Toward an Understanding of Nonlinear Electrochemical Transport

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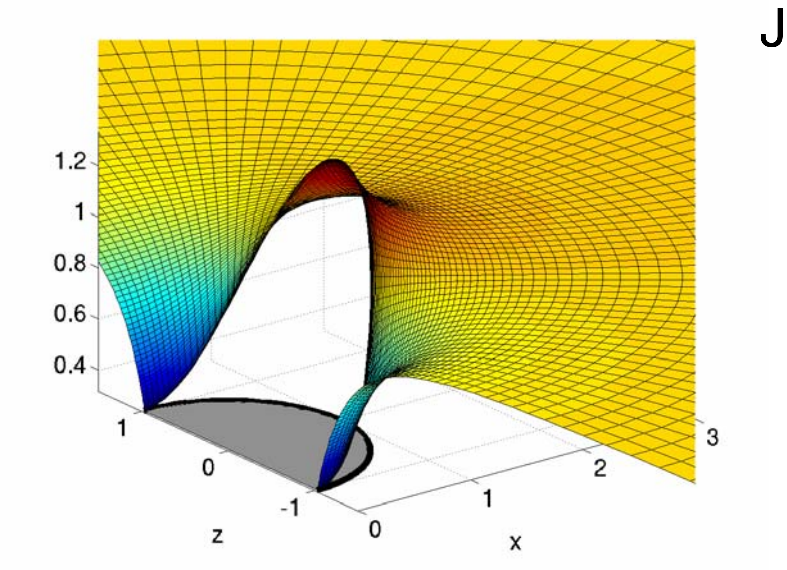
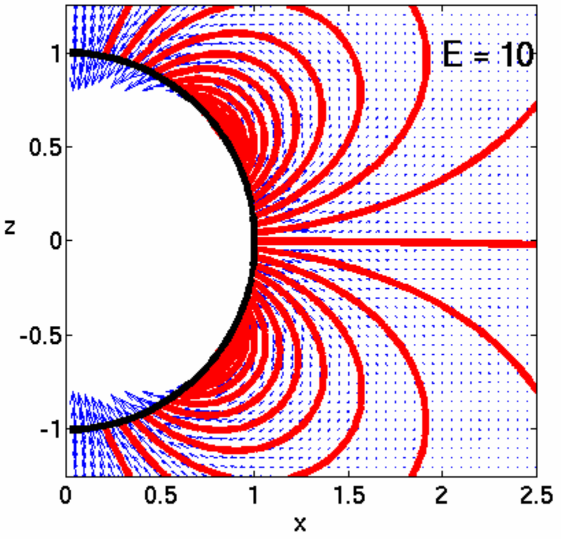




“Rules” for Talk

- Somewhat Informal
- Interrupt to ask questions
- “The ***journey*** is more important than the destination”

Outline

- ✓ Motivation
- Mathematical Model
- Nonlinear Transport Around Conductors

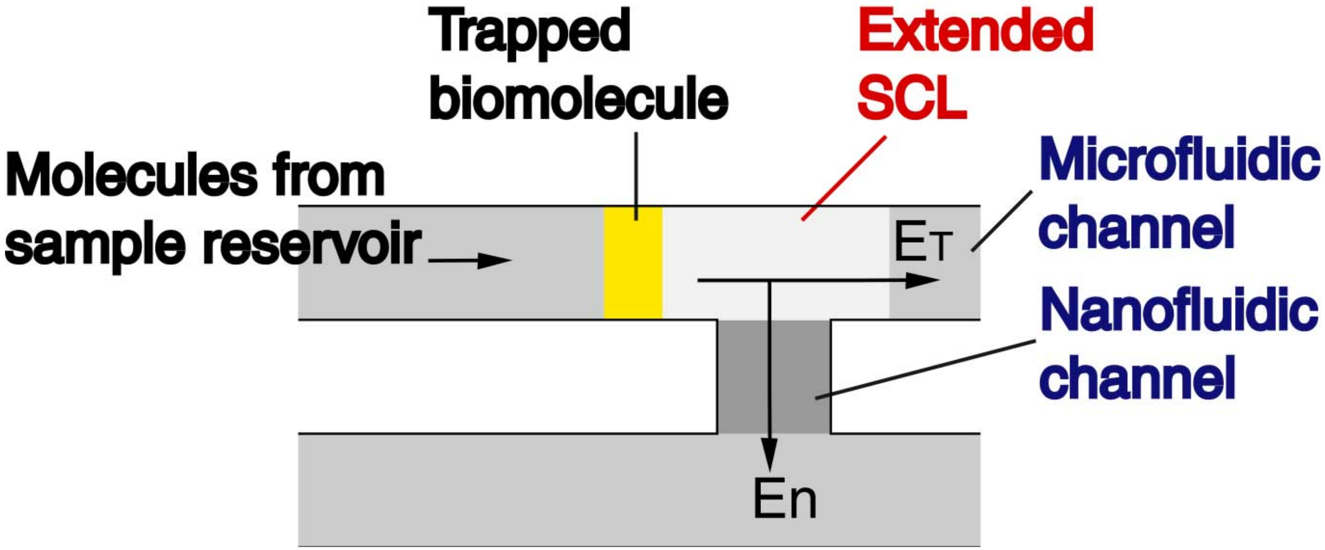
ICEO Microfluidic Devices

QuickTime™ and a
DV/DVCPRO - NTSC decompressor
are needed to see this picture.

Movie courtesy of J. Levitan and M. Bazant (MIT)

- Ion transport crucial to flow
- Theory lags experiment
- Hard to decouple physical processes at high applied fields

Nanofluidic Biomolecule Trapping



NOTE: SCL = Space-Charge Layer

Image of courtesy Y.-C. Wang and J. Han (Mech. Eng., Bio. Eng., EECS at MIT)

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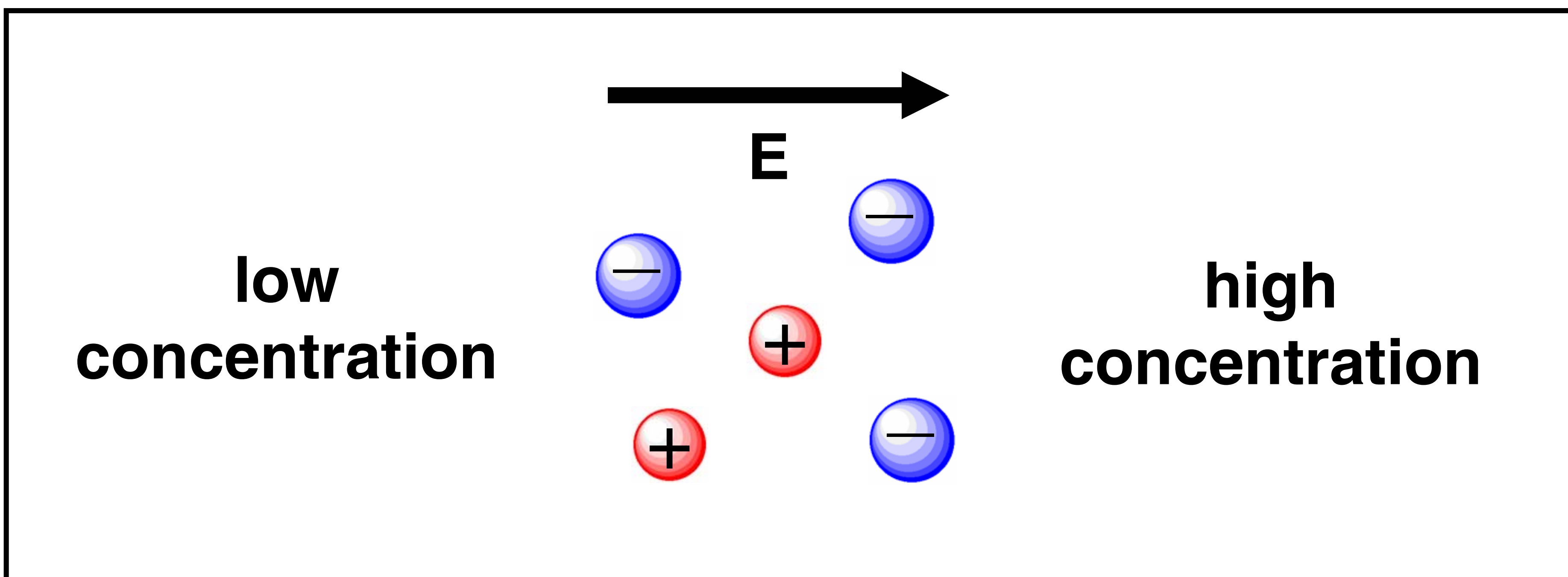
Nernst-Planck Equation

diffusion

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot F_i = \nabla \cdot (\nabla c_i + z_i c_i \nabla \phi)$$

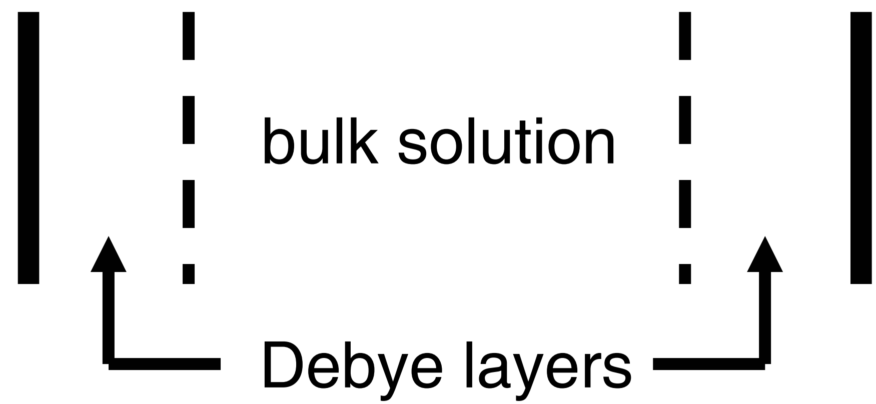
electromigration



Poisson Equation

$$-\epsilon^2 \nabla^2 \phi = \rho = \sum_i z_i c_i$$

$$\epsilon \equiv \frac{\lambda_D}{L} = \frac{\text{Debye length}}{\text{system size}}$$

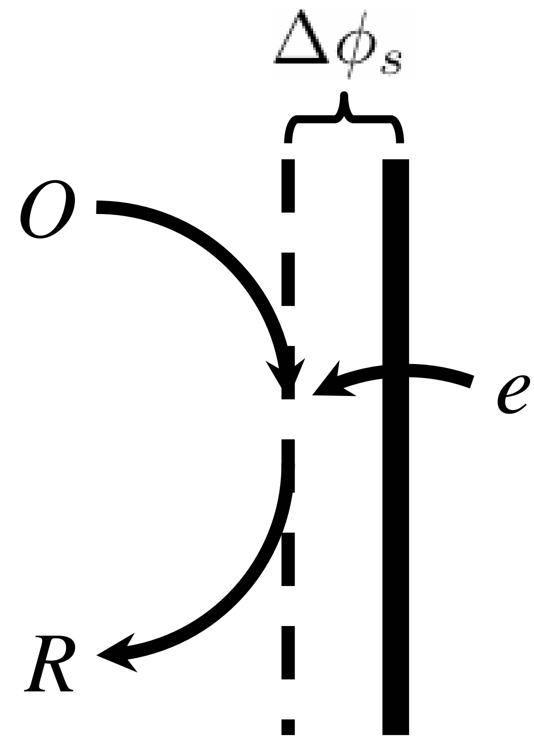


- Typically: $\epsilon \approx 10^{-4} - 10^{-3}$

Charge Density Significant Only in Boundary Layer!

Faradaic Electrode Reactions

$$O + e \underset{k_a}{\overset{k_c}{\rightleftharpoons}} R$$



Reaction Boundary Conditions

$$F_O \cdot \hat{n} = r(c_O, c_R, \Delta\phi_s)$$

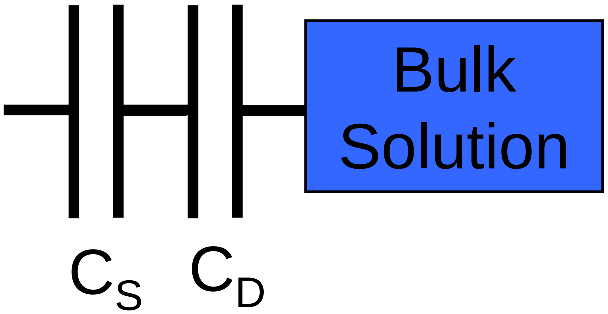
$$F_R \cdot \hat{n} = -r(c_O, c_R, \Delta\phi_s)$$

$$r\left(c_O, c_R, \Delta\phi_s\right) = k_c c_O \exp\left(-\alpha_c \Delta\phi_s\right) - k_a c_R \exp\left(\alpha_a \Delta\phi_s\right)$$

Double Layer Capacitance

- Grahame

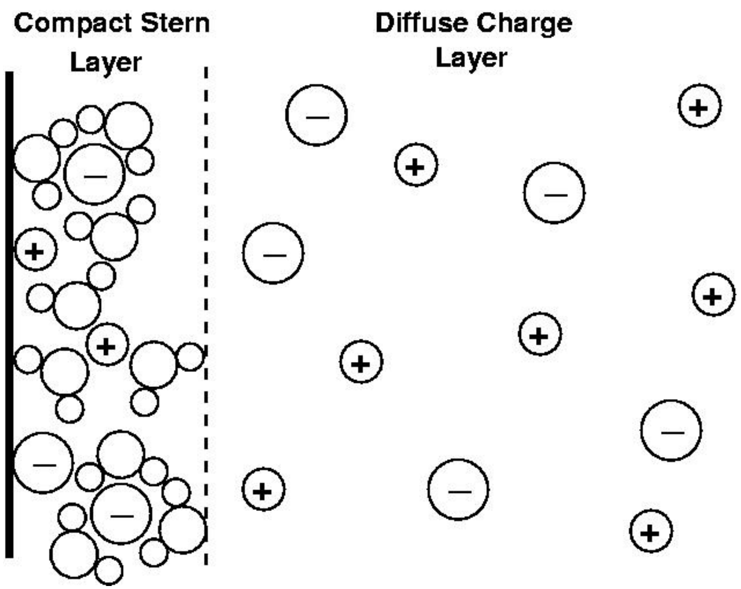
$$\Delta\phi_s = -\int_0^{-\epsilon\frac{\partial\phi}{\partial n}} \frac{d\sigma}{C_S(\sigma)}$$



- Gouy-Chapman-Stern

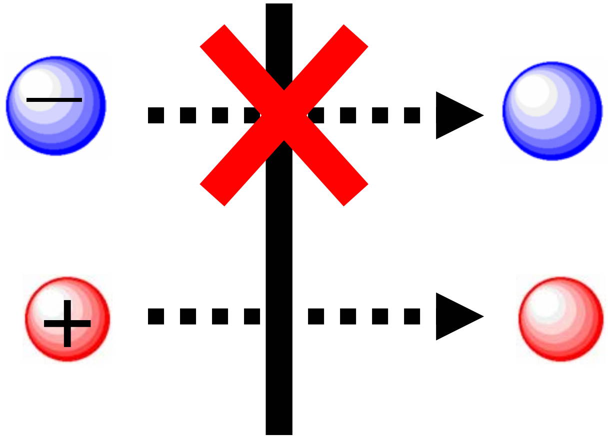
$$\Delta\phi_s = \delta\epsilon\frac{\partial\phi}{\partial n}$$

$$\delta^{-1} = \begin{array}{l}\text{effective}\\ \text{Stern capacitance}\end{array}$$



No-Flux BCs for Inert Ions

$$F_i \cdot \hat{n} = 0$$



Outline

- Motivation
- Mathematical Model

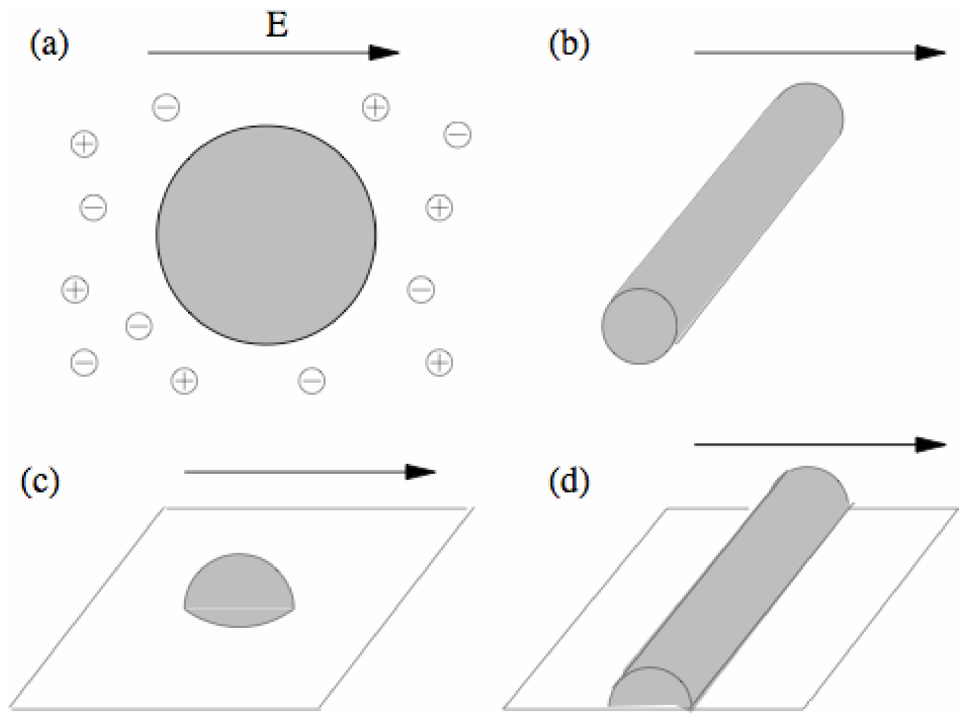
✓ Nonlinear Transport Around Conductors

Model Problems in Nonlinear Electrokinetics

sphere cylinder

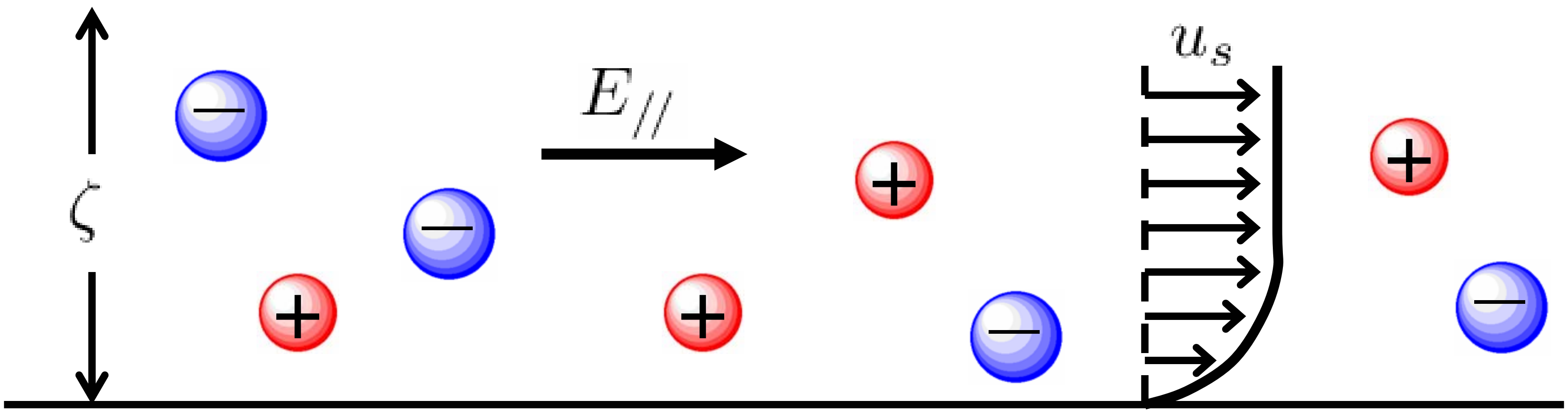
metal colloidal particles:

metal surface patterns or electrodes in microchannels:



We analyze *nonlinear* electrochemical relaxation in these geometries as a first step toward a theory of induced-charge electro-osmosis (or ACEO) in *large electric fields*.

Intuition Behind Electrokinetics



- *Surface* charge transport induces effective slip velocity

$$u_s = -\frac{\varepsilon\zeta}{\eta} E_{//}$$

- Slip velocity drives *bulk* fluid flow

- No pressure gradients required for flow

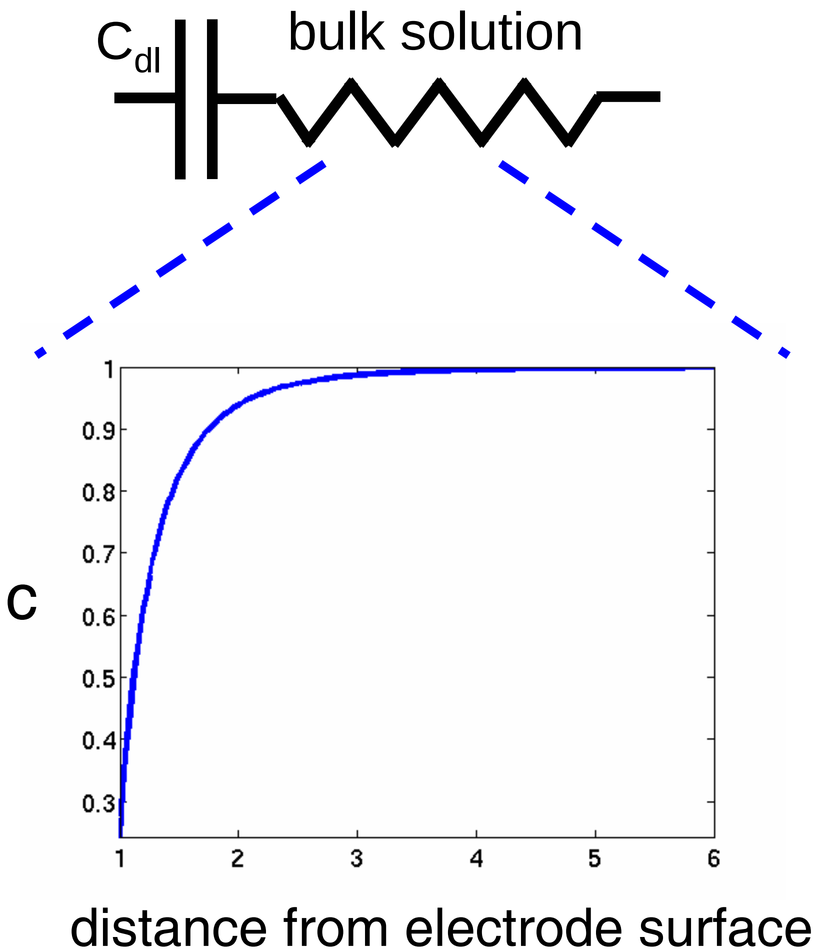
Electrochemical Circuit Models

Simonova (1977), Ramos et al (1999), Ajdari (2000), Bazant/Squires (2004)

- Uniform concentration profile: $c_{\pm} = \text{const}$
- Bulk solution = linear resistor: $j = \sigma E = -\sigma \nabla \phi$
- Double layer = capacitor: $\frac{dq}{d\zeta} = C_{dl}(\zeta)$

$$\nabla^2 \phi = 0 \qquad \frac{dq}{dt} = C_{dl} \frac{d\zeta}{dt} \propto E \cdot \hat{n}$$

Breakdown of the Circuit Model



- Concentration variations break resistor model

- Failure at $Du = O(1)$

$$Du \propto \epsilon \sinh^2 (\zeta/4)$$

$$\approx \epsilon e^{Ea} \qquad \epsilon \equiv \frac{\lambda_D}{a}$$

Bazant, Thornton, Ajdari (2004)

Beyond the Circuit Model

- Nernst-Planck Ion Transport

$$\frac{\partial c_\pm}{\partial t} = \nabla \cdot (\nabla c_\pm \pm c_\pm \nabla \phi)$$

- Local Electroneutrality

$$\sum_i z_i c_i = 0$$

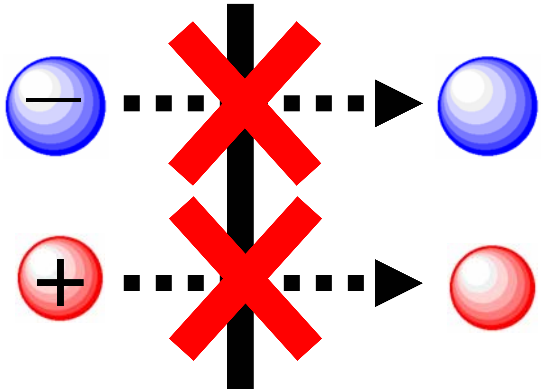
- No bulk charge accumulation

$$\nabla \cdot j = \nabla \cdot (c \nabla \phi) = 0$$

Surface Boundary Conditions

- No-Flux (blocking electrodes)

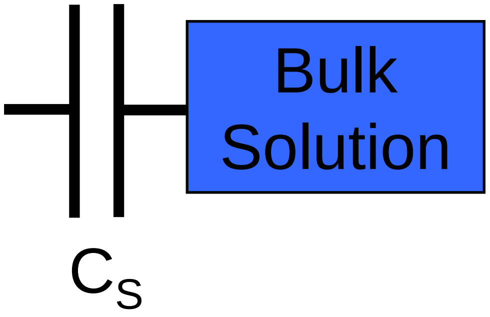
$$\frac{\partial c_\pm}{\partial n} + c_\pm \frac{\partial \phi}{\partial n} = 0$$



- Surface (Stern) Capacitance

$$\Delta\phi_s = v - \phi\big|_{r=1} = \delta\epsilon\frac{\partial \phi}{\partial n}$$

δ^{-1} = effective Stern capacitance

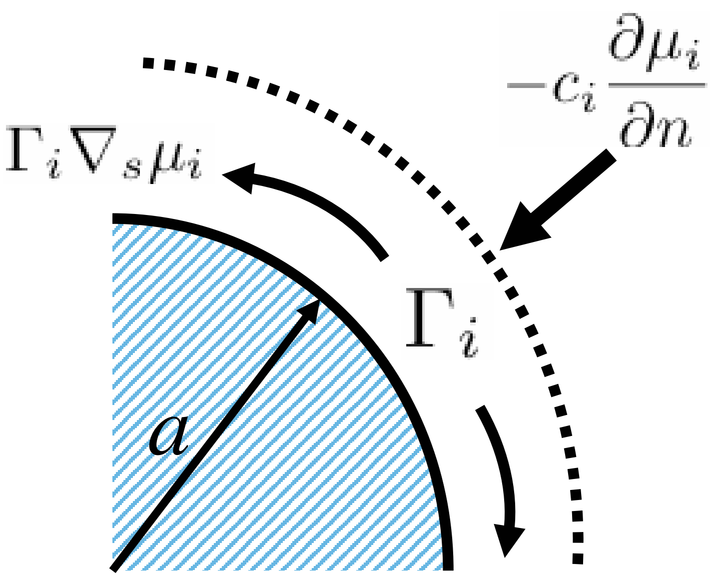


Surface Conservation Laws

Bikerman (1933-1940), Dukhin/Deryaguin/Shilov (1965-1970)
Chu/Bazant (2006)

surface transport → normal flux into DL

$$\frac{\partial \Gamma_i}{\partial t} = \nabla_s \cdot (\Gamma_i \nabla_s \mu_i) - c_i \frac{\partial \mu_i}{\partial n}$$



2-D conservation law with driving force and source term depending only on ***bulk*** dynamics***.***

Γ_i = excess DL conc. of ion i

μ_i = bulk chemical potential of ion i

Derivation of Surface Conservation Laws

- Only ***excess*** quantities are asymptotically integrable over boundary layers

$$\int_{DL} c_i dz$$

OK

$$\int_{DL} \left(c_i - c_i^{bulk}\right) dz$$

- Analysis ***must*** be done carefully. Asymptotic limit is $\epsilon \longrightarrow 0$ ***not*** $z \longrightarrow \infty$.

Effective Boundary Conditions for PNP Equations

- Individual Ionic Species

$$\frac{\partial \Gamma_i}{\partial t} = \nabla_s \cdot (\Gamma_i \nabla_s \mu_i) - \hat{n} \cdot c_i \nabla \mu_i$$

$$\mu_i = \log c_i + z_i \phi \qquad \Gamma_i = 2\epsilon \sqrt{c_i} \left(e^{-z_i \zeta/2} - 1 \right) / |z_i|$$

- Charge and Excess Salt Concentration

$$\epsilon \frac{\partial q}{\partial t} = \epsilon \nabla_s \cdot (q \nabla_s \log c + w \nabla_s \phi) - c \frac{\partial \phi}{\partial n}$$

$$\epsilon \frac{\partial w}{\partial t} = \epsilon \nabla_s \cdot (w \nabla_s \log c + q \nabla_s \phi) - \frac{\partial c}{\partial n}$$

Steady-state Response to Large Electric Fields

- Harmonic neutral salt profile and steady continuity equation

$$\frac{\partial c}{\partial t} = \nabla^2 c \qquad \nabla \cdot (c \nabla \phi) = 0$$

0

- Quasi-equilibrium double layers

$$c_{\pm}(z) = c^{bulk}(X, Y, Z) e^{\mp \psi(z)}$$

non-uniform bulk concentration

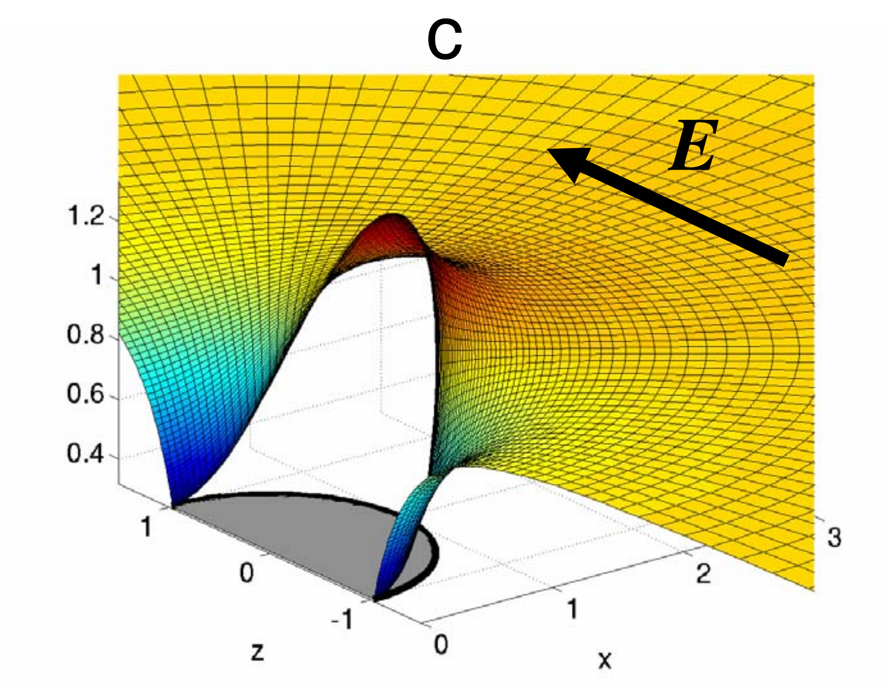
Numerical Solution Procedure

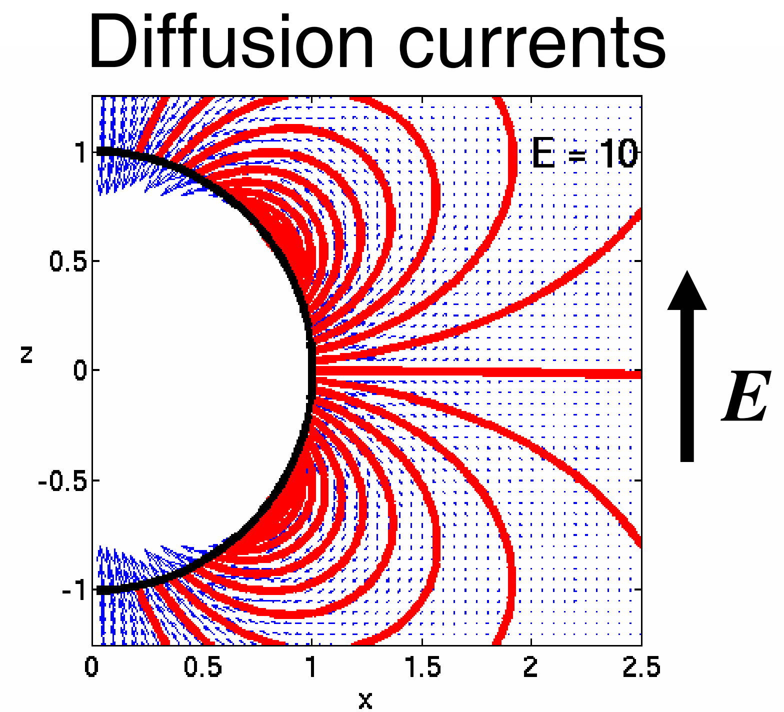
1. Discretize governing equations and BCs
   - 2D-pseudospectral grid and differentiation matrix
2. Solve nonlinear equations using Newton's method with continuation
   - Exact Jacobian computed using direct matrix method
3. Analyze/visualize results

High-Performance Algorithm

→ Pure MATLAB Simulation!

Concentration Gradients





$E = 10$, $\epsilon = 0.01$, $\delta = 1$

Expect diffusio-osmosis (= flow due to gradients in bulk salt concentration)

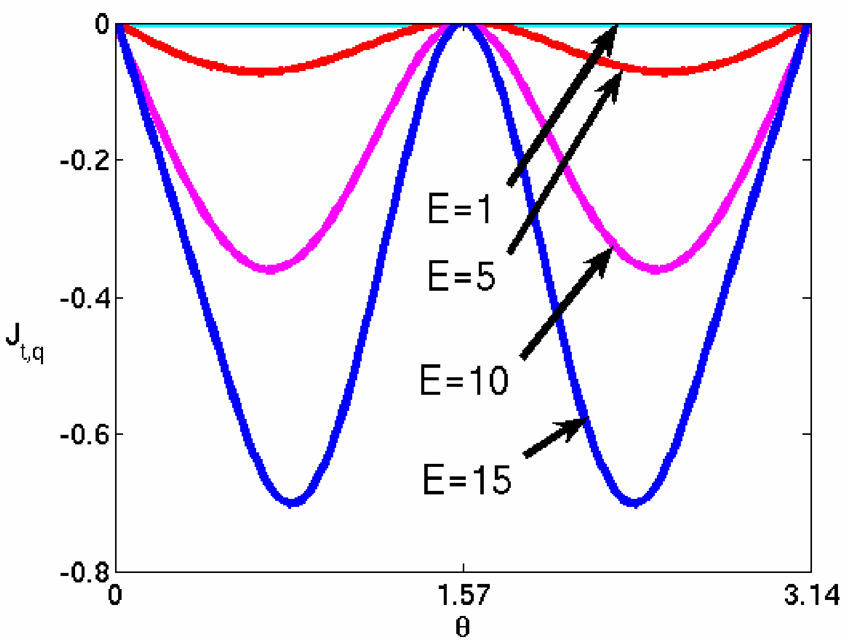
Deryaguin (1964)

$$u_s = \frac{\epsilon\zeta}{\eta}\nabla_s\phi - f(\zeta)\nabla_s \log c$$

Enhanced Surface Currents at High Fields

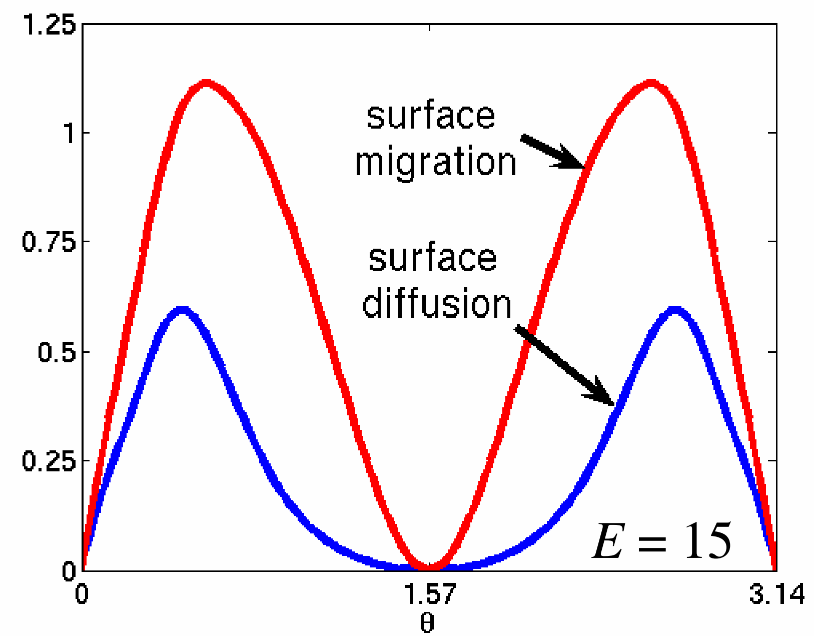
$$J_{t,q} = \epsilon q \nabla_s \log c + \epsilon w \nabla_s \phi$$

Surface Current



$$\epsilon = 0.01 \quad \delta = 1$$

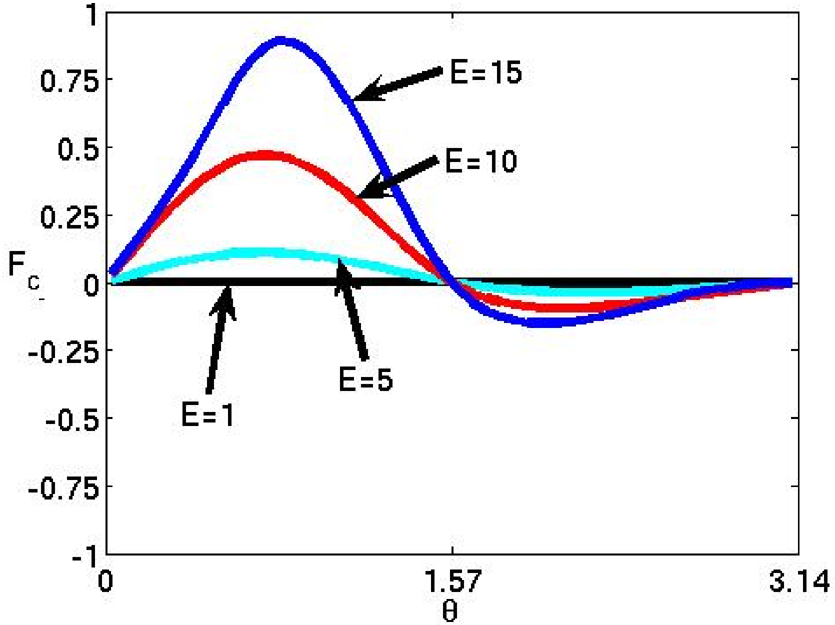
Migration vs. Diffusion



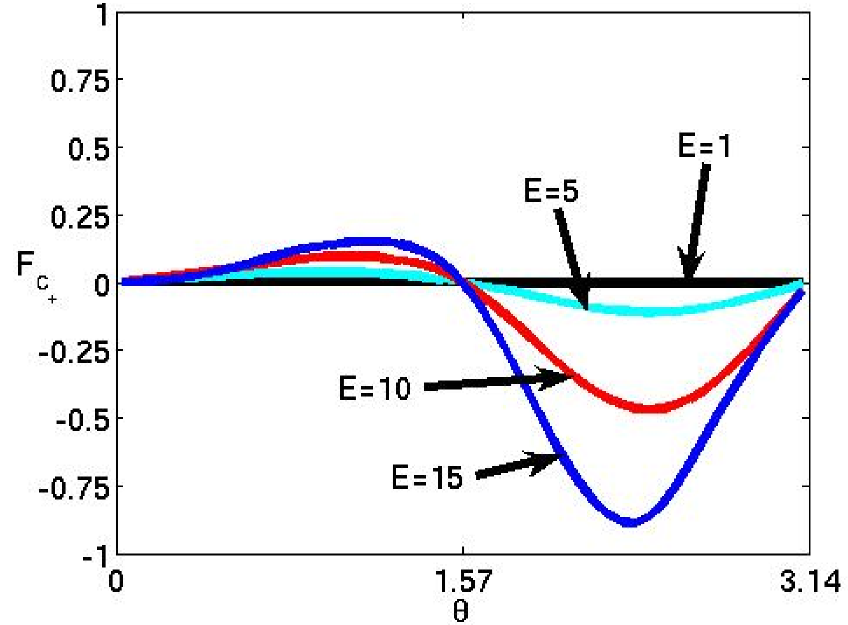
$$\frac{[\text{surface diffusion}]}{[\text{surface migration}]} = \tanh\left(\frac{ze\zeta}{4kT}\right)$$

Imbalance in Surface Fluxes

Anion Surface Flux



Cation Surface Flux



$$\epsilon = 0.01 \quad \delta = 1$$

Conclusions:

- Bulk concentration gradients lead to breakdown of circuit models
- Surface conservation laws yield effective boundary conditions for bulk dynamics
- Strong concentration gradients and surface transport at "high" applied fields

Ongoing Research . . . Kilic, Bazant, Ajdari

- Effects of finite ion size on flow
- Nonlinear permittivity due to solvent molecule alignment
- Viscoelectric effects

Acknowledgements

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