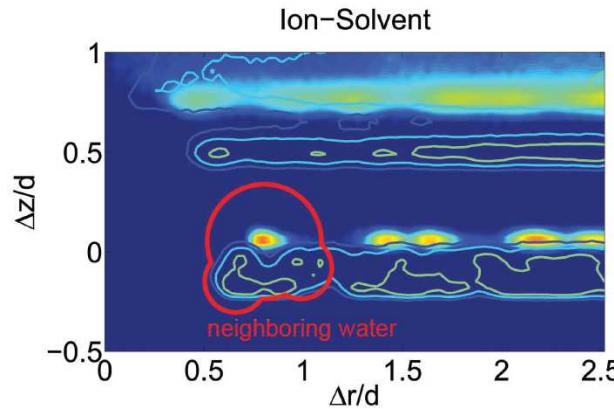
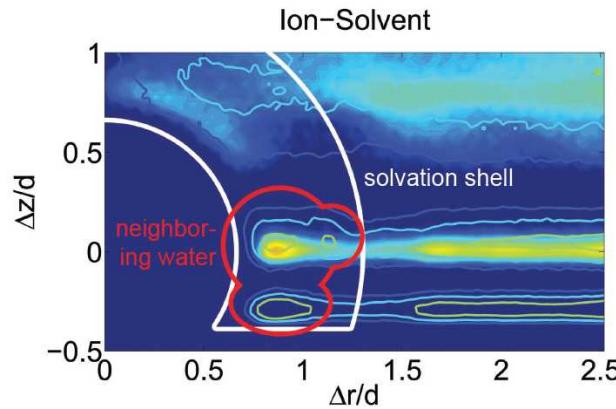
Conclusion & Future Work

- MD models to study effect of molecular solvent and structured surfaces on electric double layer
- Dielectric permittivity not constant near wall – yields much stronger Coulombic interactions and decreased capacitances
- Surfaces perturb maximum packing fraction, reduce capacitance
 - Future: How will more complex solvents behave?

Please e-mail me at: jonlee@sandia.gov

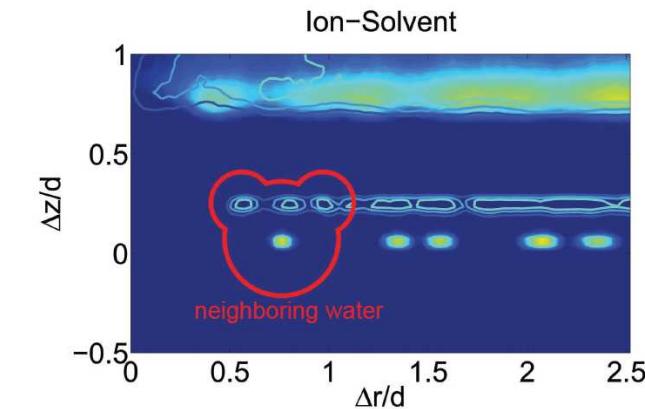
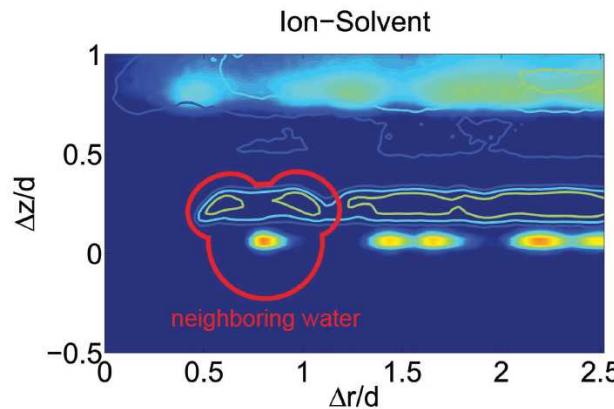
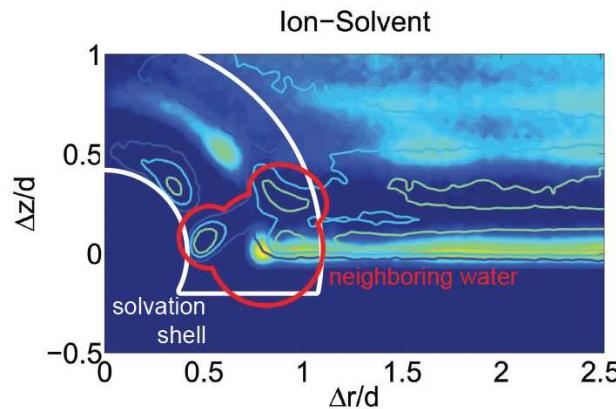
Correlation Contours

Anode:

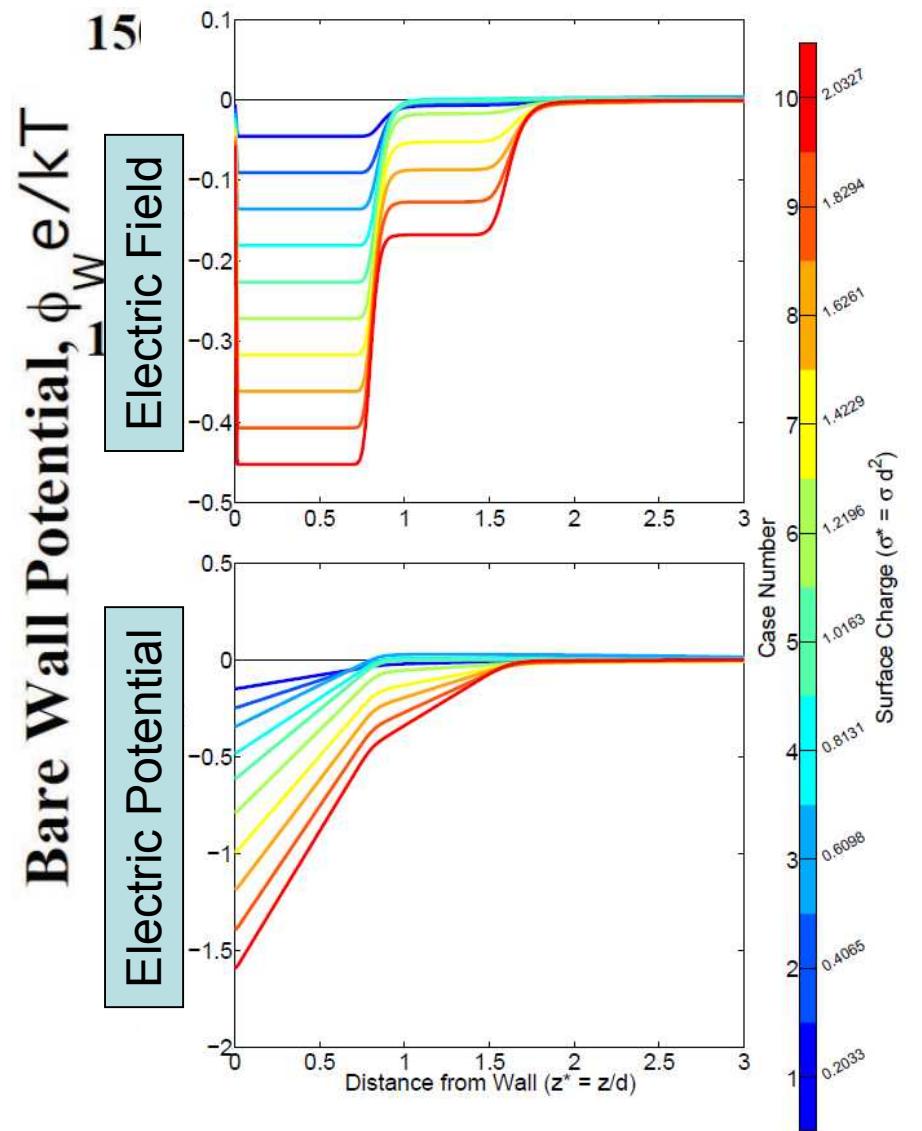
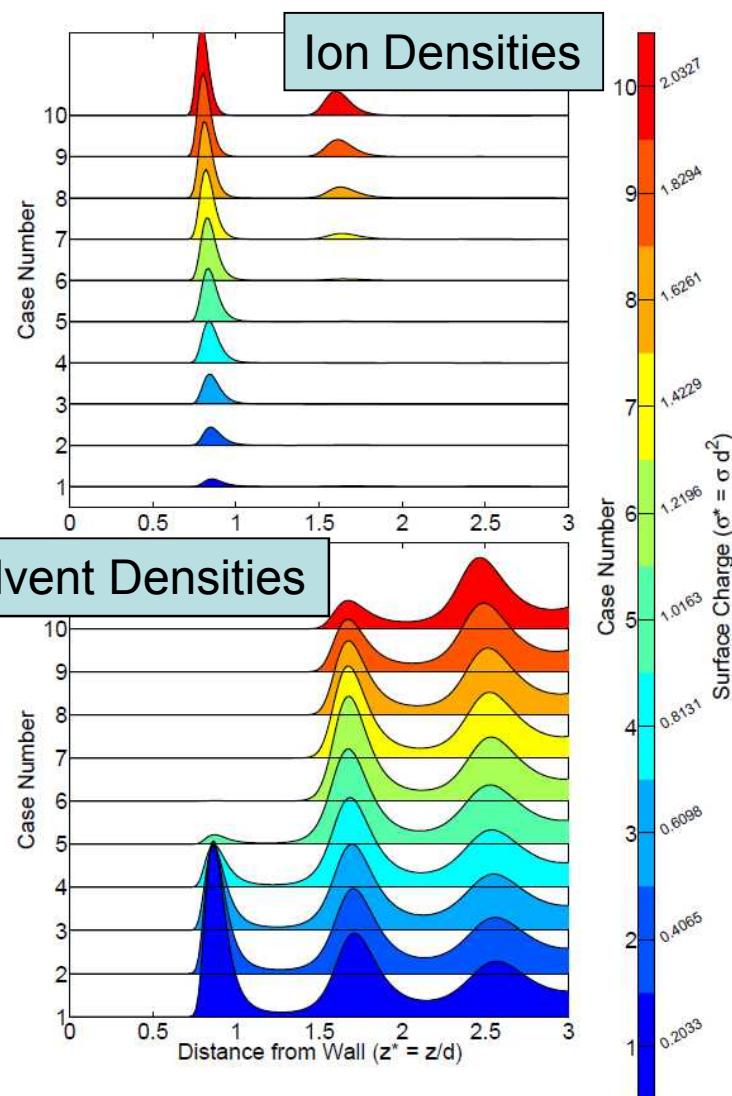


Cathode:

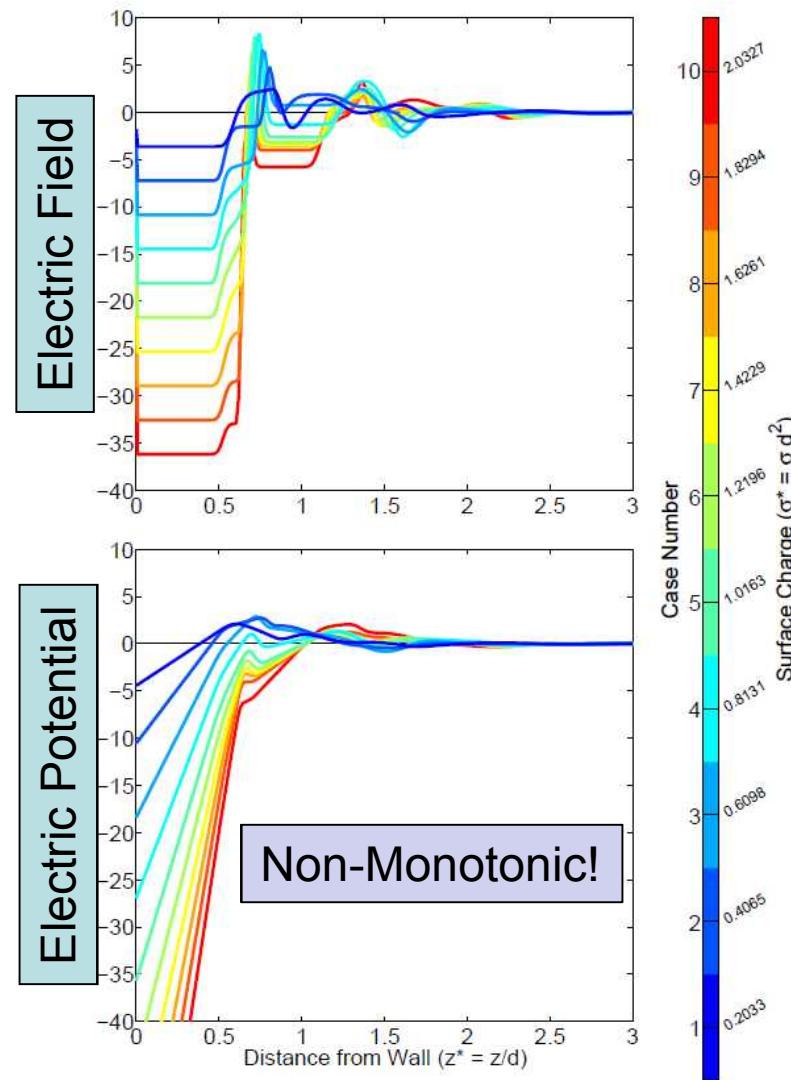
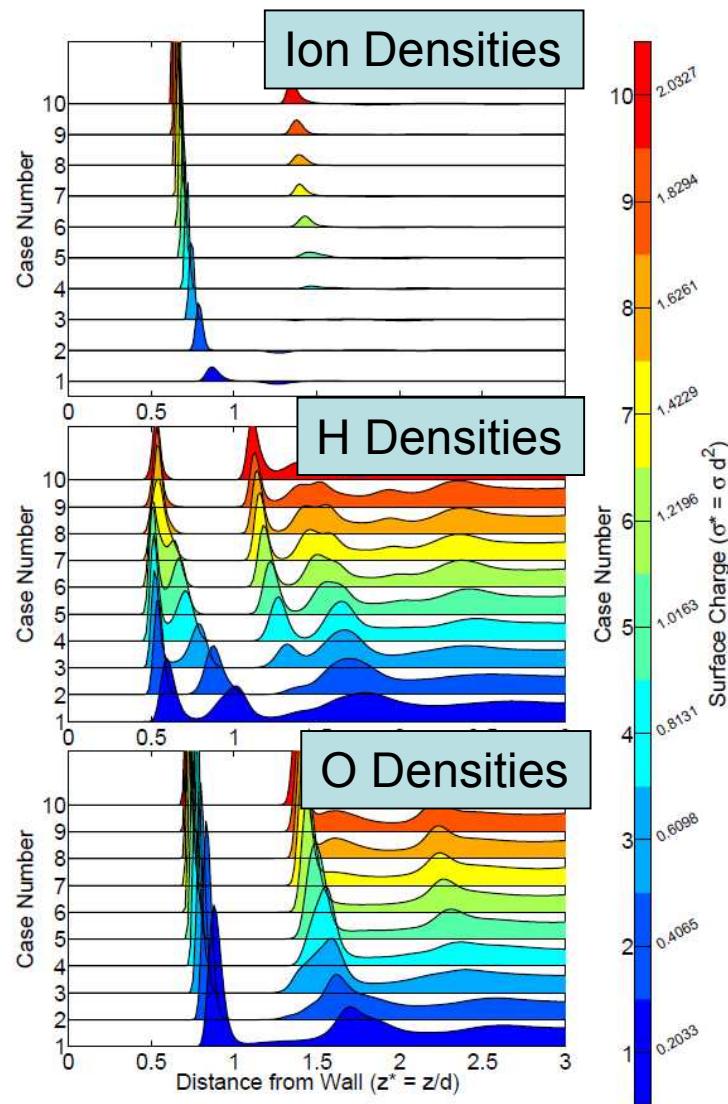
Increasing surface charge



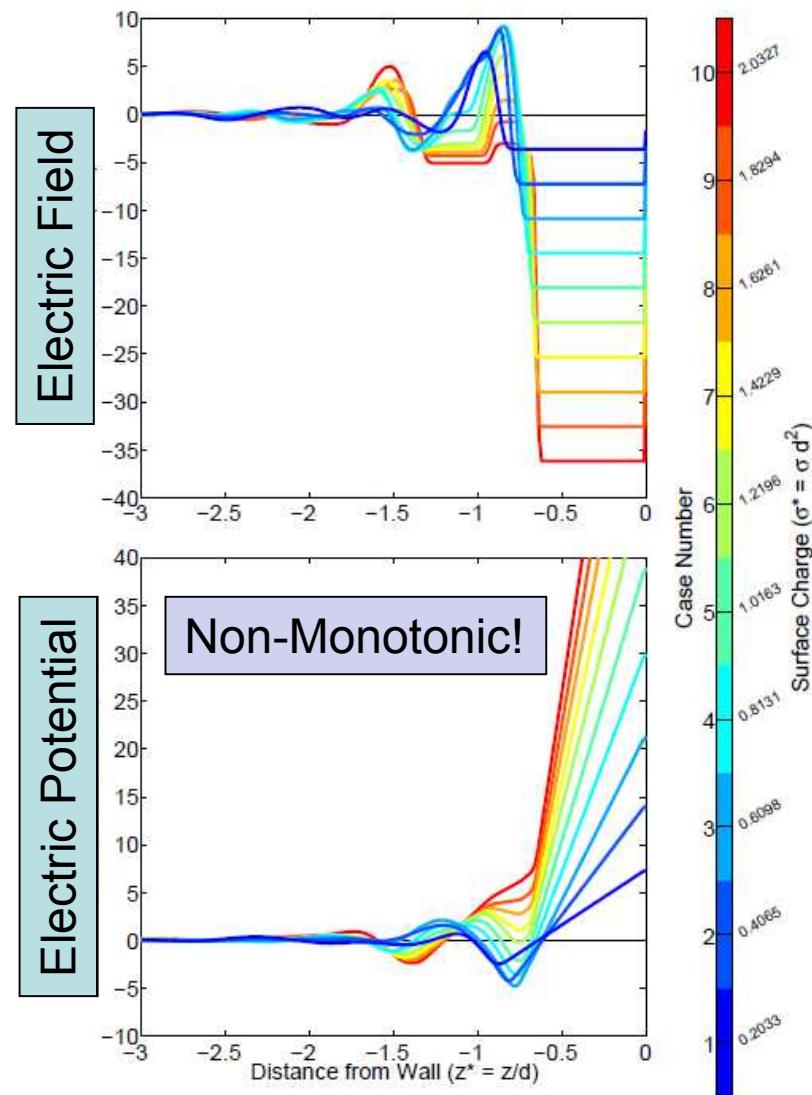
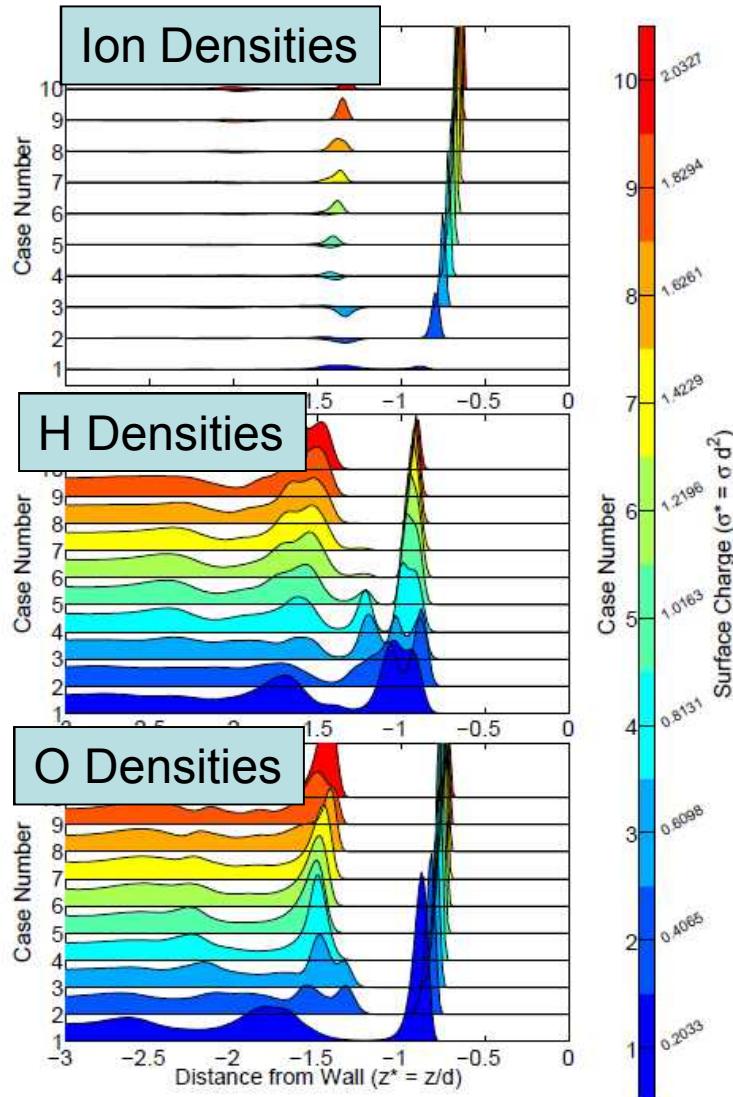
3CM Results



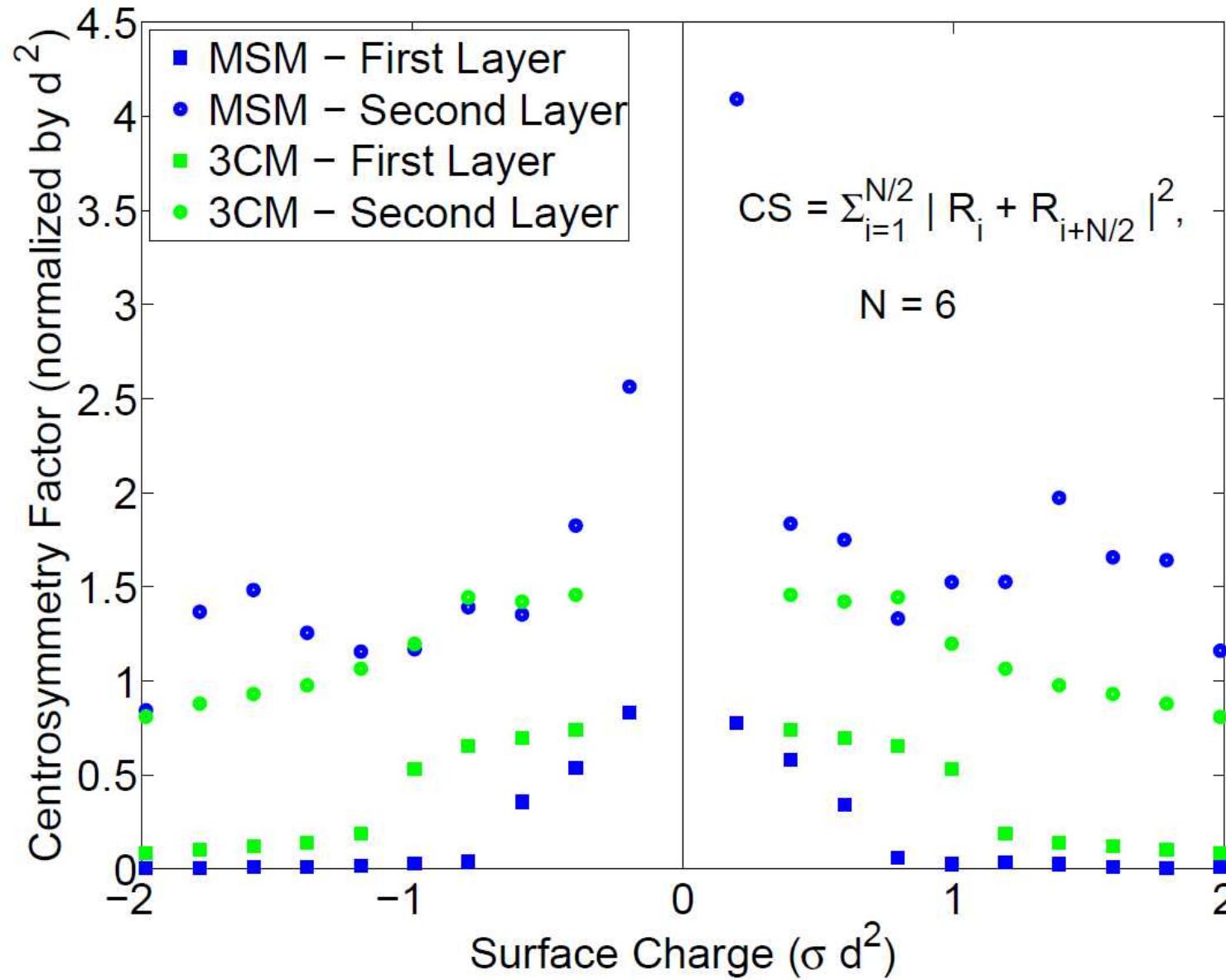
MSM Results (Anode only)



MSM Results (Cathode only)



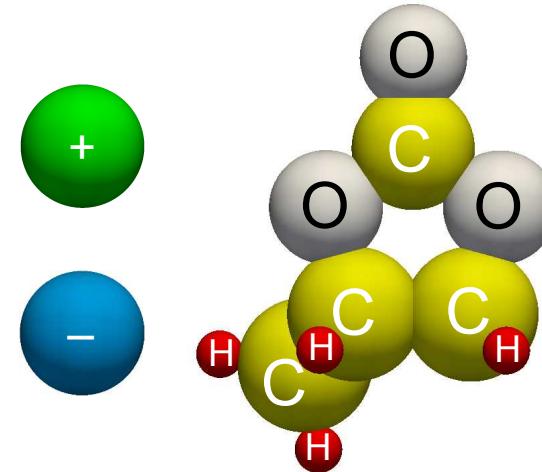
Structure of Adsorbed Layers



Work in Progress

Propylene Carbonate (PC) Solvent

- + and – ions
- Explicitly described PC molecule
- Dielectric constant = 1
- Model also includes explicit graphite substrate



Propylene Carbonate (low charge)

