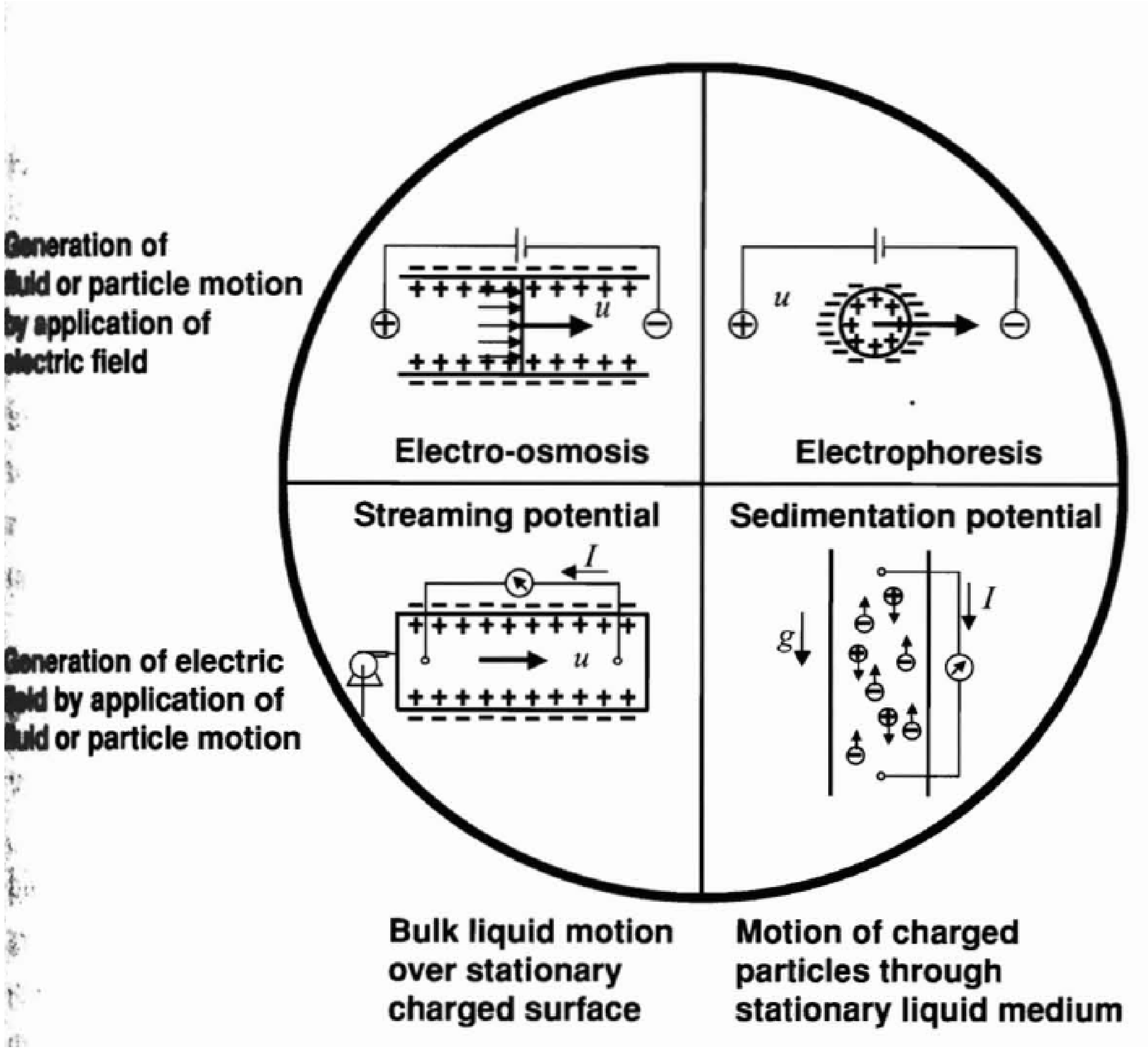
# Lecture 8

Electrokinetic effects.
Electroosmosis and
electrophoresis.

# Electrokinetic effects

- **Electrophoresis:** movement of charged surface (e.g. particle or molecule) relative to a stationary liquid.
- **Electroosmosis:** movement of liquid relative to a stationary charged surface (e.g. capillary tube)
- **Sedimentation potential**: electric potential created by moving charged particles
- **Streaming potential**: electric potential created by liquid moving relative to charged surface
- **Dielectrophoresis**: movement of uncharged particles with polarizability different from the liquid.

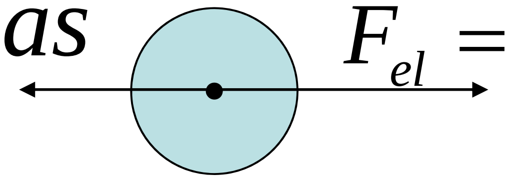
# Electrokinetic effects



# Electrophoresis

- Let’s consider a charged spherical particle in a low conductivity liquid.

$$F_{drag} = 6\pi\eta a\vec{s}$$



$$\vec{F}_{el} = Ze \cdot \vec{E}$$

- the drift velocity is:

$$\vec{u}_{ep} = \frac{Ze \cdot \vec{E}}{6\pi\eta a} = \mu_{ion} \cdot \vec{E}$$

- the equation is valid also for ions (except $H^+$and $OH^-$) assuming hydration radius of approx. 0.2nm (one layer of water molecules).

# Origin of electroosmosis

- Most of the materials carry some charge on the surface (due to adsorption, presence of partially dissociated groups etc.)

- This charge will be screened by the ions in the solution

- If an external voltage is applied the ions will start to move in the electric field and cause the flow of the liquid

# Charge on Si surface

- In the case of oxides the dominating mechanism of surface charging is the dissociation of hydroxyl groups on the surface

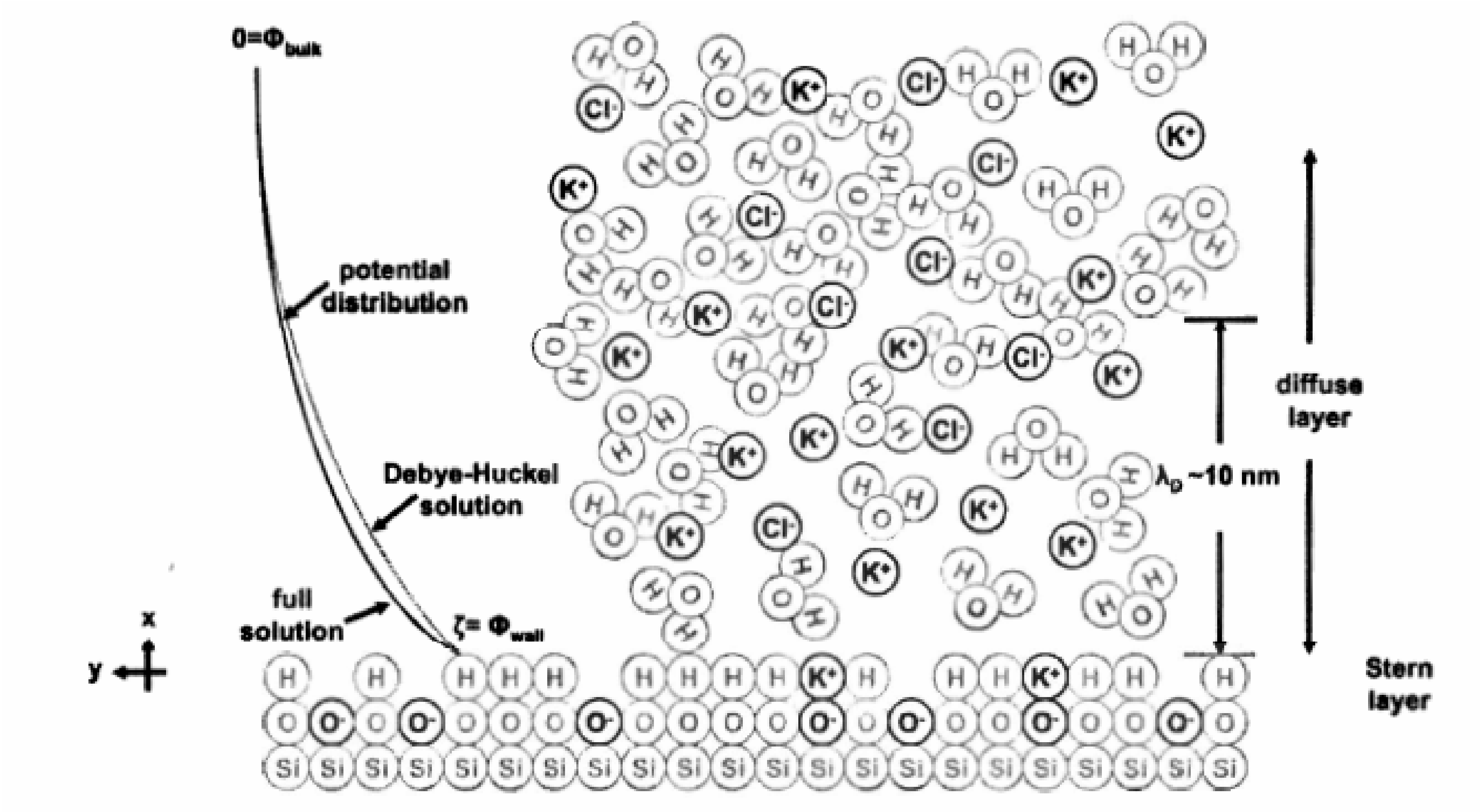
$$\sim SiOH_2 \rightleftharpoons \sim SiOH + H^+$$

$$\sim SiOH \rightleftharpoons \sim SiO^- + H^+$$

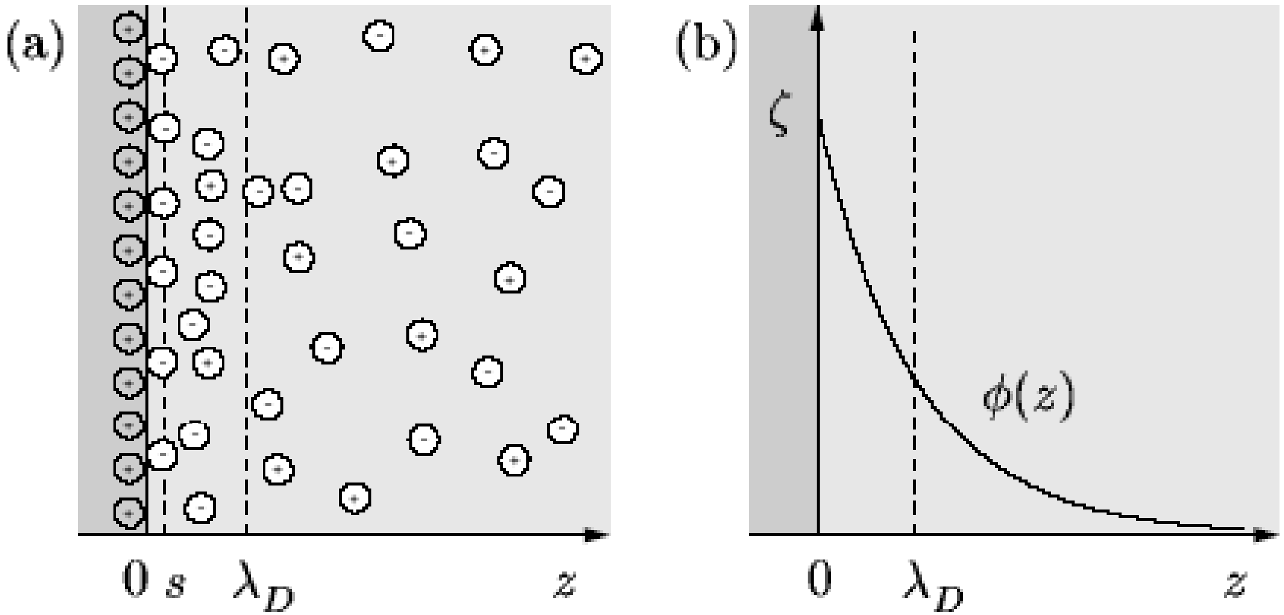
pzc ~ pH 1.8 - 3.4

# Origin of electroosmosis

- Ionic structure of the solid (silicon) - liquid (electrolyte) interface



# Debye layer in an electrolyte




- The potential at the Stern layer next to the surface is called zeta-potential ζ.

# Debye layer

- We can find the charge and potential distribution by linking thermodynamics and electrodynamics:
  - The equilibrium condition: all ions have the same chemical potential:

$$\mu_{\pm}(r) = \mu_0(r) + kT\ln\left[\frac{c_{\pm}(r)}{c_0}\right] \pm Ze\varphi(r);\ \nabla\mu_{\pm}(r) = 0$$

$$kT\nabla\ln\left[\frac{c_{\pm}(r)}{c_0}\right] = \mp\nabla Ze\varphi(r)$$

the boundary conditions: $c_{\pm}(\infty) = c_0;\ \ \varphi(\infty) = 0$

$$c_{\pm}(r) = c_0\exp\left[\mp\frac{Ze}{kT}\varphi(r)\right]$$

# Debye layer

- Now we can link charge distribution and it's electrical potentials using Poisson equation

$$\begin{cases} \nabla^2 \varphi(r) = -\dfrac{\rho_e(r)}{\varepsilon} \\ \rho_{el} = Ze\left[c_+(r) - c_-(r)\right] = -2Zec_0 \sinh\left[\dfrac{Ze}{kT}\varphi(r)\right] \end{cases}$$

- Poisson-Boltzmann equation

$$\nabla^2 \varphi(r) = 2\frac{Zec_0}{\varepsilon} \sinh\left[\frac{Ze}{kT}\varphi(r)\right]$$

# Debye-Hückel approximation

- In the limit of small zeta-potential: $Ze\zeta \ll kT$

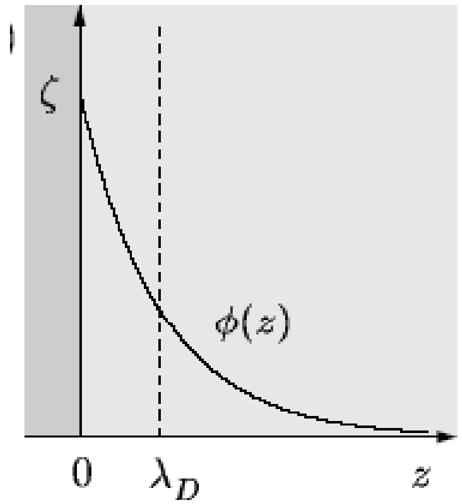
$$\nabla^2 \varphi(r) = 2\frac{(Ze)^2 c_0}{kT\varepsilon}\varphi(r) = \frac{1}{\lambda_D{}^2}\varphi(r)$$

$$\lambda_D = \sqrt{\frac{\varepsilon kT}{2(Ze)^2 c_0}} \approx \sqrt{\frac{1mM}{Z^2 c_0}} 9.6nm$$

# Debye-Hückel approximation: an infinite wall

- 1-D situation of a potential/charge distribution next to an infinite wall

$$\nabla^2 \varphi(z) = \frac{1}{\lambda_D^{\ 2}} \varphi(z)$$




the solution should be in the form: $\varphi(z) = C_1 e^{-z/\lambda_D} + C_2 e^{z/\lambda_D}$

the boundary conditions: $\varphi(\infty) = 0 \quad \varphi(0) = \zeta$

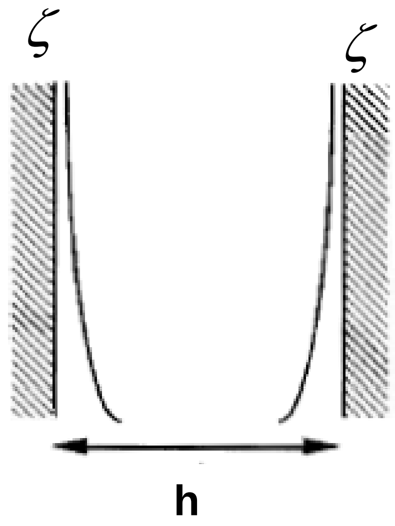
solution:

$$\varphi(z) = \zeta \exp\left[-\frac{z}{\lambda_D}\right]$$

$$\rho_{el}(z) = -\varepsilon \frac{\partial^2 \varphi}{\partial z^2} = -\frac{\varepsilon \zeta}{\lambda_D^{\ 2}} \exp\left[-\frac{z}{\lambda_D}\right]$$

# Debye-Hückel approximation: parallel plate channel

- 1-D situation of a potential/charge distribution in a parallel plate channel




$$\nabla^2 \varphi(z) = \frac{1}{\lambda_D{}^2} \varphi(z)$$

the solution should be in the form: $\varphi(z) = C_1 e^{-z/\lambda_D} + C_2 e^{z/\lambda_D}$

the boundary conditions:

$$\varphi(-h/2) = \zeta \quad \varphi(h/2) = \zeta \quad \left. \frac{\partial \varphi}{\partial z} \right|_{z=0} = 0$$

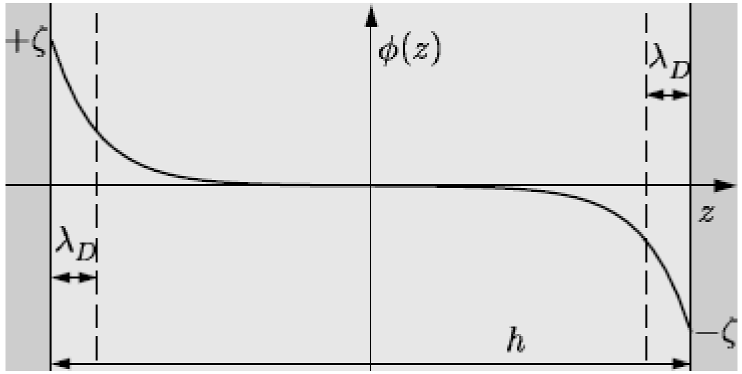
solution:

$$\varphi(z) = \zeta \frac{\cosh\left[z/\lambda_D\right]}{\cosh\left[h/2\lambda_D\right]}$$

$$\rho_{el}(z) = -\varepsilon \frac{\partial^2 \varphi}{\partial z^2} = -\frac{\varepsilon \zeta}{\lambda_D{}^2} \frac{\cosh\left[z/\lambda_D\right]}{\cosh\left[h/2\lambda_D\right]}$$

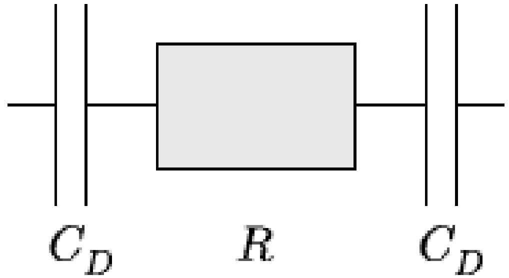
# Capacitance and characteristic frequency of a double layer

- The Debye layer acts as an electrical capacitor
- The capacitance of the Debye layer:




$$q_{el} = \int_0^{\infty} \left[ -\frac{\varepsilon\zeta}{\lambda_D{}^2} \exp\left( -\frac{z}{\lambda_D} \right) \right] dz = -\frac{\varepsilon}{\lambda_D} \zeta$$

$$C_D = \frac{\varepsilon}{\lambda_D}$$




$$\tau_{RC} = RC = \left( \frac{h}{\sigma_{el} A} \right) \left( \frac{1}{2} \frac{\varepsilon}{\lambda_D} A \right) = \frac{1}{2} \frac{h\varepsilon}{\sigma_{el} \lambda_D}$$

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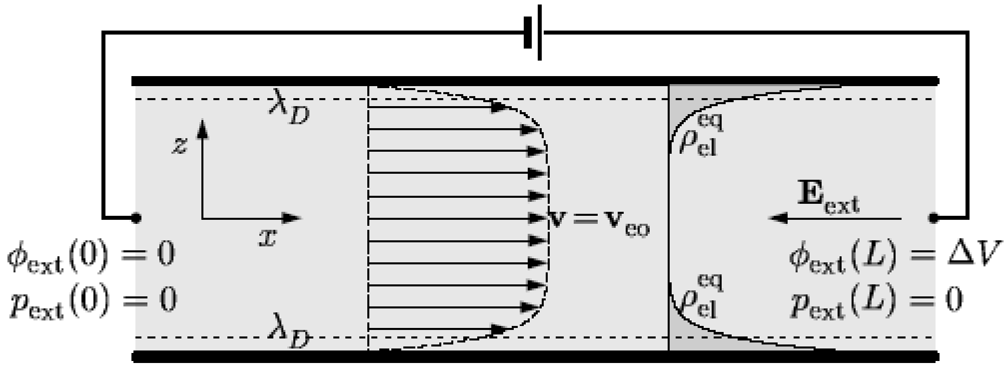
- Typically, for 1mM solution:

$\lambda_D = 9.6nm; h = 100\mu m, \sigma_{el} = 10^{-3} S/m; \varepsilon = 78\varepsilon_0$ ⇨ $\tau_{RC} = 3.6ms$

# Electroosmosis

- We have an extra body force in the Navier-Stokes equation due to electrical field:




$$\rho\left[\frac{\partial\vec{v}}{\partial t} + \left(\vec{v}\cdot\nabla\right)\cdot\vec{v}\right] = -\nabla p_{ext} + \eta\nabla^2\vec{v} - \rho_{el}\nabla\varphi_{ext}$$

$$E_{ext} = -\nabla\varphi$$

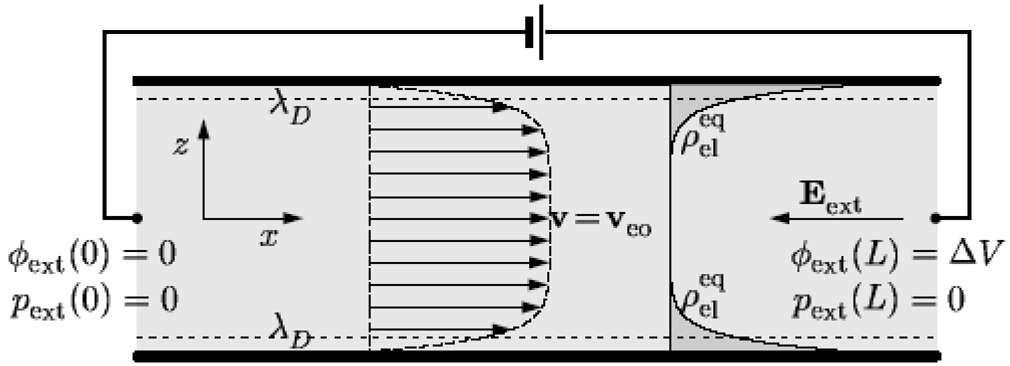
- Comments:
  - we assume that the external potential doesn't change the charge distribution
  - for continuous EO flow, some electrochemical processes on electrodes are required

# Electroosmosis

$$\rho\left[\frac{\partial\vec{v}}{\partial t}+(\vec{v}\cdot\nabla)\cdot\vec{v}\right]=-\nabla p_{ext}+\eta\nabla^2\vec{v}-\rho_{el}\nabla\varphi_{ext}$$

$$\vec{v}=\left(v_x(z),0,0\right)$$

$$\nabla p_{ext}=0$$



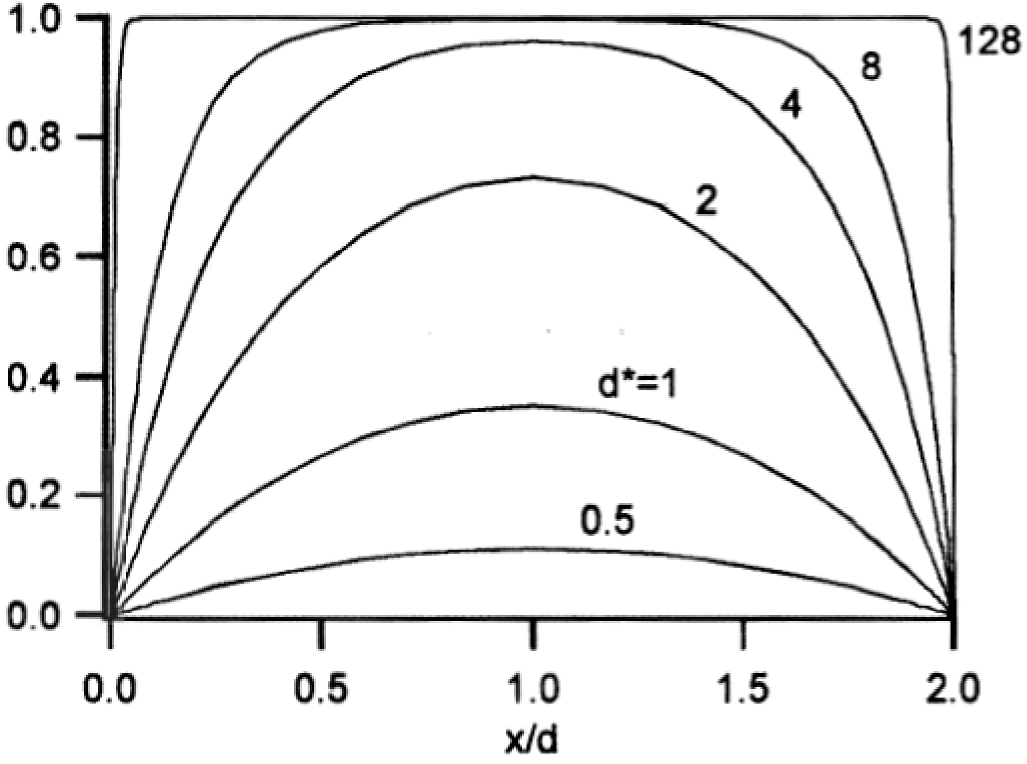

$$0=\eta\frac{\partial^2 v_x}{\partial z^2}+\varepsilon\frac{\partial^2\varphi_{eq}}{\partial z^2}E \qquad \text{or} \qquad \frac{\partial^2}{\partial z^2}\left[v_x(z)+\frac{\varepsilon E}{\eta}\varphi(z)\right]=0$$

- the boundary conditions: $v_x(-h/2)=v_x(h/2)=0$
- the solution $v_x(z)=\left[\zeta-\varphi_{eq}(z)\right]\frac{\varepsilon E}{\eta}=\frac{\varepsilon\zeta}{\eta}E\left[1-\frac{\cosh\left[z/\lambda_D\right]}{\cosh\left[h/2\lambda_D\right]}\right]$

$v_{EO}$

# Electroosmosis

- Flow velocity profile between  parallel plates




$$u^{*} = u\left(\varepsilon\zeta E / \mu\right)^{-1}$$

$$d^{*} = d / \lambda_{D}$$

# Electroosmotic flow

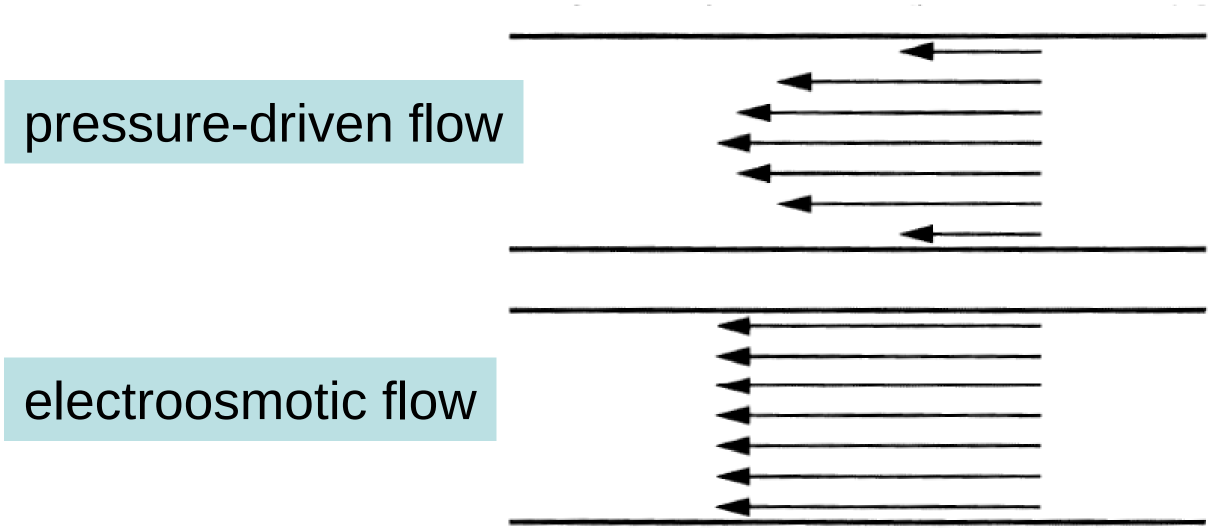
- typical values are: $\zeta \approx 100\,mV;\ \lambda_D \approx 10nm;$
- As we see, if electric field is applied across a tube filled with electrolyte a fairly uniform plug flow is produced (vs. parabolically pressure driven)

dielectric constant

zeta potential

$$u = -\frac{\varepsilon\varsigma}{\mu}E$$

viscosity



# Measuring of zeta potential

- tracking electroosmotic velocities
- streaming potential:
  - if a pressure driven flow is applied to an electrolyte, a potential will build up

$$\Delta V = \frac{\varepsilon\zeta}{\sigma\mu}\Delta p$$

Helmholtz-Smoluchowski equation

# Electrophoretic effect

- Electrophoresis: motion of electrically charged molecule of particles in response to electric field
  Electrophoretic velocity

zeta potential at the particle surface

$$u = \frac{\varepsilon \varsigma}{\eta} E \qquad \lambda_d \ll d \quad \text{(particle size)}$$

$$u = \frac{2}{3}\frac{\varepsilon \varsigma}{\eta} E \qquad \lambda_d \gg d$$

Generally: $\mu_{ep} = A\frac{\varepsilon \varsigma}{\eta} E; \;\; \mu_{net,j} = \mu_{eo} + \mu_{ep,j}$

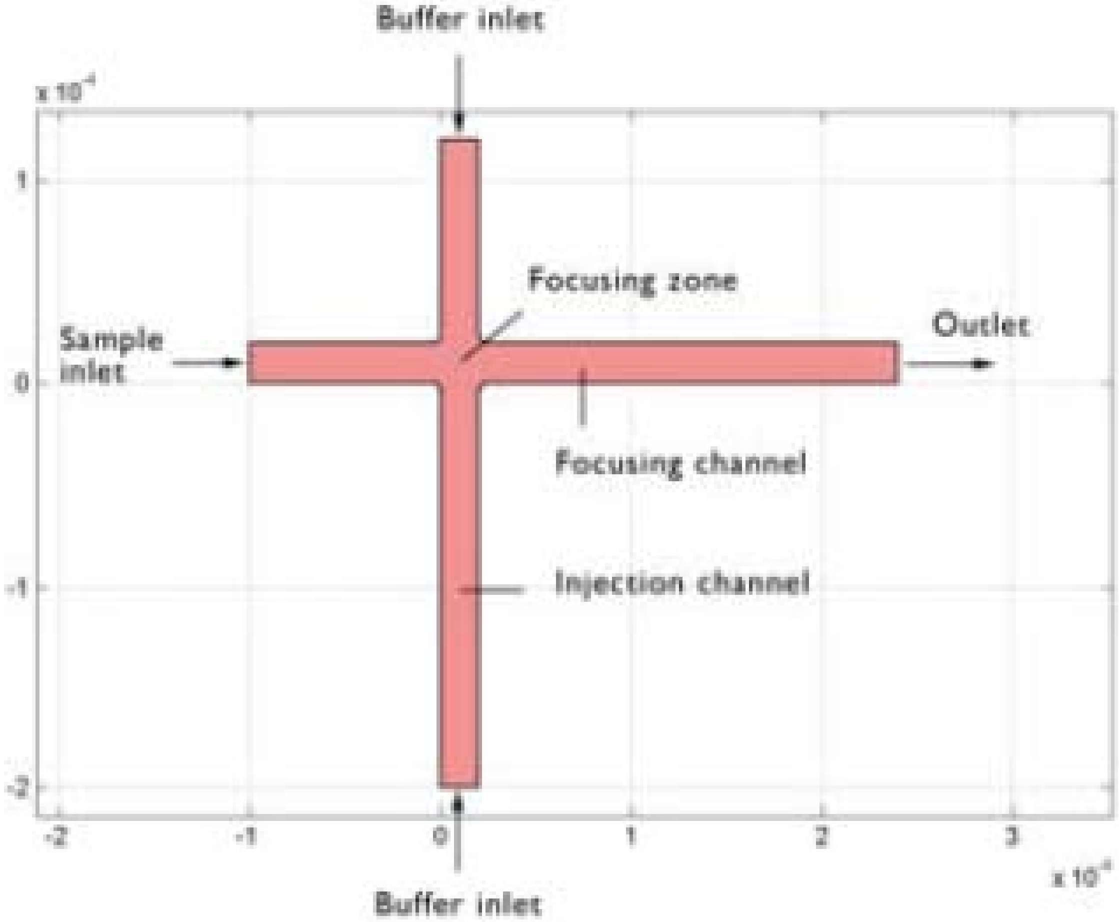
Resolution of electrophoretic system: $R_{mn} = \frac{\Delta t_{mn}}{w}$

$\Delta t_{mn} \propto t$

$w \propto \sqrt{t}$

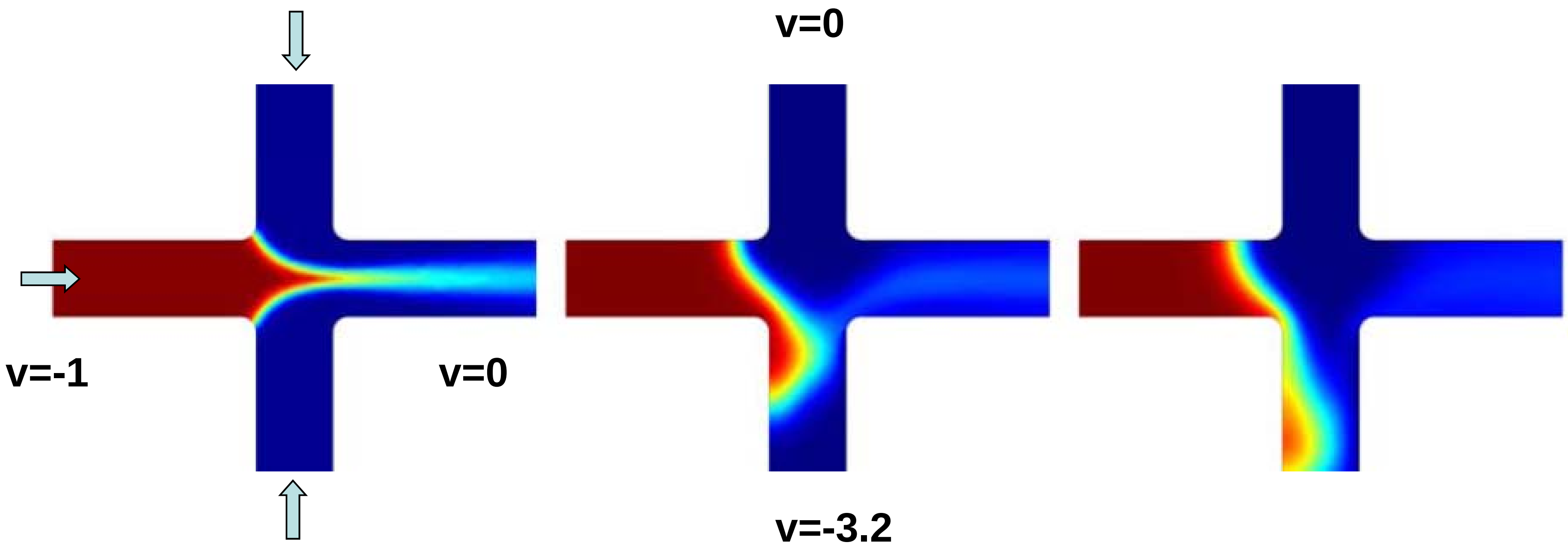
# Electrokinetic valve

- Geometry



# Electrokinetic valve

- Technique




Focusing

Injection