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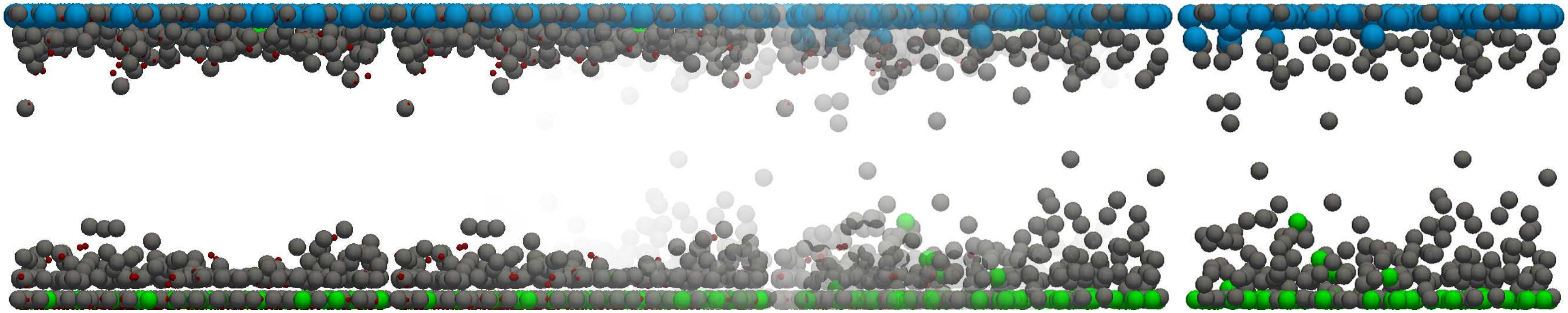

Molecular Dynamics Models of the Electric Double Layer for Large Zeta Potentials

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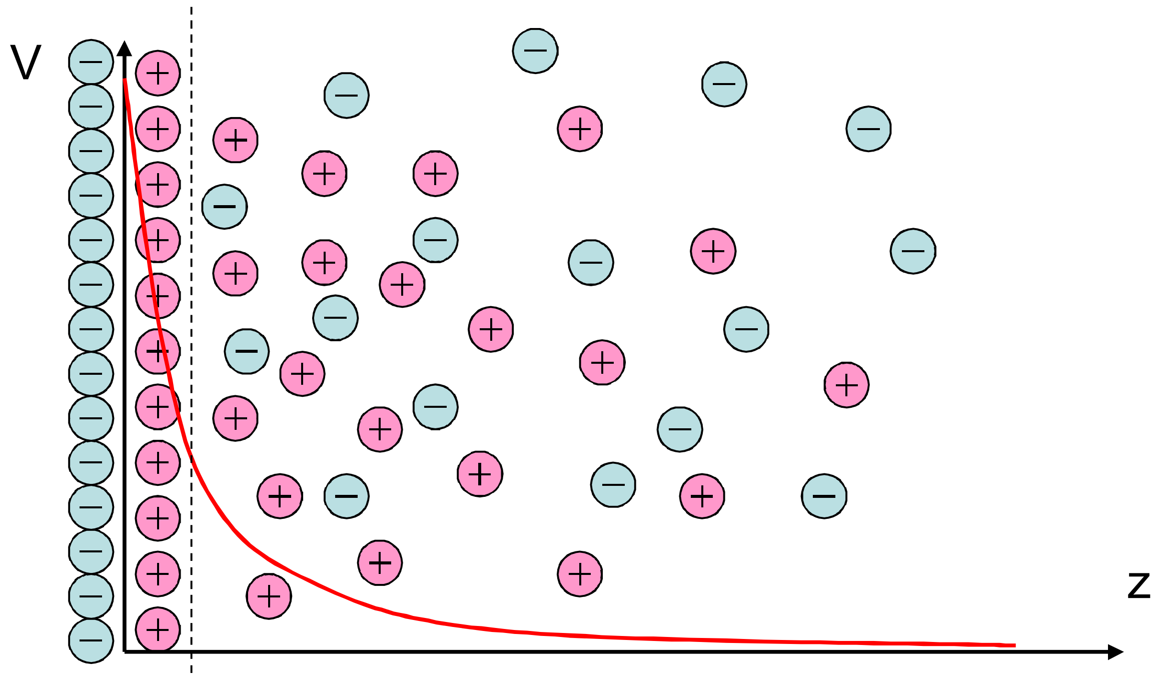
Electric Double Layer



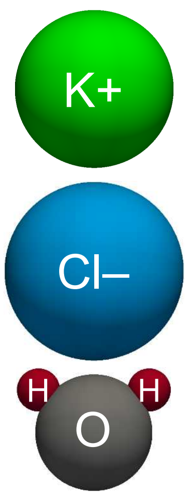
Existing Models

- Classical Poisson-Boltzmann (PB)
- Classical Density Functional Theory (DFT)

Molecular Dynamics Models

Polar Solvent Model

- K+ and Cl– ions
- Explicitly described H_2O molecules
- Dielectric constant = 1

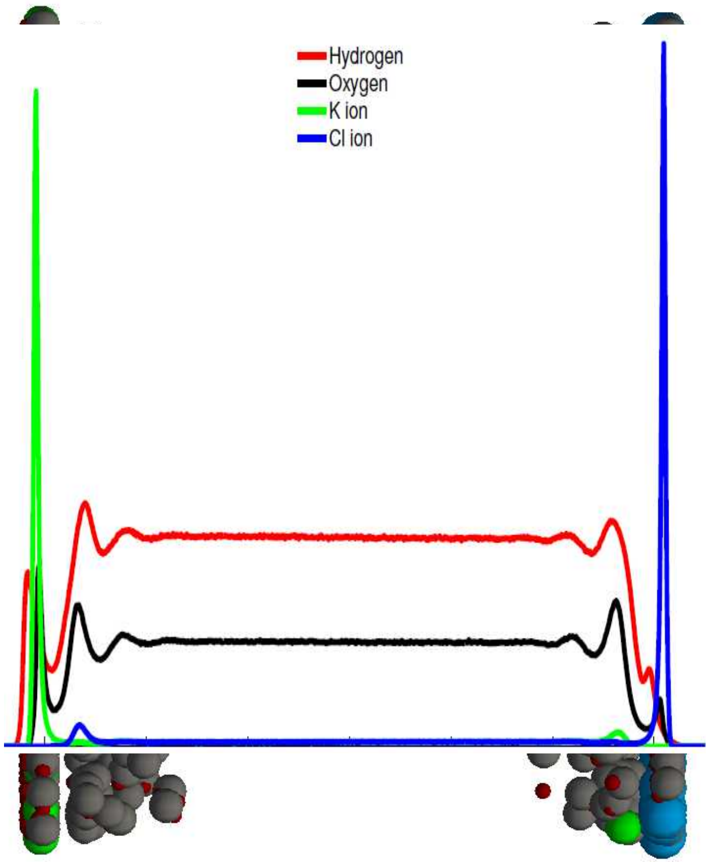


Nonpolar Solvent Model

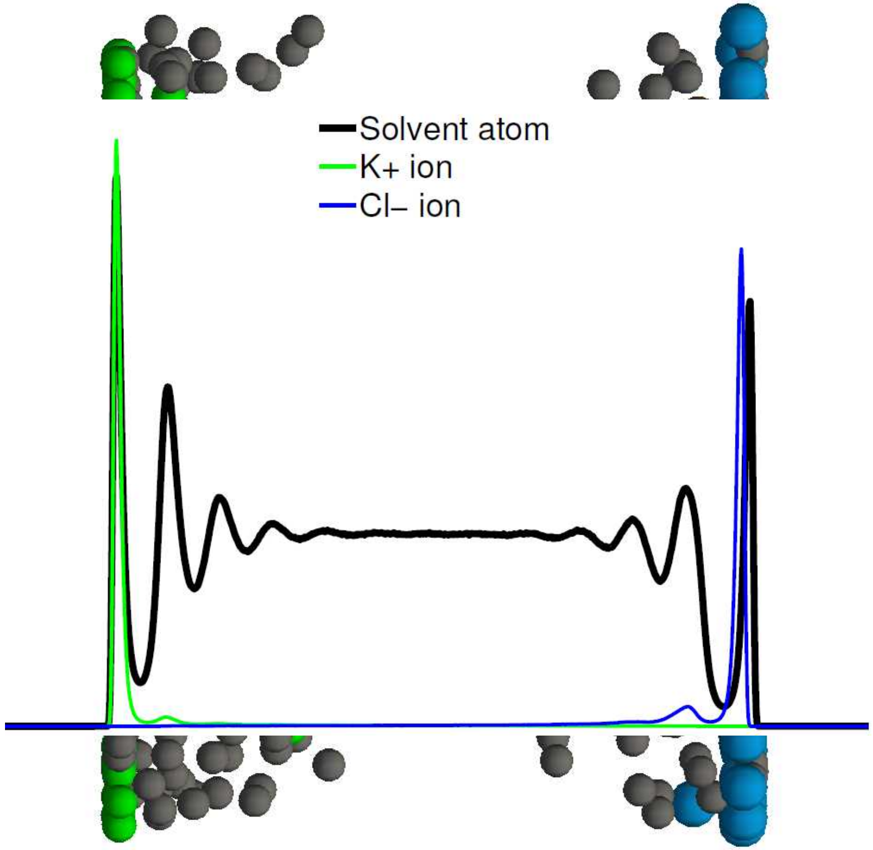
- + and – ions
- Nonpolar, neutral atoms represent H_2O molecule
- Dielectric constant = 80

Steady State Configurations

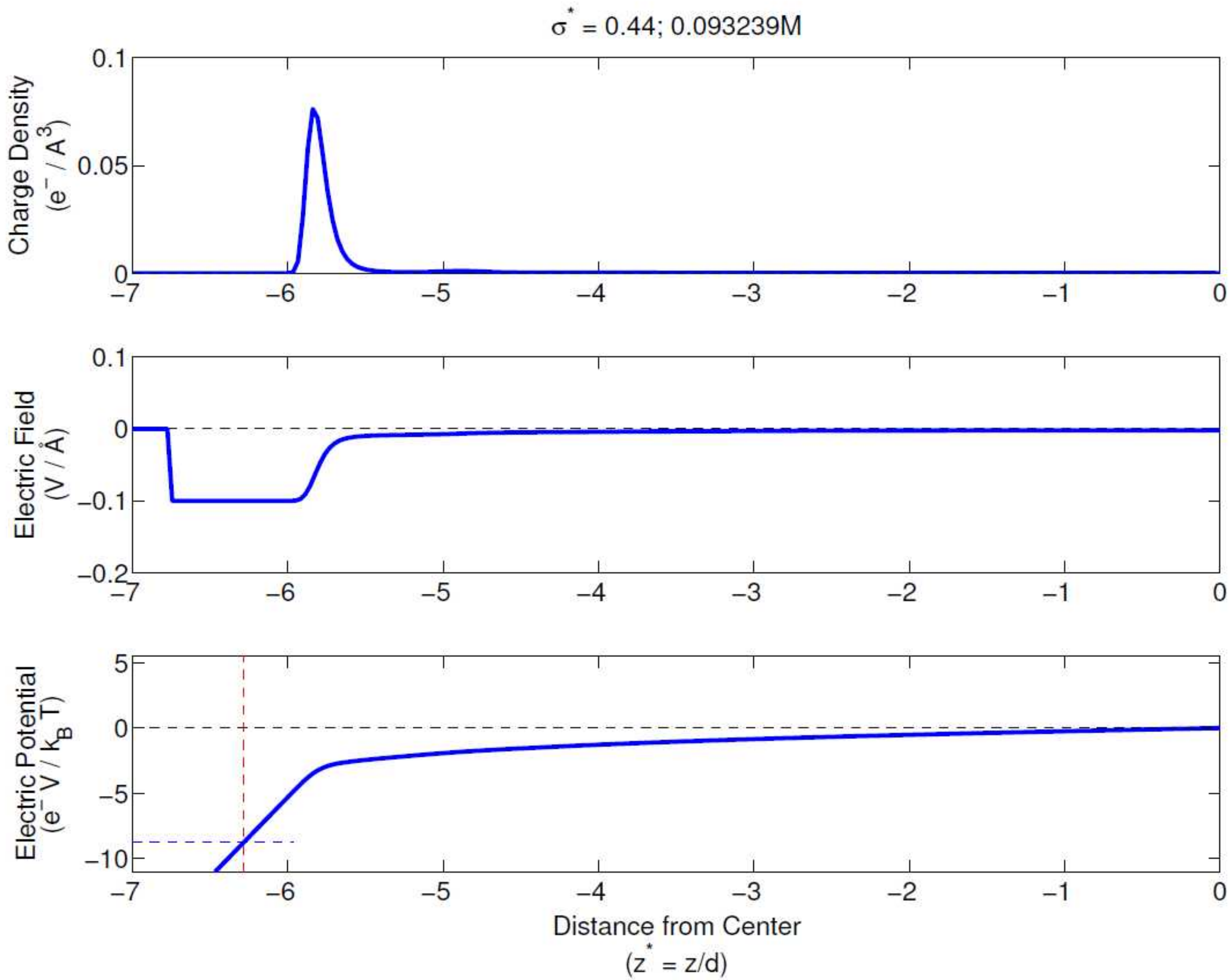
Polar Solvent Model



Nonpolar Solvent Model



Electric Potential Profiles



MD vs. Classical DFT vs. PB

Three Component Models:

MD & 1D Classical DFT

- + and – ions
- Nonpolar, neutral atoms represent H_2O molecule
- Dielectric constant = 80

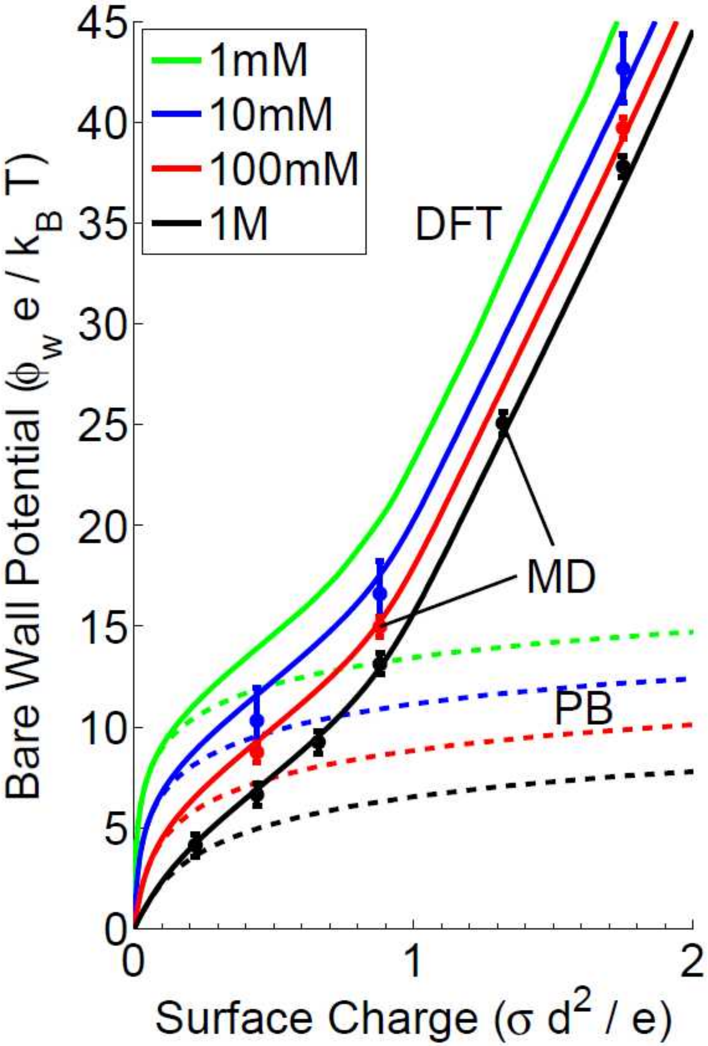
Simple Primitive Model:

Classical Poisson-Boltzmann

- + and – ions
- Solvent represented by dielectric constant = 80
- Exponential form

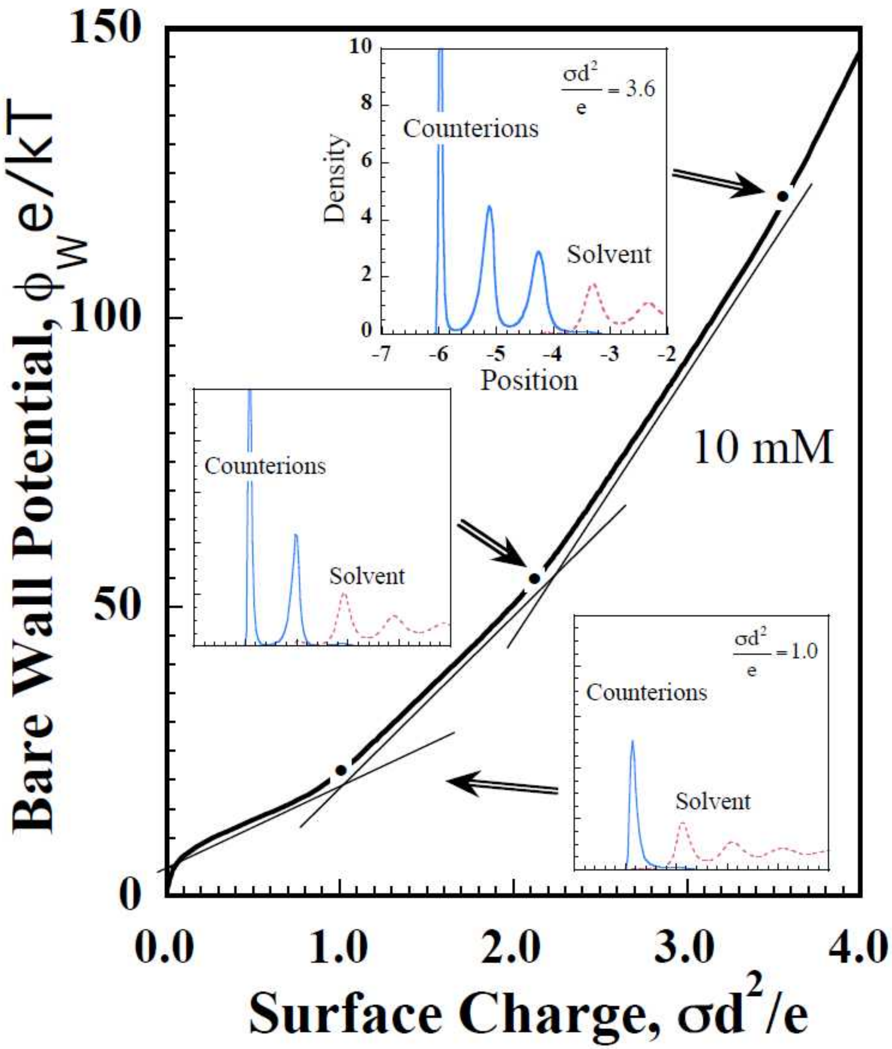
Deviation from Poisson-Boltzmann

- Non-polar Solvent MD model deviates from Poisson-Boltzmann theory
- Consistent with findings from Classical DFT simulations
- Capacitance of channels is shown to decrease significantly for high loading cases



Layer Filling Phenomenon

- DFT results to explore larger parameter space
- Inflection points signify solvent peak depletion – not counterion peak saturation
- Counterion peaks continue to grow as loading increases



Conclusion & Future Work

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- MD models developed to understand electric double layer in nanochannels
- Nonpolar solvent model illuminates physics that debunk PB theory at high surface charges
- Ongoing effort to achieve better agreement between polar and nonpolar solvent models

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