Electrokinetic effects

Diffuse ions

fluid flow, particle motion

Electric fields
Electrokinetic effects

Field-driven motion

Electro-osmotic flow

Diffuse ions

fluid flow, particle motion

Electric fields

Paul et al. '99

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Electrokinetic effects

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$qE$

Diffuse ions

Fluid flow, particle motion

Electric fields

Electrophoresis

Happy 200th Birthday!

“Notice sur un nouvel effet de l'électricité galvanique”

F.F. Reuss 1809

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Electrokinetic effects

Field-driven motion

Electro-osmotic flow

$qE$

Paul et al. ‘99

Flow-driven fields

Streaming potential

Electrophoresis

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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.

Potentially highly transformative, in the exothermic sense

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

Source: youtube

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A modern renaissance in electrokinetics

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

DNA translocation

Nanofluidic Diode

Energy Harvesting

Overlimiting Currents in Electrochemical Systems

Concentration Polarization at Micro/Nano Interfaces

Salt “de-mixing”

Keyser et al. 2006

Karnik et al. 2007

van der Heyden et al. 2007

Yossifon & Chang 2008

Kim et al. 2005

Leinweber et al. 2006

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How most of you view water.

Water, $\varepsilon = 80$
Water dissolves ions...

\[ \text{Water, } \varepsilon = 80 \]

\[ \text{OH}^- \quad \text{H}^+ \quad \text{Na}^+ \quad \text{Cl}^- \quad \text{etc.} \]
Ions ‘screen’ charged surfaces

Screening length $\lambda_D$ varies from $\sim 1 – 10^3$ nm

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Electric fields: body force on fluid

net force within screening cloud
Electro-osmosis: field drives flow

'\textit{slip'} velocity (conveyor belt) \( u_s = -\frac{\varepsilon\zeta}{\eta} E \)
“Standard Model” for electrokinetics

...what lurks behind all the cartoons I’ll show.

(1) Fluid flow: low-Re flow

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

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

(2) Electrostatics

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

(3) Ion conservation

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

**diffusion**  
**advection**  
**electrostatic**
Microfabrication: natural surface charge inhomogeneities

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

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

Violates ion conservation!
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

**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”? 

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

- Can be very long!

No geometric length scale: “Healing length” emerges

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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

Field & flow “heal” over length scale \( \lambda_H = \frac{\sigma_s}{\sigma_B} \)

Khair & Squires, JFM 08
Question: what happens to the ions...

At first:
Seems ok
Question: what happens to the ions...

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-$\zeta$: can be solved exactly
  - Steady-state concentration and fields
  - Oscillatory concentration and fields
  - Suddenly-applied field -- evolution of “concentration polarization”
- High-$\zeta$ 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

Loss of (+) ions: Need inward field
Gain of (+) ions: Need outward field
Gain of (-) ions: Need inward field
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 distribution

Natural time scale: \( \tau_D \sim \lambda^2 / D \)

\[ t = 10^{-3} \tau_D \]

\[ t = 10^{-2} \tau_D \]

\[ t = \tau_D \]

\[ t = 10 \tau_D \]
Convection and diffusion of salt

Electro-osmotic Peclet number:

\[ \text{Pe}_E = \frac{U_{EOF} L}{D} \sim \frac{\epsilon \zeta E \lambda}{\mu D} \]
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:

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

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

Salt “de-mixing”

Leinweber & Tallarek 2005
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 & steric effects**

- Universal EK mobility
- Of highly-charged bodies
- Surface conduction determines mobility
- Remarkable Collapse!

**Gating in ‘tunable’ nanoconstrictions**

**Squires, preprint**

**Roughness effects**

Khair & Squires, PoF 09, JFM 09

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Inhomogeneous surface transport

- **Surface charge gradients:**
  - Ion conservation necessitates bulk field perturbations
  - At step changes: “healing length” $\sim \sigma_S / \sigma_B$ 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
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References

Concentration polarization

Electrokinetic formation of salt concentration gradients

Permeselective membrane

Salt Source

Salt Sink

High Salt

Low salt

CP in porous granules

CP across nanochannels

See e.g. Rubinstein

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

Tallarek et al 2005

Kim, Han et al 2007

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