Presented at the COMSOL Conference 2008 Boston

Dependence of Potential and Ion Distribution on Electrokinetic Radius in Infinite and Finite-length Nano-channels

Jarrod Schiffbauer[*,1], Josh Fernandez[2], Will Booth[1], Kathleen Kelly[3], Aaron Timperman[3] and Boyd Edwards[1]

[1]Physics Dept. West Virginia University, [2]Chemical Engineering Dept, WVU, [3]Dept. of Chemistry, WVU

Abstract:

A site-binding/dissociation model is used to determine surface charge in numerical studies of the equilibrium potential and ion distributions inside infinite and finite-length nano-channels. This model allows us to investigate the response of surface (zeta) potential to environmental parameters such as reservoir salt concentration, solution pH and wall separation. The resulting ion and potential distributions in the electric double-layer (EDL) are used to calculate near-equilibrium charge and fluid transport through a nano-channel, demonstrating the possibility of flow-reversal at low salt concentration.

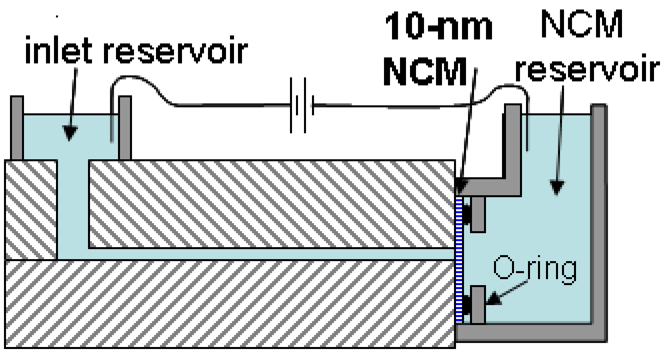
Keywords: Nanofluidics, Poisson-Boltzmann equation, electrokinetic transport

Outline:

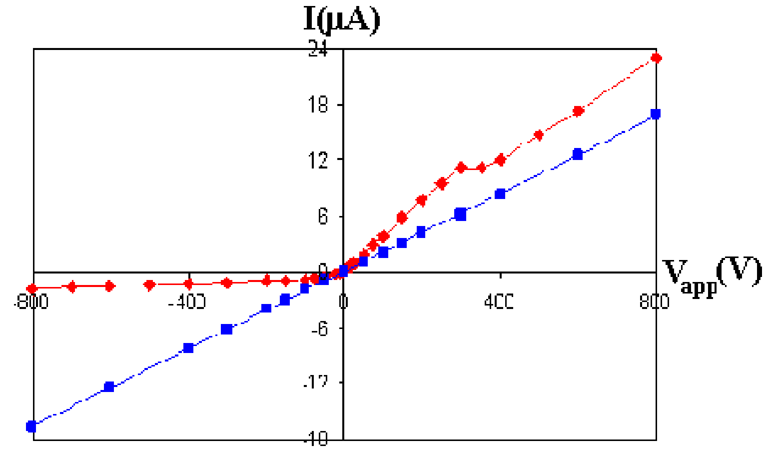
- Introduction
- Theory
- Computational method
- Results
- Conclusions and on-going work

Introduction: NCM pre-concentrator experiments

Device geometry

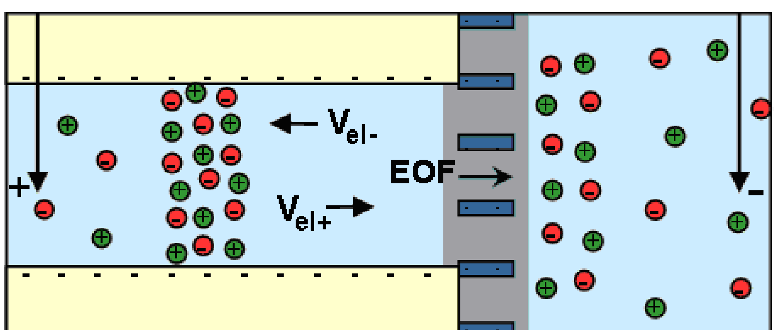


I-V characteristic

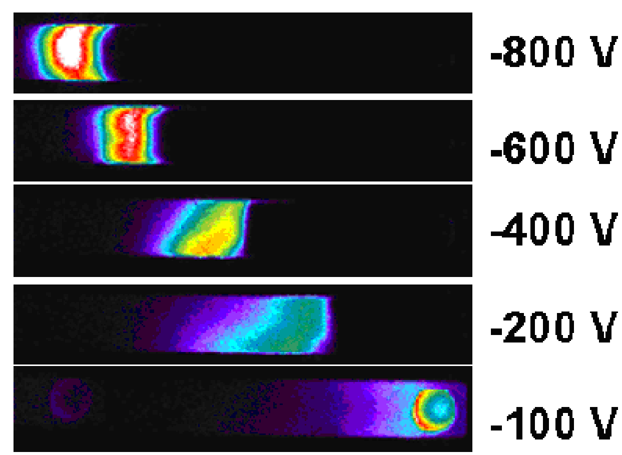


NCM (red) and no NCM (blue)

Schematic of NCM/NMI device in "off" state



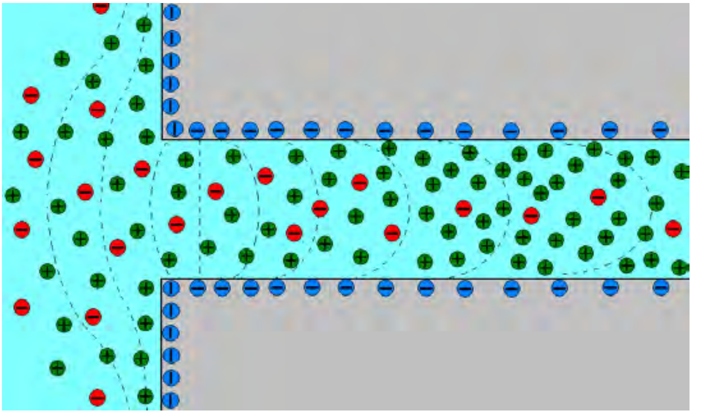
"Off" state concentration enhancement



(NCM/NMI at far right)

Introduction: NCM modeling

- Model concentration enhancement and depletion effects as function of applied voltage, pore radius, porosity, bulk solution composition, etc.
- First, develop a simple model of transport through membrane that is capable of responding to changes in applied fields and solution chemistry



Three modes of transport to consider:

•electrophoretic transport
•electro-osmosis
•diffusion

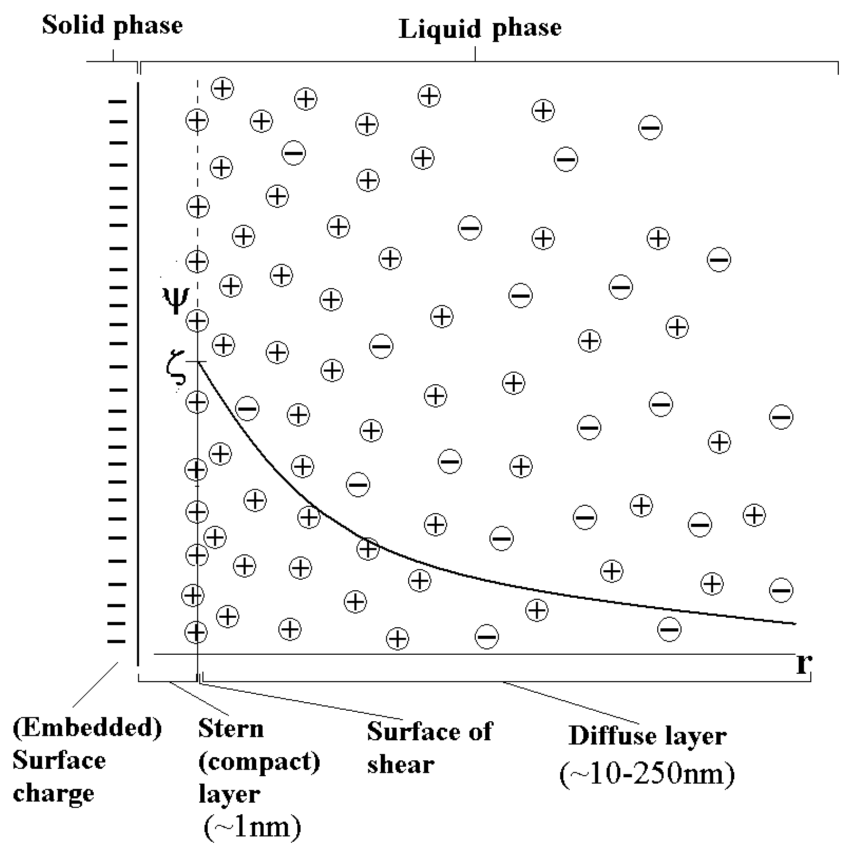
The first two depend directly on the surface(zeta) potential and here we demonstrate how surface potential may vary with bulk ion concentration and proximity to other charged surfaces.

CAVEAT: All we seek at this point is a qualitative understanding!

Theory: Gouy-Chapman EDL

Continuum model that treats diffuse layer of ions in neutral solution with constant ε

Identifies ζ-potential and surface potential, Stern layer capacitance neglected (finite size of ions, etc.)



Theory: Poisson-Boltzmann model

The nonlinear Poisson-Boltzmann equation and squared inverse Debye length:

$$\nabla^2 \Psi = 2(\kappa a)^2 \sinh(\Psi) \qquad \kappa^2 = \frac{e^2}{kT}\frac{n_o}{\varepsilon}$$

The boundary conditions:

$$\left.\frac{d\Psi}{d\rho}\right|_{\rho=0} = 0 \qquad \left.\frac{d\Psi}{d\rho}\right|_{\rho=1} = -\frac{ea}{kT}\frac{\sigma_s(\Psi(1))}{\varepsilon}$$

With dimensionless coordinate and potential

$$\rho \equiv \frac{r}{a} \qquad \Psi \equiv \frac{e\psi}{kT}$$

Theory: Site-binding/dissociation

$$AH \leftrightarrow A^{-} + H^{+}$$

$$\sigma_s(\Psi_s) = -\left(\frac{e}{S}\right)\frac{d}{\exp(-\Psi_s) + d}$$

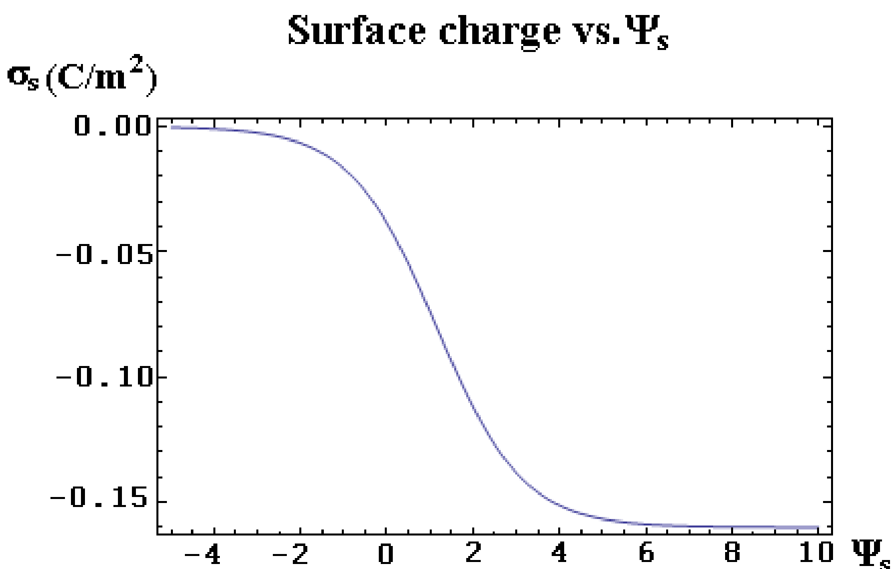


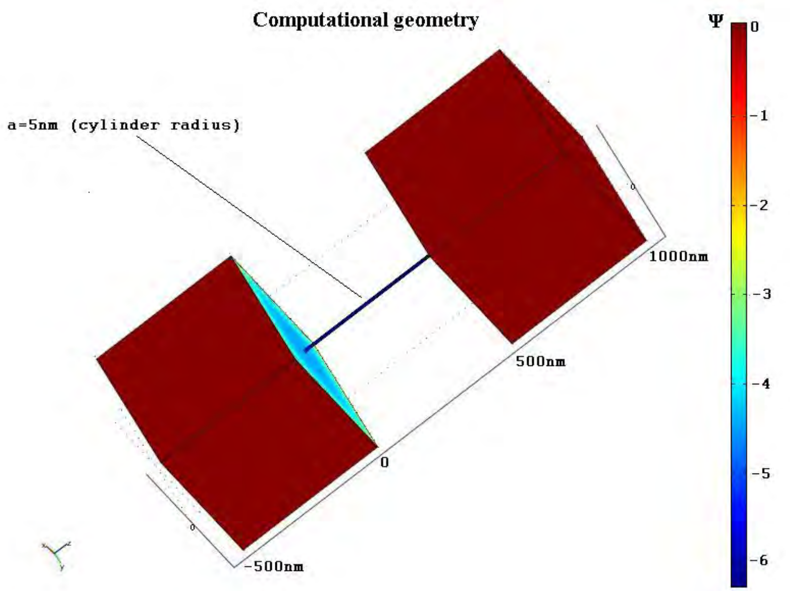
Figure shows surface charge vs. dimensionless potential at fixed reservoir pH for pK=7.5 (experimental value for silica)

$$d \equiv \frac{Z}{H} = \frac{10^{-\mathrm{pK}}}{10^{-\mathrm{pH}}}$$

$$\Psi_s \equiv \frac{e\zeta}{kT}$$

Computational method

- Coefficient form for PDE modes, stationary nonlinear problem
- Direct solvers, free meshes
- Various geometries:
  - Infinite cylindrical
  - Finite cylindrical
  - Finite length 2D channels

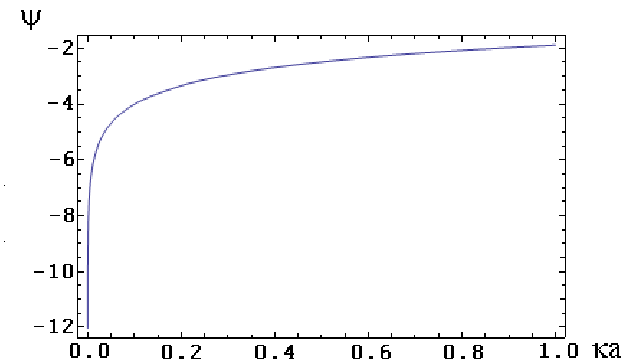


Results:

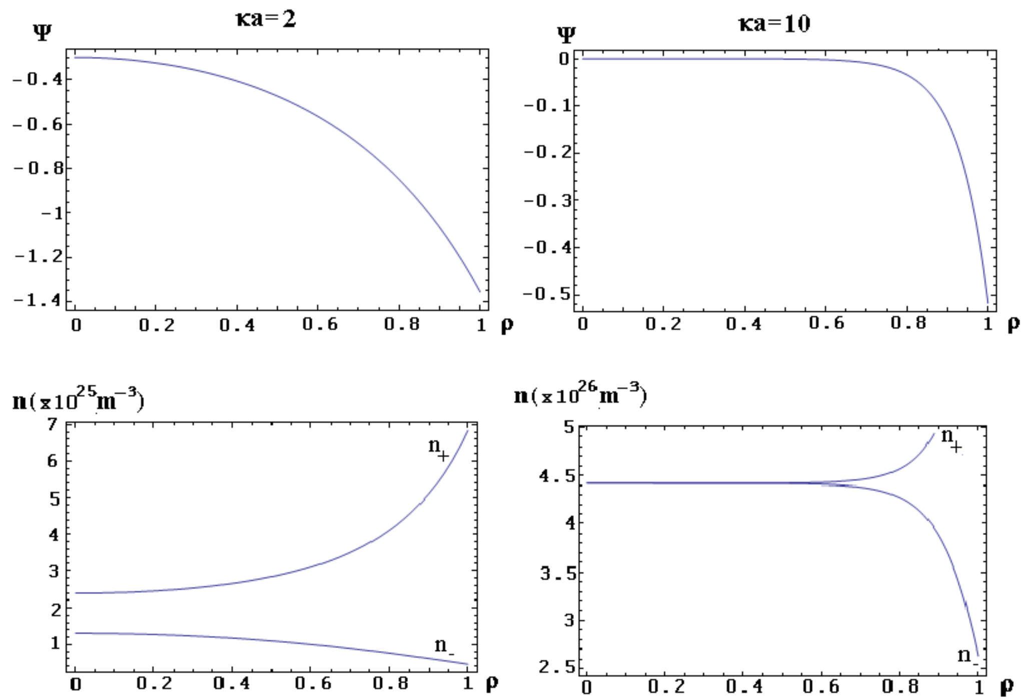
- Infinite nanochannels
- Finite nanochannels
- Transport (current-voltage characteristics)

Infinite nanochannels

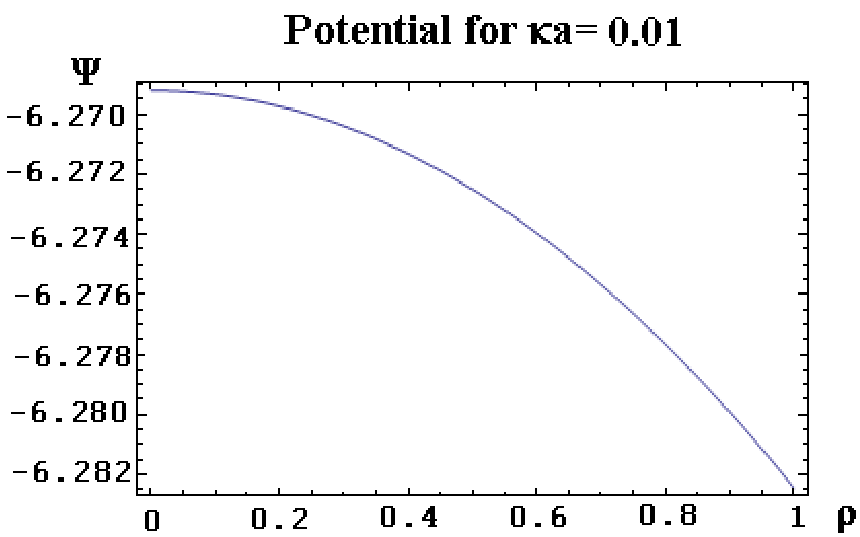
Surface potential vs. electrokinetic radius (κa)

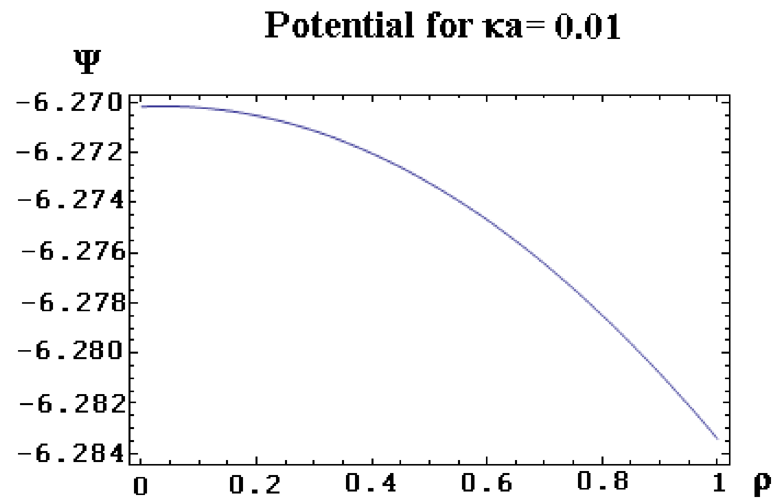


Potential and ion distributions



Infinite and finite nanochannels

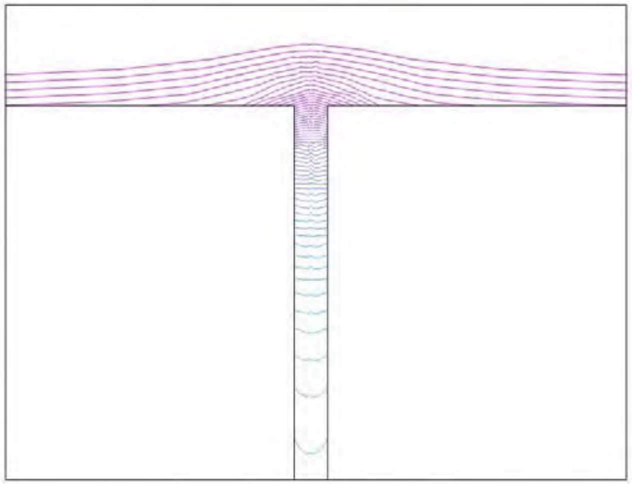


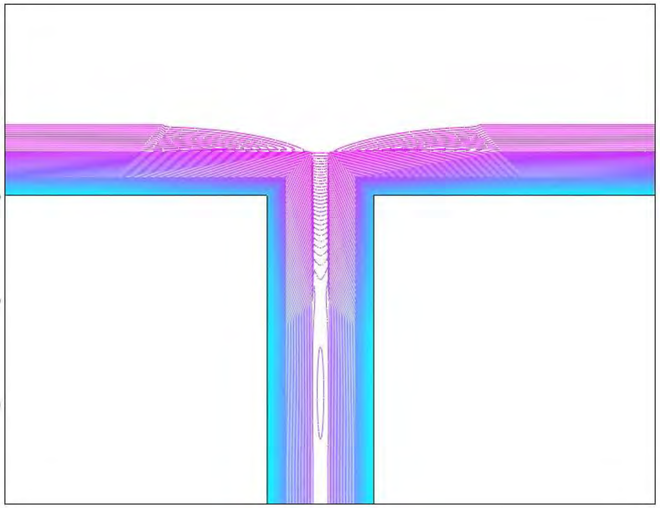


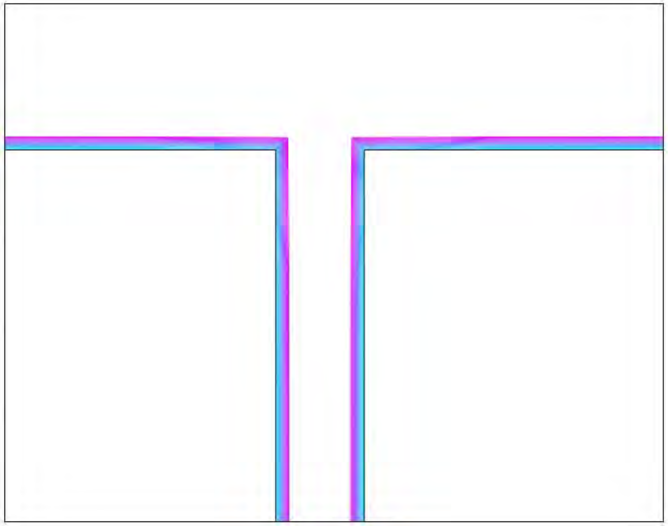
(Taken from a cross-section at the middle of the finite 5nm nanochannel)

Radial dependence of dimensionless potential in infinite (left) and center of a finite cylinder (right) of radius a= 5 nm

Finite nanochannels

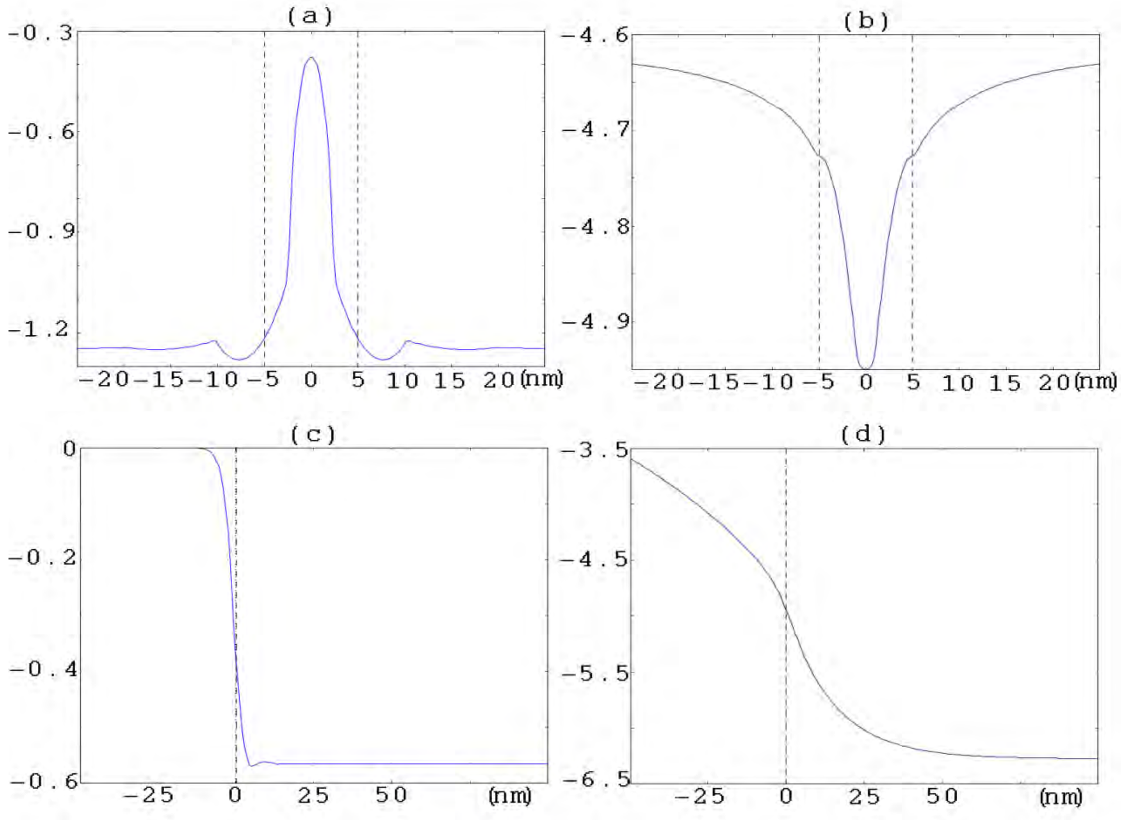






Equipotential surfaces near pore mouths for (clockwise from above) κa= 0.01, 2, and 10 for a=5 nm channels.

Finite nanochannels



Dimensionless potential on exterior membrane surface near pore mouth for (a) $\kappa a = 2$ and (b) $\kappa a = 0.01$. Below are on-axis potentials near the pore mouths (dashed lines) for (c) $\kappa a=2$ and (d) $\kappa a= 0.01$

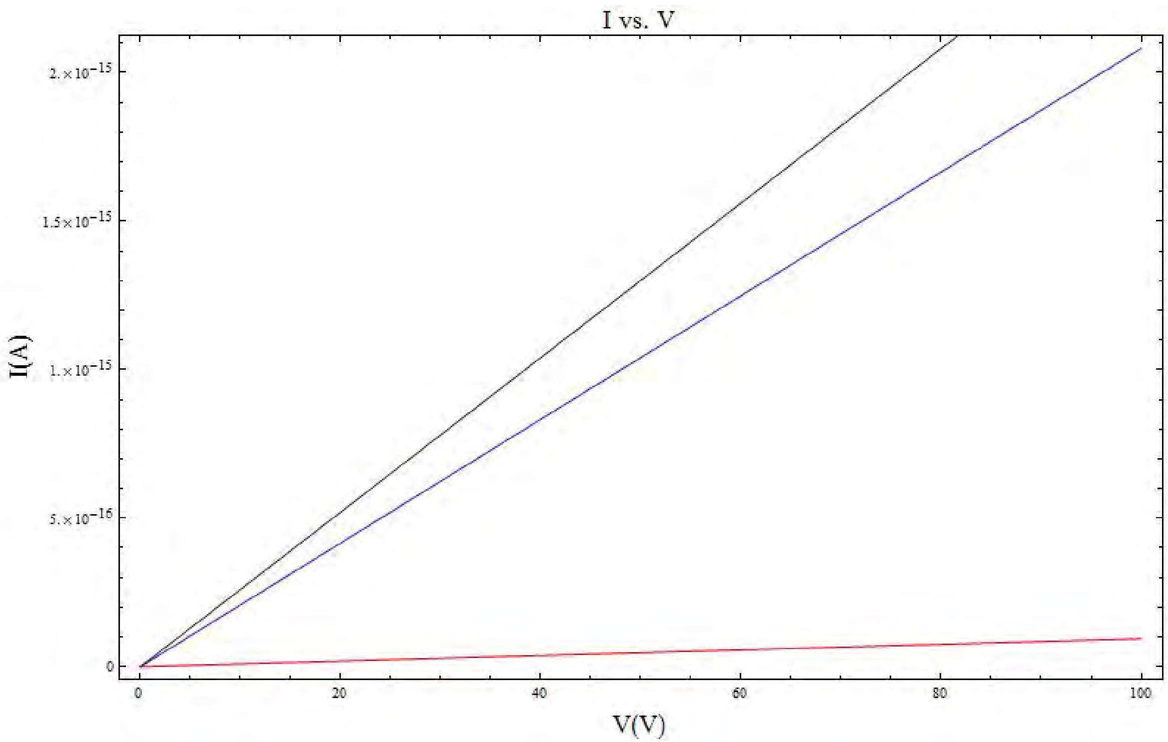
Current flow

Quasi-equilibrium equation for current-voltage relations

$$I = \Gamma(\kappa a)E_{\mathrm{app}}$$

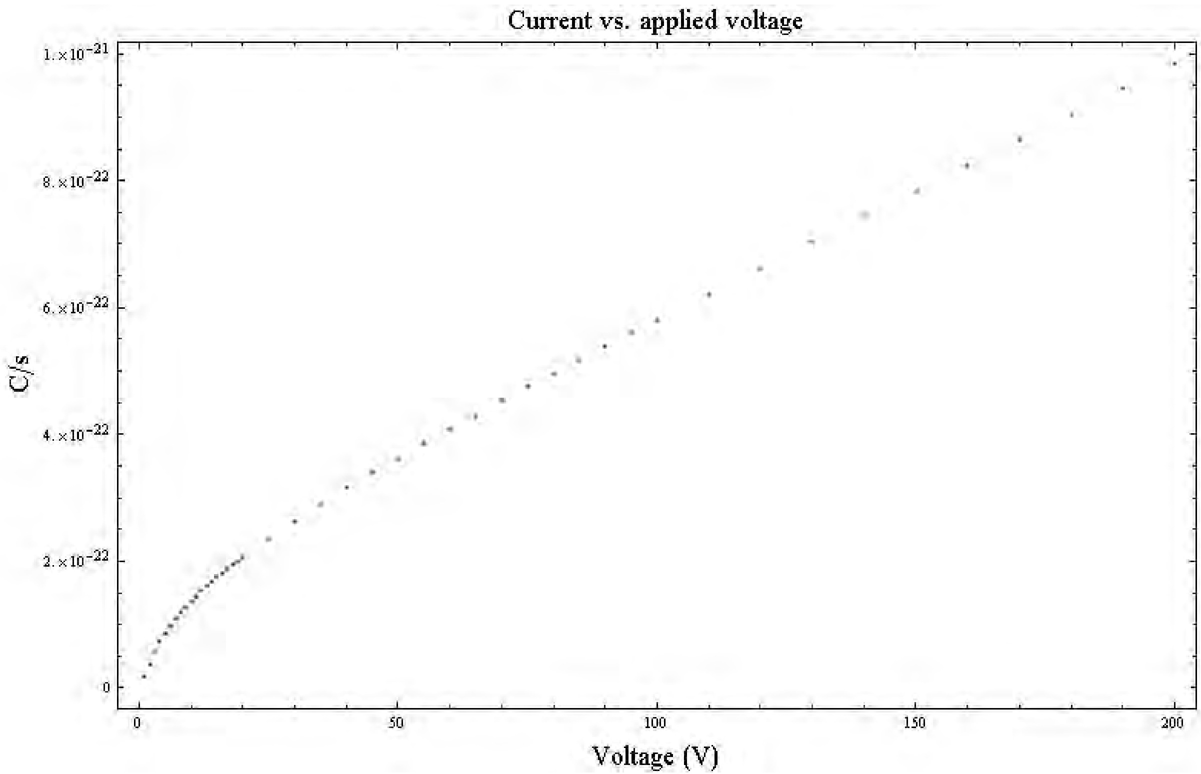
$$\Gamma(\kappa a) = -\frac{2\epsilon kT}{e}(\kappa a)^2 \left[\left(\mu_b - \frac{\epsilon kT\eta}{e}\right)\left(\Psi_s \int \sinh(\Psi)d\Omega\right)_{\kappa a} - \frac{\epsilon kT\eta}{e}\left(\int \Psi \sinh(\Psi)d\Omega\right)_{\kappa a} \right]$$

Quasi-equilibrium I-V



Quasi-equilibrium current vs. voltage for infinite cylinders (‘classical’ electrokinetics) for a = 5 nm, μ_b=5 X 10^{-8} m^2/Vs for κa = 0.01 (red), 2 (blue), and 10 (black) using site-binding surface charge model

Non-equilibrium I-V curve(PNP)



Current vs. voltage for non-equilibrium PNP model, finite-length channel with end-effects and diffusion, a=30 nm (no EOF.) Constant surface charge of $-0.5\mathrm{X}10^{-22}$ C/nm^2.

Conclusions:

- We have demonstrated how EDL overlap affects potential and ion distribution using a simple model for dissociation of surface groups
- We have investigated potential and ion distributions in a variety of geometries.
- We have used these models to consider classical electrokinetic transport and have begun non-equilibrium studies using a restricted (PNP) model

On-going work:

- Consider the effects of varying degrees of overlap in PNP models
- Reconcile the infinite-cylinder prediction of possible flow reversal with finite-channel models and basic physics (what part of the model breaks down at strong overlap?)
- Building bigger and better models:
  - PNP with variable surface charge models
  - Full non-equilibrium transport including EOF at the nano-micro interface

Thank you!

Thank you all for your attention, and the authors would like to thank the following for financial support:

NSF grant number EPS-0554328, the WVNANO initiative, and the WVU Physics Dept.