# The Francois Frenkiel Award Lecture: Fundamental aspects of Concentration Polarization

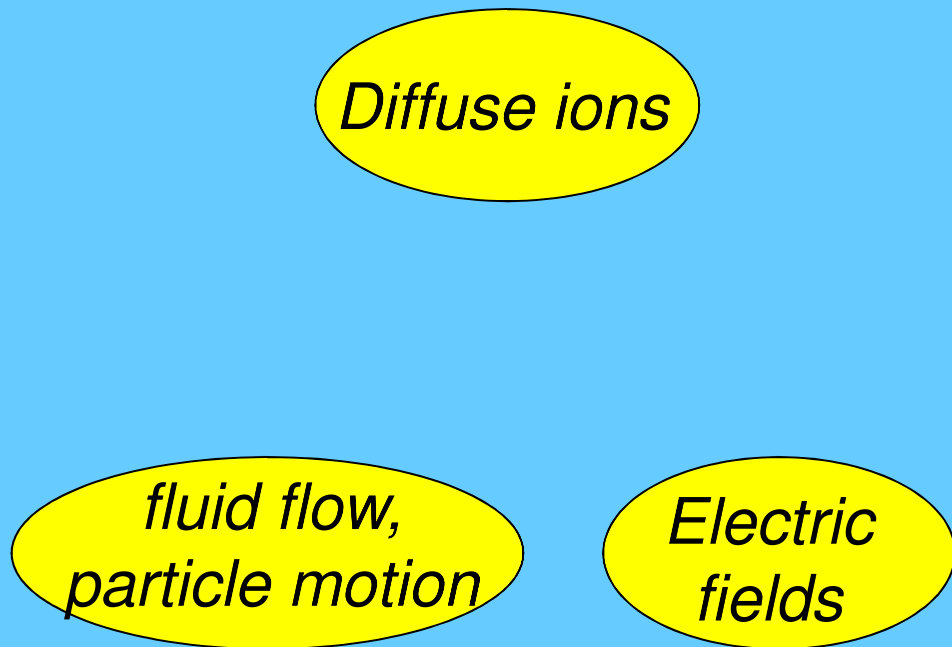
**Todd Squires**

**Aditya Khair**

**Chemical Engineering**

**University of California, Santa Barbara**

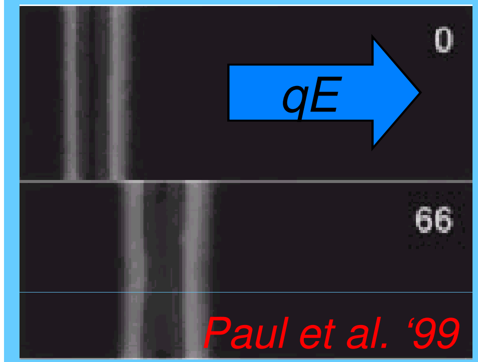
# Electrokinetic effects

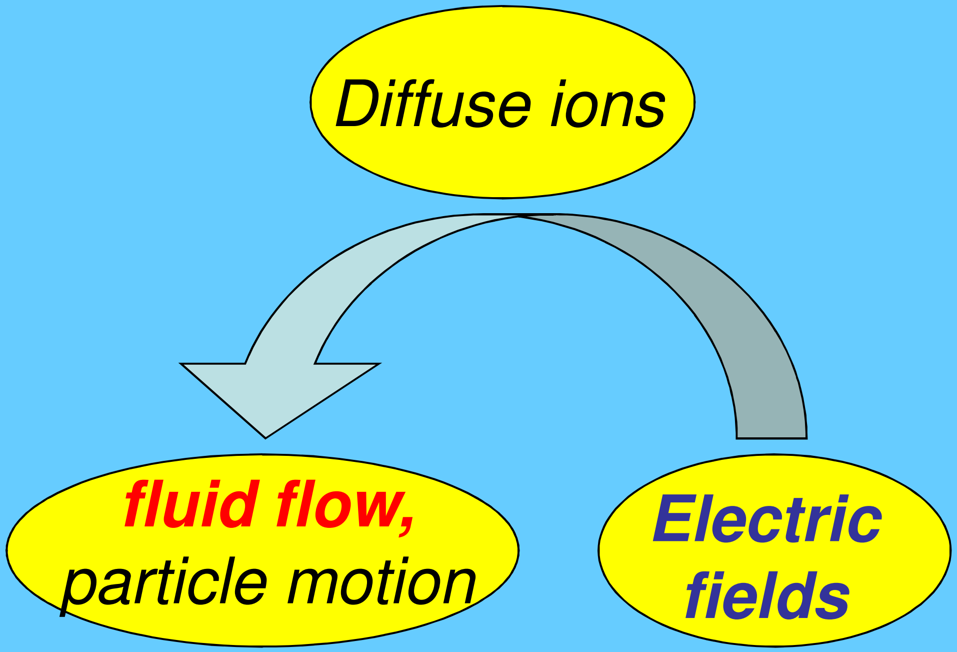


# Electrokinetic effects

***Field-driven motion***

**Electro-osmotic flow**

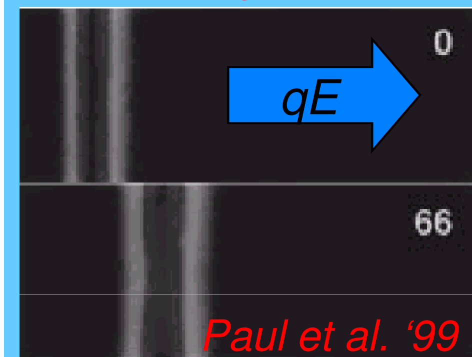


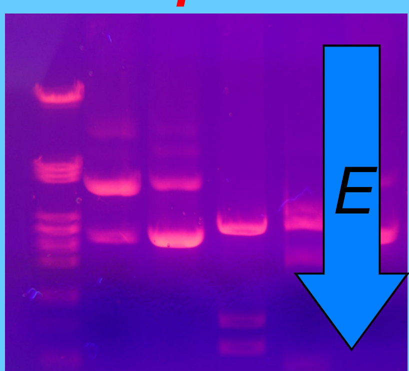
# Electrokinetic effects

## *Field-driven motion*

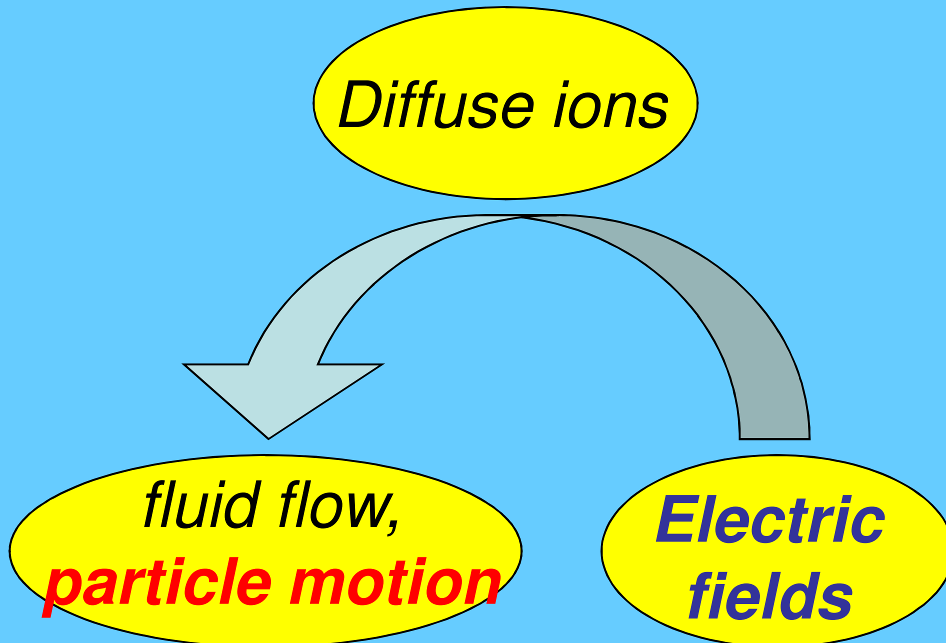
***Electro-osmotic flow***




***Electrophoresis***




(Wikipedia)




***Happy 200th Birthday!***

***"Notice sur un nouvel effet de l'électricité galvanique"***

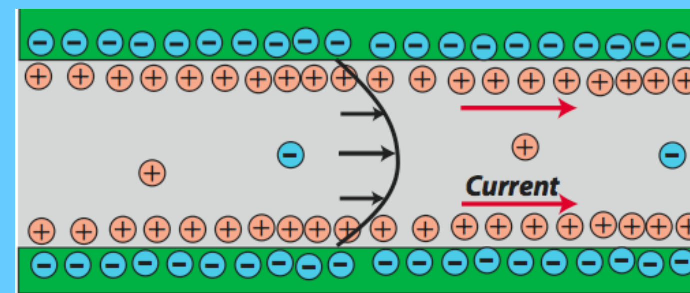
***F.F. Reuss 1809***

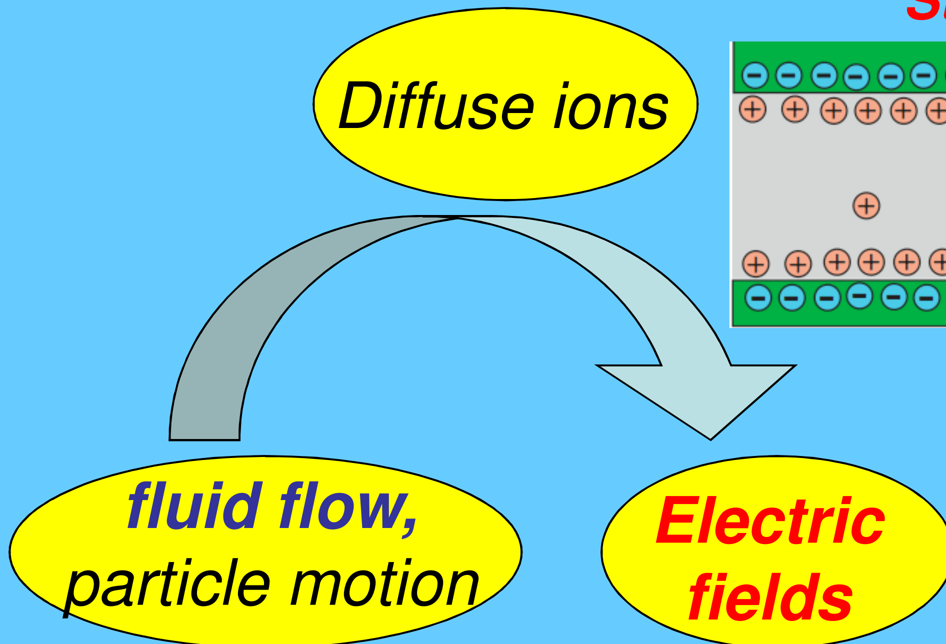
# Electrokinetic effects

## *Field-driven motion*

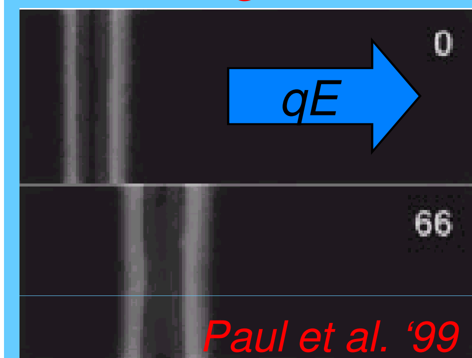
## *Flow-driven fields*

***Streaming potential***

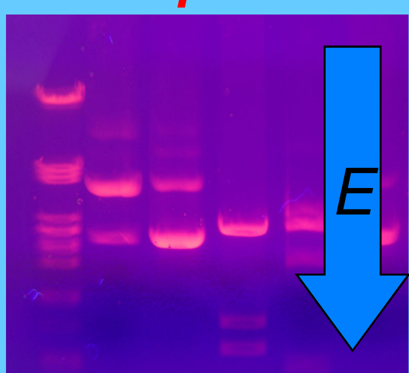



***Electro-osmotic flow***




***Electrophoresis***




(Wikipedia)

***Happy 200th Birthday!***

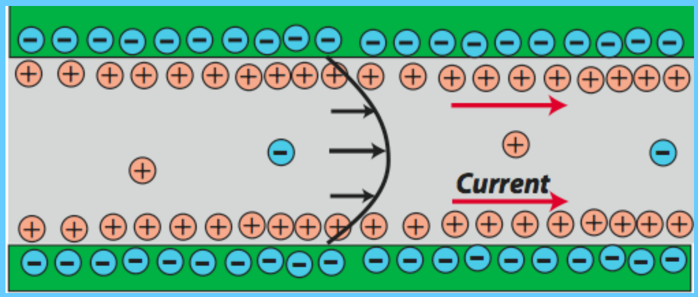
***"Notice sur un nouvel effet de l'électricité galvanique"***

***F.F. Reuss 1809***

# Broader impacts of electrokinetics research

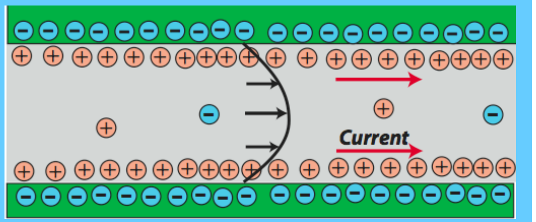
## Convective charge separation in low-conductivity fluids

**Streaming potential**



# Broader impacts of electrokinetics research

## Convective charge separation in low-conductivity fluids




QuickTime™ and a
decompressor
are needed to see this picture.

*Source: youtube*

***Potentially highly transformative, in the exothermic sense***

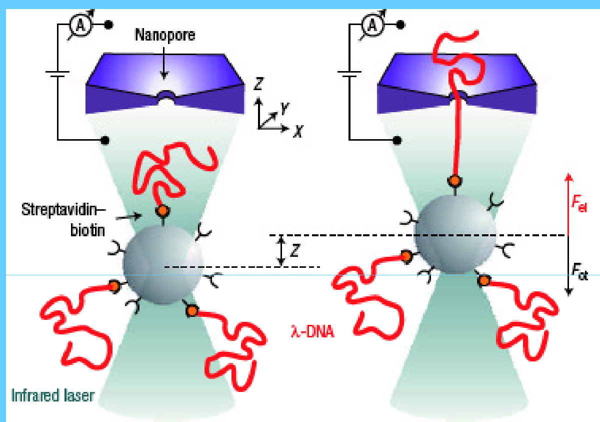
***My Outreach to you: please remember to ground your gas containers.***

# *A modern renaissance in electrokinetics*

## Microfabrication:

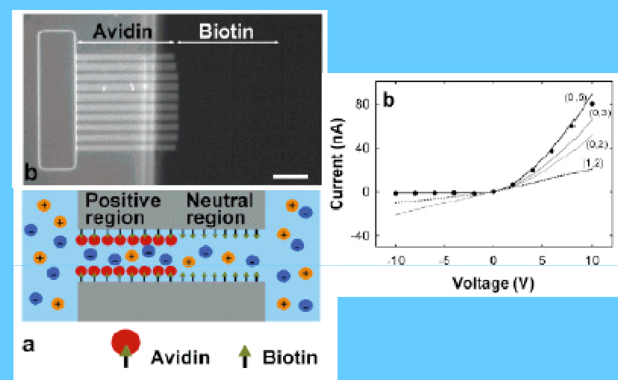
**Fields and flows provide many new ways to control micro & nano-scale transport**

### *DNA translocation*



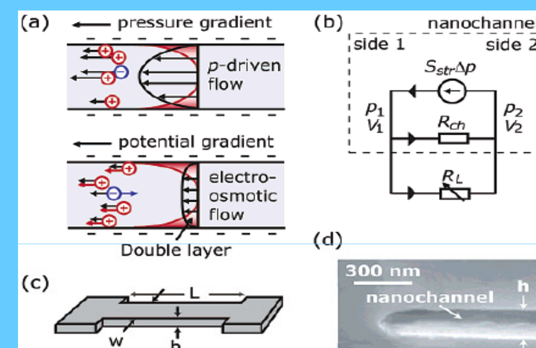

*Keyser et al. 2006*

### *Nanofluidic Diode*



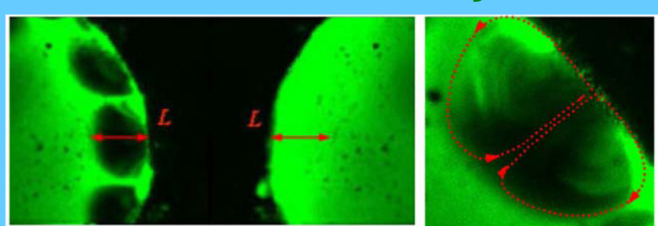

*Karnik et al. 2007*

### *Energy Harvesting*



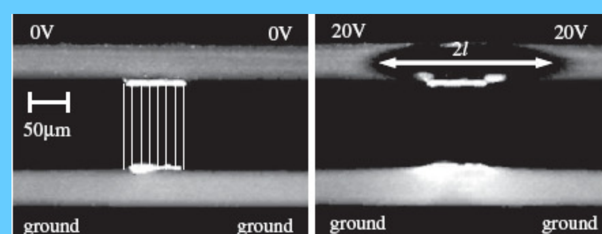

*van der Heyden et al. 2007*

### *Overlimiting Currents in Electrochemical Systems*




*Yossifon & Chang 2008*

### *Concentration Polarization at Micro/Nano Interfaces*



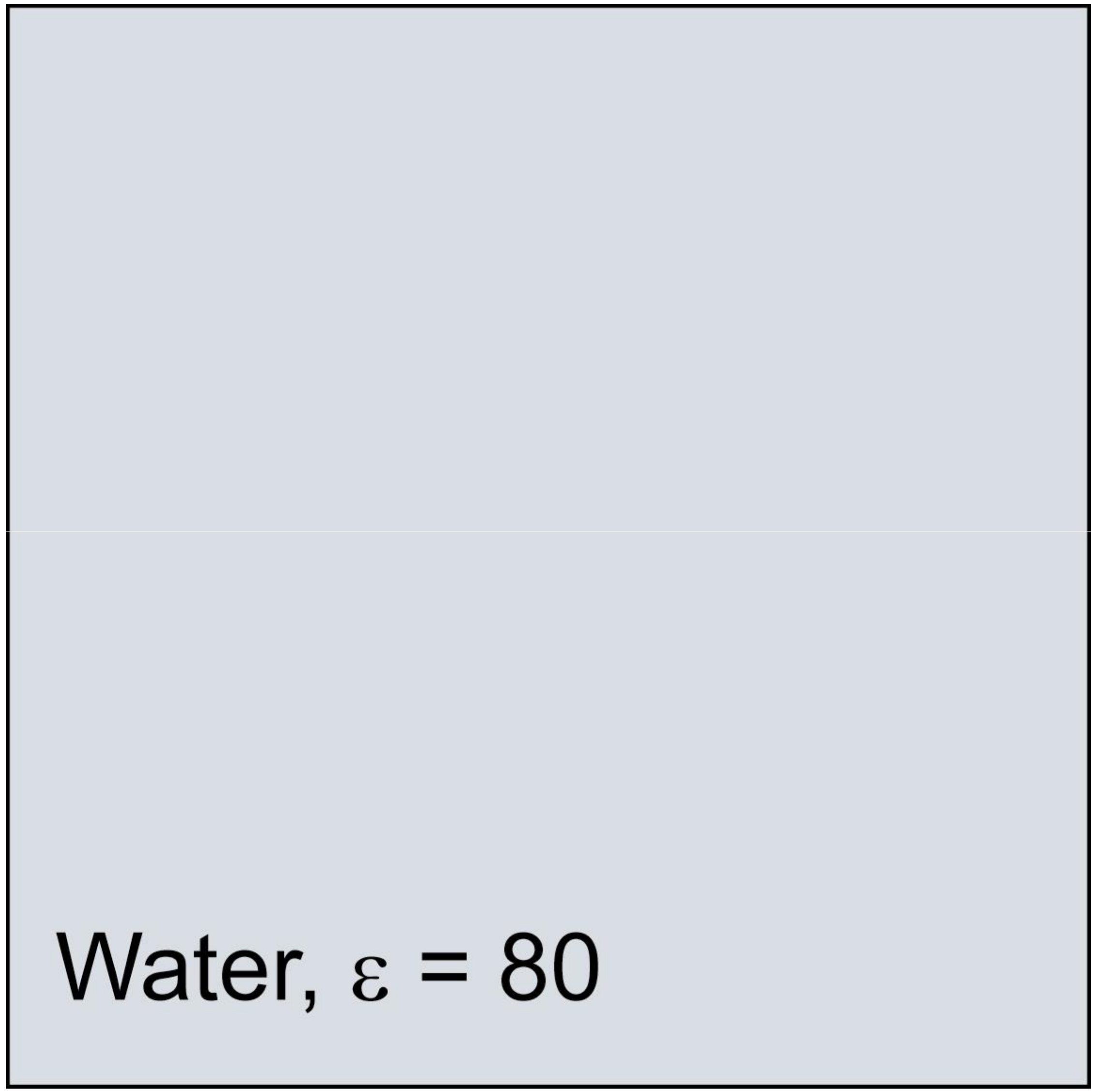

*Kim et al. 2005*

### *Salt "de-mixing"*

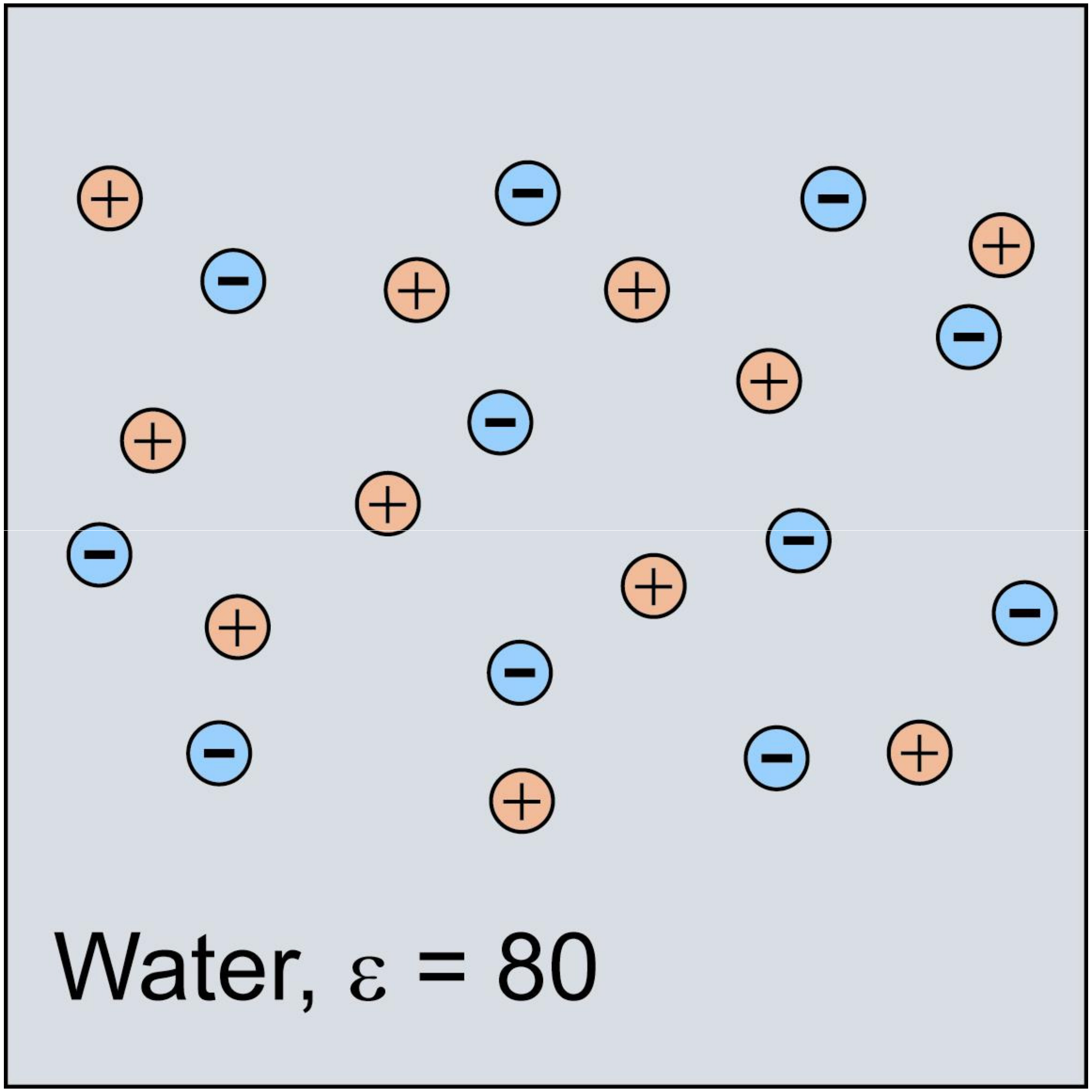
QuickTime™ and a decompressor are needed to see this picture.

*Leinweber et al 2006*

# *How most of you view water.*

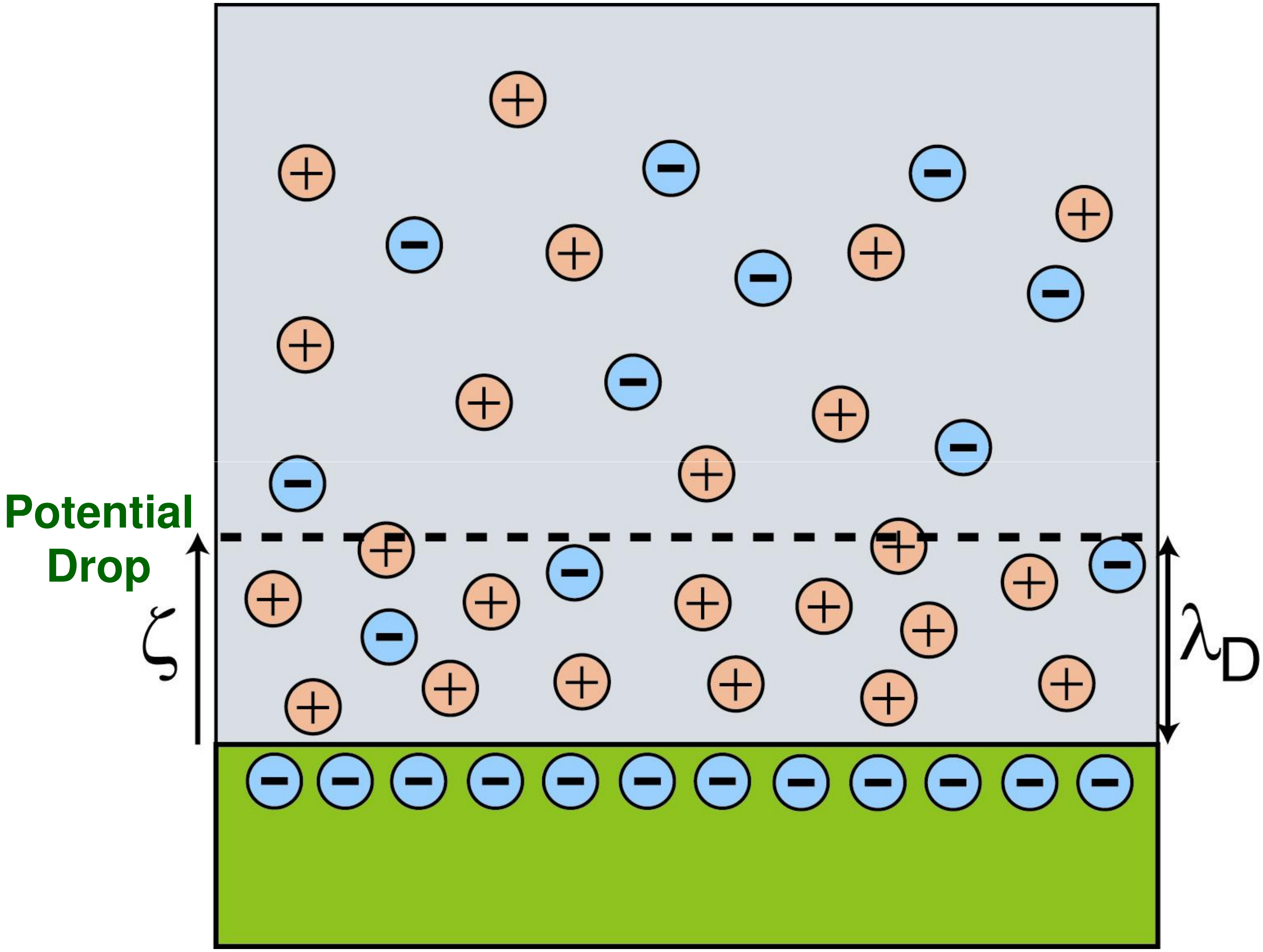


# *Water dissolves ions...*



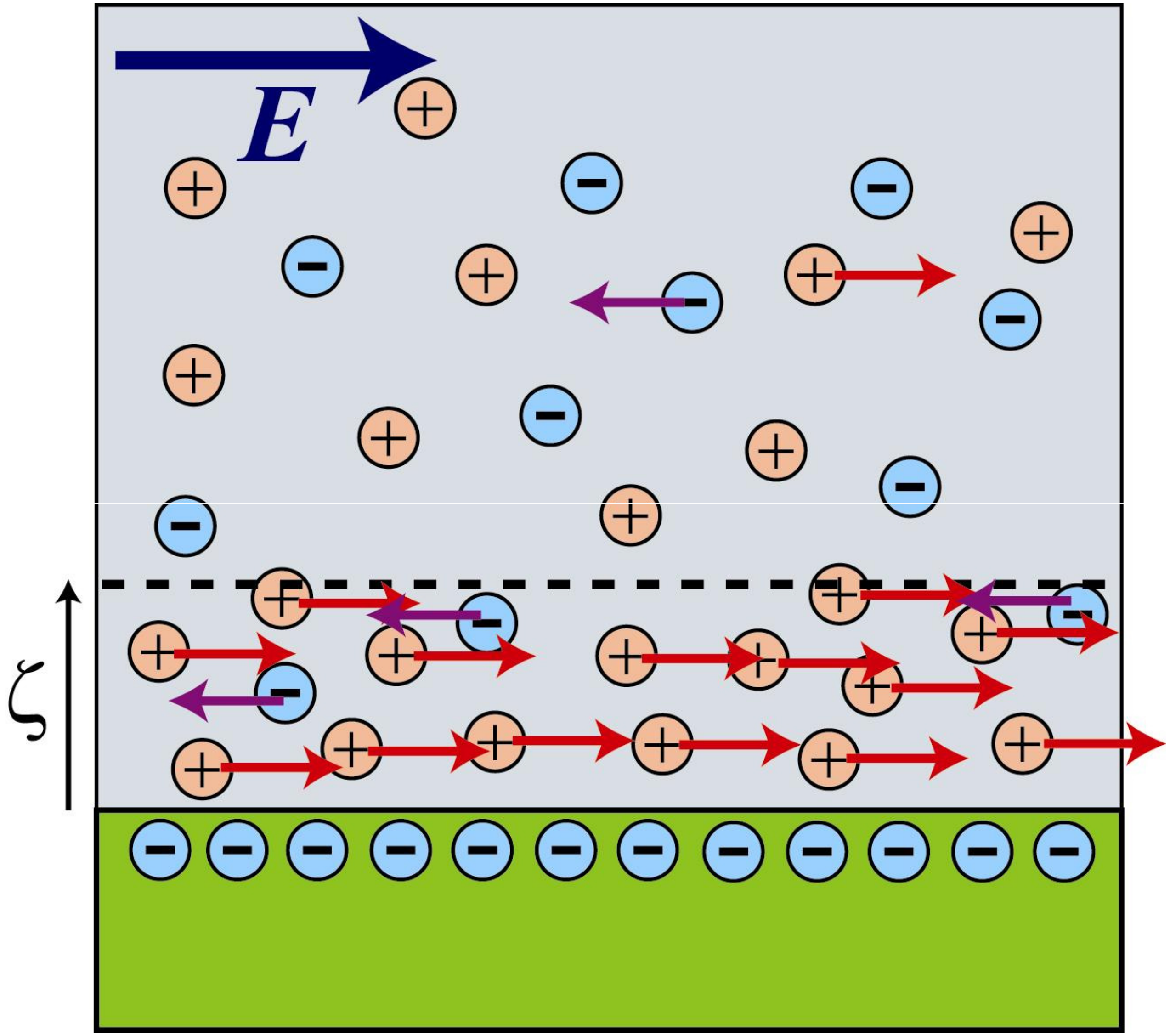

$OH^-$
$H^+$
$Na^+$
$Cl^-$
*etc.*

# Ions 'screen' charged surfaces



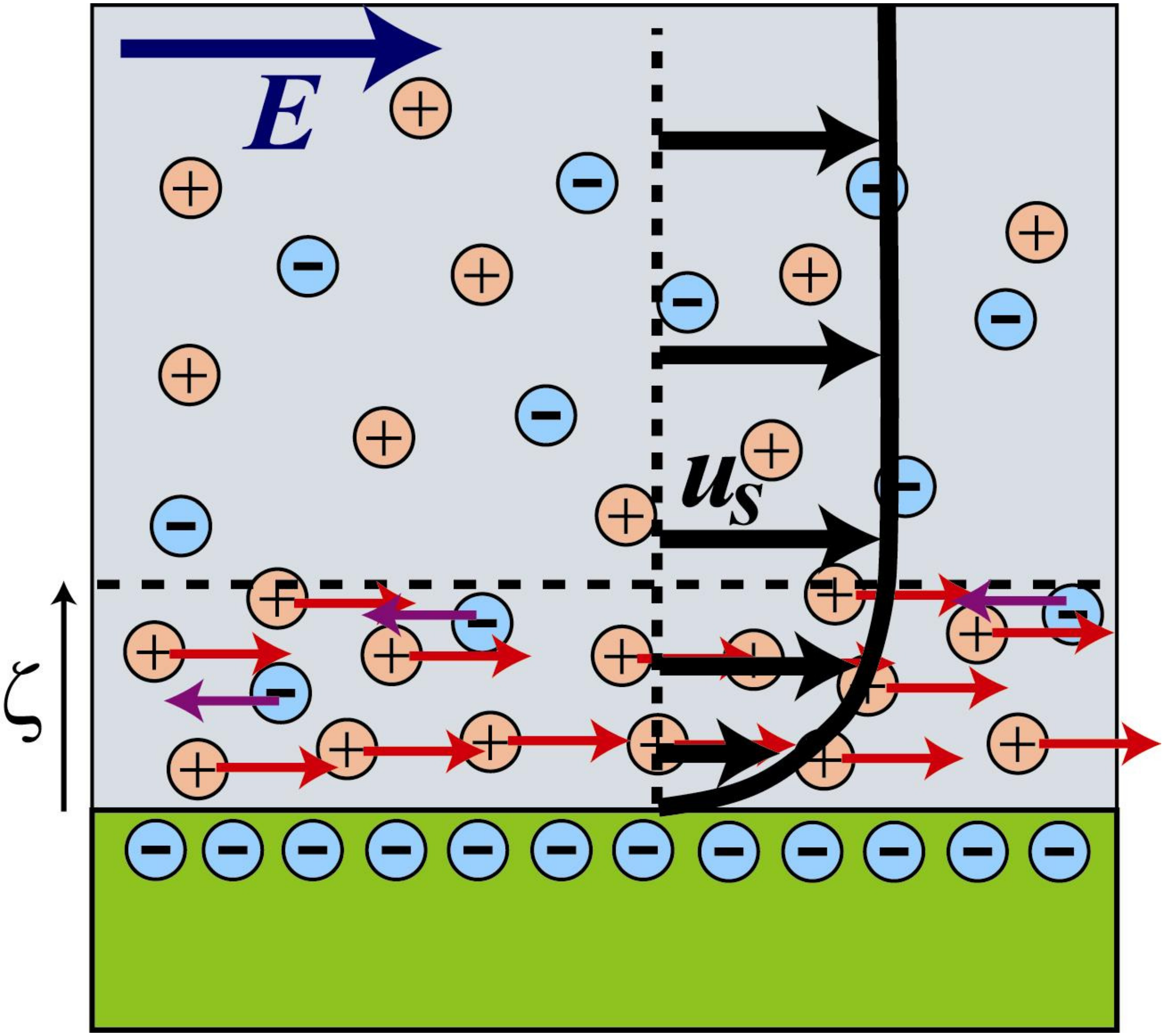

**screening length $\lambda_D$ varies from ~1 – $10^3$ nm**

# Electric fields: body force on fluid




net force within screening cloud

# Electro-osmosis: field drives flow




'slip' velocity (conveyor belt) $u_s = -\frac{\epsilon\zeta}{\eta}E$

# "Standard Model" for electrokinetics

***…what lurks behind all the cartoons I'll show.***

## (1) Fluid flow: low-Re flow

$$\eta\nabla^2\vec{u} - \nabla p - e(n_+ - n_-)\nabla\phi = 0$$

$$\nabla\cdot\vec{u} = 0$$

Coupled, Nonlinear PDE's

## (2) Electrostatics

$$\nabla^2\phi = -\frac{e(n_+ - n_-)}{\epsilon_w}$$

Common Approach:
Matched asymptotics
With "thin" double-layers

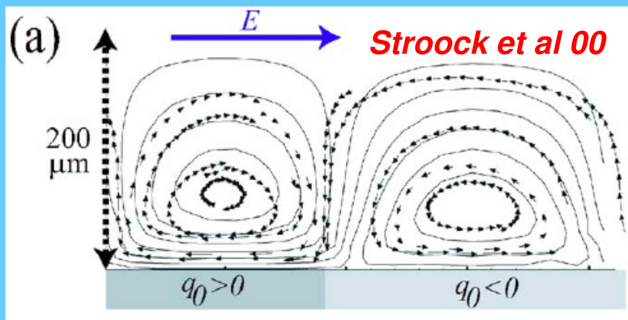
## (3) Ion conservation

$$\vec{j}_\pm = -D\nabla n_\pm + \vec{u}n_\pm \mp \frac{eD}{k_BT}n_\pm\nabla\phi$$

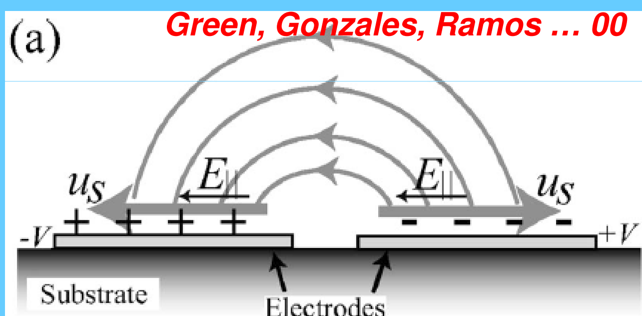
*diffusion* — *advection* — *electrostatic*

# Microfabrication: natural surface charge inhomogeneities

***Andy Pascall & TMS***



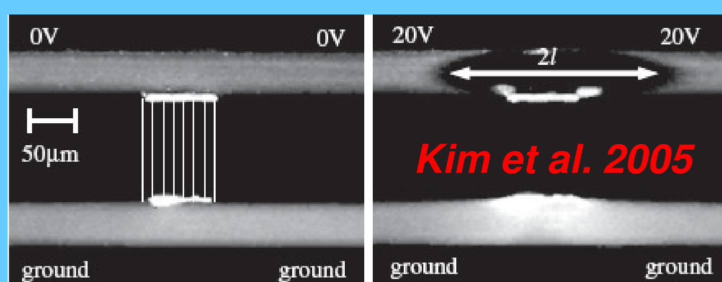





*Leinweber & Tallarek 2005*

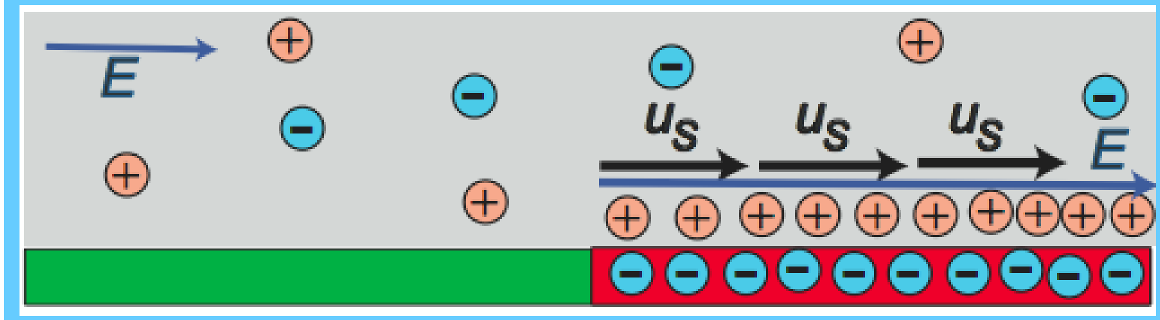
QuickTime™ and a
decompressor
are needed to see this picture.

QuickTime™ and a
decompressor
are needed to see this picture.



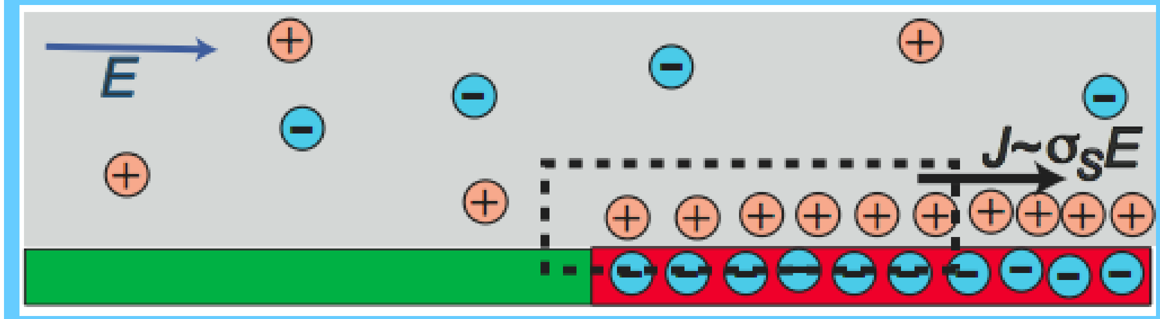

**Theory: J. Anderson, Ajdari, Stone, Long, Ghosal, Yariv, TMS, many many others**

# Surface charge discontinuity




***Electro-osmotic flow:***
***Similarity solution***
***outside double-layer***
***Yariv (2004)***

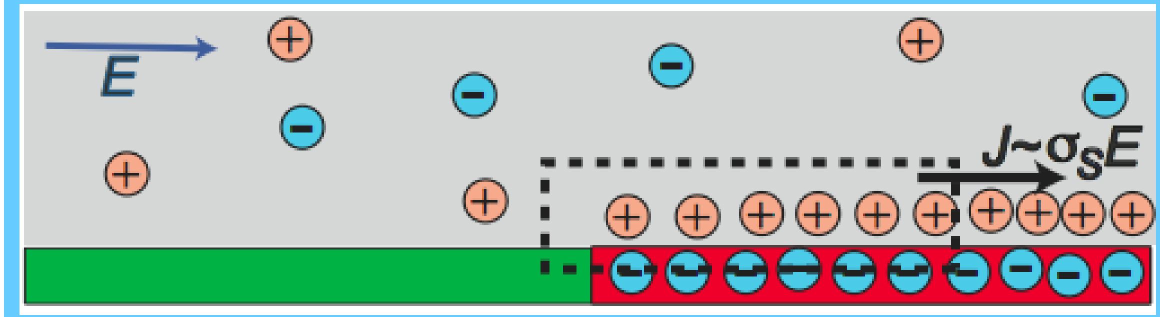
# Surface charge discontinuity




*Violates ion conservation!*

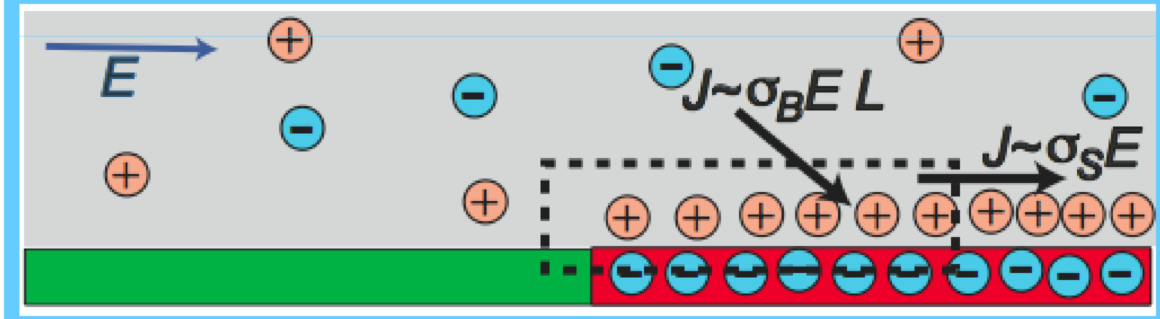
***Electro-osmotic flow: Similarity solution outside double-layer Yariv (2004)***

# Surface charge discontinuity




***Electro-osmotic flow:***
***Similarity solution outside double-layer***
***Yariv (2004)***

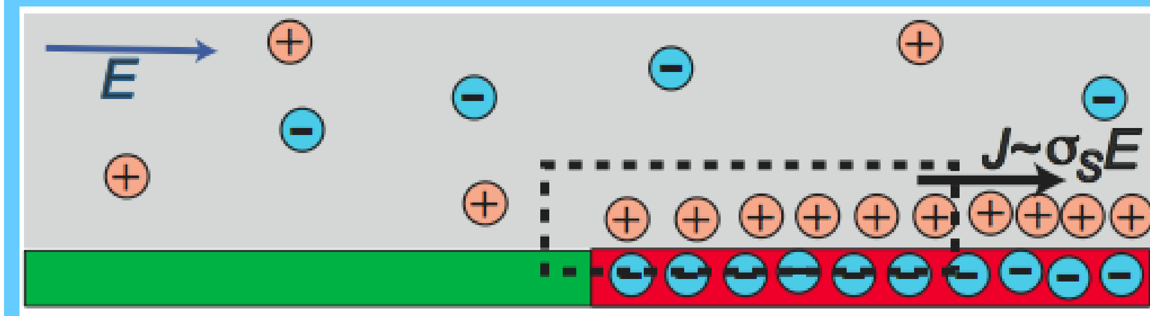
***Violates ion conservation!***




***Ion conservation:***

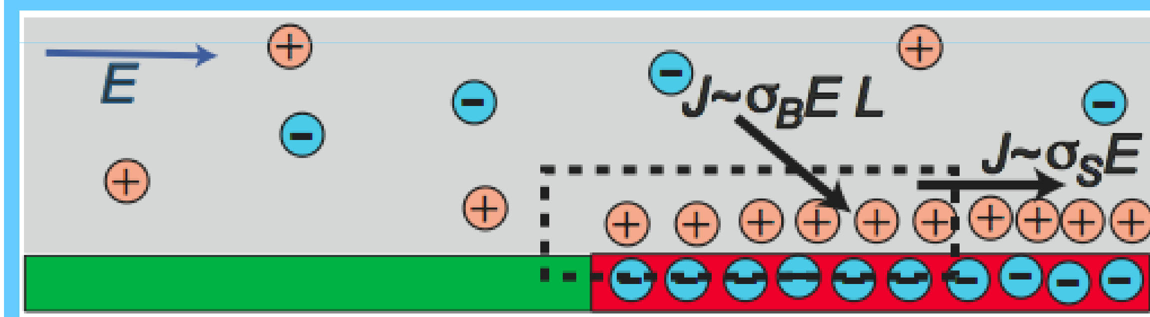
- Field pulled in from bulk
- How far downstream (L) before standard "parallel field"?

# Surface charge discontinuity




*Violates ion conservation!*

***Electro-osmotic flow: Similarity solution outside double-layer Yariv (2004)***




***Ion conservation:***

- Field pulled in from bulk
- How far downstream (L) before standard "parallel field"?

$$J_{\mathrm{in}} = J_{\mathrm{out}}$$

$$L = \frac{\sigma_S}{\sigma_B} \sim \lambda_D e^{e\zeta/k_B T}$$

- Can be very long!

***No geometric length scale: "Healing length" emerges***

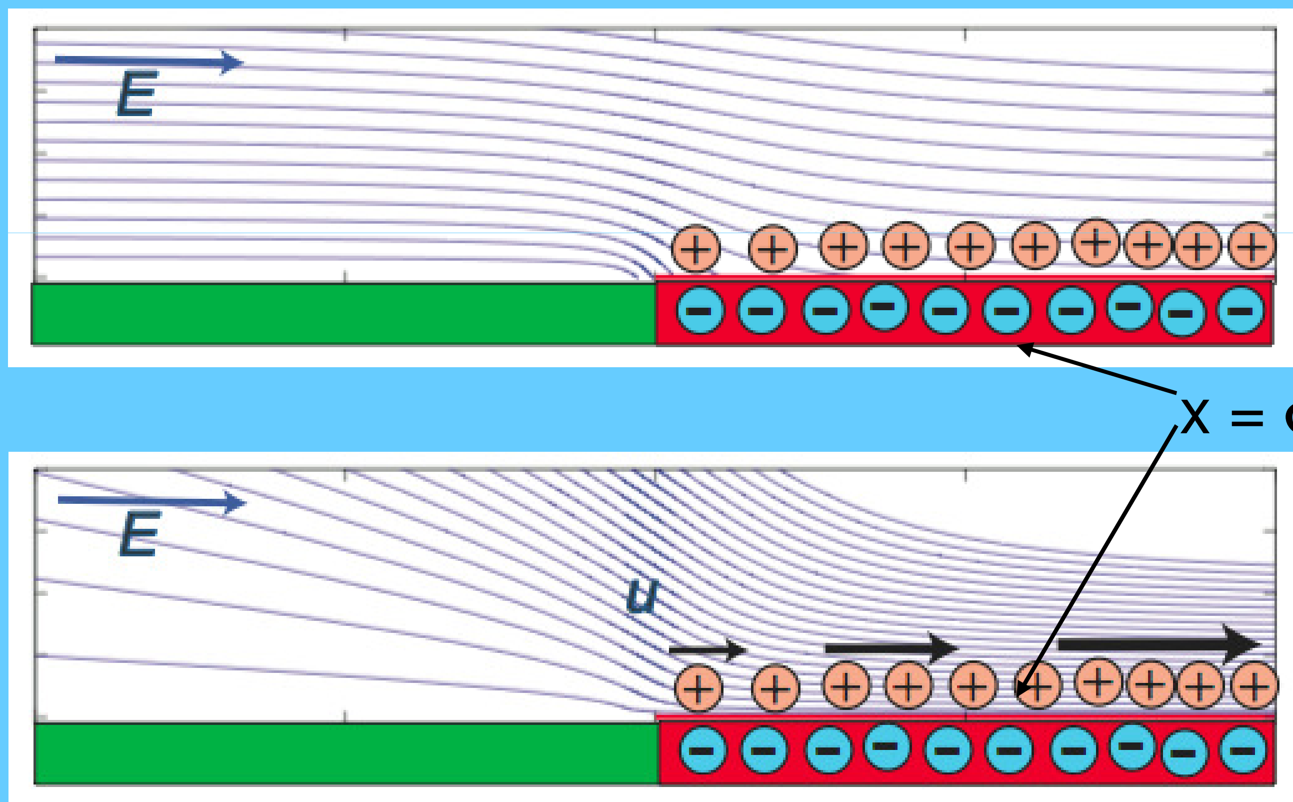
# *Universal flow problem:*
## *scale by healing length*

- *Ion conservation alters electrostatic boundary condition*

$$\sigma_B \frac{\partial \phi}{\partial y} = \frac{\partial}{\partial x}\left(\sigma_s(x)\frac{\partial \phi}{\partial x}\right)$$

**Electric Field Lines**

**Flow Stream Lines**



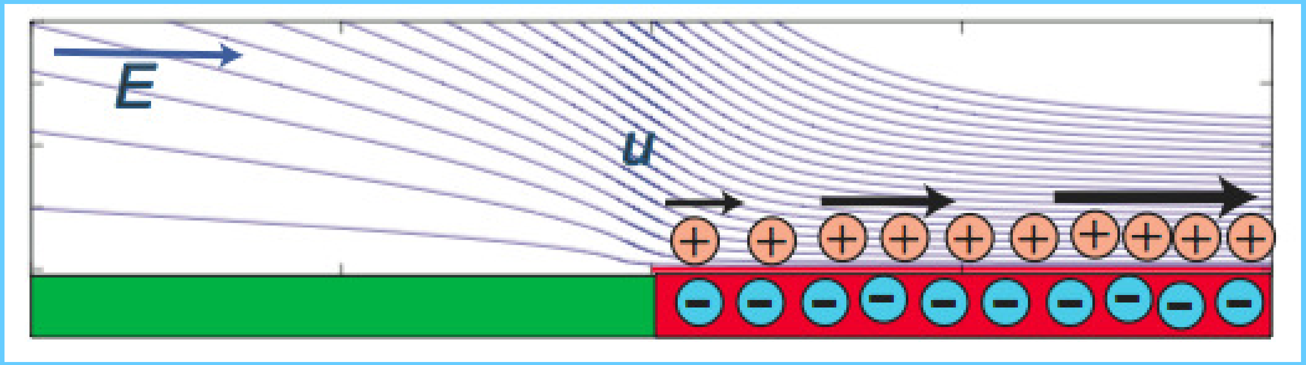

$x = \sigma_s/\sigma_B$

**Field & flow "heal" over length scale $\lambda_H = \sigma_s/\sigma_B$**

*Khair & Squires, JFM 08*

# *Question: what happens to the ions…*

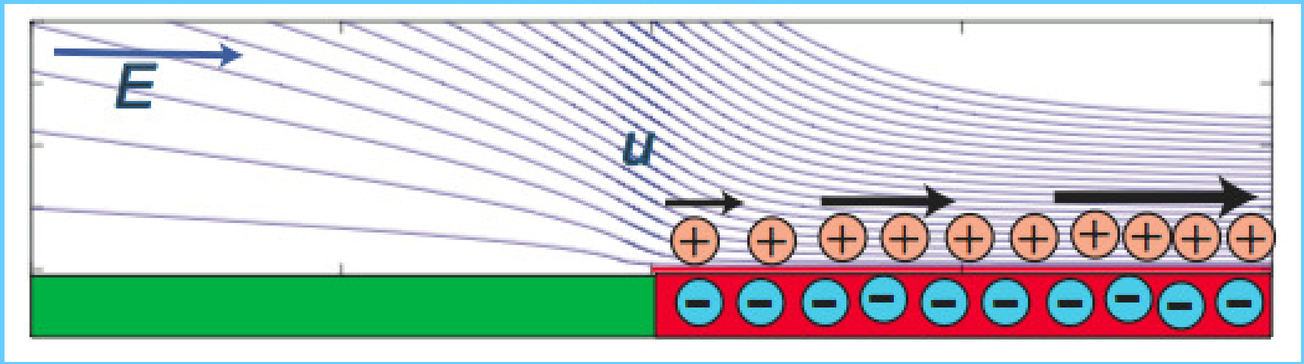
Electric
Field
Lines



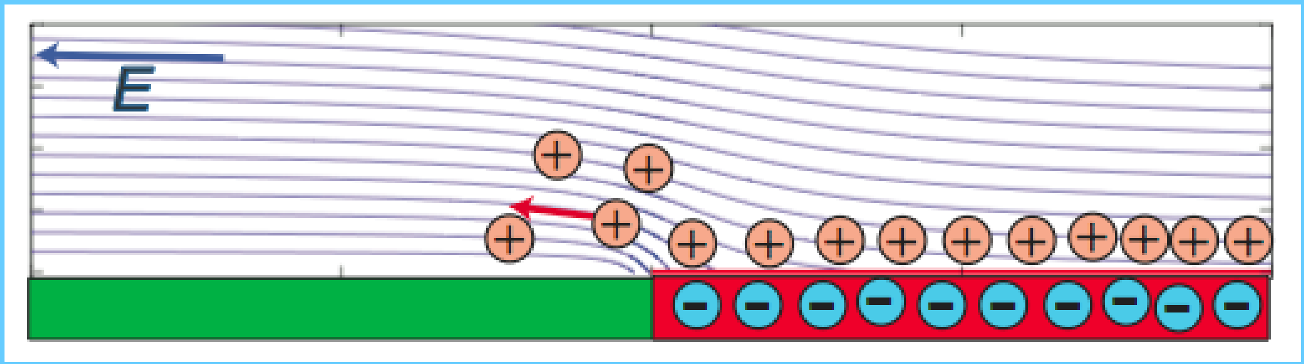

**At first:
Seems ok**

# *Question: what happens to the ions…*

**Electric Field Lines**




**At first: Seems ok**



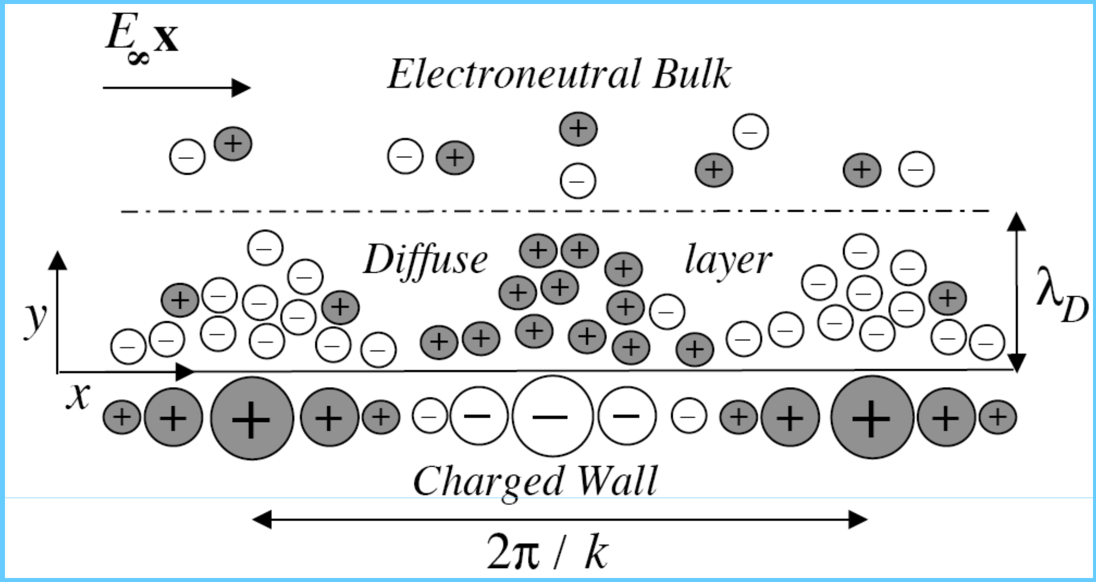

**Reverse field: Ion accumulation**

***Steady state solution?***

# *Inhomogeneous surface transport: Ion conservation*

***Khair & Squires, PoF (08)***

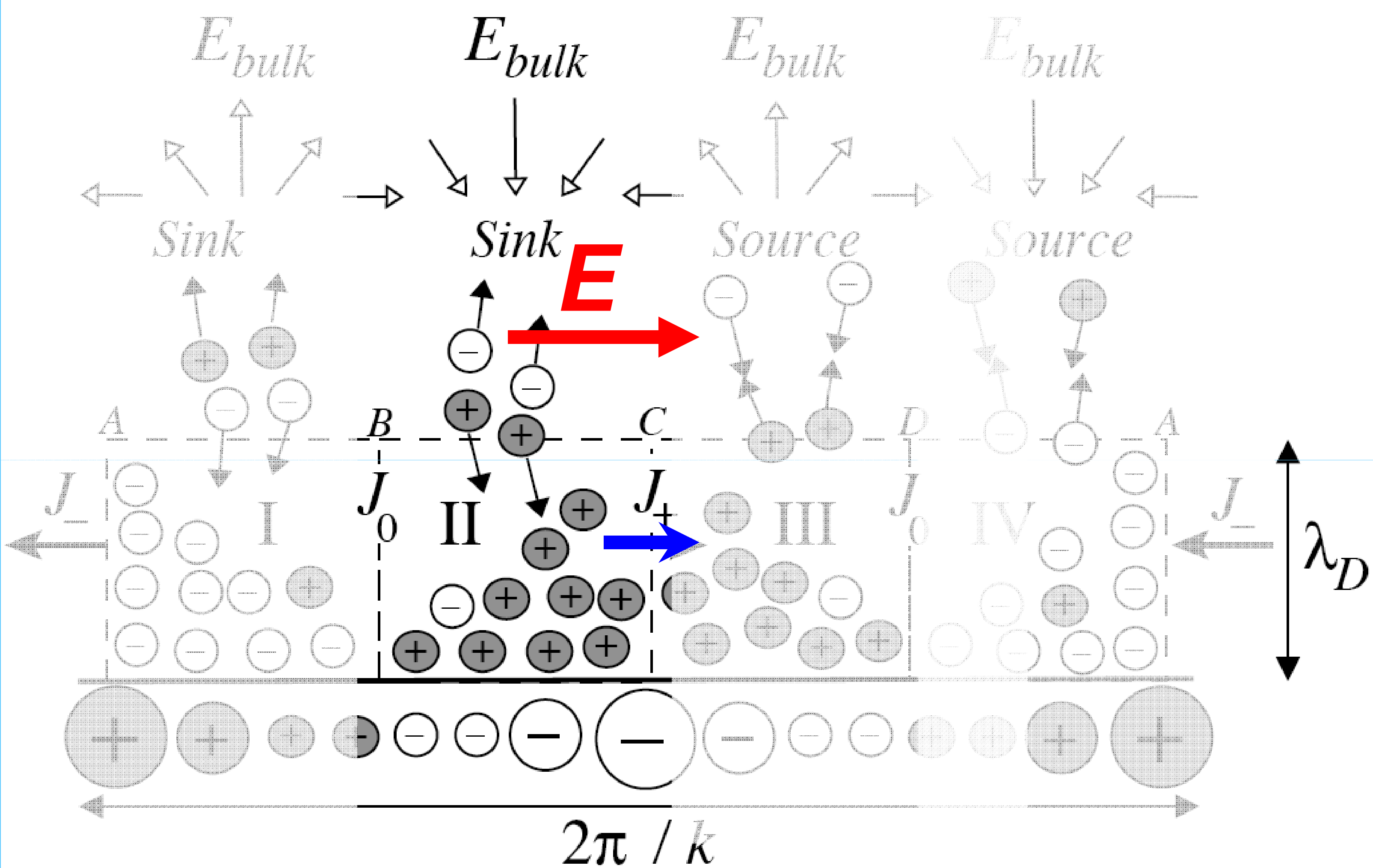
**Simplest model system**




## *Electro-osmosis over a periodically-varying charged surface*

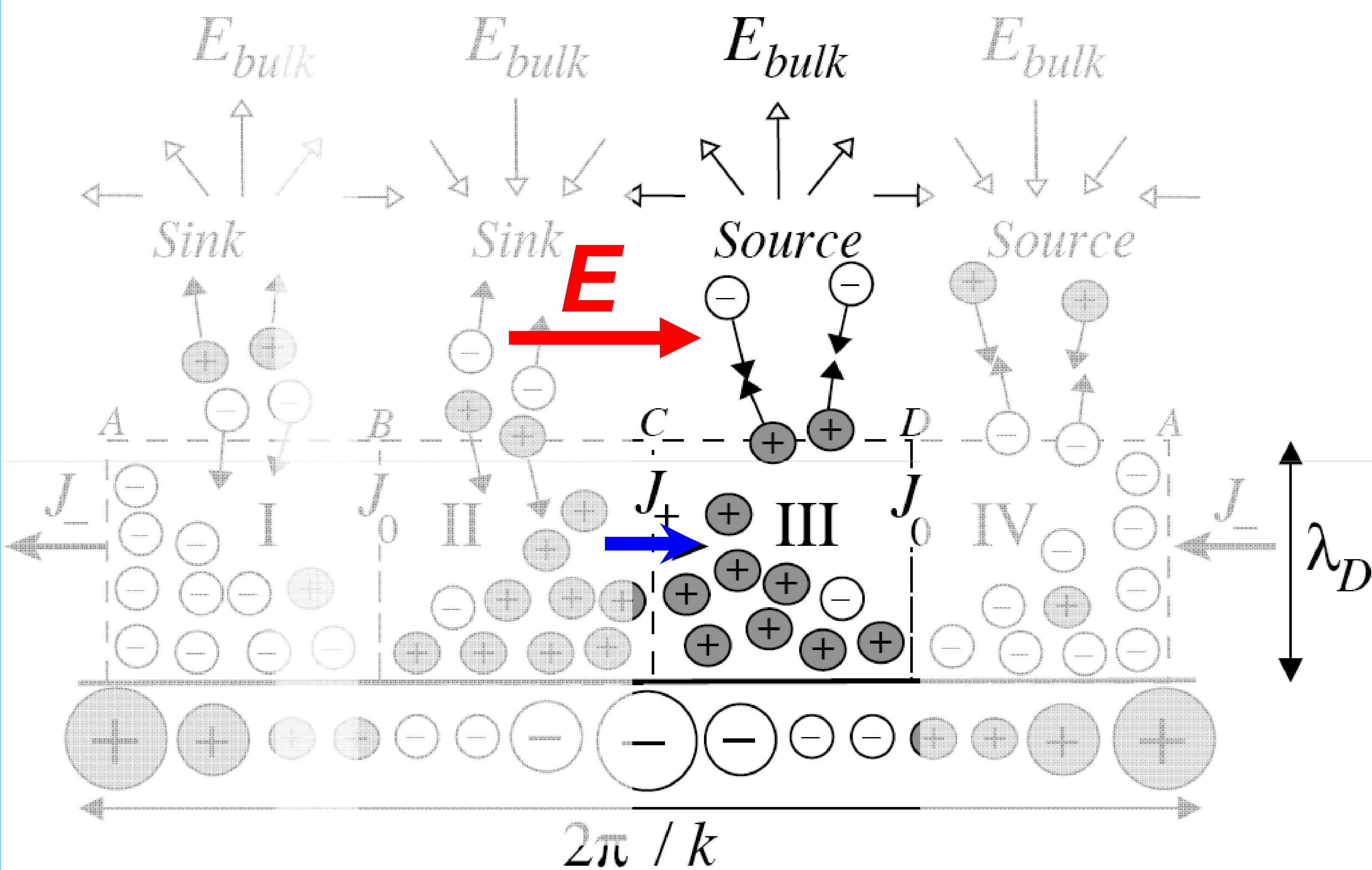
- **Low-ζ: can be solved exactly**
  - Steady-state concentration and fields
  - Oscillatory concentration and fields
  - Suddenly-applied field -- evolution of “concentration polarization”
- **High-ζ also amenable to analysis**
- **Avoids field curvature effects**
- **Convective transport due to EOF**

# Concentration Polarization




Loss of (+) ions:
Need inward field

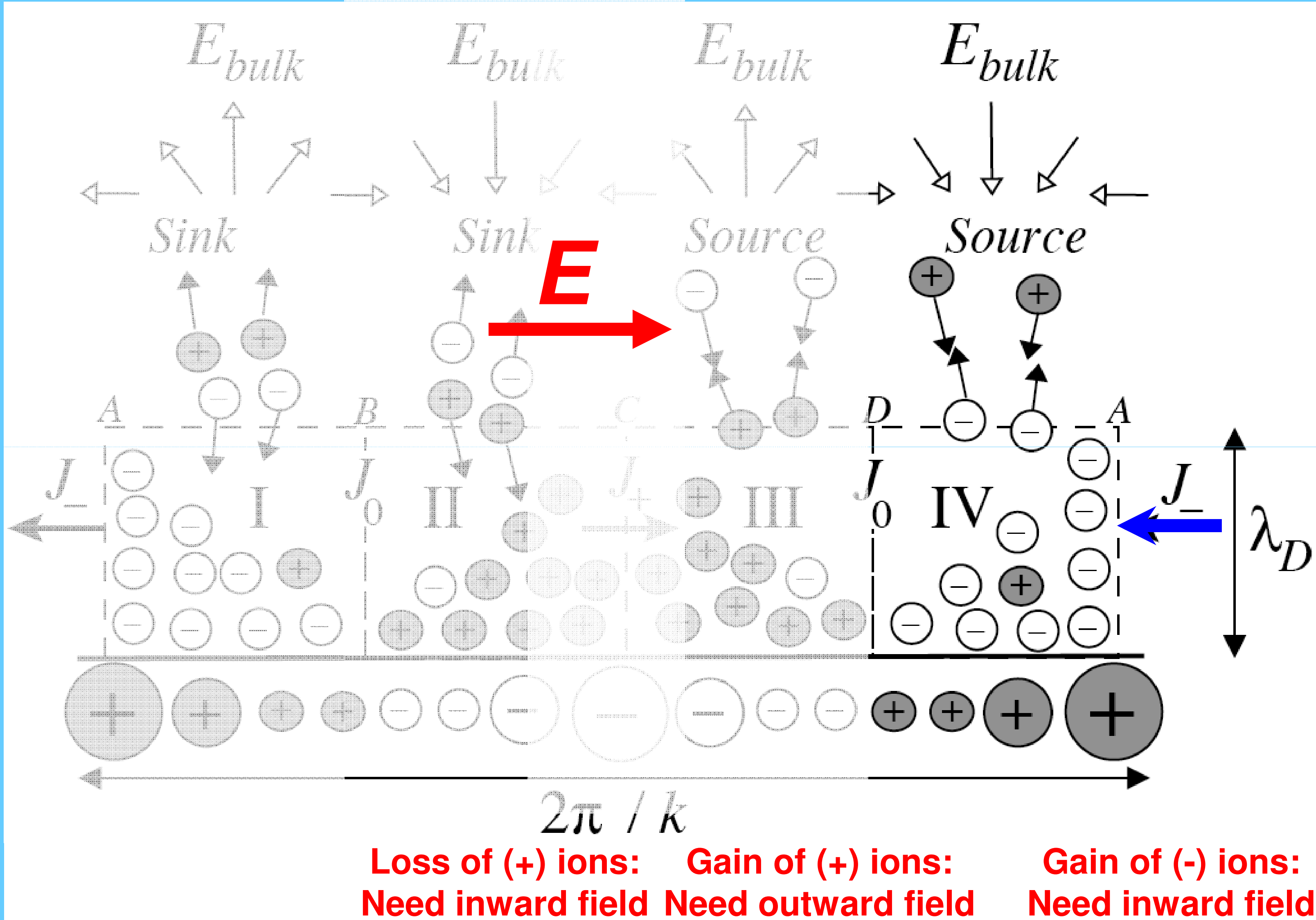
# Concentration Polarization



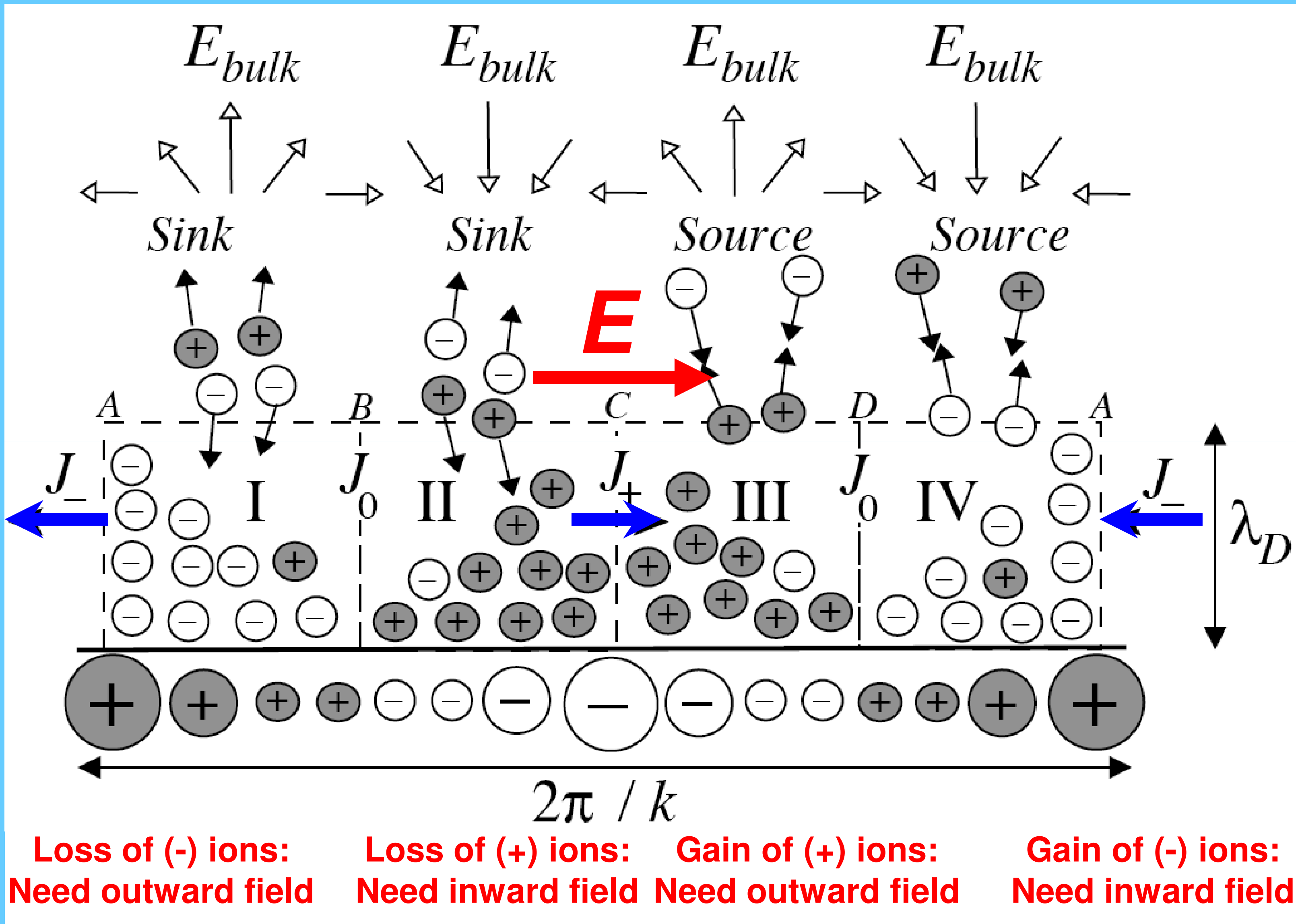

Loss of (+) ions: Need inward field

Gain of (+) ions: Need outward field

# Concentration Polarization



# Concentration Polarization




*This is a cartoon. All details emerge quantitatively from analysis*

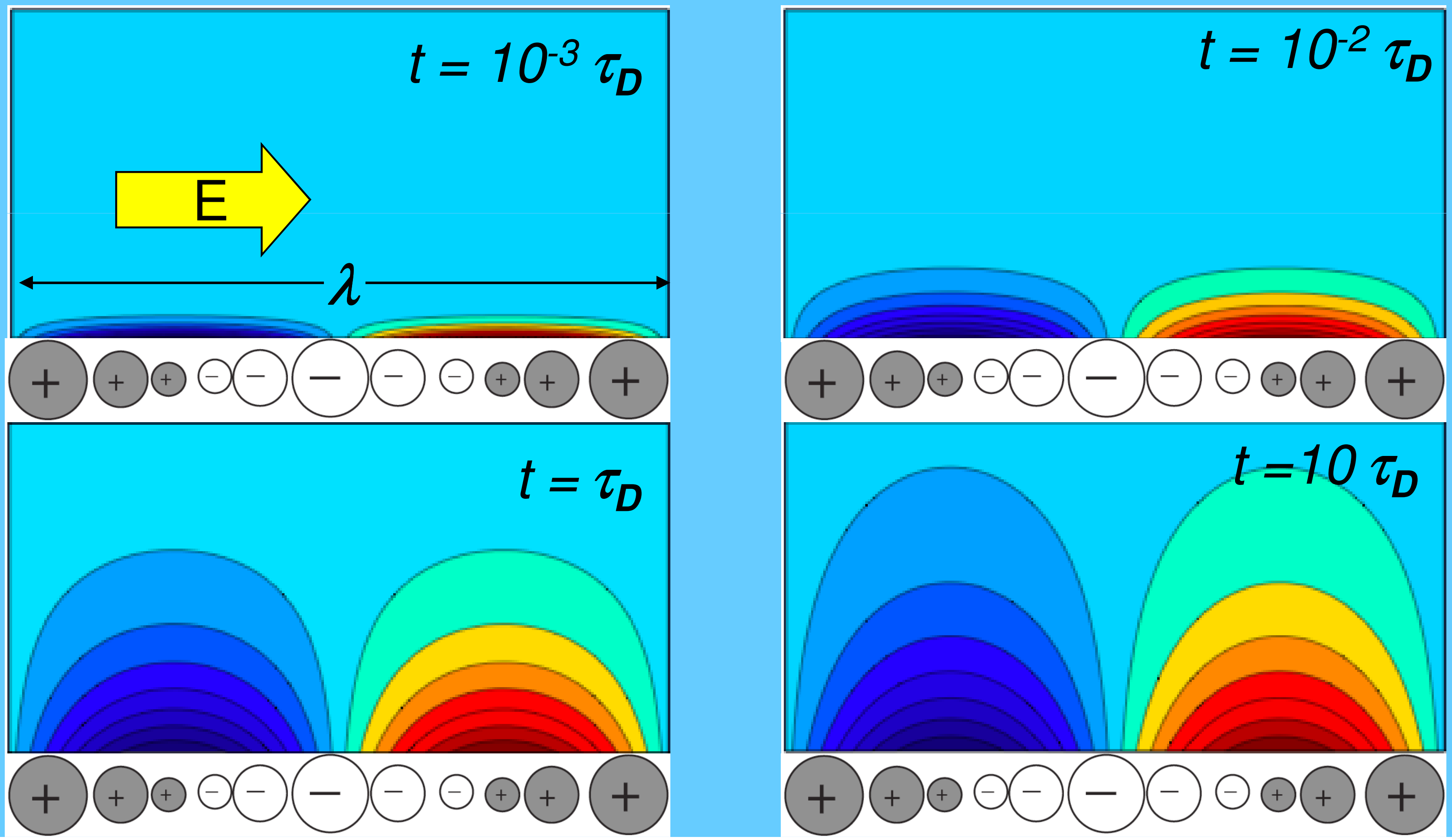
# Concentration polarization

suddenly-applied field

***Outside DL: Salt transport via diffusion***

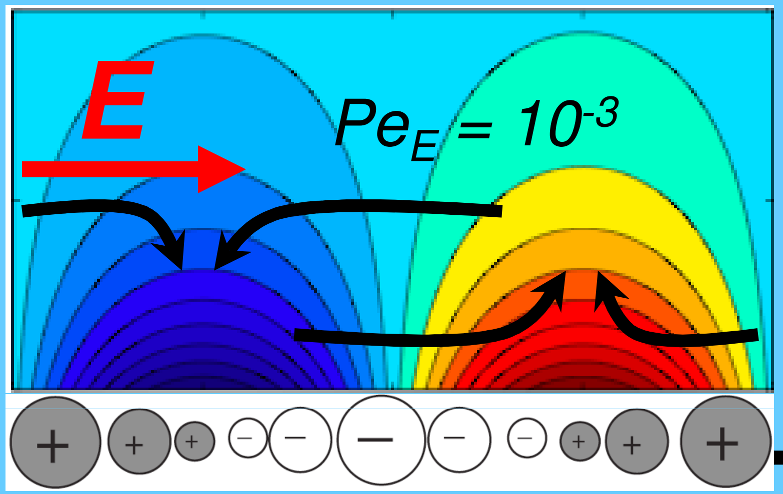
**Inhomogeneous double-layer: salt source/sink disribution**

***Natural time scale: $\tau_D \sim \lambda^2/D$***



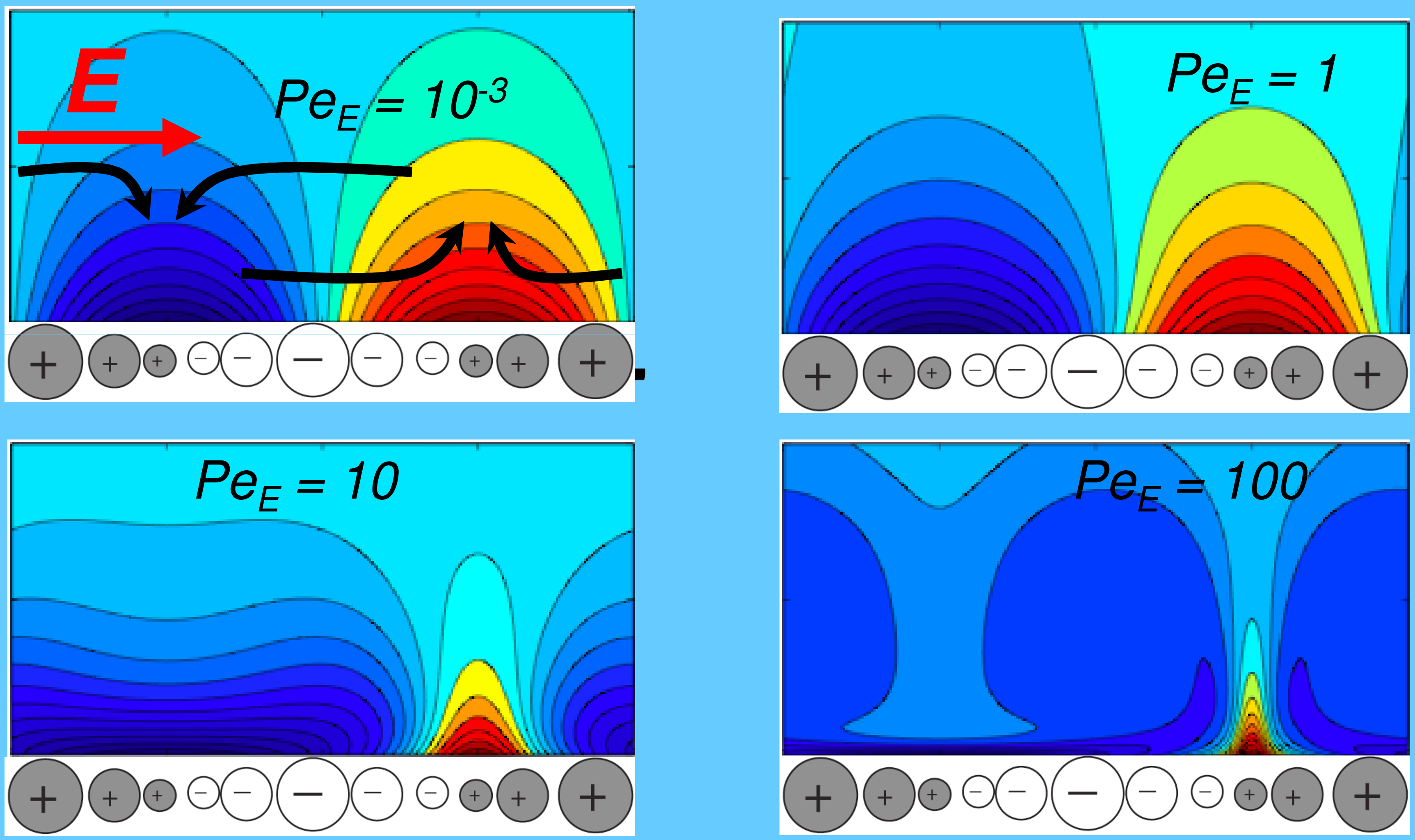
# Convection and diffusion of salt

**Electro-osmotic Peclet number:** $$Pe_E = \frac{U_{EOF} L}{D} \sim \frac{\epsilon \zeta E \lambda}{\mu D}$$



# Convection and diffusion of salt

***Electro-osmotic Peclet number:*** $Pe_E = \frac{U_{EOF}L}{D} \sim \frac{\epsilon\zeta E\lambda}{\mu D}$

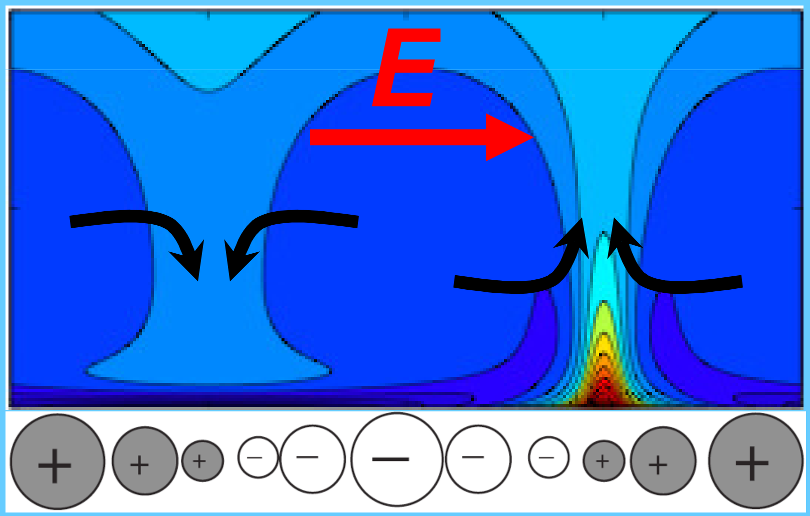



*Flow asymmetry gives concentration asymmetry, form salt plumes*

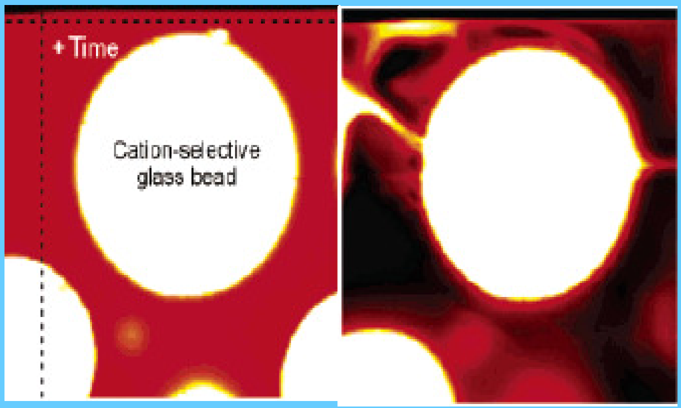
# Convection-diffusion: salt plumes

*Electro-osmotic Peclet number:*

$$Pe_E = \frac{U_{EOF}L}{D} \sim \frac{\epsilon\zeta E\lambda}{\mu D}$$




**CP + Convection**

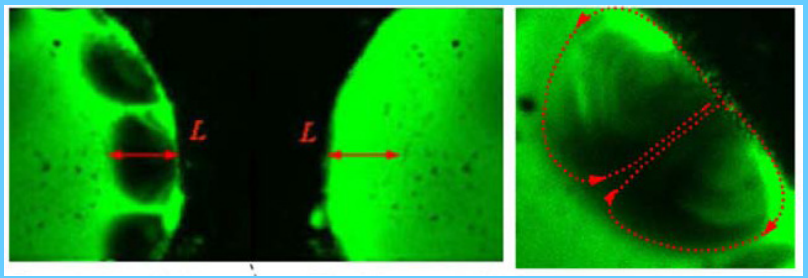



*Leinweber & Tallarek 2005*

*Salt "de-mixing"*

QuickTime™ and a
decompressor
are needed to see this picture.

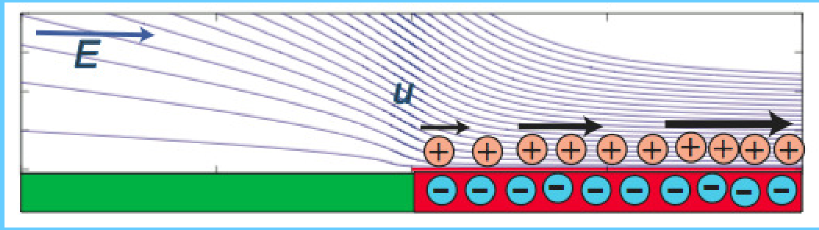
*Leinweber et al 2006*




*Yossifon & Chang 2008*

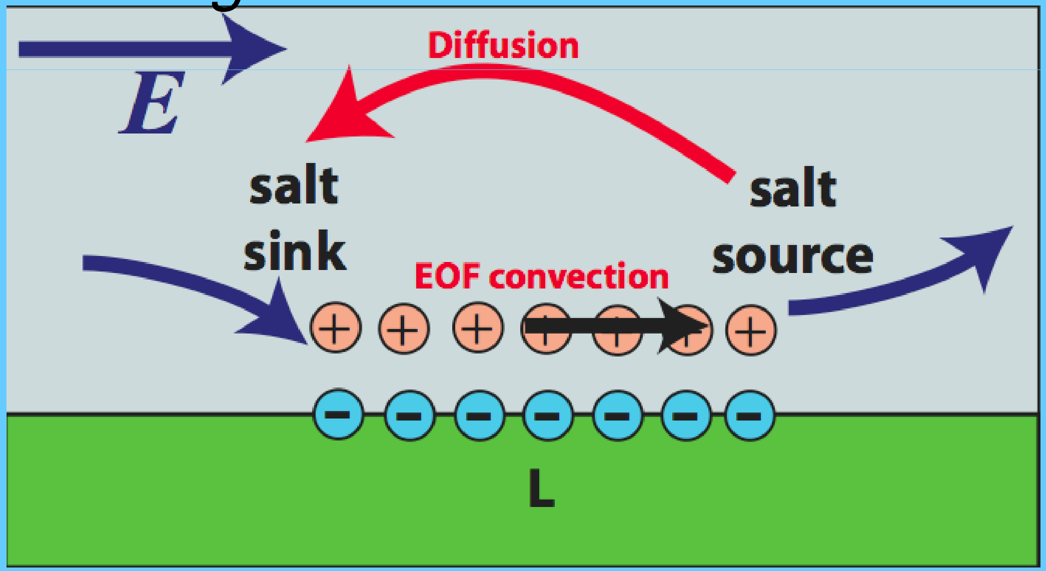
# Surface charge discontinuities

***2D diffusion from line source/sink: ill-posed.***




***Regularization mechanisms:***

- *Convective transport from EOF*
  - *Convection-diffusion boundary layer, 'upwind' stabilizes*
  - *Downwind: salt gradually reduced*
- *Plate ends, providing a line source of salt*

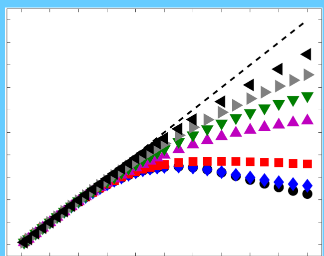



*Time scale to reach steady state:*

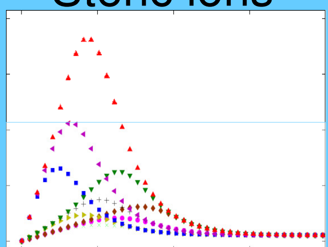
- *diffusion time $L^2/D$*
- *convection time $L/U_{EOF}$*

# Where we've since gone

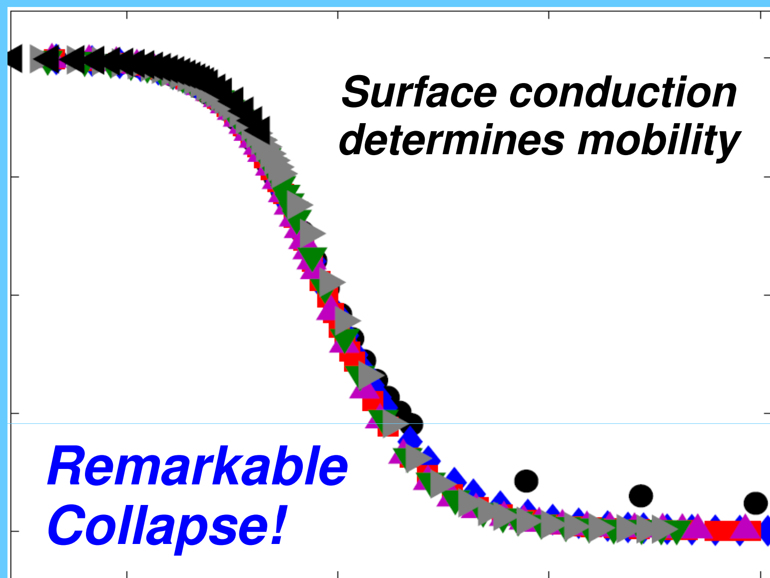
***Electrophoresis with slip & sterics***



Steric ions

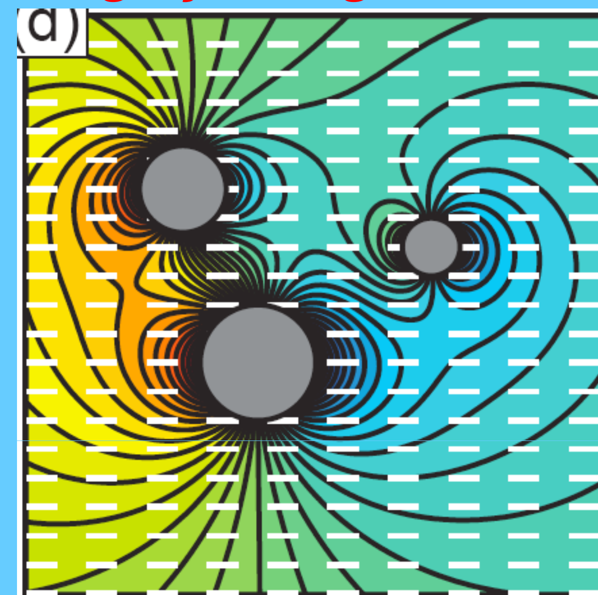


Partial Slip




***Khair & Squires, PoF 09, JFM 09***

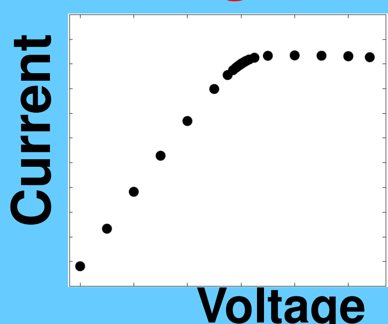
***Universal EK mobility***
***Of highly-charged bodies***

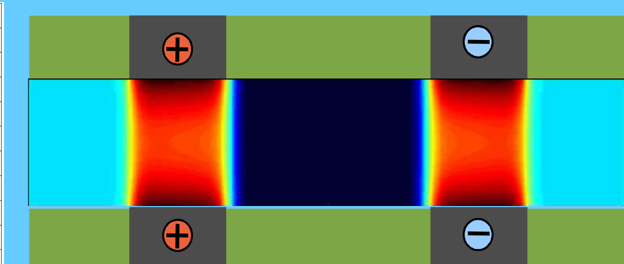



***Squires, preprint***

***Roughness effects***

***Gating in 'tunable' nanochannels***

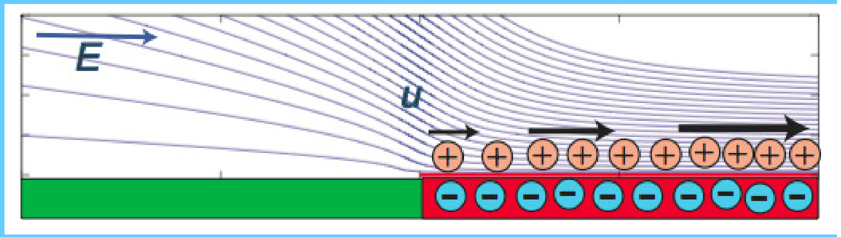


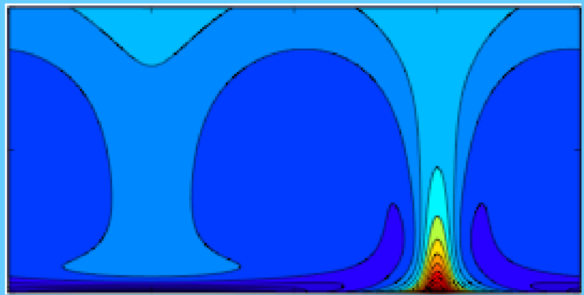
QuickTime™ and a
decompressor
are needed to see this picture.

# *Inhomogeneous surface transport*

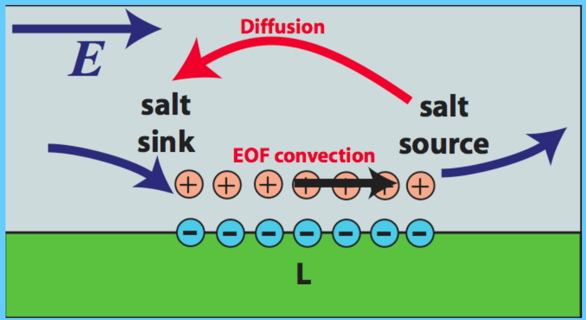
- **Surface charge gradients:**
  - Ion conservation necessitates bulk field perturbations
  - At step changes: "healing length" ~ $\sigma_S / \sigma_B$ can be *long*




  - Field into/out of DL creates sources/sinks of salt
  - Concentration Polarization
    - *Established over 'macro' time and length scales*
    - *Nontrivially influenced by convection with EOF*



  - *Step Change:*
    - *ill defined without regularization*
      - *Trailing edge - diffusive dipole*
      - *Convection with EOF - boundary layer*



# Acknowledgments

**The Frenkiel Award Committee & DFD Community**
**Aditya Khair,**
**Andy Pascall, Rob Messinger**
**Carl Meinhart**

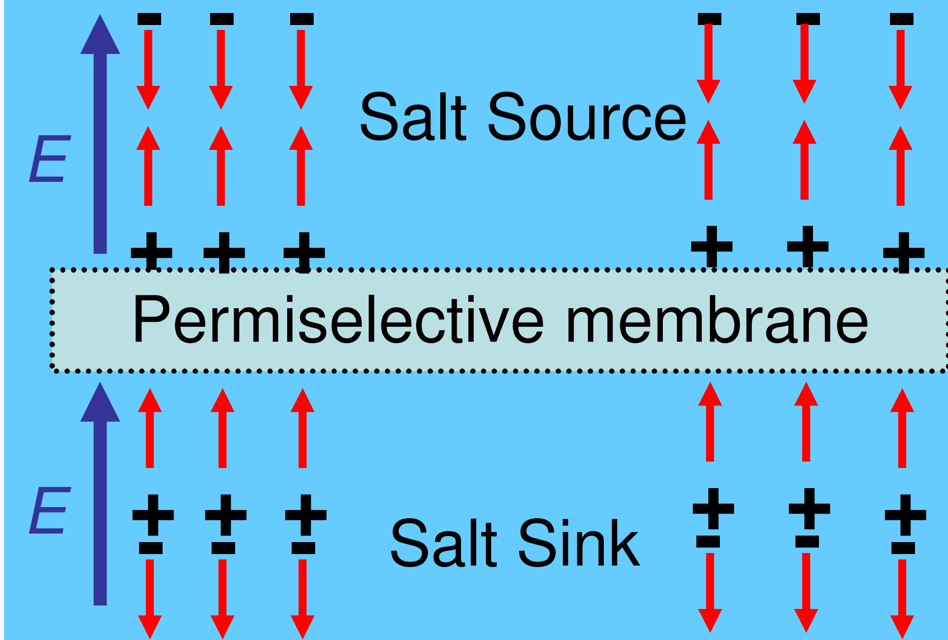
## References

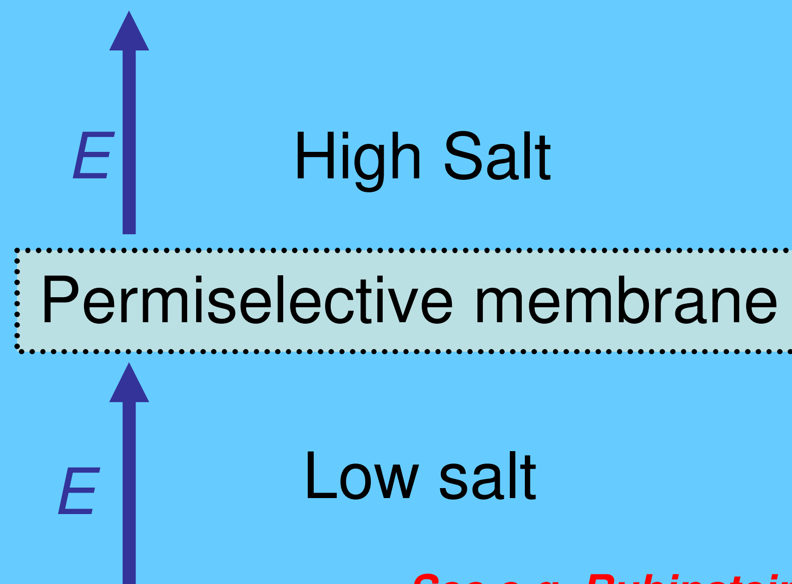
•Khair & Squires "Fundamental aspects of concentration polarization arising from non-uniform surface transport", *Phys. Fluids* 20, 087102 (2008)
•Khair & Squires, *J. Fluid Mech*. 615, 323-334 (2008)

ICB NSF NNIN UCSB nanofab Arnold and Mabel BECKMAN

# Concentration polarization

## *Electrokinetic formation of salt concentration gradients*



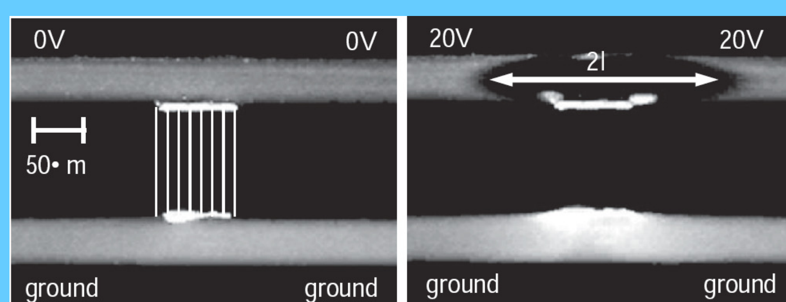

***See e.g. Rubinstein***

**CP in porous granules**

QuickTime™ and a
decompressor
are needed to see this picture.

***Tallarek et al 2005***

**CP across nanochannels**




***Kim, Han et al 2007***

- **Induced-charge electrokinetics (e.g. Chu & Bazant)**