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Electrokinetics and Electrohydrodynamics of Microsystems

Induced-Charge Electrokinetic Phenomena

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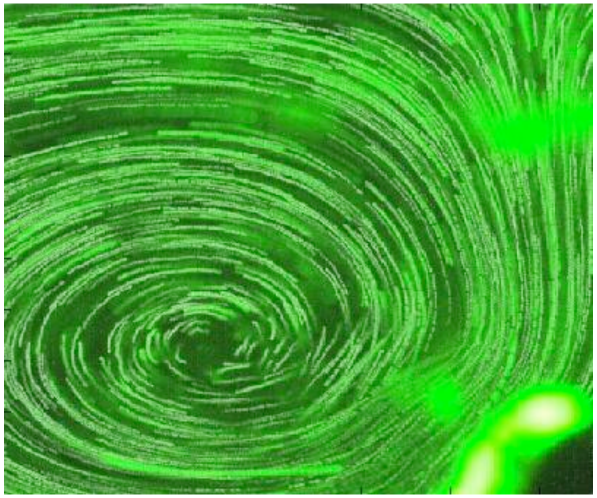
Lectures

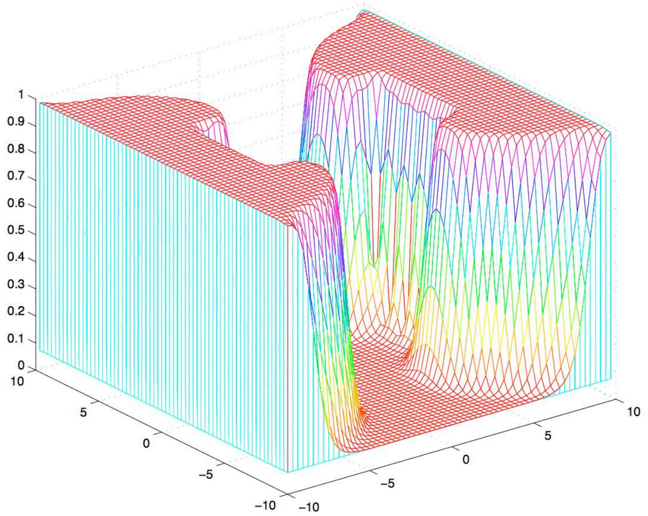
1. Introduction
2. Low-voltage theory
3. Particle motion
4. Fluid motion
5. Large-voltage theory

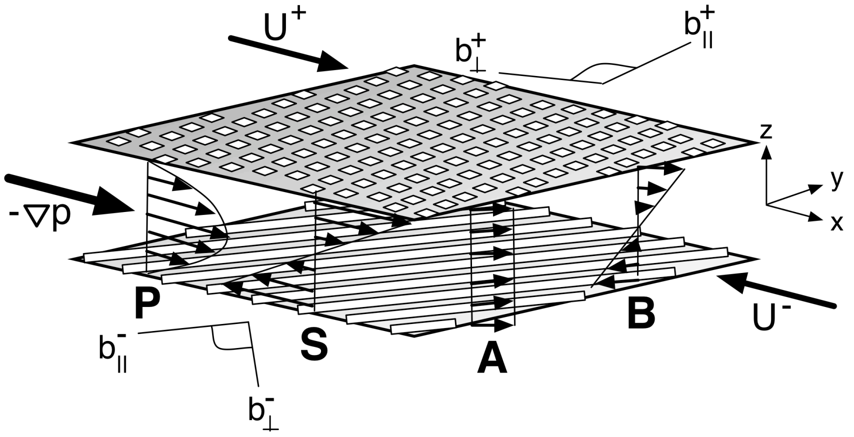


Research Interests

Electrochemical Energy Systems

- *Li-ion batteries*
- *Fuel cells*
- *Super-capacitors*
- *Sensitized Solar Cells*





Microfluidics

- *Superhydrophobic surfaces*
- *Desalination / separations*
- *Nonlinear electrokinetics*

Also: Granular flow, statistical physics, applied math…

Acknowledgments: Electrokinetics

PhD Students:

- Jeremy Levitan (Mech. Eng., 2005)
- Kevin Chu (Applied Math. 2005),
- Sabri Kilic (Applied Math. 2008)
- Damian Burch (Applied Math. 2009)
- JP Urbanski (Mech. Eng. 2005, Thorsen)

Postdocs:

- Yuxing Ben (2004-2006)
- Chien-Chih Huang (2007-2009)

Undergraduate Students:

- Jakub Kominiarczuk (BS Thesis, 2007)
- Kapil Subramanian
- Andrew Jones
- Brian Wheeler
- Matt Fishburn

Collaborators:

- Armand Ajdari (ESPCI, France)
- Henrik Bruus (DTU, Denmark)
- Antonio Ramos (Sevilla, Spain)
- Todd Thorsen (MIT)
- Brian Storey (Olin College)
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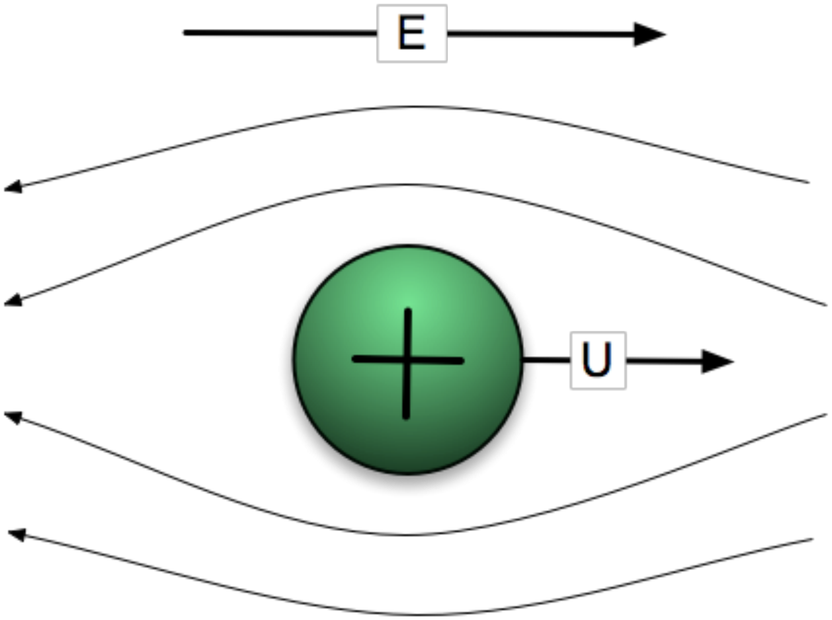
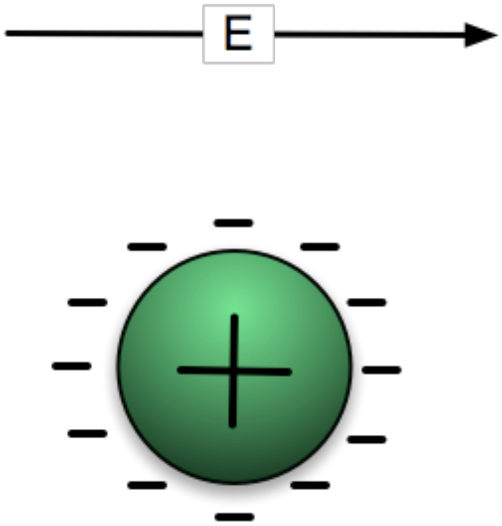
Overview of Linear Electrokinetic Phenomena

Electrokinetic particle motion



Non-conducting viscous liquid, e.g. oil drops in air, Millikan 1900

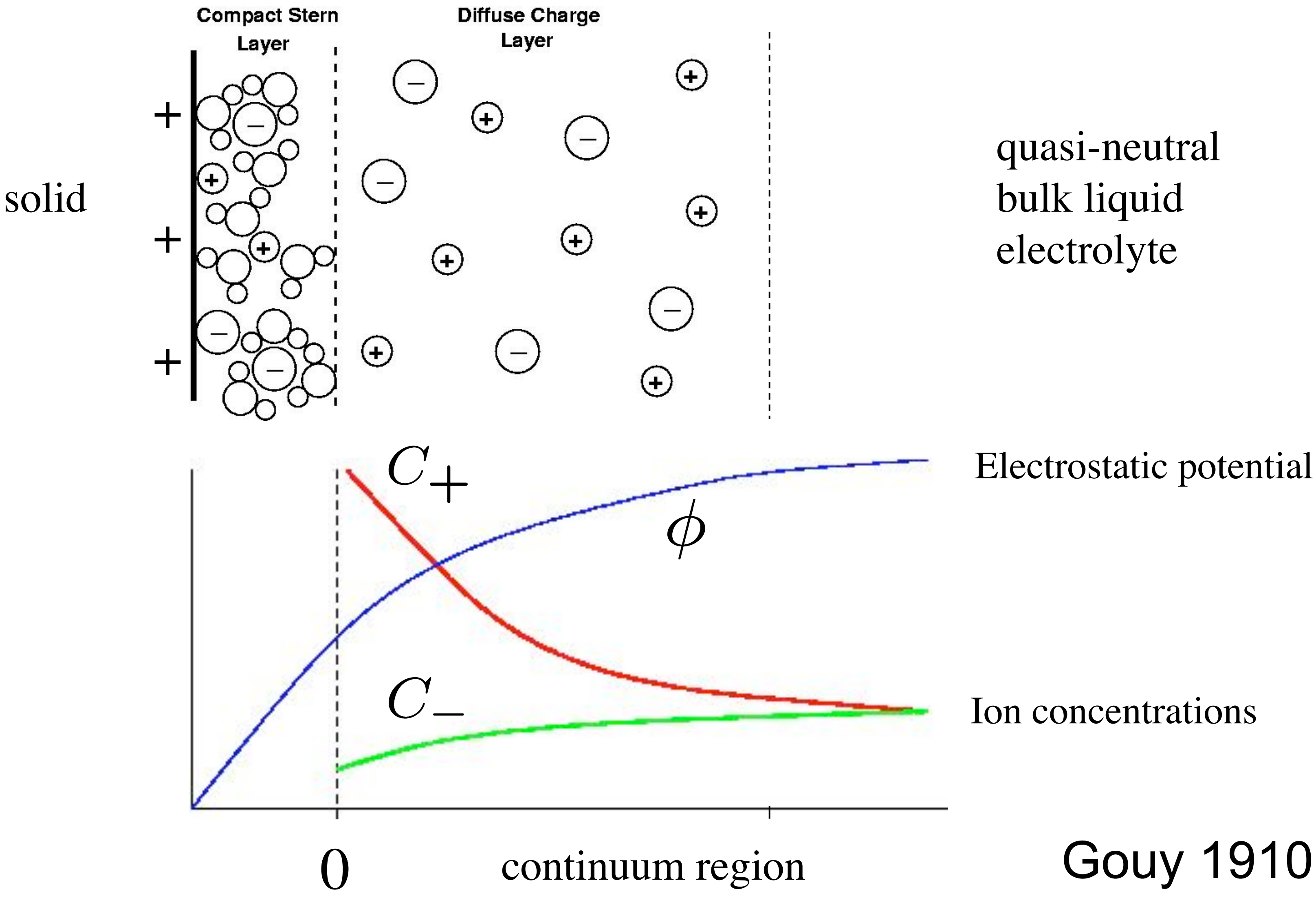
$$U = \frac{qE}{6\pi\eta R}$$



Electrolyte (salt solution) e.g. clay particles in water, Reuss 1808

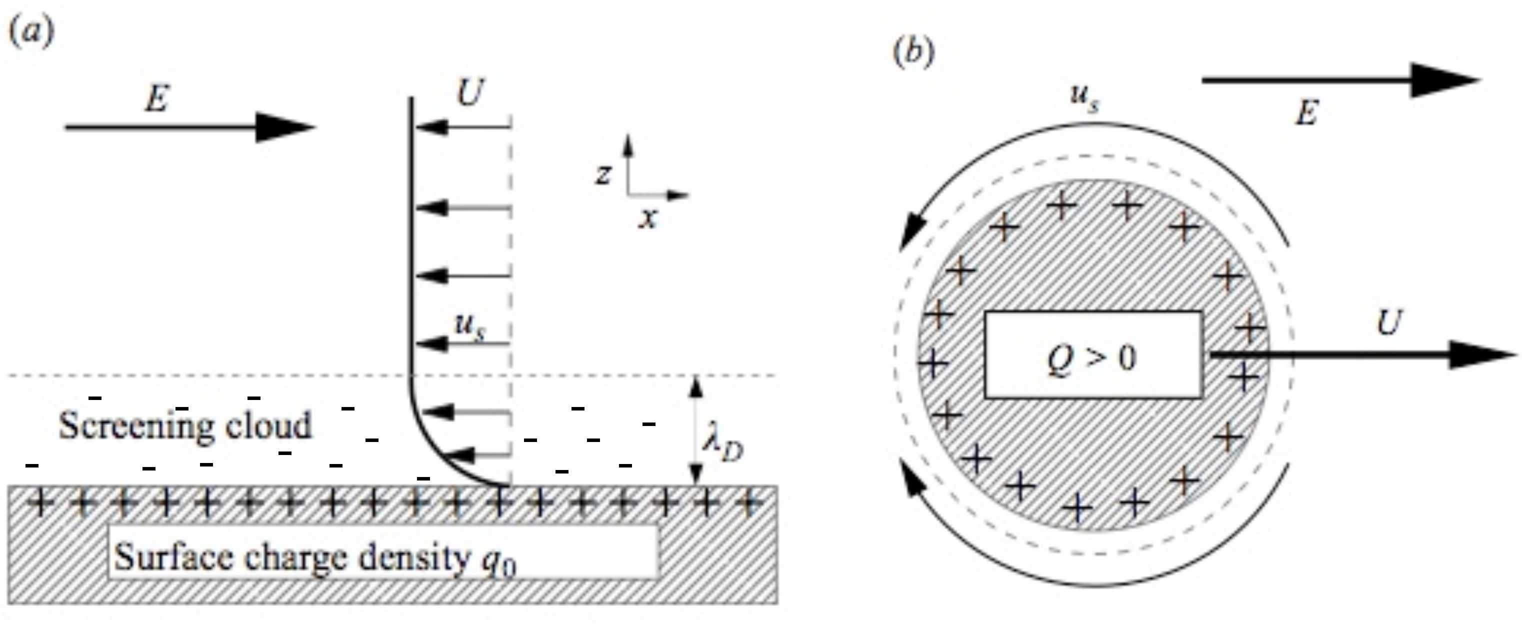
$$q_{total} = 0, \quad U = 0?$$

The Electric Double Layer



Gouy 1910

Electrokinetics in electrolytes



(a) Electro-osmosis = fluid slip across the double layer, as an electric field pushes on the screening cloud

(b) Electrophoresis = particle motion due to electro-osmosis

Classical Theory

- *Quasi-equilibrium thin double layers*
- *Fixed surface charge (or zeta potential)*

Effective fluid "slip" outside the double layer

$$u_s = M_{EO} \nabla_t \phi + M_{DO} \nabla_t \ln c$$

Electro-osmotic mobility (general result)

$$M_{EO} \equiv \frac{\varepsilon_{bulk}\zeta}{\eta_{bulk}} = \int_0^{\psi_D} \frac{\varepsilon}{\eta} d\psi \approx \frac{\varepsilon_{bulk}\psi_D}{\eta_{bulk}}$$

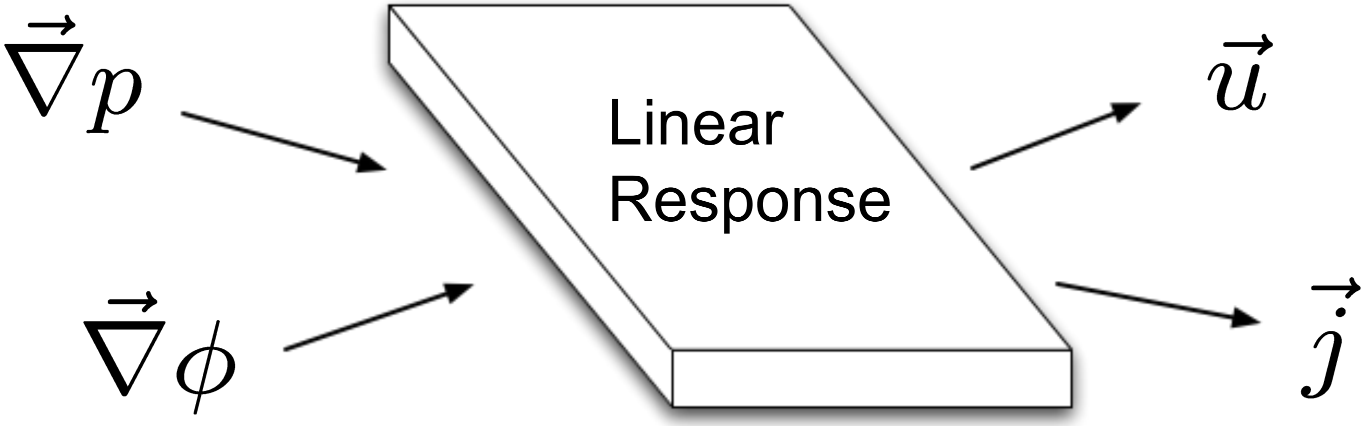
Helmholtz-Smoluchowski

Diffisio-osmotic mobility (dilute z:z electrolyte)

$$M_{DO} = \frac{4\varepsilon_{bulk}}{\eta_{bulk}} \ln\cosh\left(\frac{ze\zeta}{4kT}\right)$$

Derjaguin-Dukhin

Linear Electrokinetics: 1. Fluids

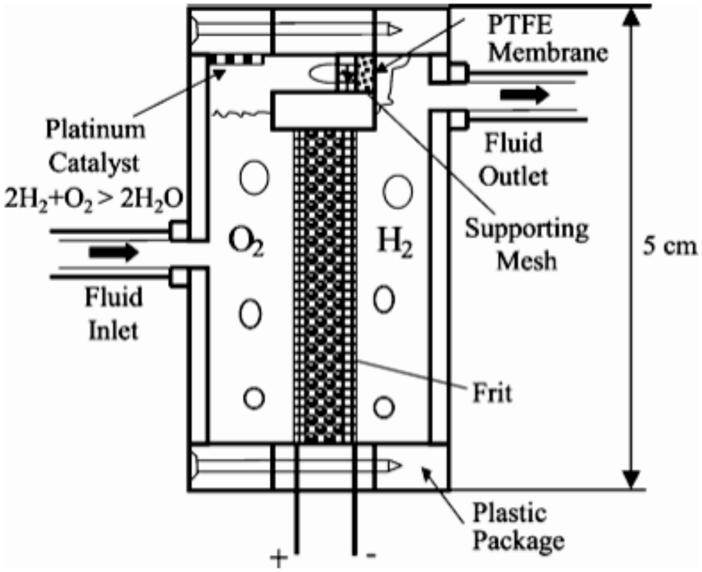


- <u>Helmholtz:</u> electro-osmotic flow
- <u>Onsager:</u> streaming potential & current (inverse effects)
- <u>Ajdari:</u> transverse couplings (anisotropic surfaces)

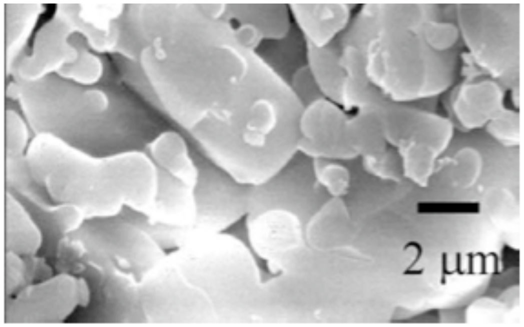
- uniform zeta, thin double layers: potential flow (no vortices)
- No net response to AC forcing

Some Applications

- Forward effect: DC EO Pumps
- Small channels (porous media) lead to large pressure (>10atm)
- Disadvantages:
  - High voltage (100 V)
  - Faradaic reactions
  - Gas management
  - Hard to miniaturize
- Inverse effect: “Electrokinetic energy conversion” (harvest streaming voltage)

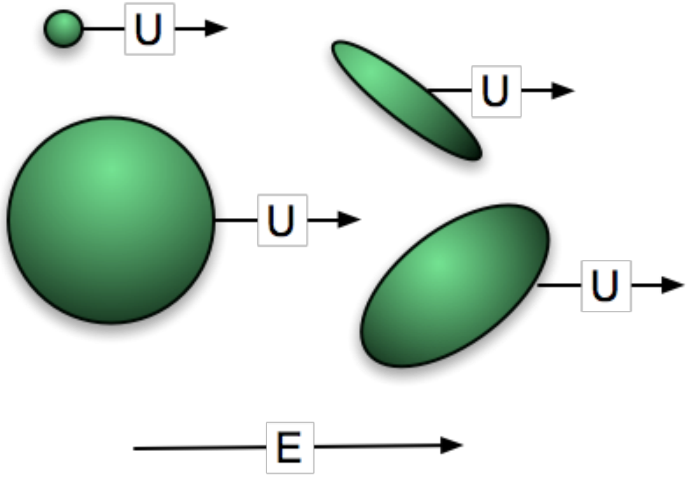


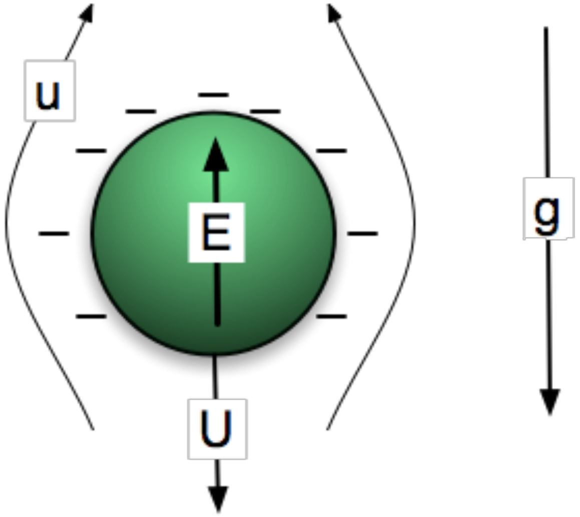
Yau et al, JCIS (2003)



Porous Glass

Linear Electrokinetics: 2. Particles





- Smoluchowski: electrophoresis
- Onsager: sedimentation potential, induced dipole
- Dukhin, Deryaguin: surface conduction (large charge)
- Anderson, Ajdari: transverse motion, rotation

- uniform zeta, thin double layers: cannot separate particles!

Overview of
Nolinear “Induced-Charge”
Electrokinetic Phenomena

Examples of Nonlinear Electrokinetic Phenomena in Electrolytes

-Shilov (1976): dipolophoresis (DEP + electrophoresis)

-Dukhin (1986): 2nd kind electrophoresis
-Rubinstein & Zaltzman (2000): Electro-osmotic instability and super-limiting current at ion-exchange membranes

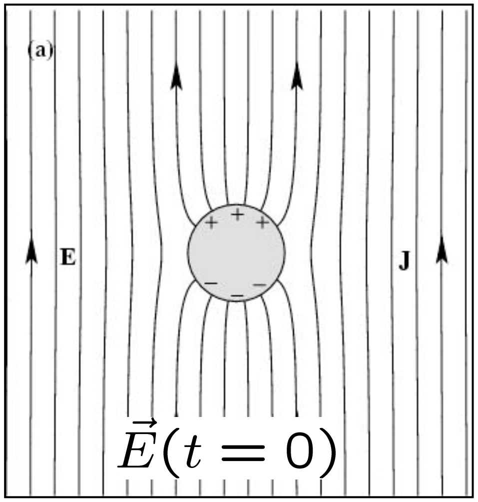
-Santiago (2004): Two-fluid electrokinetic instability in microchannels

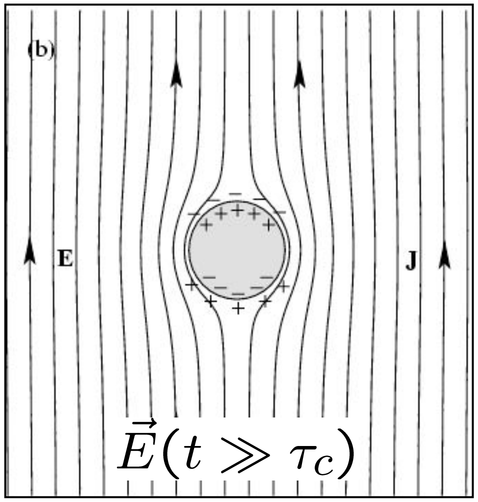
-Murtsovkin (1986): EO flows around metal particles
-Saville (1997): AC colloidal self-assembly on electrodes
-Ramos (1999): AC electro-osmosis
-Ajdari (2000): AC pumping with electrode array

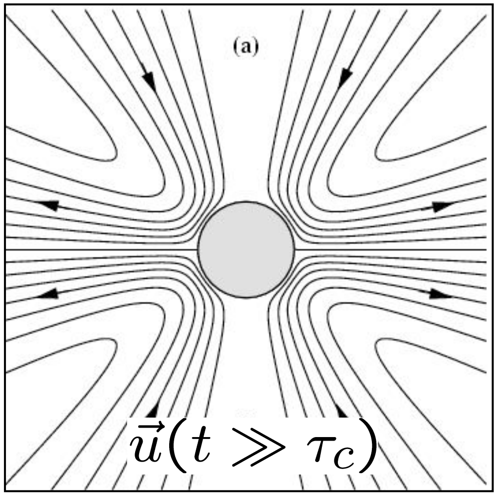
“Induced-Charge Electro-osmosis”

= *nonlinear* electro-osmotic slip at a *polarizable* surface

Example: An uncharged metal cylinder in a suddenly applied DC field







$$\zeta \sim ER \;\Rightarrow\; u \sim \varepsilon R E^2/\eta$$

ICEO flow persists in an AC field (< charging frequency).

Gamayunov, Murtsovkin, Dukhin, Colloid J. USSR (1986) - flow around a metal sphere
Bazant & Squires, Phys, Rev. Lett., J Fluid Mech, (2004) - mathematical theory, microfluidic applications

Double-layer polarization and ICEO flow

A conducting cylinder in a suddenly applied uniform E field.

Electric field

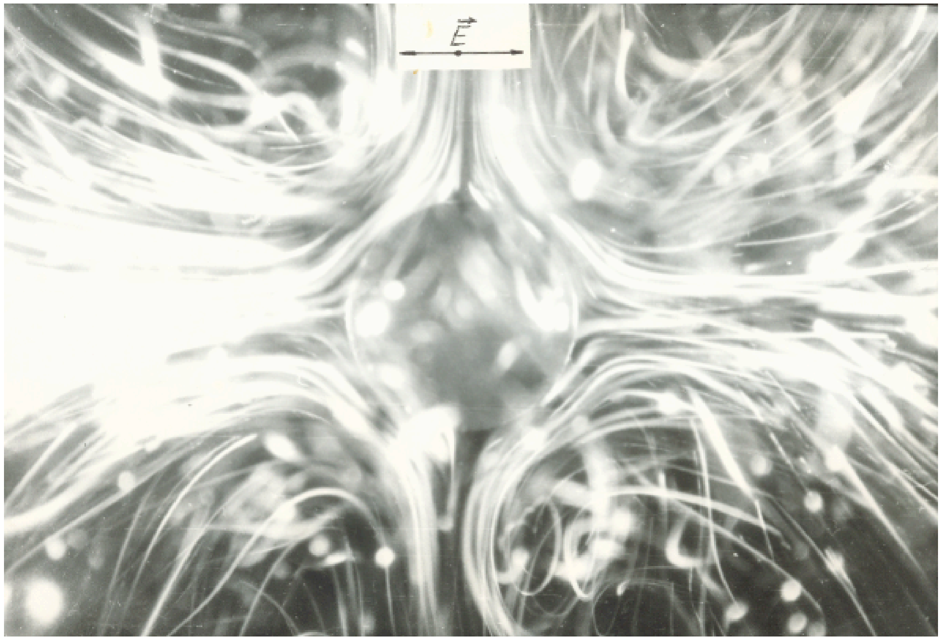
ICEO velocity

Movies: numerical solution of the Poisson-Nernst-Planck/Navier-Stokes equations by Y. Ben, 2005 ($\lambda/a=0.005$)

We will analyze this problem in Lecture 2.

A pioneer, ahead of his time

Vladimir A. Murtsokvin (work from 1983 to 1996)

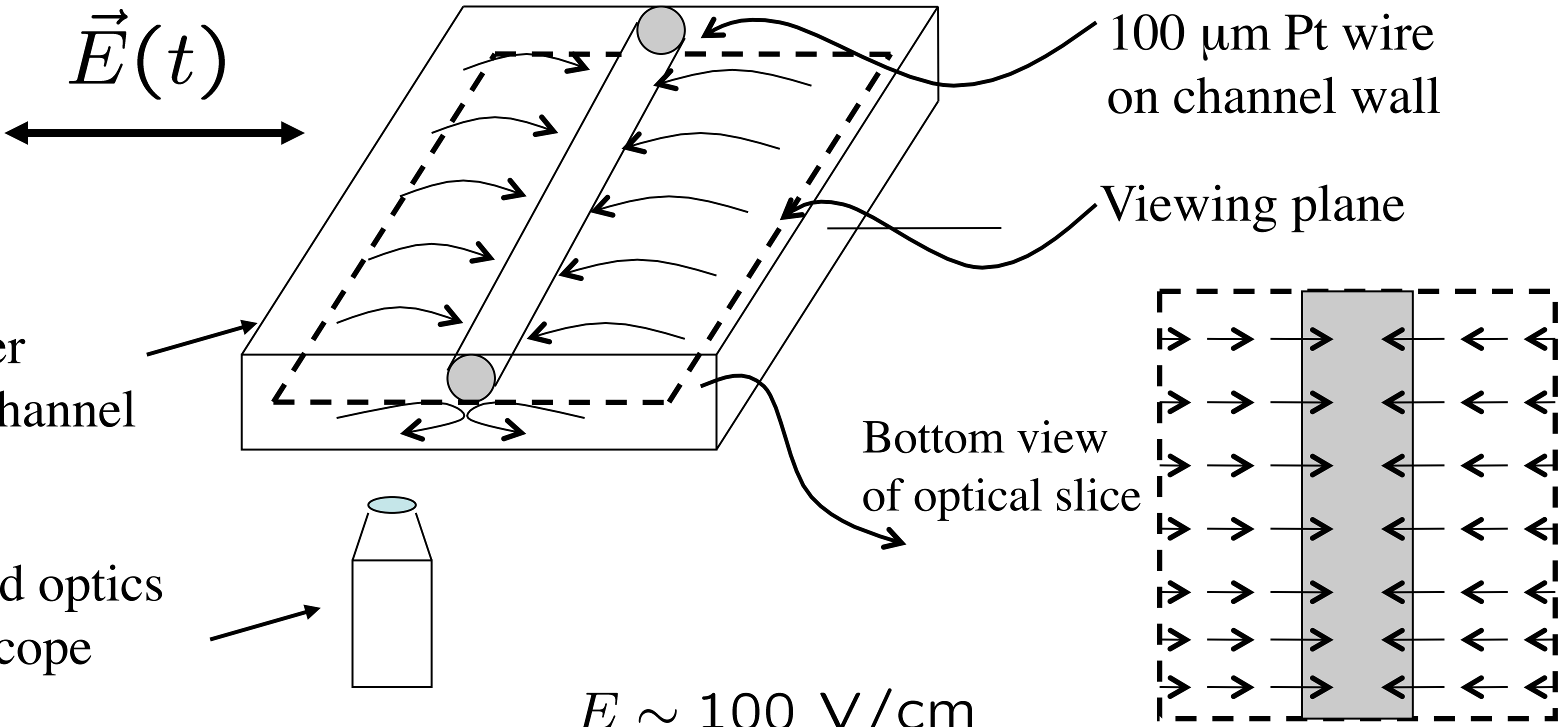


“ICEO” flow around an metal particle (courtesy of Andrei Dukhin)

The subsequent development of micro/nanotechnology has created many new opportunities for basic science and applications of nonlinear electrokinetic phenomena.

Experimental Observation of ICEO

Jeremy Levitan, PhD Thesis in Mechanical Engineering, MIT (2005)



100 μm Pt wire
on channel wall

Viewing plane

PDMS
polymer
microchannel

Bottom view
of optical slice

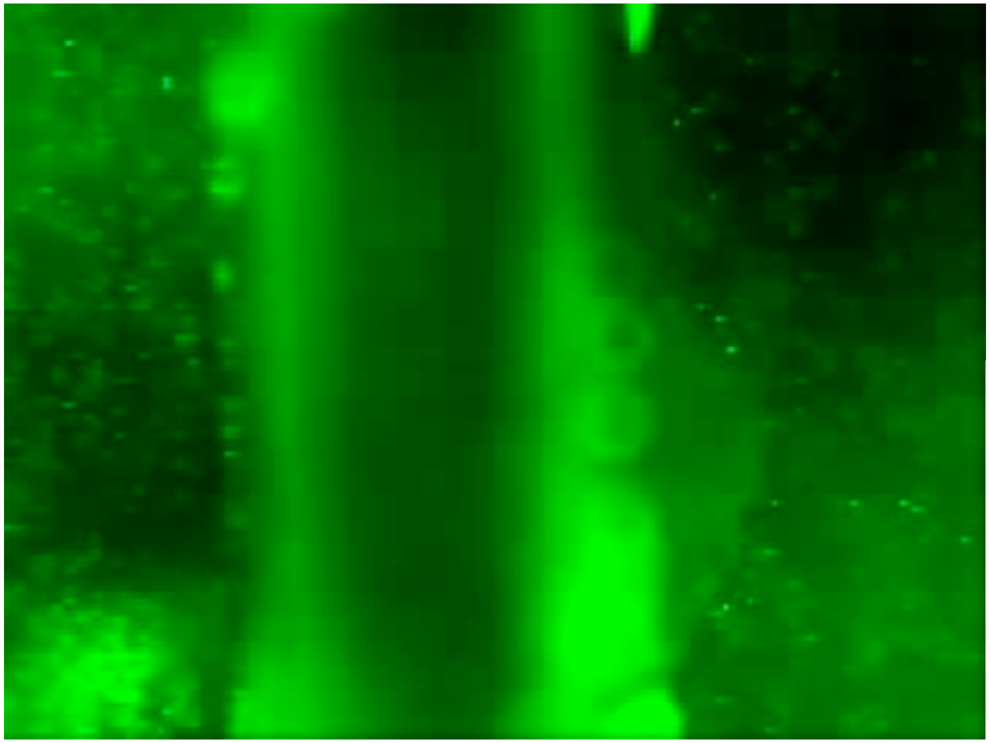
Inverted optics
microscope

Micro-particle image velocimetry (μPIV) to map the velocity profile

$E \sim 100$ V/cm
$\omega \sim 100$ Hz AC
$u \sim 100\ \mu$m/s
$C \sim 0.1$ mM KCl

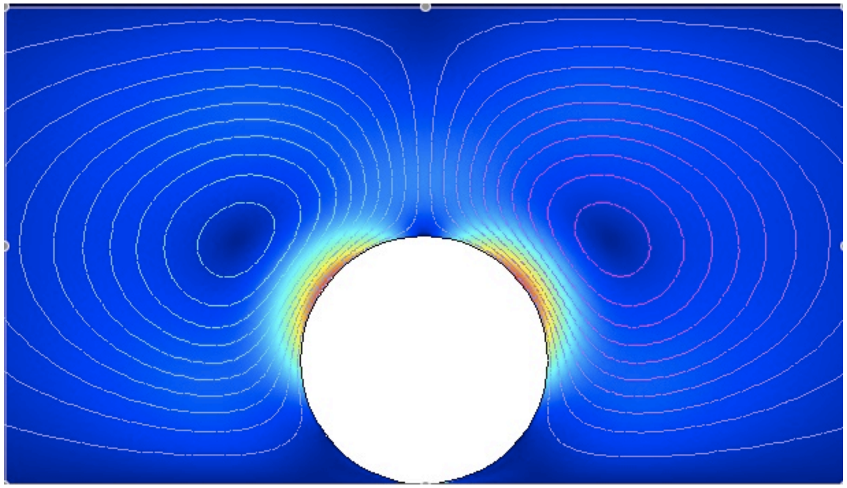
ICEO Experiments

J. A. Levitan, S. Devasenathipathy, V. Studer,
Y. Ben, T. Thorsen, T. M. Squires & M. Z. Bazant,
Colloids and Surfaces (2005)

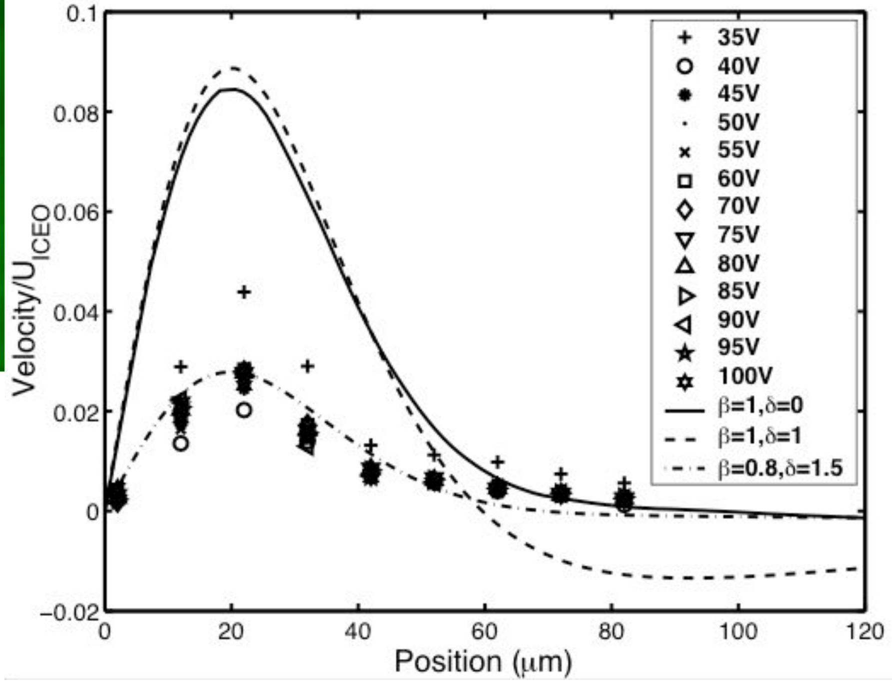


Movie: 5 μm optical slice sweeping
100 μm Pt cylinder (top view)
100 V/cm, 300 Hz, 0.1 mM KCl

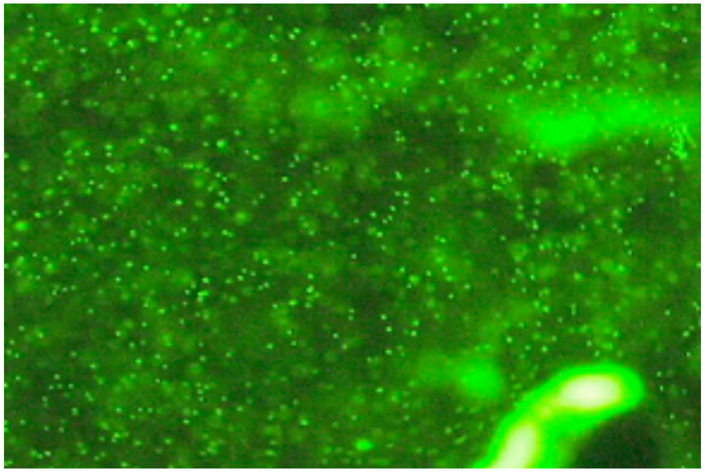
Simulated flow (side view)



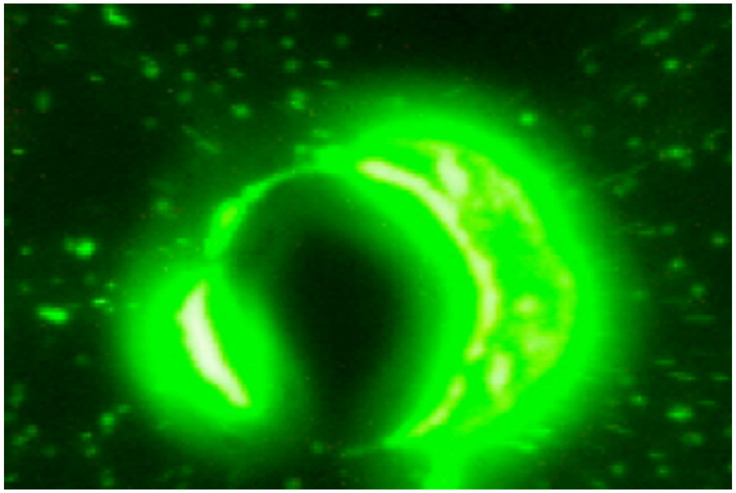
Collapse of experimental data



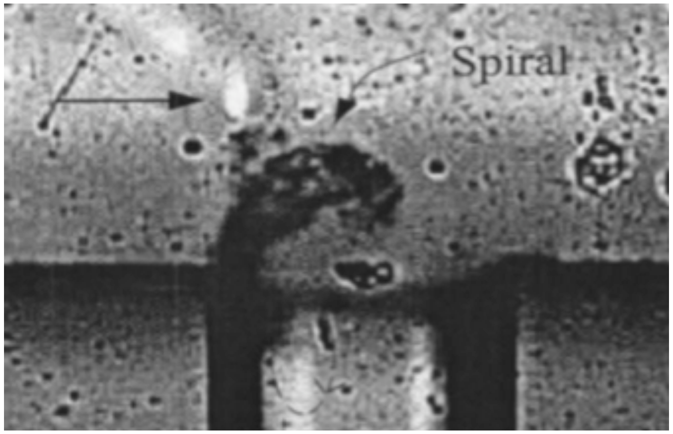
Examples of ICEO in Microfluidics



Flow around a metal post

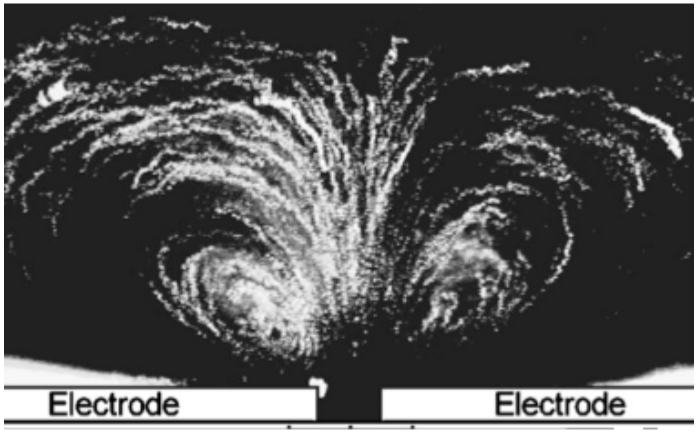


Fixed-potential ICEO



DC jet at a dielectric corner

Thamida & Chang (2002)

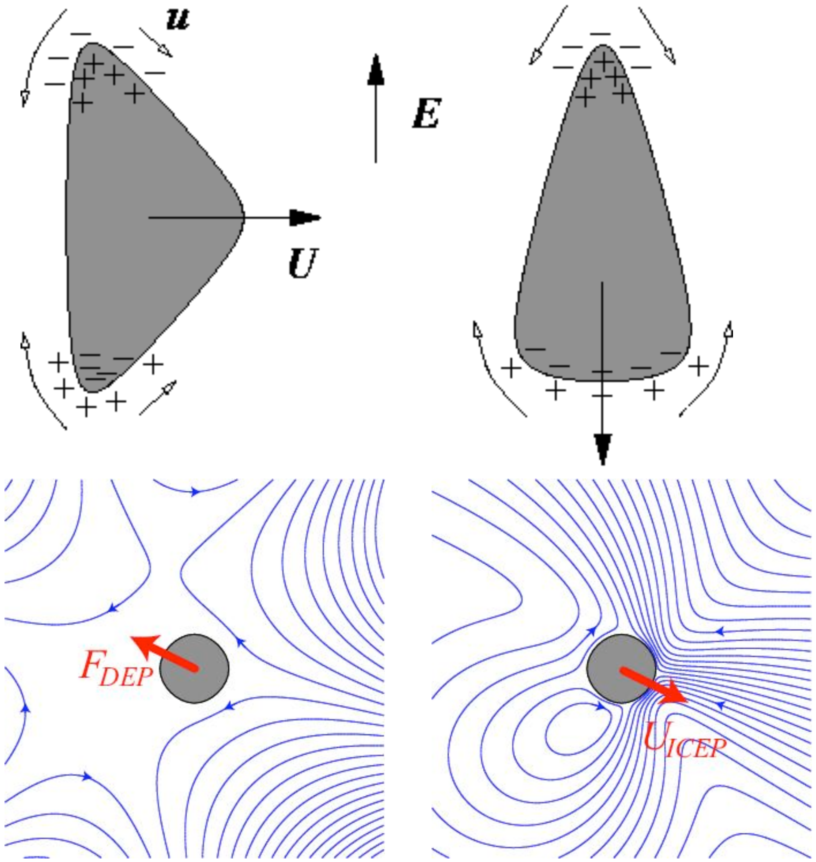


AC electro-osmosis

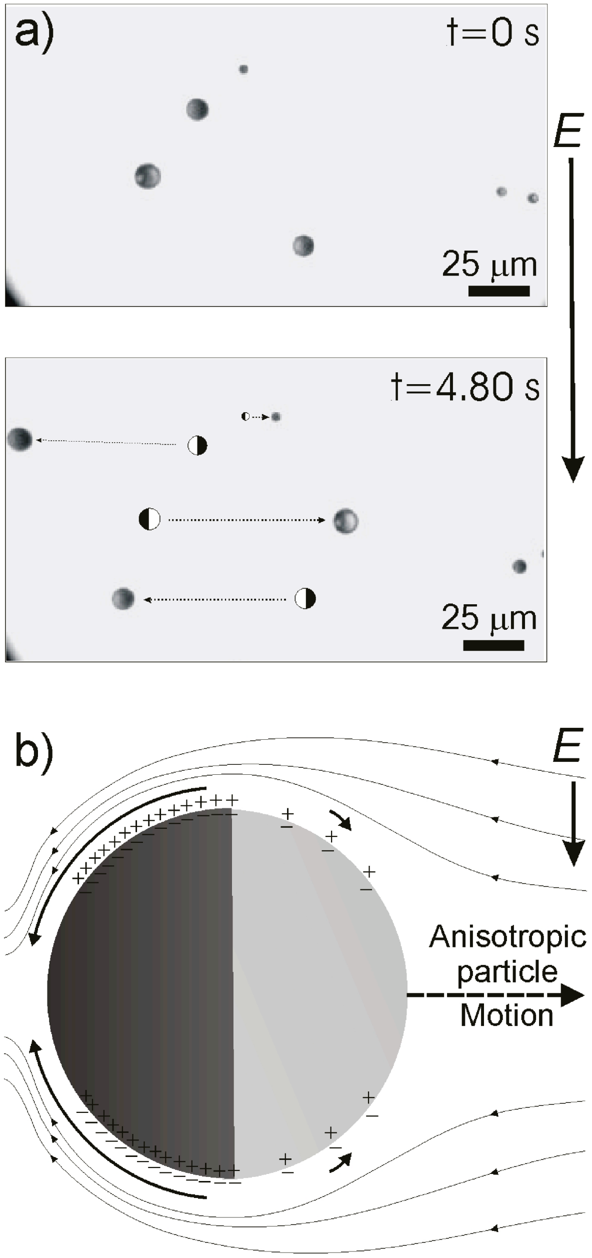
Ramos et al (1999), Ajdari (2000)

Broken Symmetries:
I. Particle Motion

(Lecture 3)



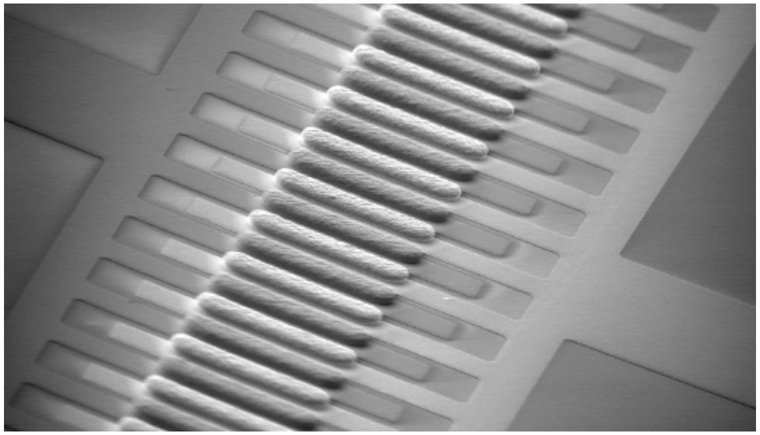
Squires & Bazant, J. Fluid Mech. (2006)



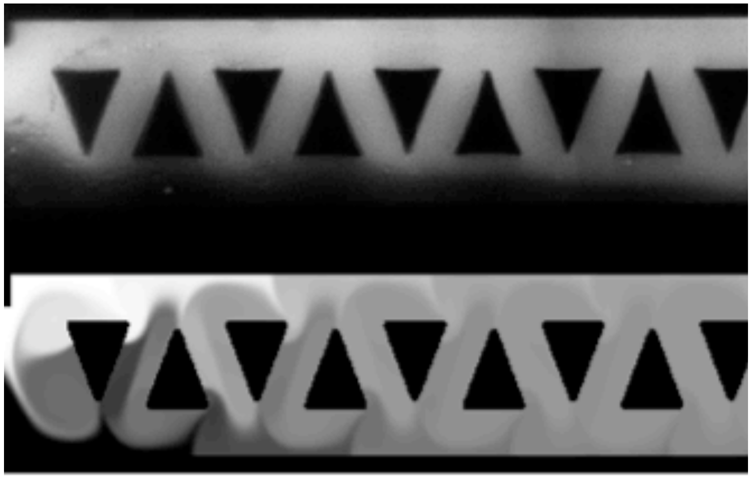
Gangwal et al, Phys. Rev. Lett. (2008)

Broken Symmetries: II. Fluid Motion

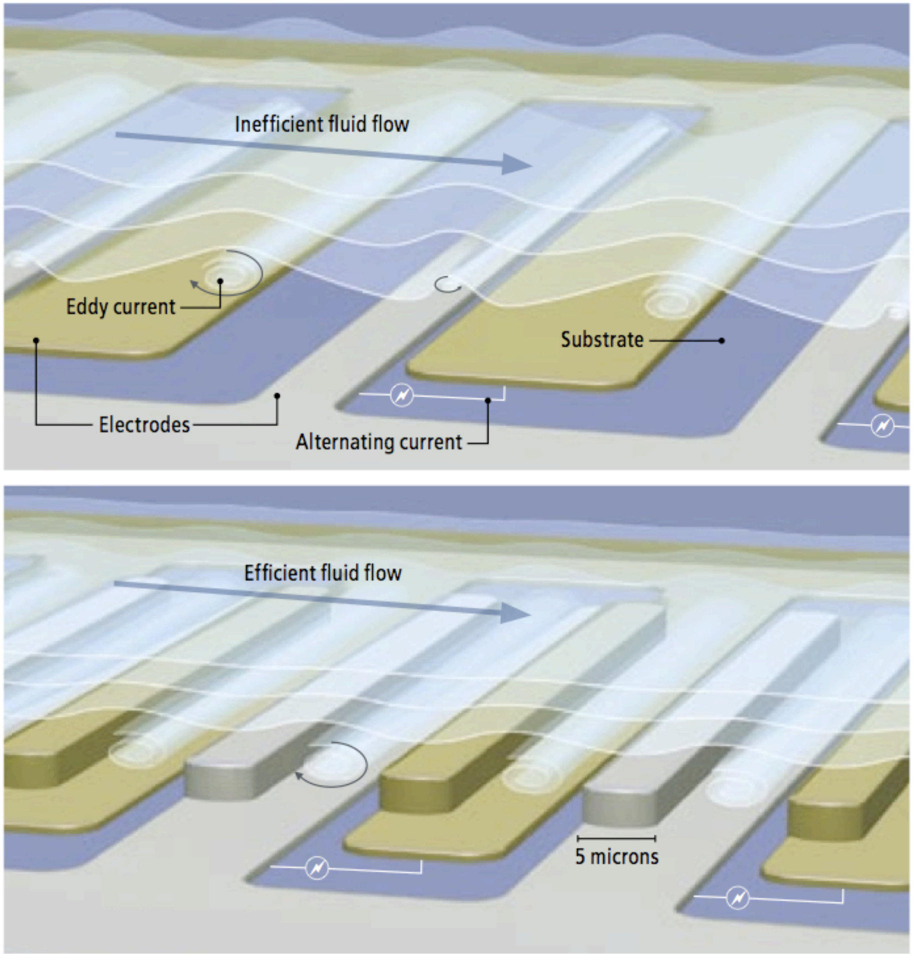
(Lecture 4)



Urbanski et al, Appl Phys Lett (2006)



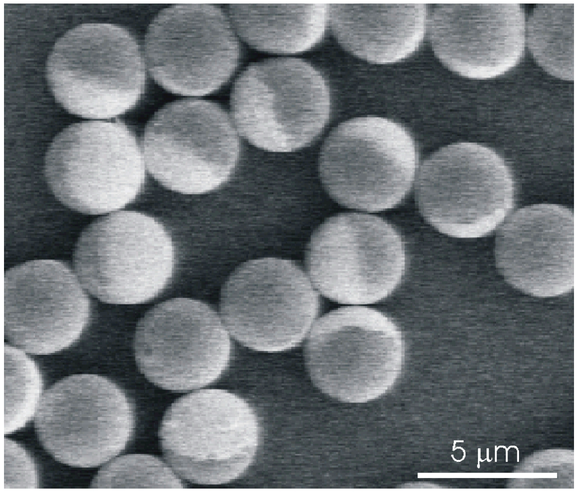
Harnett et al, Lab on a Chip (2008)

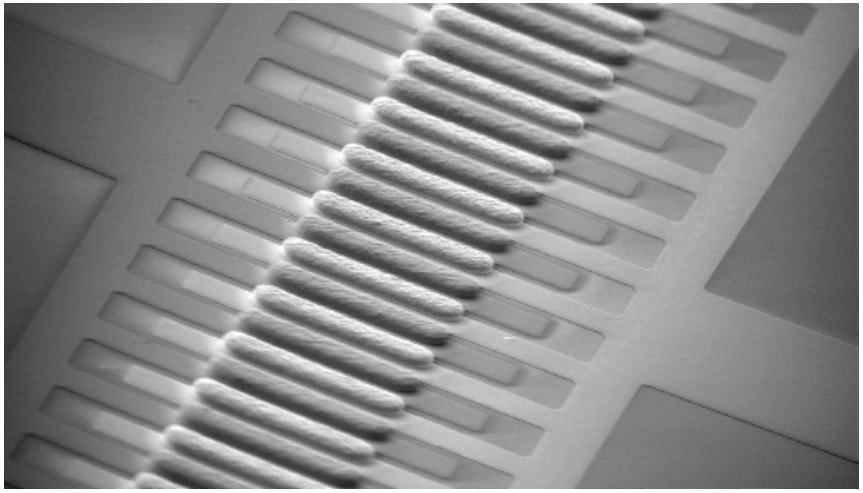


Choi, Scientific American (2007)
Bazant & Ben, Lab on a Chip (2006)

Lecture 1: Conclusion

Induced-charge / AC electrokinetics provides many opportunities for new science and applications.





Papers, slides… http://web.mit.edu/bazant/www/ICEO