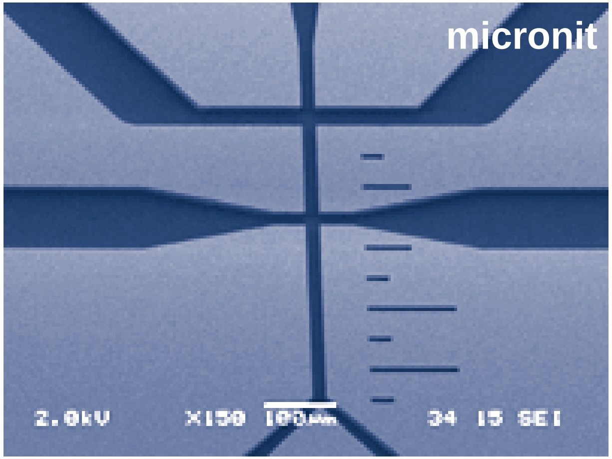
Numerical Simulation of Non-Equilibrium Electroosmotic Flow in Micro- and Nanochannels



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Overview

Brief Introduction to Electroosmosis

- ✓ EDL (Electric Double Layers)
- ✓ Basics of electroosmostic flow

Numerical Model

- ✓ Non-equilibrium model (Nernst-Planck Eq.)
- ✓ Boundary conditions at charged walls

Numerical Simulations

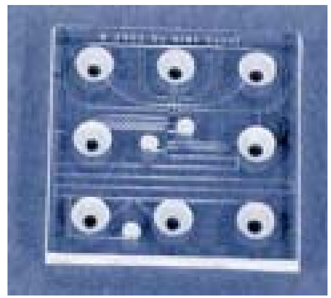
- ✓ EOF in simple channel
- ✓ Relaxation to Boltzmann equilibrium in nanopores
- ✓ EOF in a micro-nano pore

Microfluidic Devices

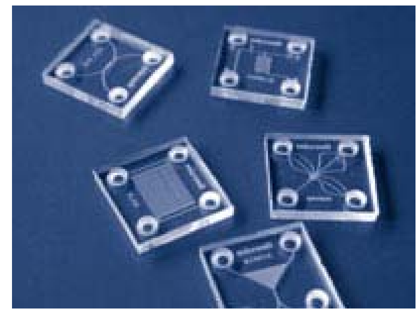
LOC(Lab-on-a-chip) / μ-TAS(Total Analysis System)

- ✓ Stone, Strook, Ajdari, *Ann. Rev. Fluid Mech*. (2004)
- ✓ Bousse et al., *Ann. Rev. Biophys. Biomol. Sci*. (2000)

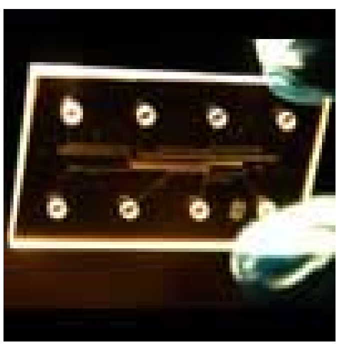
ChemLab, Sandia National Lab.



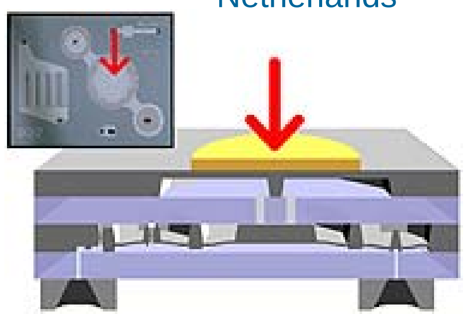
Biochip, N. Kunst
Wageningen Univ.,
Netherlands



Customized glass chips,
www.micronit.com



Microchip, NASA



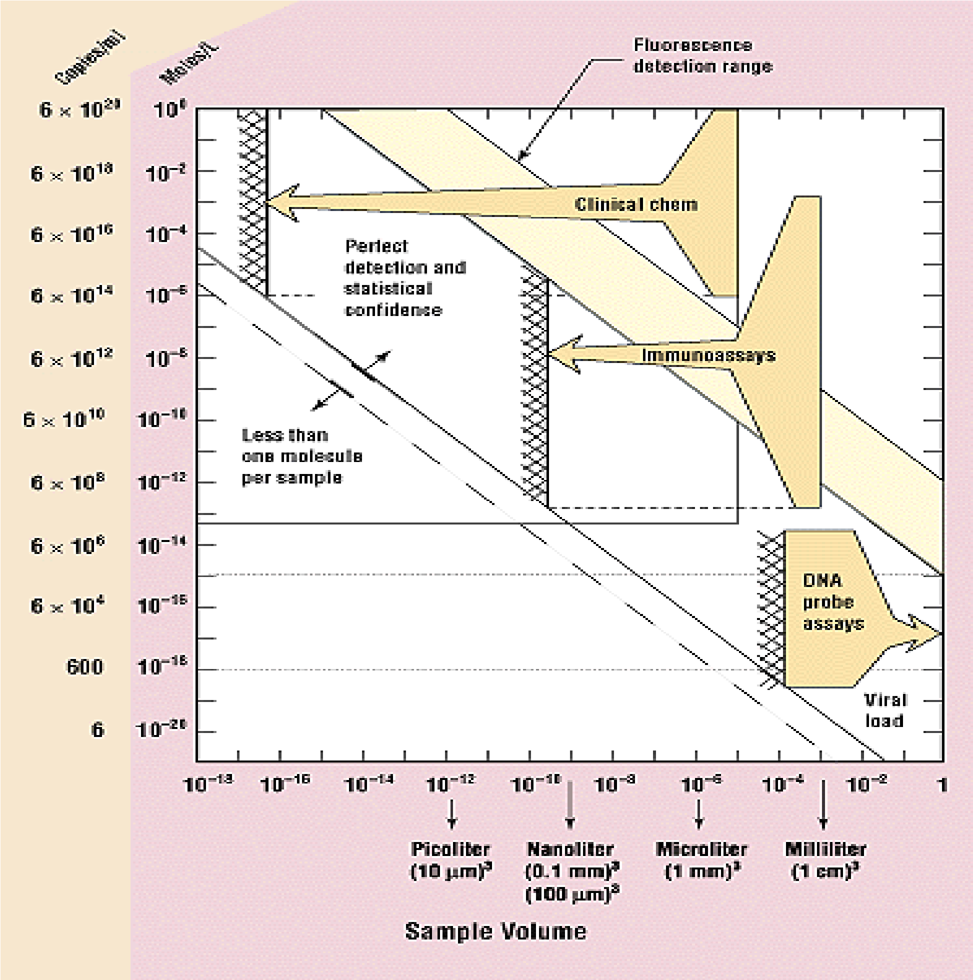
Micropump, Debiotech, Switzerland
www.debiotech.com

Nanochip®Electric Microarray,
www.nanogen.com

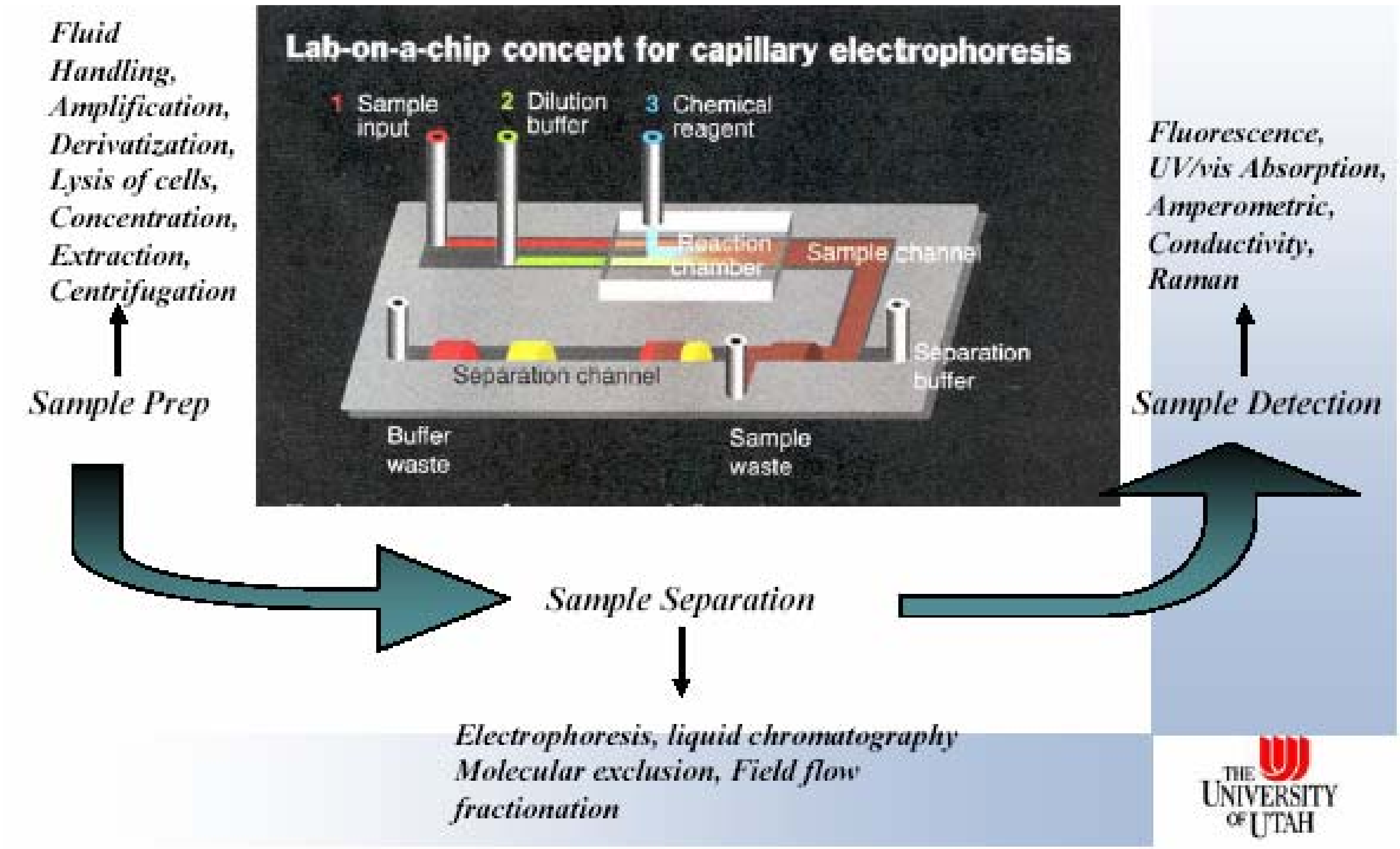
Miniaturization

Miniature Clinical Diagnostic System

- ✓ Fast, on-site, real-time testing
- ✓ High-resolution, low-mass
- ✓ Localized heating possible



Concept of Lab-on-a-Chip



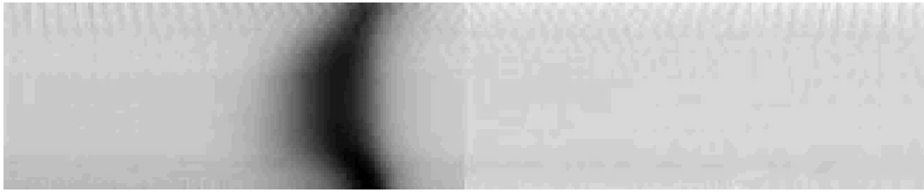
B. Gale, Univ. of Utah

How to Manipulate Micro Flows

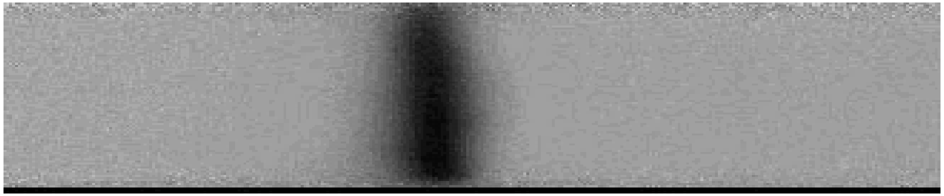
Driving Forces

- ✓ Pressure gradient
- ✓ Capillary : Surface Tension or its gradients
- ✓ Electric fields : *Electroosmosis* / Dielectrophoresis
- ✓ Magnetic fields / Centrifuge / Acoustic streaming

Pressure-driven flow

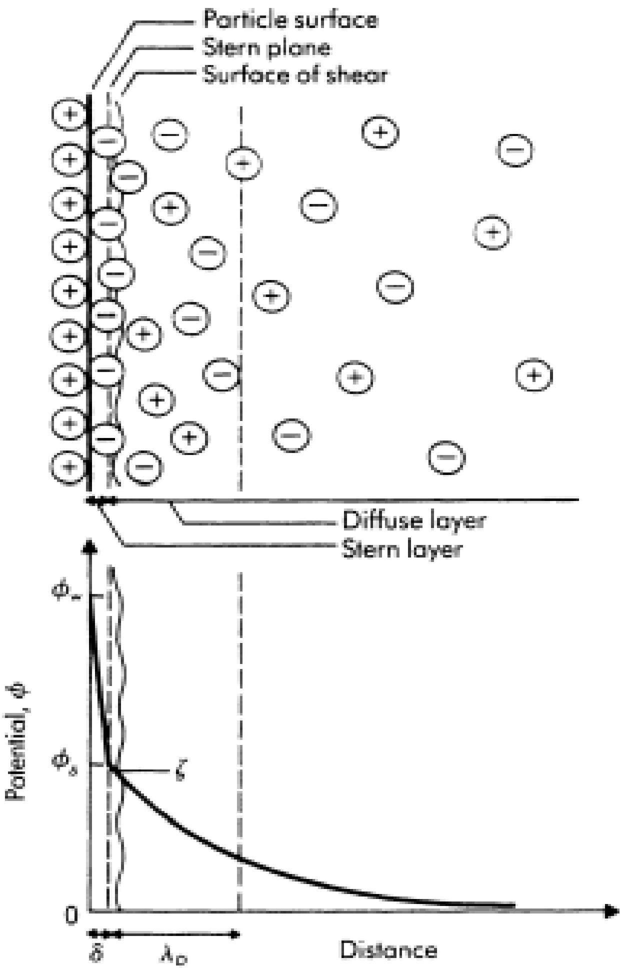


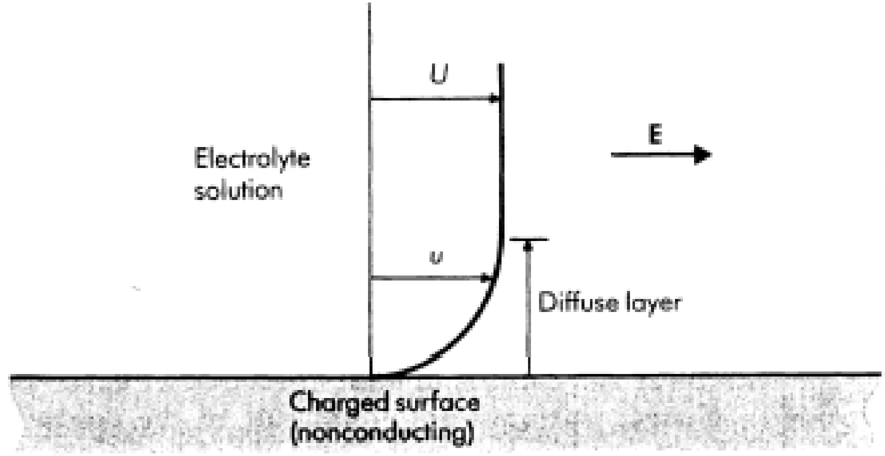
Electroosmotic flow



Source: Stanford Microfluidics Laboratory, microfluidics.stanford.edu

Electric Double Layers





Debye length $$\lambda_D = \left(\frac{\varepsilon k T}{2 n_0 e^2 z^2} \right)^{1/2}$$

Nominal EOF Velocity $$U = -\frac{\varepsilon \zeta E}{\eta}$$

λ_D ~ 10nm for n_0=1mM

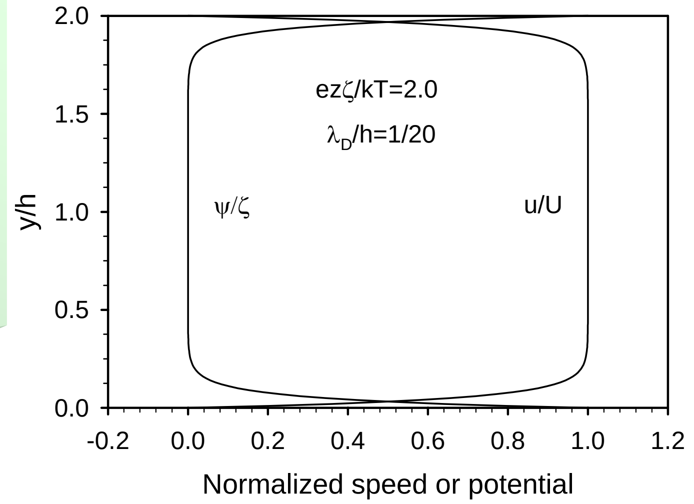
U ~ 1mm/s for E=1kV/m, ζ=50mV

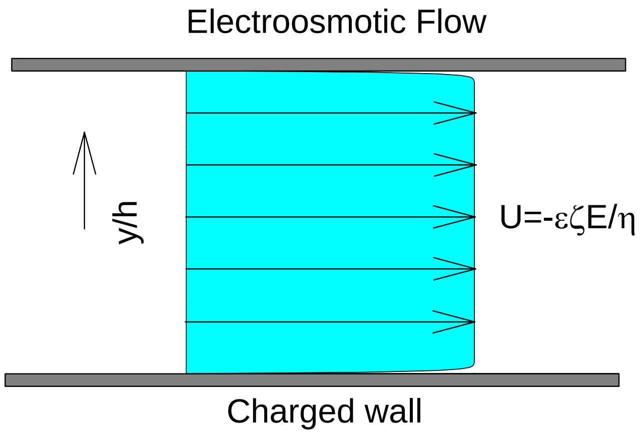
Probestein, *Physicochemical Hydrodynamics* (1993)

EOF in Microchannels

Ideal Electrokinesis

- Cummings et al., *Anal Chem*., (2000)
- $\lambda_D/h \ll 1$, and $h/L \ll 1$
- Similitude between flow & electic field outside EDL : $u = cE$





Plug-like EOF

- $h \sim 10\text{-}100\mu m \gg \lambda_D$
- Negligible EDL structure
- Slip boundary condition

EDL : Boltzmann Distribution

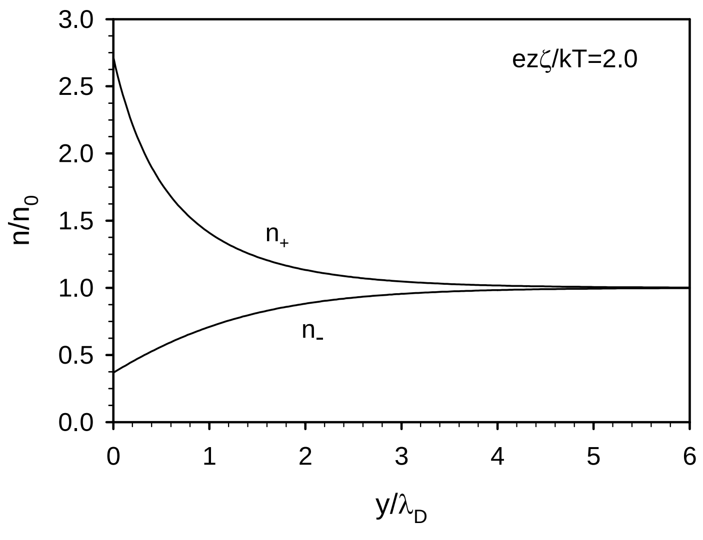
Charged plate immersed in a infinite domain of electrolyte

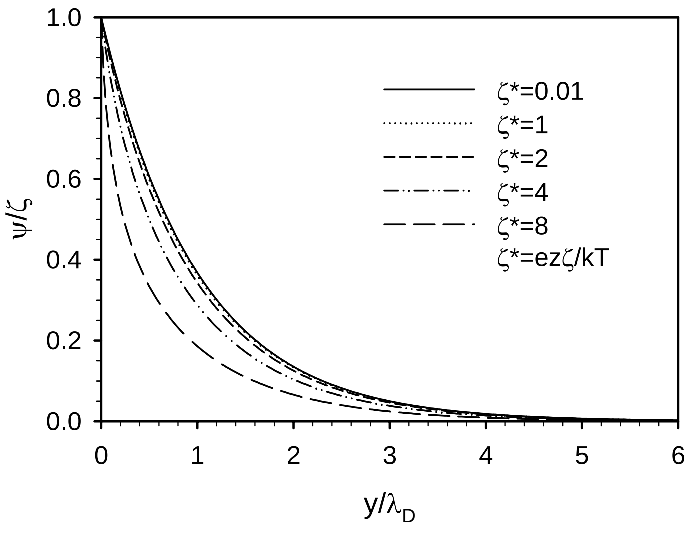
$$\frac{Dn_i}{Dt} = 0 \longrightarrow D_i \nabla n_i + \frac{ez_i n_i}{kt} \nabla \psi = 0$$

$$\nabla \cdot (\varepsilon \nabla \psi) = ez \sinh\left(\frac{ez}{kT}\psi\right)$$

$$n_i = n_{i,\infty} \exp\left(-\frac{ez_i}{kT}\psi\right)$$

$$\frac{ez}{kT}\psi = 2\ln\left[\frac{1+\tanh(\zeta^*/4)\exp(-y/\lambda_D)}{1-\tanh(\zeta^*/4)\exp(-y/\lambda_D)}\right]$$





EOF in Nanochannels

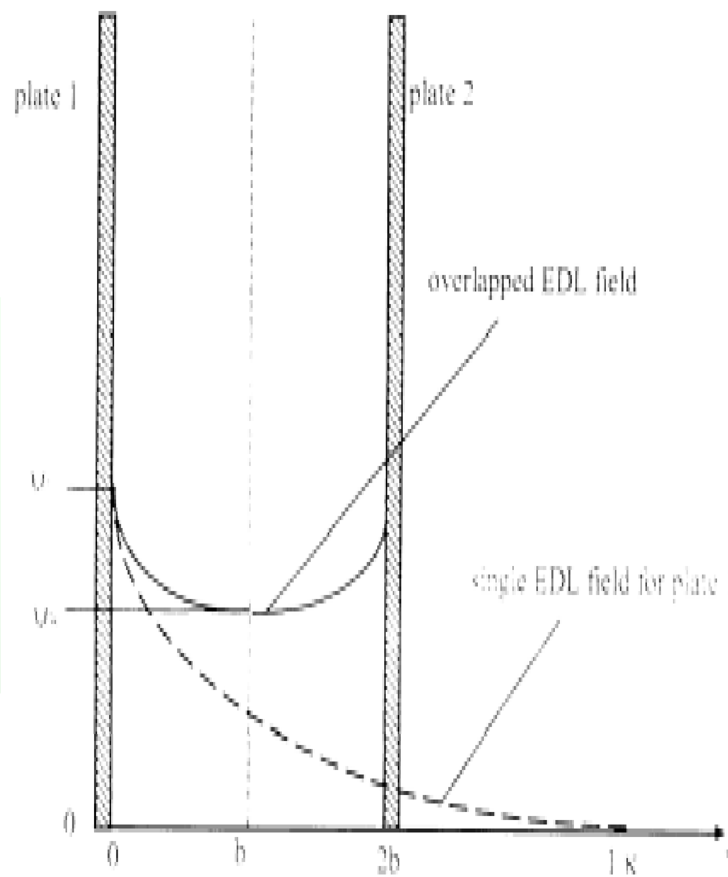
Smaller channels

- ✓ h =10nm ~ 1μm [λ_D/h → O(1)]
- ✓ Non-negligible EDL effects
- ✓ Coupled with core flow

Overlapped EDLs

- ✓ Qu & Li, J. Colloid & Int. Sci (2000)
- ✓ Conservations of mass and chemical balance in the domain
- ✓ 1D analytical solution

With reservoirs ?



Numerical Efforts

Atomistic Simulations

- ✓ MD: Freund, *J. Chem. Phys*. (2002)
- ✓ MC: Yang, Yiacoumi, Tsouris, *J. Chem. Phys*. (2002)

Continuum Simulations (Boltzmann Equilibrium)

- ✓ Patankar & Hu, *Anal. Chem*. (1998) - FVM
- ✓ Yang & Masliyah, *Int. J. Heat Mass Transfer* (1998) - FVM
- ✓ Bianch, Ferrigna & Girault, *Anal. Chem.* (2000) - FEM

Continnum Simulations (Non-Equilibrium)

- ✓ Lin & Yang, *J. Micromech. Microeng*. (2002) : Non-equilibrium equation set but equilibrium B.C

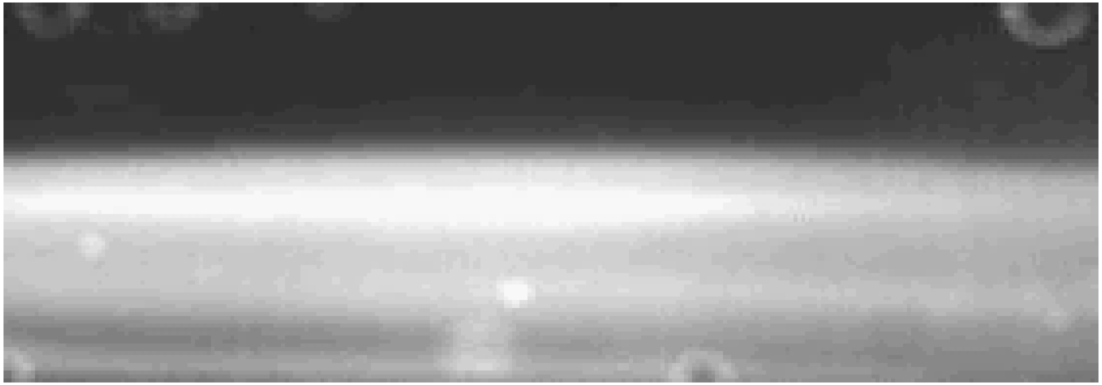
Why Non-equilibrium?

External sources

- ✓ Transient Process, Start-up and Shut-down
- ✓ Utilization of AC currents (e.g., electrophoretic separation)

Intrinsic sources

- ✓ Time-dependent buffer chemistry (e,g., variation of pH)
- ✓ Flow instabilities



Source: Stanford Microfluidics Laboratory, microfluidics.stanford.edu

Present Model

Physical Model

- ✓ Guoy-Chapman Model
- ✓ Time-dependent Nernst-Planck equations
- ✓ *Decomposition of potential*
- ✓ *Boundary conditions based on surface charge density*

Numerical Model

- ✓ Finite volume method on structured grid
- ✓ Collocated grid arrangement
- ✓ Fractional time step method
- ✓ Parallelization based on multi-block approach

Guoy-Chapman Model

Navier-Stokes Equation

$$\rho \frac{D\vec{u}}{Dt} = -\nabla p + \nabla \cdot (\eta \vec{u}) + \rho_e \vec{E}$$

$$\vec{E} = \nabla \Phi$$

Net Charged Density

$$\rho_e = \sum e z_i n_i$$

Poisson Equation

$$\nabla \cdot \left(\varepsilon \nabla \Phi \right) = -\rho_e$$

Nernst-Planck Equation

$$\frac{Dn_i}{Dt} = \nabla \cdot (D_i \nabla n_i) + \nabla \cdot \left(\frac{e z_i n_i}{kt} \nabla \Phi \right)$$

Equilibrium Model

Boltzmann Equilibrium

$$\frac{Dn_i}{Dt} = 0 \longrightarrow D_i \nabla n_i + \frac{ez_i n_i}{kt} \nabla \Phi = 0$$

$$n_i = n_{i,\infty} \exp\left(-\frac{ez_i}{kT} \Phi \right)$$

Poisson-Boltzmann Equation

$$\nabla \cdot \left(\varepsilon \nabla \Phi \right) = ez \sinh\left(\frac{ez}{kT} \Phi \right)$$

Debye-Huckel Approximation

$$\left| \frac{ez\Phi}{kT} \right| << 1 \longrightarrow \nabla \cdot \left(\varepsilon \nabla \Phi \right) = 2 \frac{e^2 z^2}{kT} \Phi$$

Decomposition of Potential (I)

$$\Phi = \phi + \psi$$

ϕ: potential due to external electric field
ψ: natural (intrinsic) potential due to EDL

$$\Delta\varepsilon / \varepsilon << 1$$

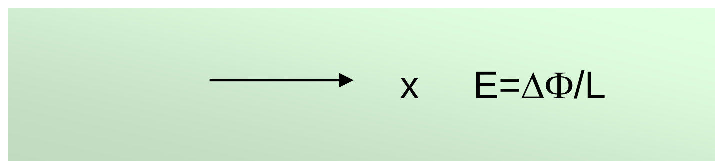
$$\nabla \cdot \left(\varepsilon \nabla \Phi\right) = -\rho_e$$

$$\nabla \cdot \left(\varepsilon \nabla \phi\right) = 0$$

$$\nabla \cdot \left(\varepsilon \nabla \psi\right) = -\rho_e$$

$\Phi = \Delta\Phi \dfrac{x}{L} + \zeta$ on charged wall

$\Phi = \Delta\Phi$ at inlet

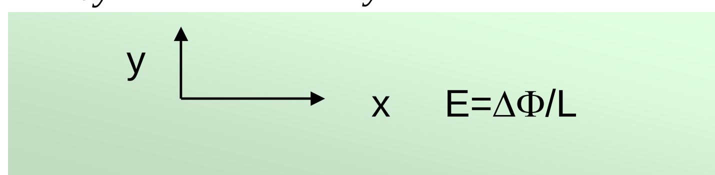


$\Phi = 0$ at outlet

Lin & Yang (J. Colloid & Int. Sci, 2002)

$\dfrac{\partial \phi}{\partial y} = 0 \quad a\psi + b\dfrac{\partial \psi}{\partial y} = c$ on charged wall

$\phi = \Delta\Phi$, $a\psi + b\dfrac{\partial \psi}{\partial y} = c$ at inlet



$\phi = 0$, $a\psi + b\dfrac{\partial \psi}{\partial y} = c$ at outlet

Kwak & Hasselbrink (2004)

Decomposition of Potential (II)

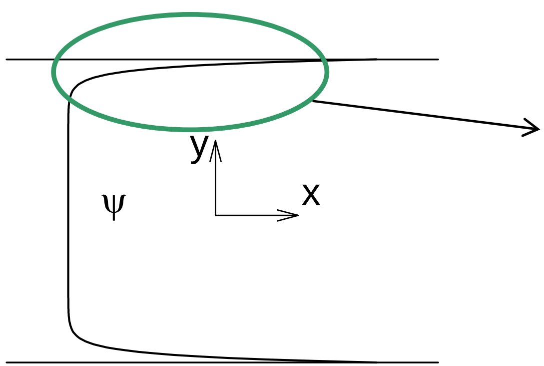
Treatment of electric body force

$$\rho_e \vec{E} = -\varepsilon \nabla^2 \psi (\nabla \phi + \nabla \psi)$$

$$\vec{E} = \nabla \phi + \nabla \psi \qquad \vec{E}_{EOF} = \nabla \phi \qquad \vec{E}_{ST} = \nabla \psi$$

$$p = p' + p_{ST}$$

$$\rho_e \vec{E} = \rho_e \vec{E}_{EOF} \qquad \nabla p_{ST} = \rho_e \vec{E}_{ST}$$



$$\frac{\partial p_{ST}}{\partial y} = \rho_e \frac{\partial \psi}{\partial y}$$

No impact on EOF !!!

B.C. for Charged Wall

Traditional ζ-based Boundary Conditions

$$\psi = \zeta$$

$$n_i = n_{i,\infty} \exp\left(\frac{ez_i}{kT} \psi \right)$$

Physical meaning of ζ ?
Steady B.C. for n_i ?

σ-based Boundary Conditions

$$\varepsilon \frac{\partial \psi}{\partial n} = -\sigma$$

$$\frac{\partial n_i}{\partial b} = \frac{\sigma}{\varepsilon} \frac{ez_i}{kT} n_i$$

Physical meaningful σ
Unsteady B.C for n_i
No net flux of n_i on wall

Numerical Model

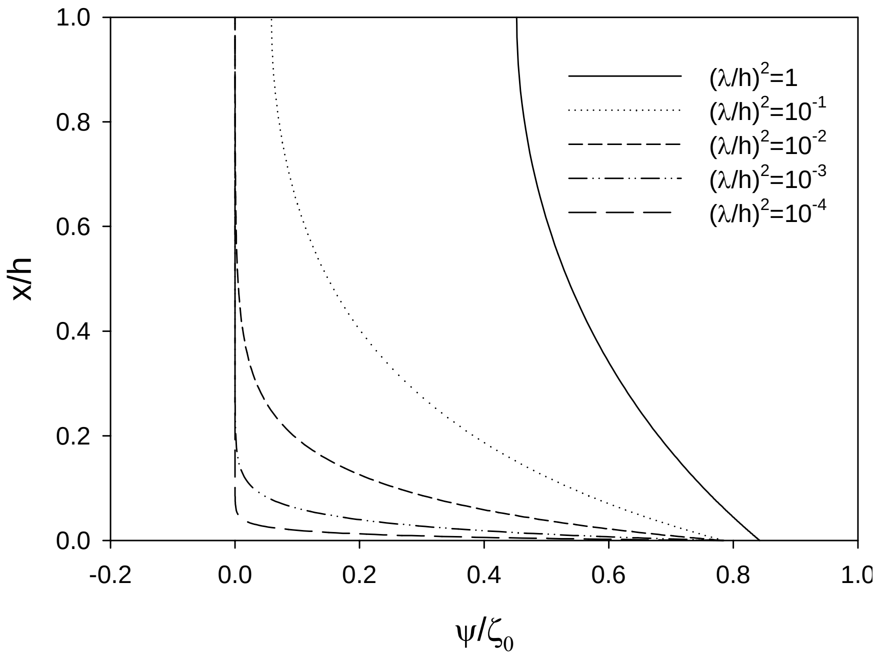
Finite Volume Model

- ✓ Collocated structured grid
- ✓ Fractional time step method
- ✓ Crank-Nicholson scheme for diffusion terms
- ✓ Implicit treatment of boundary conditions
- ✓ Pressure-driven boundary conditions applicable
- ✓ Velocity B.C. may not be specified

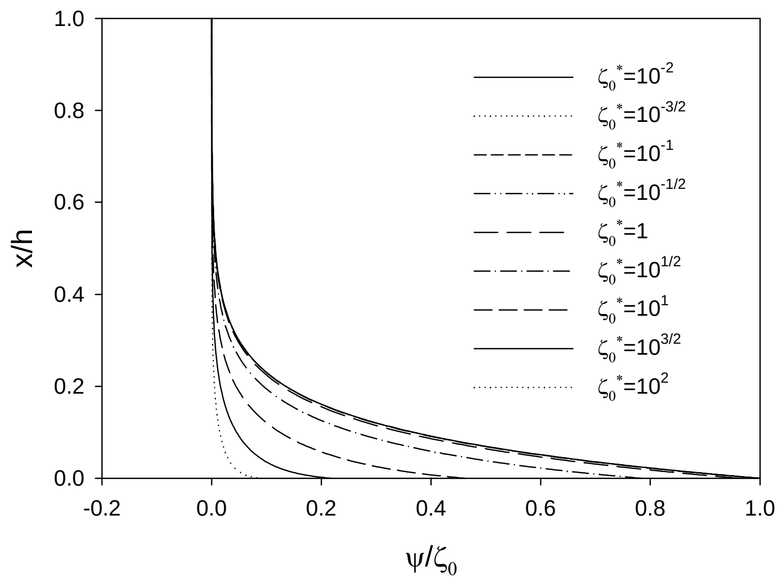
Parallelization

- ✓ Multi-block approach
- ✓ Domain decomposition
- ✓ MPI

EOF in Micro- & Nanochannels



$\lambda/h=1/10$



$\zeta_0=\sigma\lambda/\varepsilon$

$\zeta_0*=-3.16$

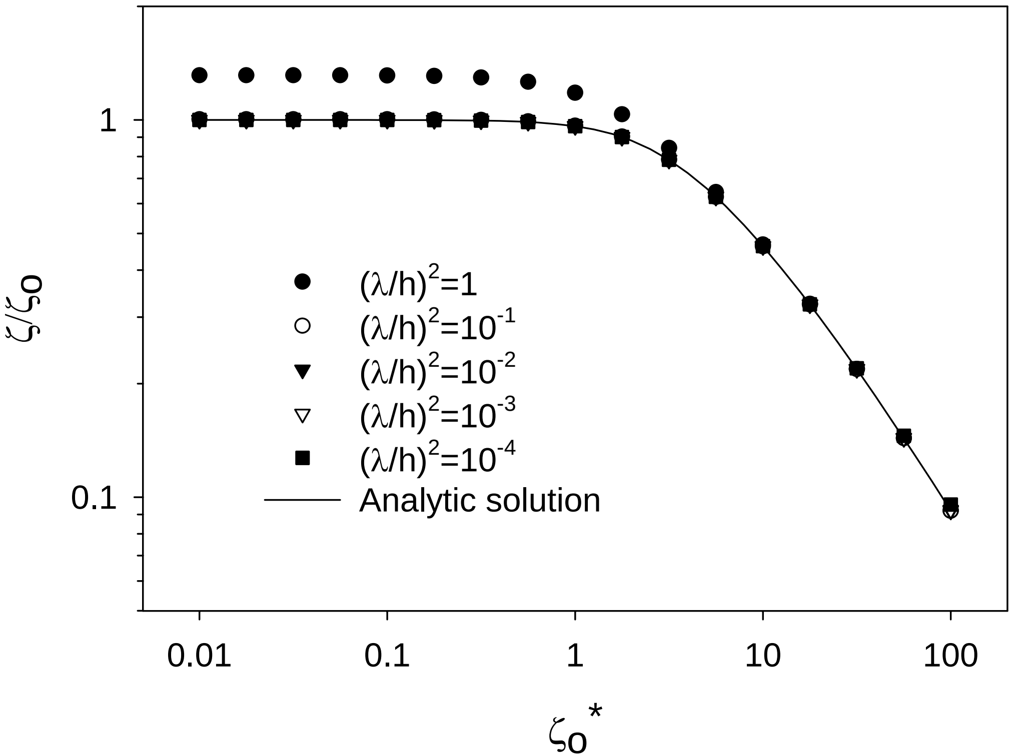
Relationship between ζ and σ

Can surface charge density be represented by the convectionally-used zeta potential ?

$\zeta_0 = \sigma\lambda/\varepsilon$:

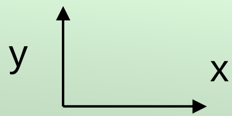
Reduced zeta potential

$\zeta_0{}^* = ez\zeta/kT$



Reservoir Effects ?

Mass conservation and chemical balance on charged wall



$E = \Delta\Phi / L$

$$\frac{\partial F}{\partial x} = 0$$

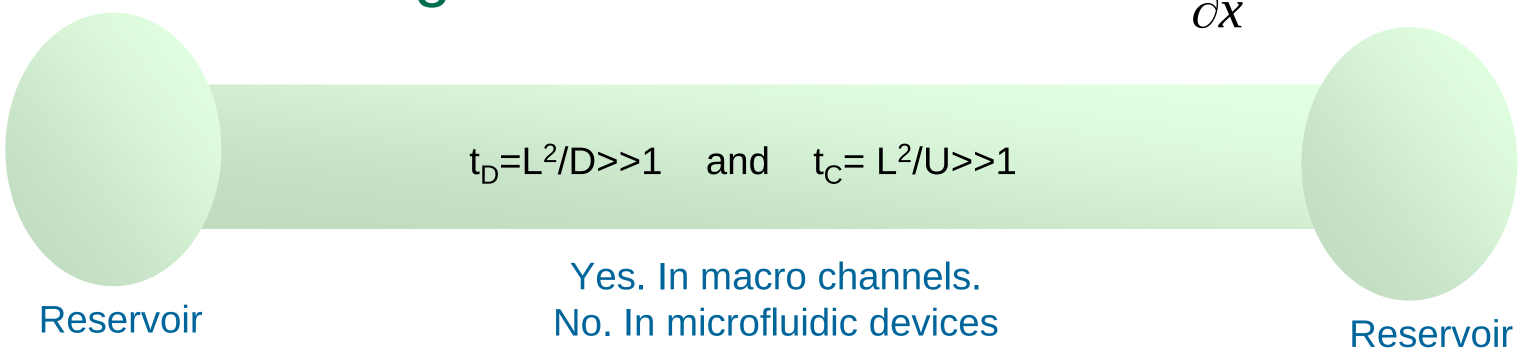
Overlapped EDLS in an infinite channel
Qu & Li (J. Colloid & Int. Sci, 2000)

$$\Phi = 0$$

at outlet

h/L<<1 guarantees infinite ?

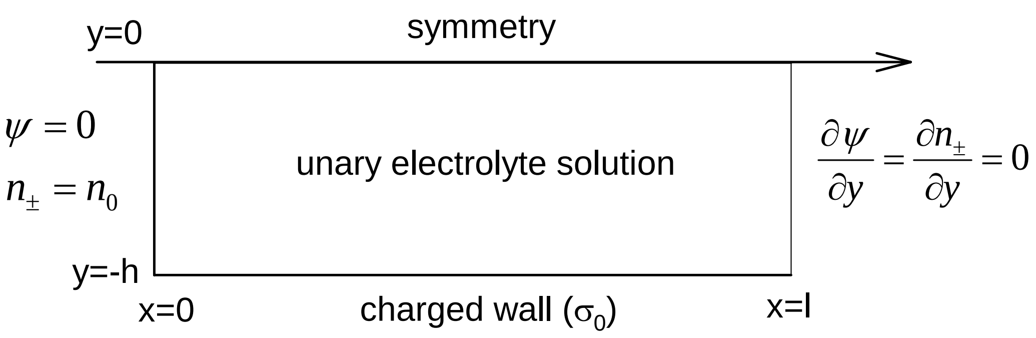
$$\frac{\partial F}{\partial x} = 0 \quad ?$$



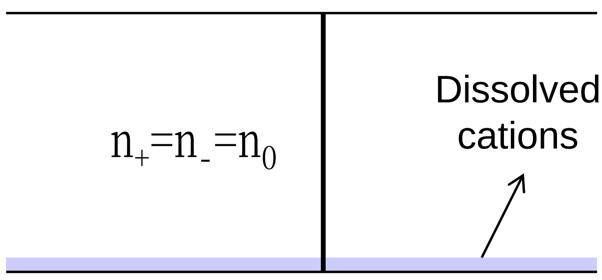
Yes. In macro channels.
No. In microfluidic devices

Problem Setup

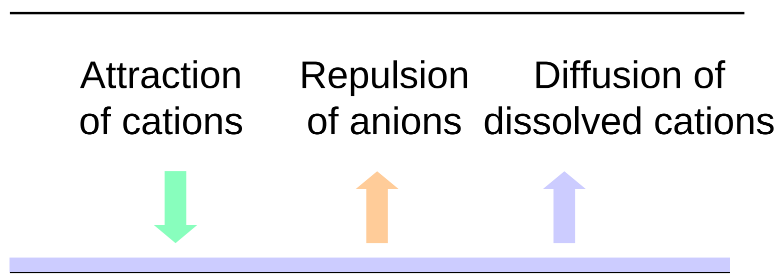
Evolution of Overlapped EDLs



$$\lambda/h=1/3,\ \zeta_0^*=ez\zeta/kT=-2.35\ \ (\zeta^*=-2, \zeta=50\text{mV})$$



Initial condition



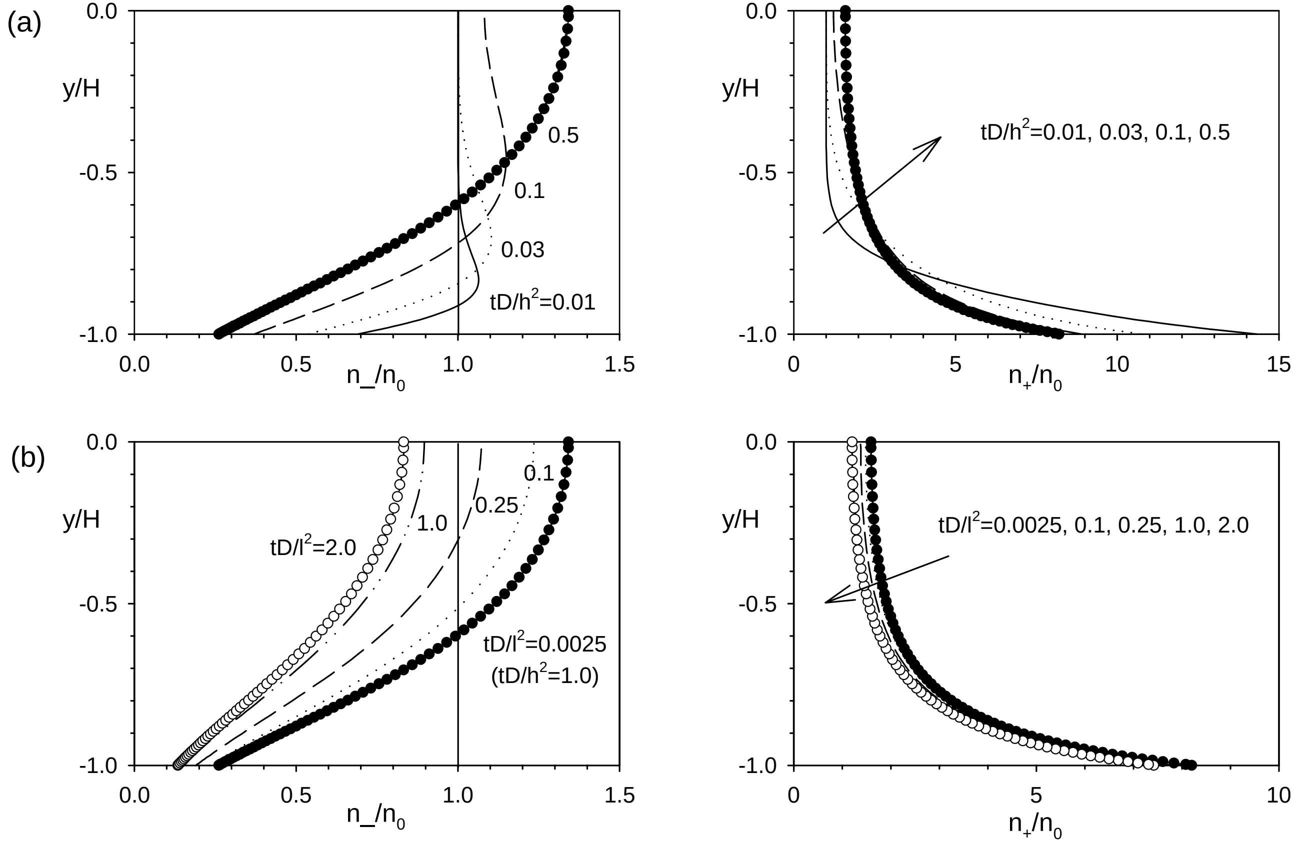
EDL evolution

Transient Evolution of EDL

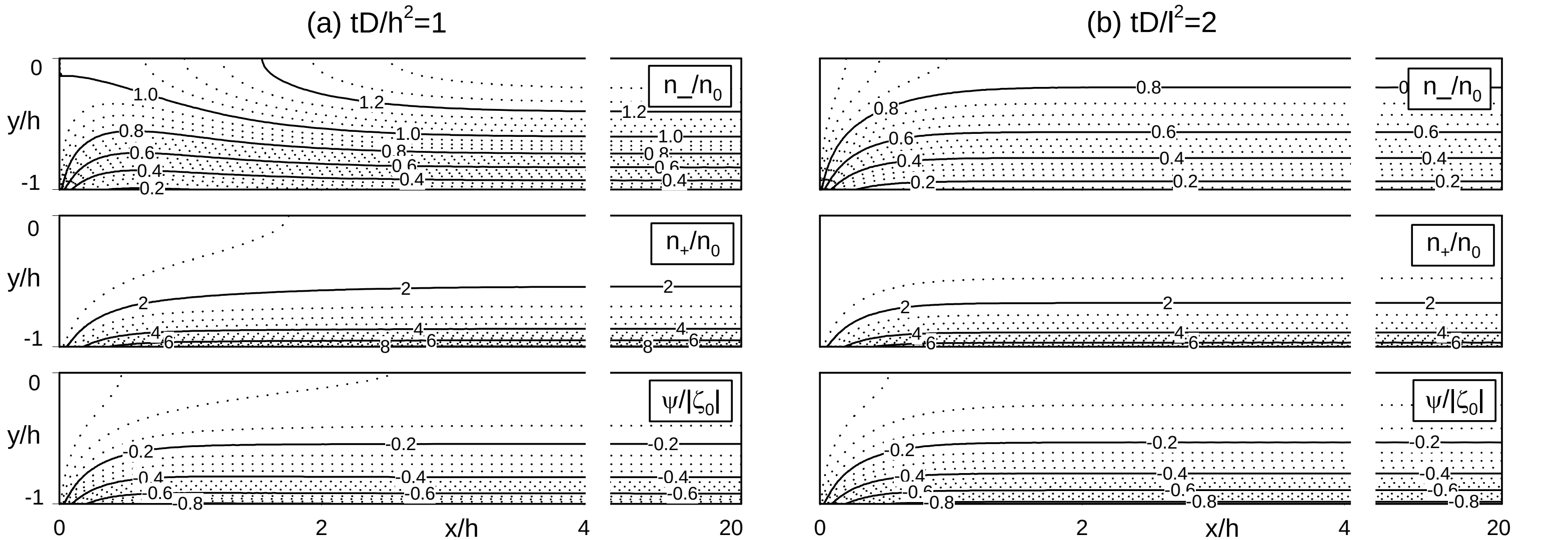
Diffusion Only

Early-time Response

Long-term transient evolution



Why Second Transient ?



after first transient process

Steady state solution

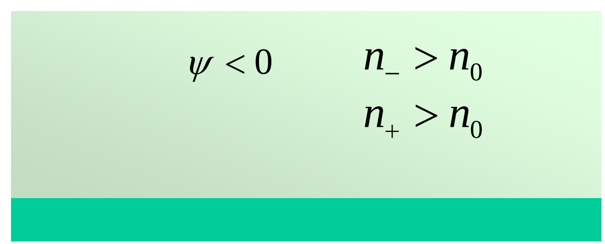
If equilibrium

$$\frac{\partial n_+}{\partial x} = -n_+ \frac{ez}{kT}\frac{\partial \psi}{\partial x}$$

$$\frac{\partial n_-}{\partial x} = +n_- \frac{ez}{kT}\frac{\partial \psi}{\partial x}$$

$$\psi = 0$$

$$n_+ = n_- = n_0$$



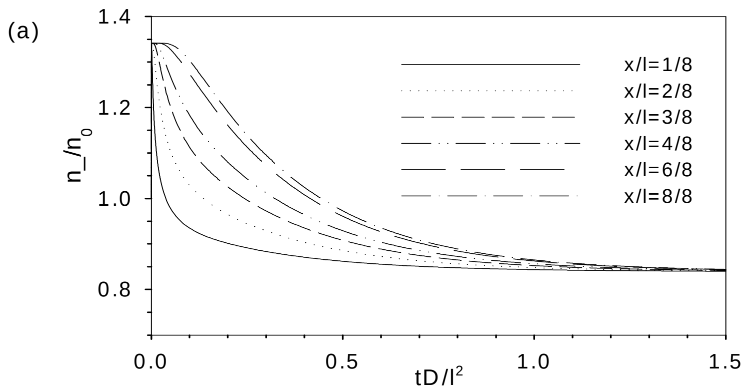
after first transient process

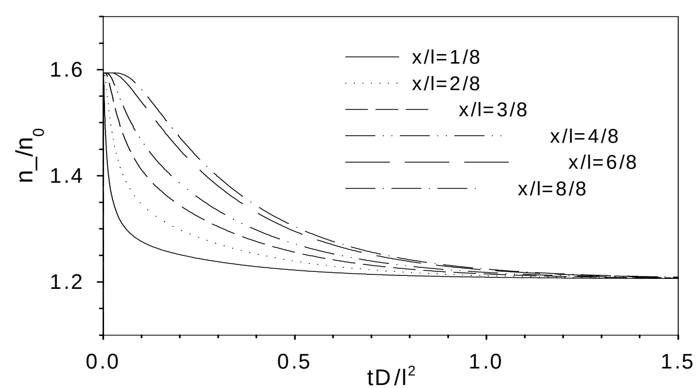
Relaxation to Boltzmann Equilibrium

Convection vs. Diffusion

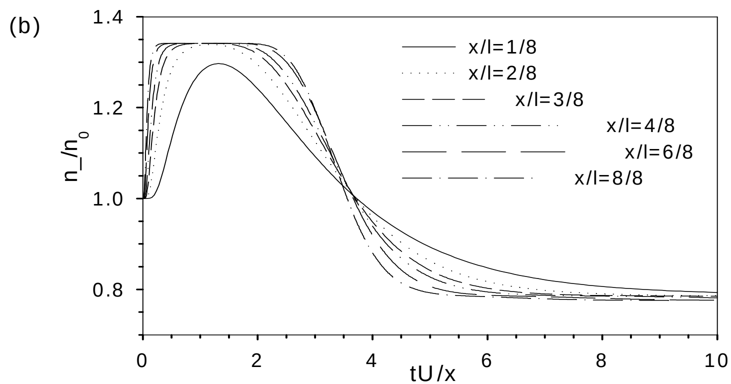
Peclet No.
Pe=Ul/D

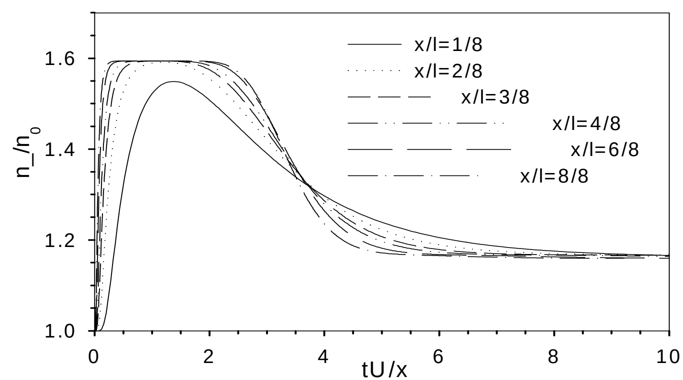
Pe=0.1



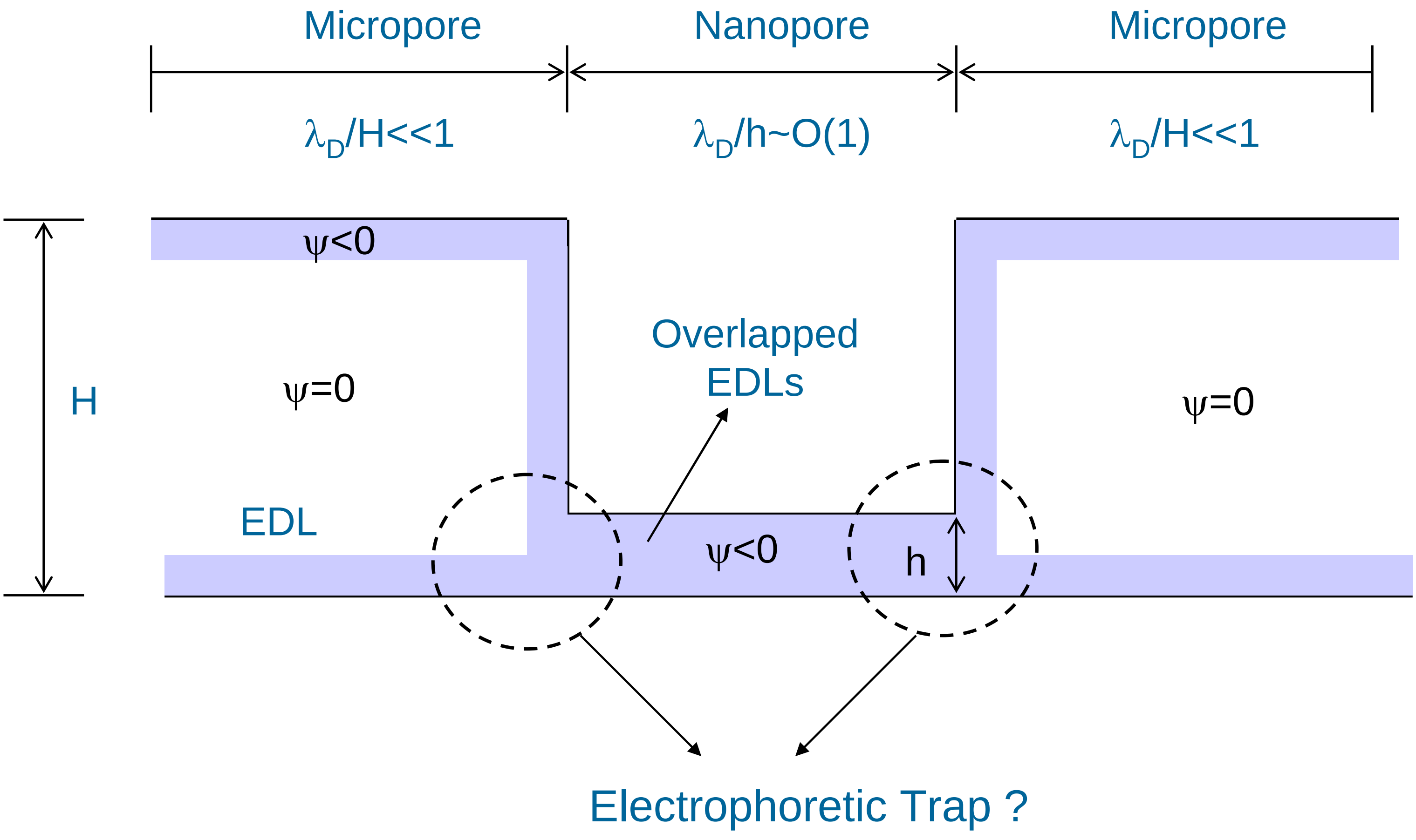


Pe=10

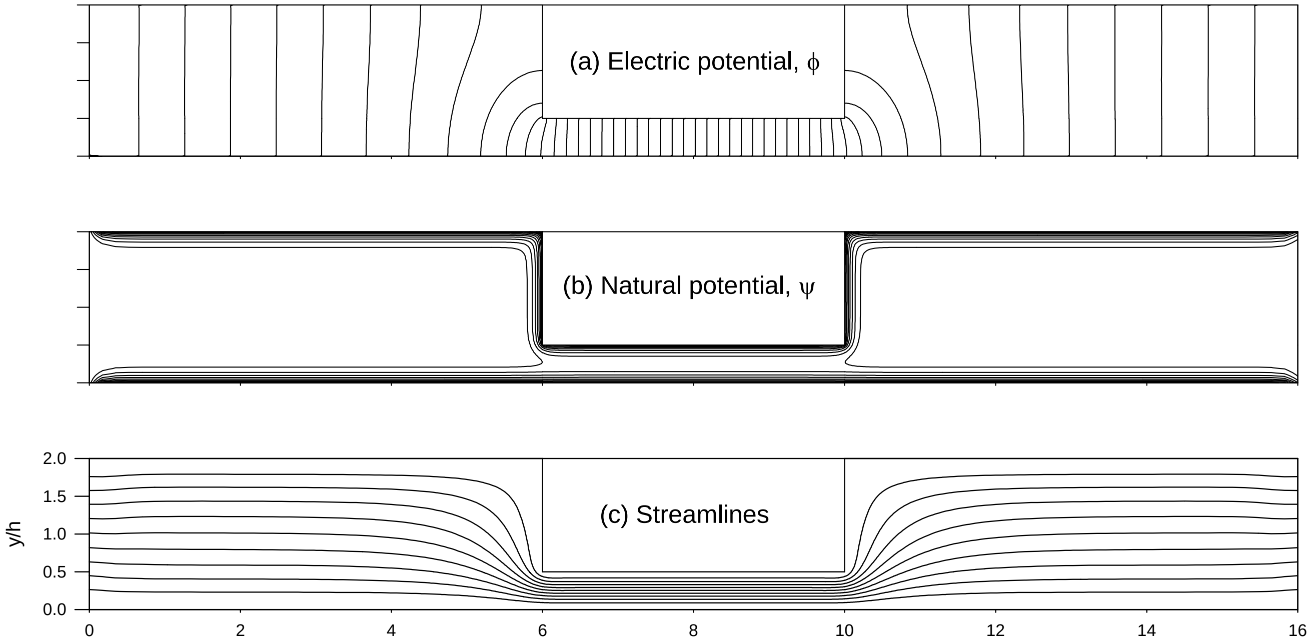




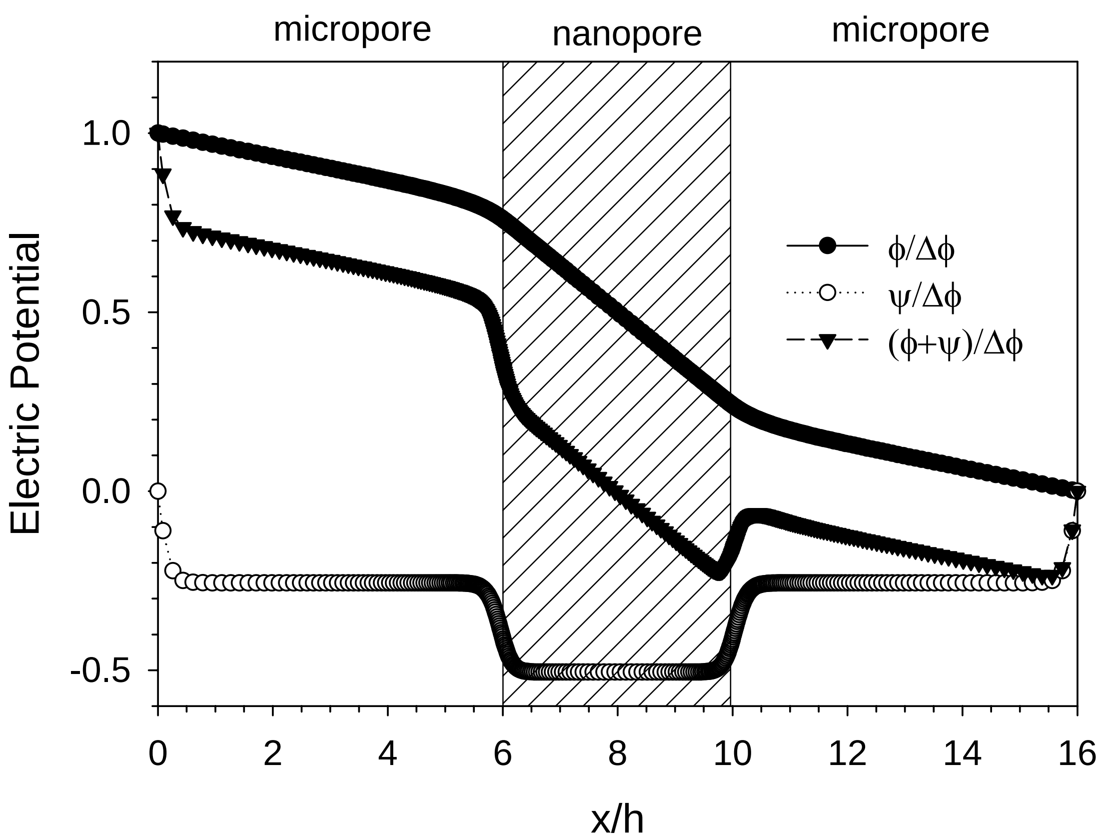
EOF in a Micro-Nano Pore



EOF in a Micro-Nano Pore



Electrophoretic Trap



Conclusion

A Numerical Model Developed

- ✓ For Non-equilibrium electroosmotic flow
- ✓ Nernst-Planck equation employed
- ✓ Boundary condition based on surface charge density
- ✓ Several problems tested

Future Work

- ✓ Include detailed buffer chemistry
- ✓ Add Electrophoretic particle tracking
- ✓ Study Electrokinesis responding to AC
- ✓ Consider control of EOF by using thermal modulation

Acknowledgements

Ernest F. Hasselbrink, Jr., (Univ. of Michigan, Ann Arbor) for leading me to the Microfluidics field and supporting my sabbatical

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Two buddies (HG IM, JW LEE) and their families living in Ann Arbor for their XXX