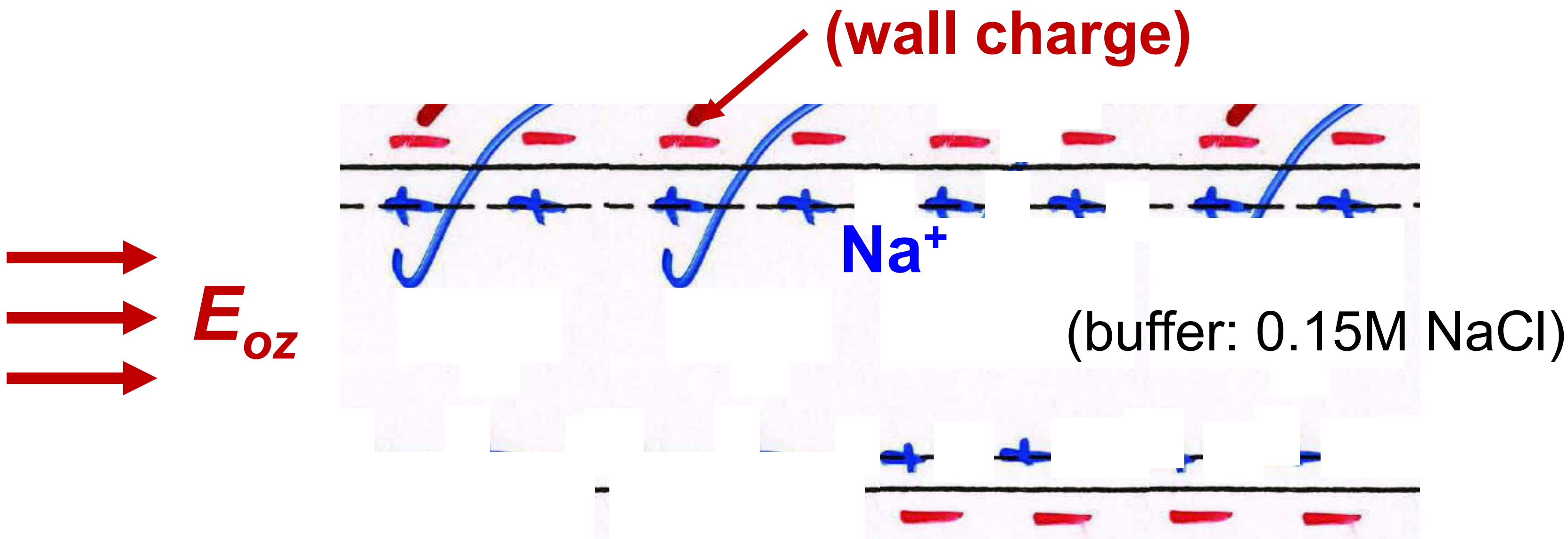
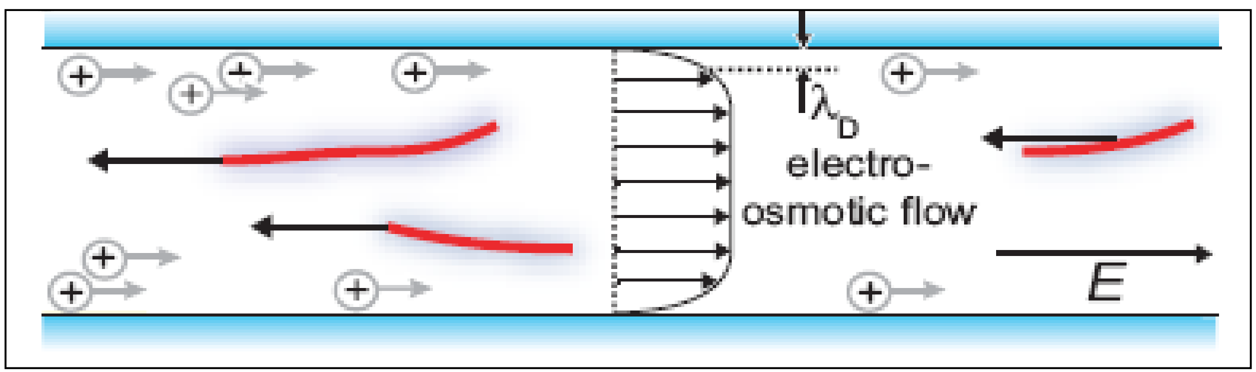
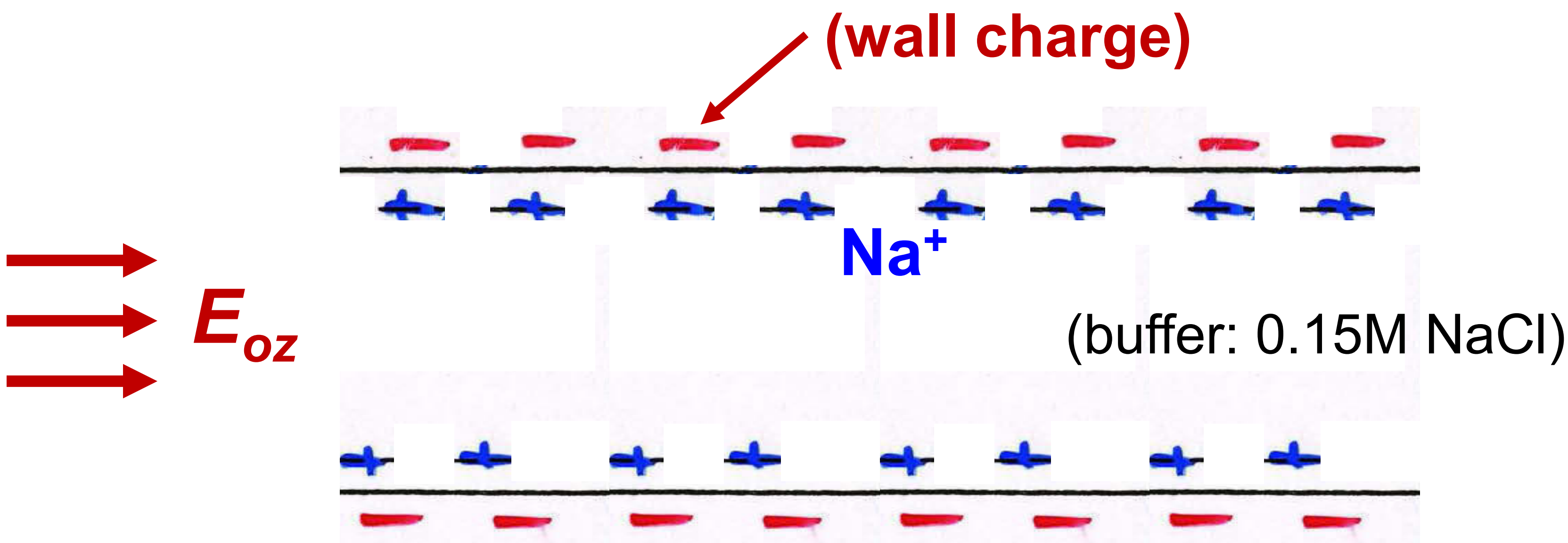
Electroosmosis





Courtesy of National Academy of Sciences. Used with permission.
Source: Van den Heuvel, M. G. L. et al. "Electrophoresis of individual microtubules in microchannels."
Proceedings of the National Academy of Sciences 104, no. 19 (2007): 7770-7775.

Electroosmosis

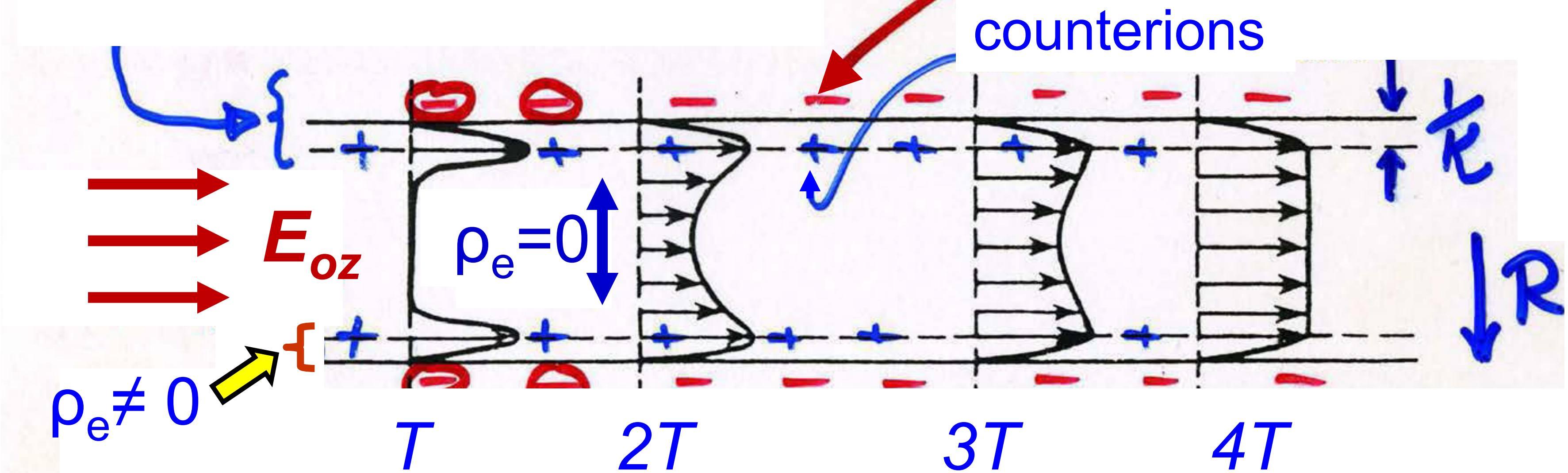


Where is the $\rho_e \underline{E}$ force on the fluid??

Electroosmosis

Electrical Double Layer

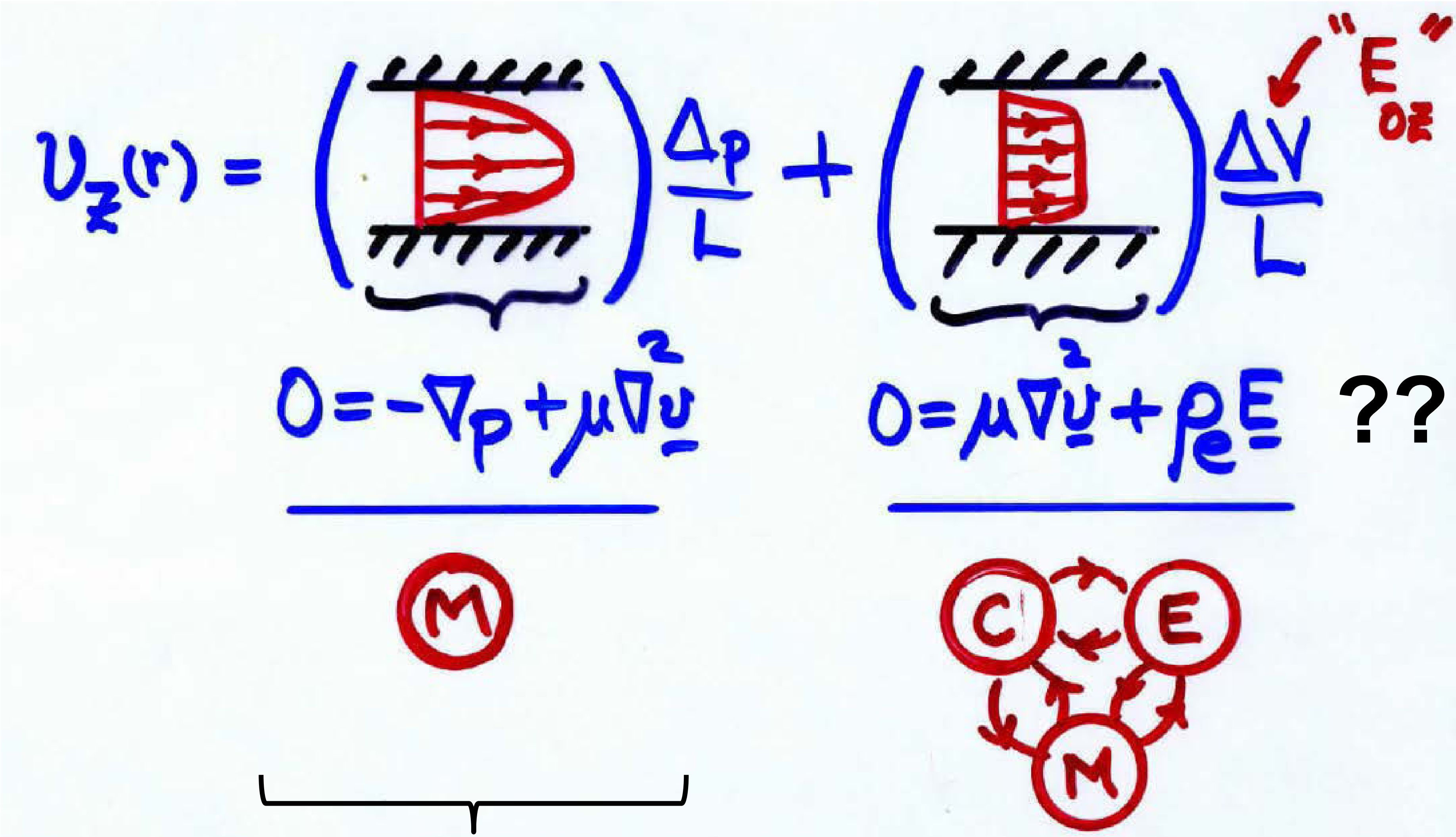
Glass, plastic, proteins: <u>surface charge on wall</u>



$$\boxed{-\nabla p + \mu \nabla^2 v + \rho_e \boldsymbol{E} = 0}$$

$$\boxed{\tau_{vd} \sim \frac{R^2}{(\mu/\rho)}}$$

Superposition



Stokes → (Poiseuille) + (Electroosmosis)

LAWS

C

$$(1)\quad \underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E}^{TOT} + c_i \underline{v}$$

$$(2)\quad (\partial c_i/\partial t) = \left[-\nabla\cdot \underline{N}_i + R_i\right]$$

E

$$(3)\quad \nabla\cdot \epsilon \underline{E}^{TOT} = \rho_e = \sum z_i F c_i$$

$$(4)\quad \underline{E}^{TOT} = -\nabla \Phi^{TOT}$$

$$(5)\quad \nabla\cdot \underline{J} = -(\partial \rho_e/\partial t)$$

$$(6)\quad \underline{J} = \sigma \underline{E}^{TOT}$$

M

$$(7)\quad \rho \frac{D\underline{v}}{Dt} = \Big(-\nabla p + \mu \nabla^2 \underline{v} + \underbrace{\rho_e \underline{E}^{TOT}}_{\nabla\cdot \epsilon \underline{E}}\Big) \simeq 0$$

$$(8)\quad \nabla\cdot \underline{v} = 0$$

Written on the Board at end of last class…..

LAWS

C

$$(1)\ \underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E}^{TOT} + c_i \underline{v}$$

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True for Chap 2 E-subsystem (alone) problems

M

$$(7)\ \rho \frac{D\underline{v}}{Dt} = \Big(-\nabla p + \mu \nabla^2 \underline{v} + \underbrace{\rho_e \underline{E}^{TOT}}_{\nabla\cdot \epsilon \underline{E}}\Big) \simeq 0$$

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LAWS

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(3) $\nabla \cdot \epsilon \underline{E}^{TOT} = \rho_e = \sum z_i F c_i$

(4) $\underline{E}^{TOT} = -\nabla \Phi^{TOT}$

(5) $\nabla \cdot \underline{J} = -(\partial \rho_e / \partial t)$

(6) $\underline{J} = \left(\sigma \underline{E}^{TOT} + \rho_e \underline{v} + (\ ) \nabla c_i\right) = \sum z_i F N_i$

M

(7) $\rho \frac{D\underline{v}}{Dt} = \left(-\nabla p + \mu \nabla^2 \underline{v} + \underbrace{\rho_e \underline{E}^{TOT}}_{\nabla \cdot \epsilon \underline{E}}\right) \simeq 0$

(8) $\nabla \cdot \underline{v} = 0$

Didn't need to find J for the Midterm

…but now fully coupled and we need these terms

LAWS

C

(1) $\underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E}^{TOT} + c_i \cancel{\underline{v}}^{\,0}$

(2) $(\partial c_i/\partial t) = \left[-\nabla\cdot\underline{N}_i + R_i\right] = 0$

(3) $\nabla\cdot\epsilon\underline{E}^{TOT} = \rho_e = \sum z_i F c_i$

(4) $\underline{E}^{TOT} = -\nabla\Phi^{TOT}$

E

(5) $\nabla\cdot\underline{J} = -(\partial\rho_e/\partial t)$

(6) $\underline{J} = \left[\sigma\underline{E}^{TOT} + \cancel{\rho_e\underline{v}}^{\,0} + (\ )\nabla c_i\right] = 0$

M

(7) $\rho\frac{D\underline{v}}{Dt} = \left(-\nabla p + \cancel{\mu\nabla^2\underline{v}}^{\,0} + \underbrace{\rho_e\underline{E}^{TOT}}_{\nabla\cdot\epsilon\underline{E}}\right) \simeq 0$

(8) $\nabla\cdot\underline{v} = 0$

Initial equilibrium (t < 0): (no E_{oz})

$N_i = 0 \rightarrow$

Poisson-Boltzmann

$$c_i(x) = c_{i0}\exp\left[-\frac{z_i F\Phi(\mathbf{r})}{RT}\right]$$

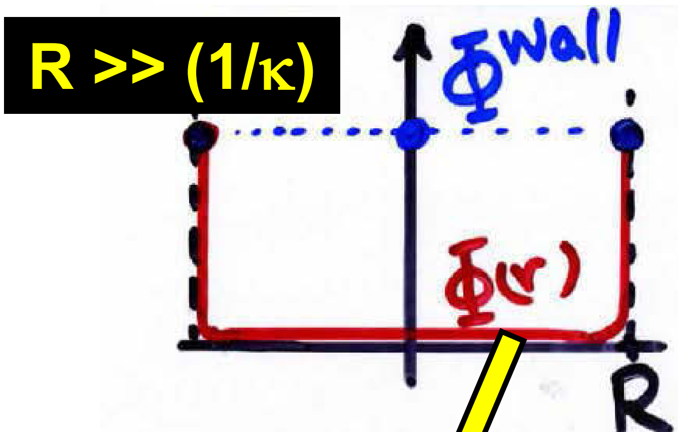
****No net J in double layer!**

Midterm:

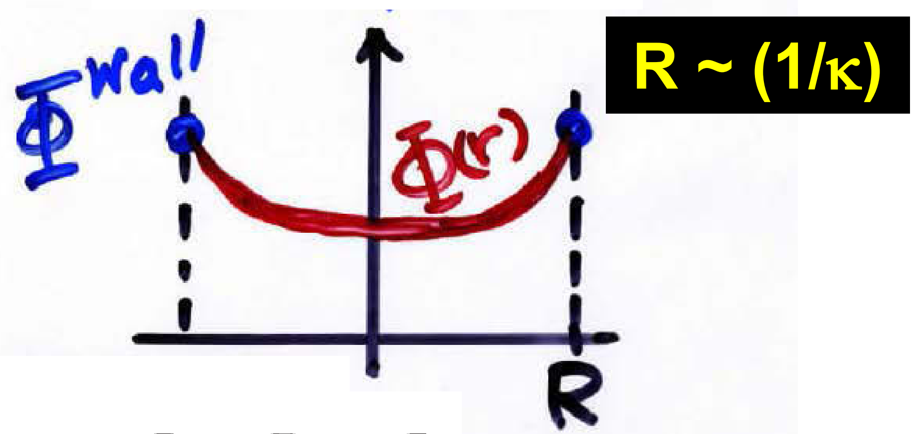
Find $\Phi^{in}(r)$ & $c_i^{in}(r)$ for $t<0$

(initial Equil; $E_{0z} = 0 = v_z$)

Microchannel



Nano-pore



$$c_i(x) = c_{i0} \exp\left[-\frac{z_i F \Phi(x)}{RT}\right]$$

from Poisson-Boltzmann

$$\boxed{\frac{d^2\Phi(x)}{dx^2} = -\frac{1}{\epsilon}\sum_i z_i F c_{i0} \exp\left[\frac{-z_i F \Phi(x)}{RT}\right]}$$

LAWS

C

(1) $\underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E}^{TOT} + c_i \underline{v}$

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M

(7) $\rho \frac{D\underline{v}}{Dt} = \left(-\nabla p + \overset{0}{\cancel{\mu \nabla^2 \underline{v}}} + \underbrace{\rho_e \underline{E}^{TOT}}_{\nabla \cdot \epsilon \underline{E}}\right)\Big|_r \simeq 0$

(8) $\nabla \cdot \underline{v} = 0$

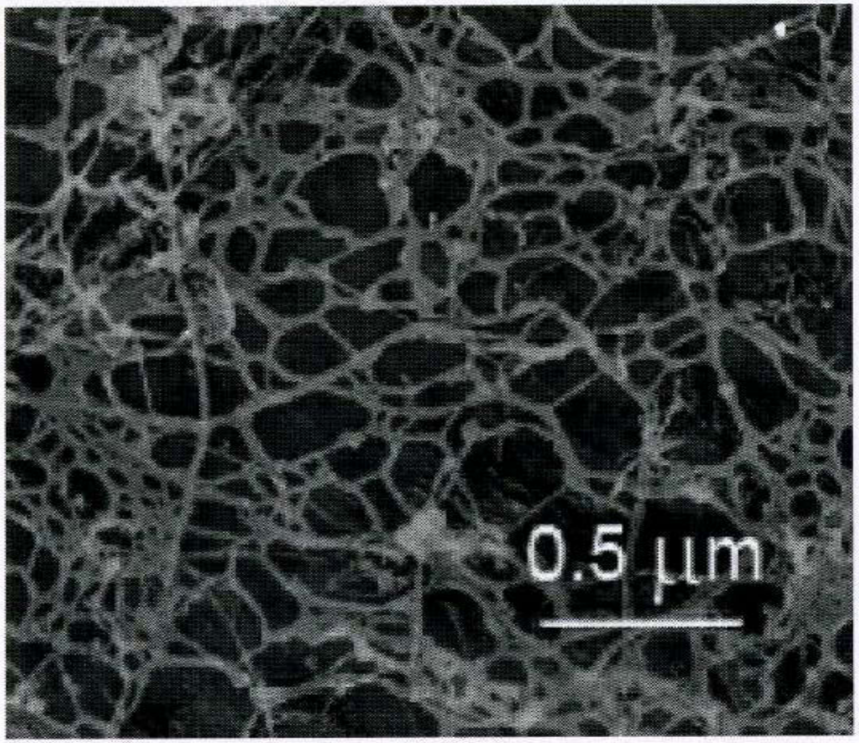
r-component of Stokes Eqn.

Initial equilibrium (t < 0): (no E_{oz})

Tissue, tumor, can SWELL due to electrostatic repulsive ("osmotic") interactions in ECM

+ $\rho_e \underline{E}$ → "Donnan Osmotic Swelling Pressure"

Tissues, Gels, Intra- and Extra-cellular space



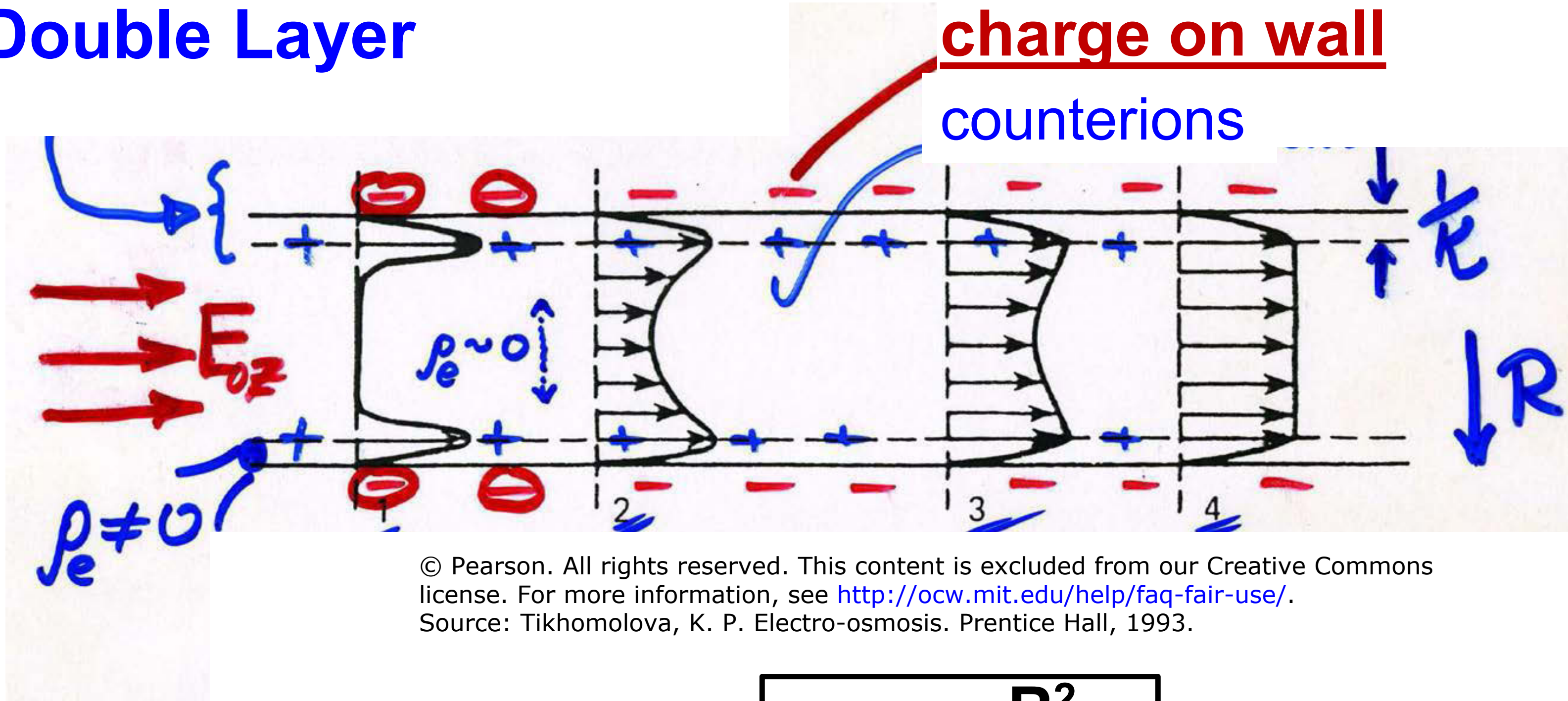
Local "nano" swelling pressure

Electroosmosis

Electrical Double Layer

Glass, plastic (PDMS), proteins: <u>surface charge on wall</u>

counterions



Source: Tikhomolova, K. P. Electro-osmosis. Prentice Hall, 1993.

$$\boxed{\tau_{vd} \sim \frac{R^2}{(\mu/\rho)}}$$

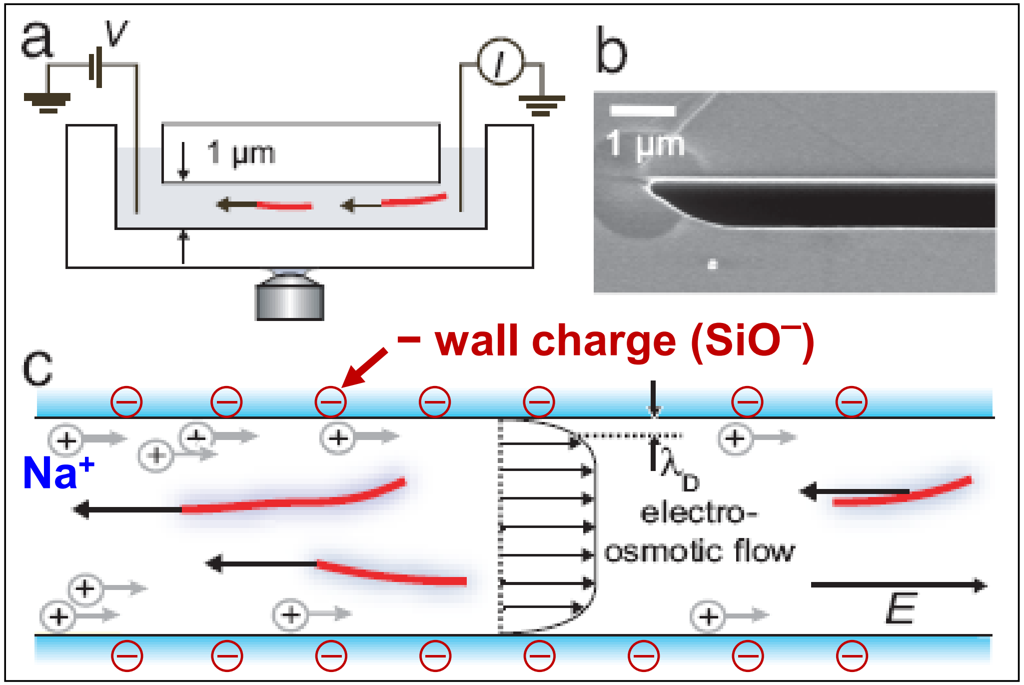
$$\boxed{-\nabla p + \mu \nabla^2 v + \rho_e \mathbf{E} = 0}$$

Electrophoresis of individual microtubules in microchannels

PNAS 2007

M. G. L. van den Heuvel, M. P. de Graaff, S. G. Lemay, and C. Dekker*

Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ, Delft, The Netherlands



Source: Van den Heuvel, M. G. L. et al. "Electrophoresis of individual microtubules in microchannels." Proceedings of the National Academy of Sciences 104, no. 19 (2007): 7770-7775.

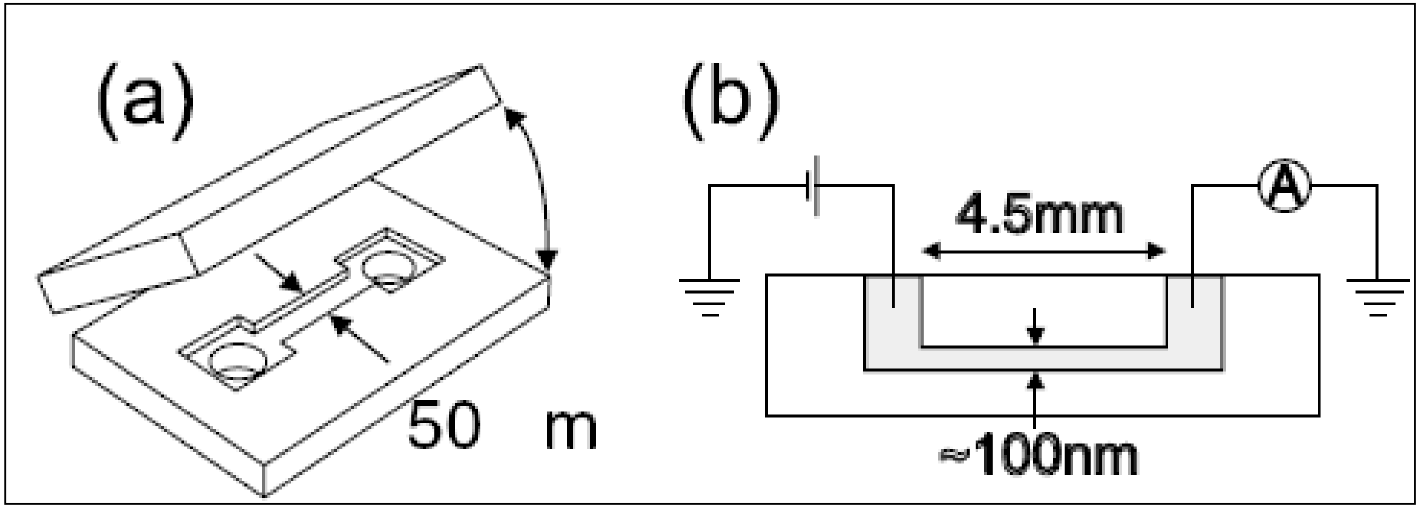
The electrophoretic mobility of molecules is a fundamental property.... In ensemble measurements, such as gel electrophoresis or dynamic light scattering, the differences between individual molecules are obscured. Here, **individual microtubules** are visible by fluorescent labeling, and their electrophoretic motion can be imaged using fluorescence microscopy

Microfabricated slit-like fluidic channels form an excellent system to confine and observe the electrophoretic motion of individual fluorescently labeled biomolecules, such as microtubules, actin filaments, or virus particles.

VOLUME 93, NUMBER 3 PHYSICAL REVIEW LETTERS 2004 week ending 16 JULY 2004

Surface-Charge-Governed Ion Transport in Nanofluidic Channels

Derek Stein, Maarten Kruithof, and Cees Dekker



Source: Stein, Derek et al. "Surface-charge-governed ion transport in nanofluidic channels." Physical Review Letters 93, no. 3 (2004): 035901.

Nanofluidic channels [Fig. 1(a)] were fabricated following a silicate bonding procedure similar to that of Wang *et al.* [12]. Briefly, channels 50 μm wide and 4.5 mm long were patterned between 1.5 mm × 1.5 mm reservoirs using electron beam lithography on fused silica substrate.

VOLUME 93, NUMBER 3 PHYSICAL REVIEW LETTERS 2004 week ending 16 JULY 2004

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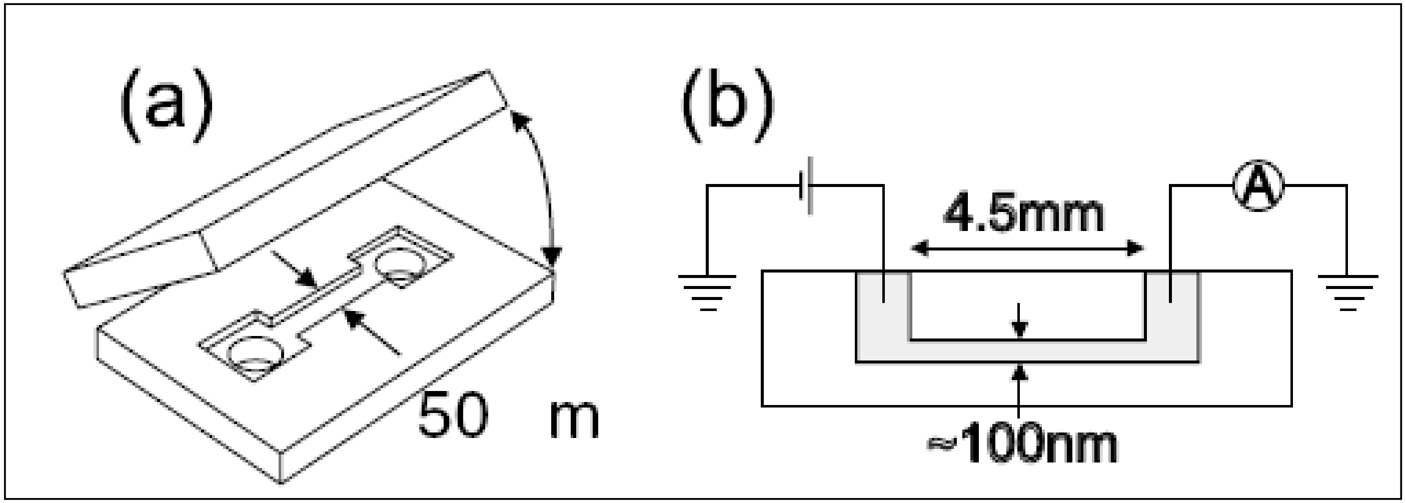

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...transport of ions in nanofluidic channels ... dominated by transport of counterions that must accumulate near charged channel walls to maintain charge neutrality. The effect is well described by an electrokinetic model that combines the Poisson-Boltzmann distribution of ions with the Navier-Stokes description of the fluid, and imposes a constant surface charge σ_d *as a boundary condition*.

Tandon, Kirby et al.

Electrophoresis 2008, *29*, 1092–1101

Zeta potential and electroosmotic mobility in microfluidic devices fabricated from hydrophobic polymers: The origins of charge

2.1.1 Ionization of surface groups

Many microfluidic substrates behave as weak acids in aqueous solutions, owing to reactivities of surface groups, *e.g.*, amines, carboxylic acids, or oxides. Glass/silica microdevices are a particularly well-studied example of such a system, due to their ubiquity in devices used for CE and other analytical techniques [9]. In glass substrates, surface silanol groups can be deprotonated in aqueous solutions leaving a negative surface charge:

$$\boxed{\mathrm{SiOH} \underset{}{\overset{K_a}{\rightleftharpoons}} \mathrm{SiO^-} + \mathrm{H^+}} \qquad (1)$$

The pK_a for this reaction is approximately 4.7 [9]. In cases like this where protonation/deprotonation of surface groups is the origin of charge, the charge-determining ions are H^+ and OH^-, and the electrokinetic properties of the system are a strong function of pH [10]. and ionic strength

Source: Tandon, Vishal et al. "Zeta potential and electroosmotic mobility in microfluidic devices fabricated from hydrophobic polymers: 1. The origins of charge." Electrophoresis 29, no. 5 (2008): 1092-1101.

Tandon, Kirby et al. *Electrophoresis* 2008, *29*, 1092–1101

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Midterm Prob 3

Source: Tandon, Vishal et al. "Zeta potential and electroosmotic mobility in microfluidic devices fabricated from hydrophobic polymers: 1. The origins of charge." Electrophoresis 29, no. 5 (2008): 1092-1101.

Tandon, Kirby et al.

Electrophoresis 2008, *29*, 1092–1101

Zeta potential and electroosmotic mobility in microfluidic devices fabricated from hydrophobic polymers: The origins of charge

Electroneutrality

$$\bar{\rho}_m(x) + \sum_i z_{i+} F \bar{c}_{i+}(x) + \sum_j z_{j-} F \bar{c}_{j-}(x) = 0$$

$$\boxed{\mathrm{SiOH} \underset{}{\overset{K_a}{\rightleftharpoons}} \mathrm{SiO^-} + \mathrm{H^+}}$$

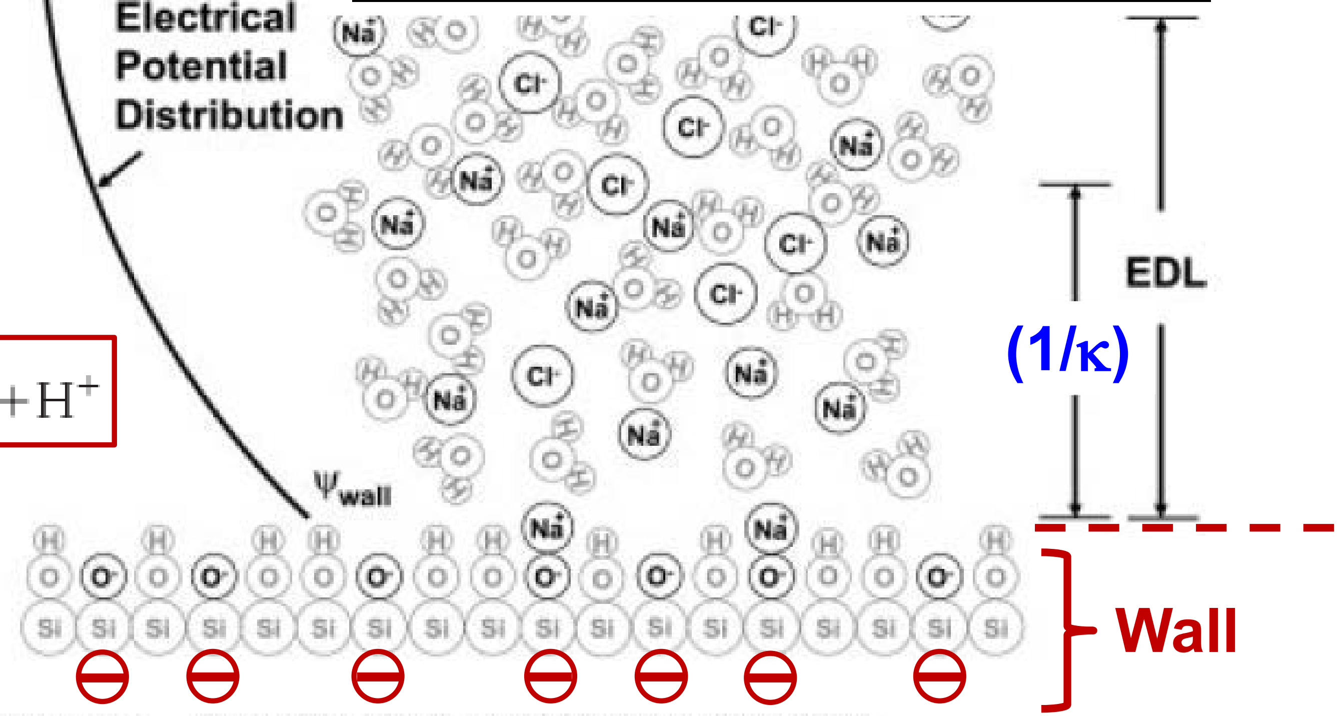


Figure 1. Scheme of the electrical double layer.

Source: Tandon, Vishal et al. "Zeta potential and electroosmotic mobility in microfluidic devices fabricated from hydrophobic polymers: 1. The origins of charge." Electrophoresis 29, no. 5 (2008): 1092-1101.

REVIEW

Microfluid Nanofluid 2009

Surface molecular property modifications for poly(dimethylsiloxane) (PDMS) based microfluidic devices

Ieong Wong · Chih-Ming Ho

Abstract: .... At present, the main challenge is the control of nanoscale properties on the surface of lab-on-a-chip to satisfy the need for biomedical applications. For example, poly(dimethylsiloxane) (PDMS) is a commonly used material for microfluidic circuitry, yet the **hydrophobic nature of PDMS surface suffers serious nonspecific protein adsorption**.

BIOMICROFLUIDICS 3, 044101 (2009)

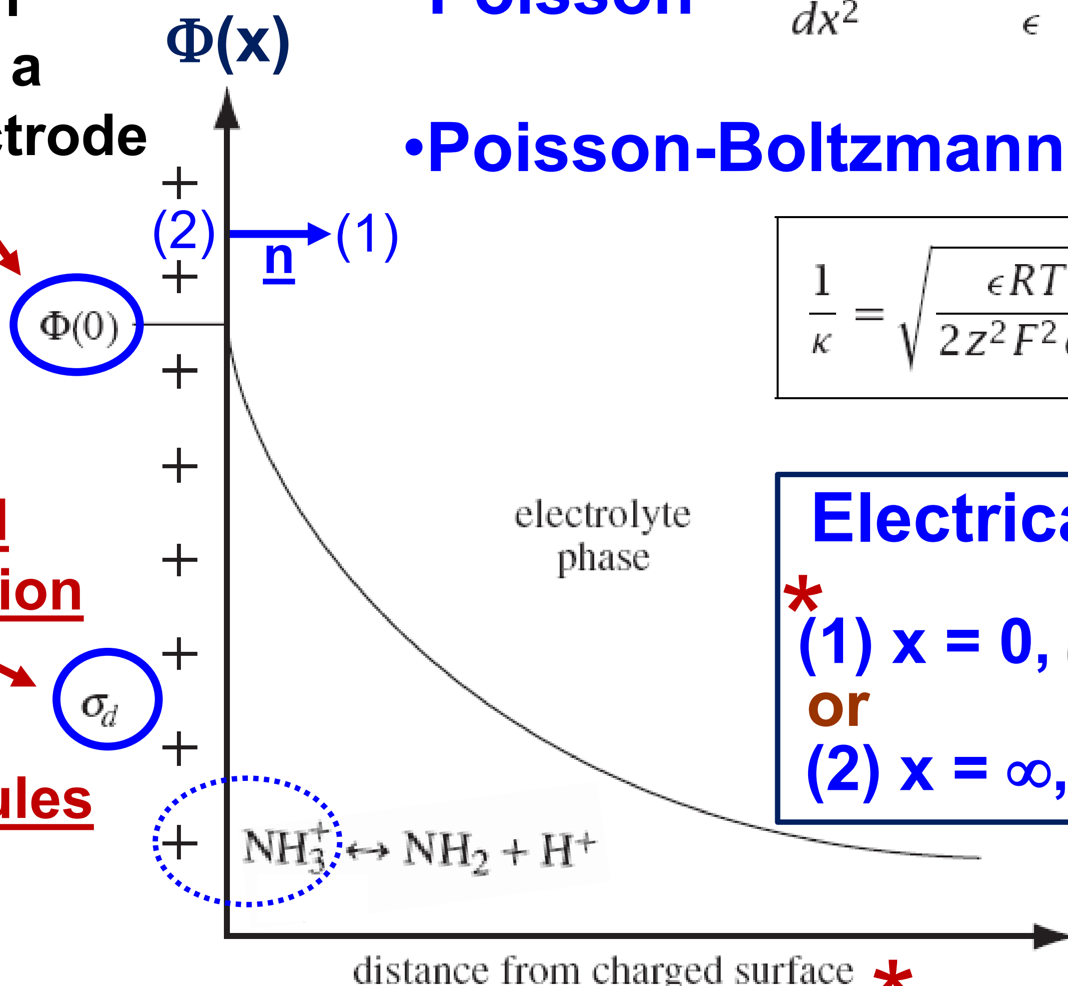
Study on surface properties of PDMS microfluidic chips treated with albumin Schrott, et al.

Electrokinetic properties and morphology of PDMS microfluidic chips intended for bioassays are studied... Albumin passively adsorbs on the PDMS surface. **Electrokinetic characteristics** electro-osmotic velocity, electro-osmotic mobility, and **zeta potential of the coated PDMS channels** are **experimentally determined** as functions of the electric field strength and the characteristic electrolyte concentration.

Review

Apply Φ_0 with "battery" if surface is a metal electrode

σ_d derived from titration of bio-surface biomolecules



•**Boltzmann** $c_i(x) = c_{i0} \exp\left[-\frac{z_i F \Phi(x)}{RT}\right]$

•**Poisson** $\frac{d^2\Phi(x)}{dx^2} = \frac{-\rho_e(x)}{\epsilon} = -\frac{1}{\epsilon}\sum_i z_i F c_i(x)$

•**Poisson-Boltzmann** $\frac{d^2\Phi(x)}{dx^2} = \kappa^2 \Phi(x)$

$$\boxed{\frac{1}{\kappa} = \sqrt{\frac{\epsilon RT}{2z^2F^2c_{i0}}} \equiv \text{Debye length}}$$

Electrical B.C.s

* **(1) x = 0,** $\sigma_d = -\epsilon \left.\frac{\partial \Phi(x)}{\partial x}\right|_{x=0}$

or

(2) x = ∞, $\Phi = 0$

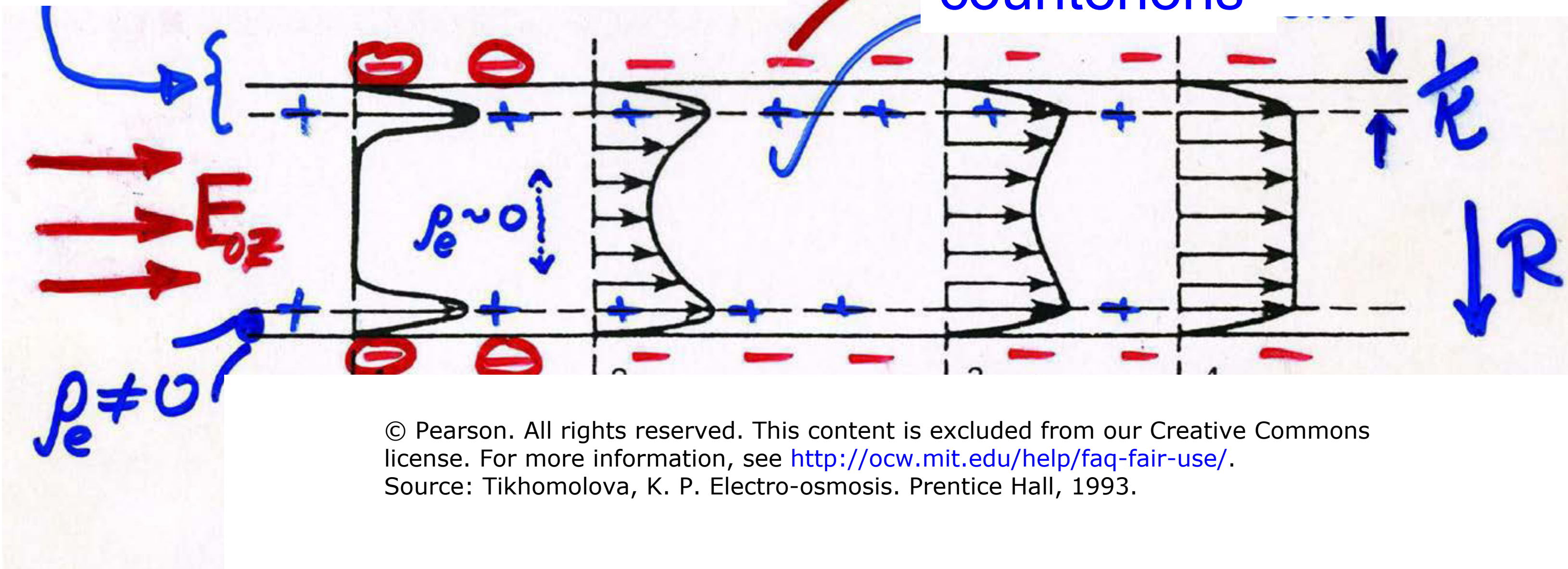
* $\underline{\mathbf{n}} \cdot (\varepsilon_1 \underline{\mathbf{E}}_1 - \varepsilon_2 \underline{\mathbf{E}}_2) = \sigma_d$

Electroosmosis

Electrical Double Layer

Glass, plastic (PDMS), proteins: <u>surface charge on wall</u>

counterions



Source: Tikhomolova, K. P. Electro-osmosis. Prentice Hall, 1993.

$$\boxed{\tau_{vd} \sim \frac{R^2}{(\mu/\rho)}}$$

$$\boxed{-\nabla p + \mu \nabla^2 v + \rho_e \mathbf{E} = 0}$$

LAWS

C

$$(1)\ \underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E}^{TOT} + c_i \underline{v}$$

$$(2)\ (\partial c_i / \partial t) = -\nabla \cdot \underline{N}_i + R_i$$

E

$$(3)\ \nabla \cdot \epsilon \underline{E}^{TOT} = \rho_e = \sum z_i F c_i$$

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$$(6)\ \underline{J} = \left(\sigma \underline{E}^{TOT} + \rho_e \underline{v} + \cancel{(\ )\nabla c_i}^{\,0}\right) = \sum z_i F N_i$$

M

$$(7)\ \rho \frac{D\underline{v}}{Dt} = \left(-\nabla p + \mu \nabla^2 \underline{v} + \underbrace{\rho_e \underline{E}^{TOT}}_{\nabla \cdot \epsilon \underline{E}}\right) \simeq 0$$

$$(8)\ \nabla \cdot \underline{v} = 0$$

$c_+ , c_- ;\ \underline{N}_+ , \underline{N}_- ;\ \underline{E} ;\ \underline{v}$

14 EQNS. IN 14 unknowns !!

Table B.3
p. 293

$$[\underline{v}\cdot\nabla\underline{v}]_z = \cancelto{0}{v_r}\frac{\partial v_z}{\partial r} + \frac{\cancelto{0}{v_\theta}}{r}\frac{\partial v_z}{\partial \theta} + v_z\cancelto{0}{\frac{\partial v_z}{\partial z}}$$

(cylindrical coord.)

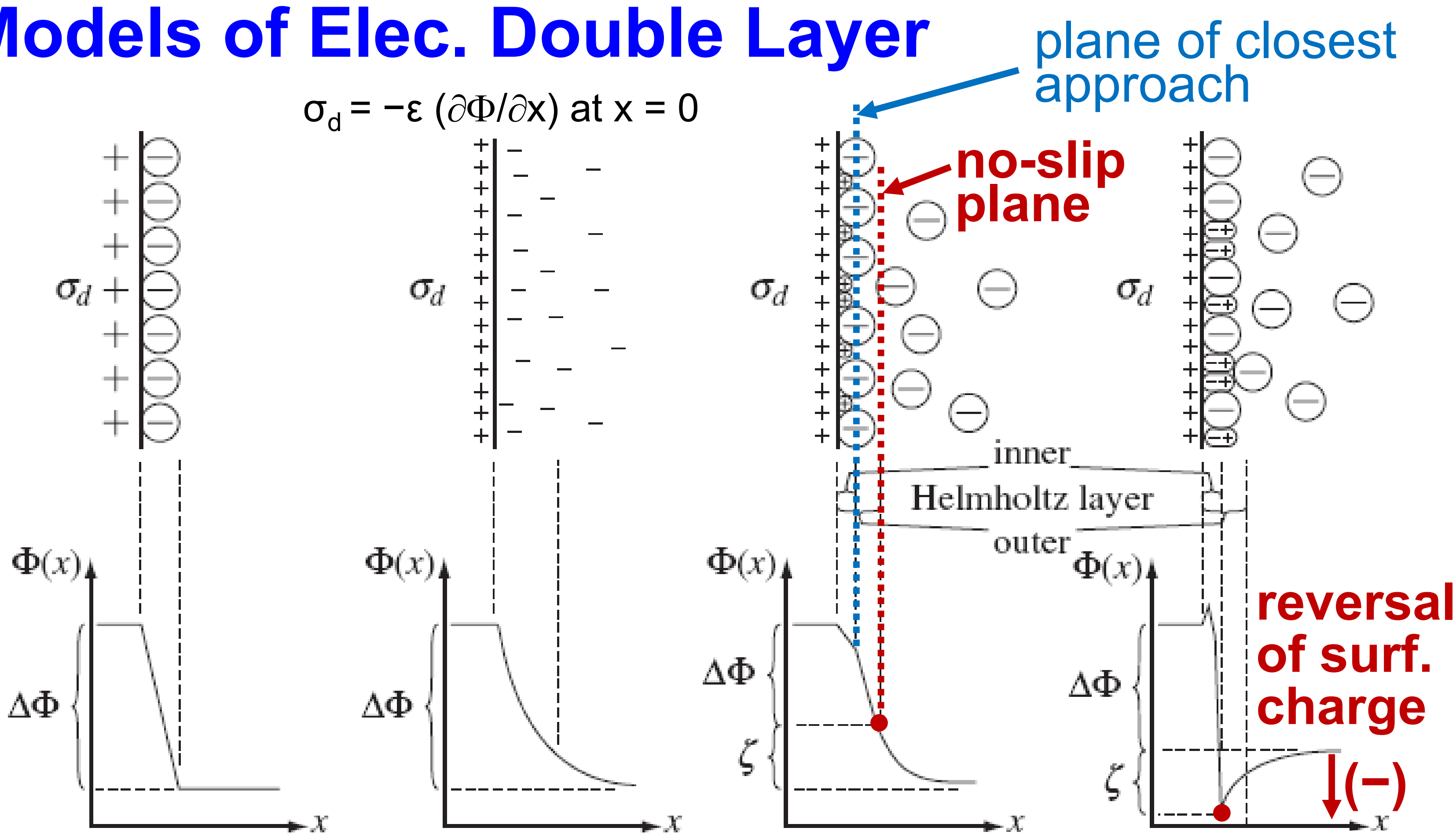
$$\rho_e = \nabla\cdot\epsilon\underline{E} = \frac{1}{r}\frac{\partial}{\partial r}(r\epsilon E_r) + \frac{1}{r}\cancelto{0}{\frac{\partial E_\theta}{\partial \theta}} + \cancelto{0}{\frac{\partial E_z}{\partial z}}$$

$$[\nabla^2\underline{v}]_z = \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v_z}{\partial r}\right) + \frac{1}{r^2}\cancelto{0}{\frac{\partial^2 v_z}{\partial \theta^2}} + \cancelto{0}{\frac{\partial^2 v_z}{\partial z^2}}\right]$$

$$\nabla\cdot\underline{v} = \left[\frac{1}{r}\frac{\partial}{\partial r}(r\cancelto{0}{v_r}) + \frac{1}{r}\cancelto{0}{\frac{\partial v_\theta}{\partial \theta}} + \cancelto{0}{\frac{\partial v_z}{\partial z}}\right] \equiv 0$$

Models of Elec. Double Layer

$\sigma_d = -\varepsilon\,(\partial\Phi/\partial x)$ at $x = 0$



Helmholtz double layer model

"Diffuse" P-B double layer model: point charges

with ion adsorption; ζ potential

with molec. adsorption; ζ potential

Electrokinetics

Zeta Potential vers (Gouy-Chapman) Potential