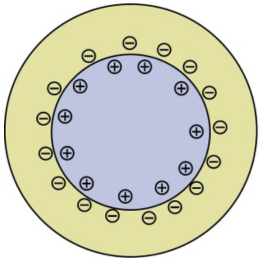
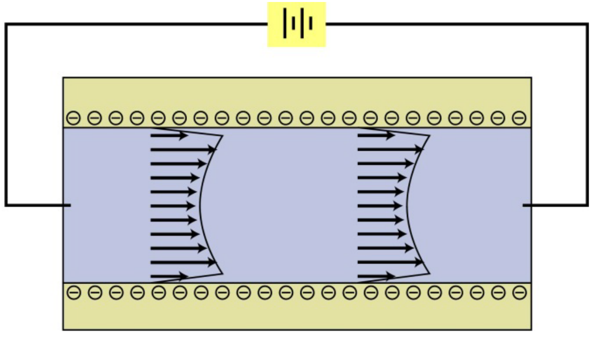
Contents

3. Physics of Microfluidic Systems

3.7. Electrokinetics

- Topics of electrokinetics (EK)
  - Electroosmosis (EO)
    - Surface charges in wall
  - Electrophoresis (EP)
    - Ionic charges in liquid bulk



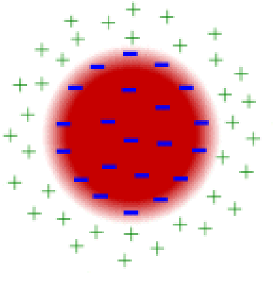


- Electrophoretic separations
  - Both phenomena observed simultaneously
  - Suppression of electroosmosis
    - Surface modification
    - Buffer solutions (pH)

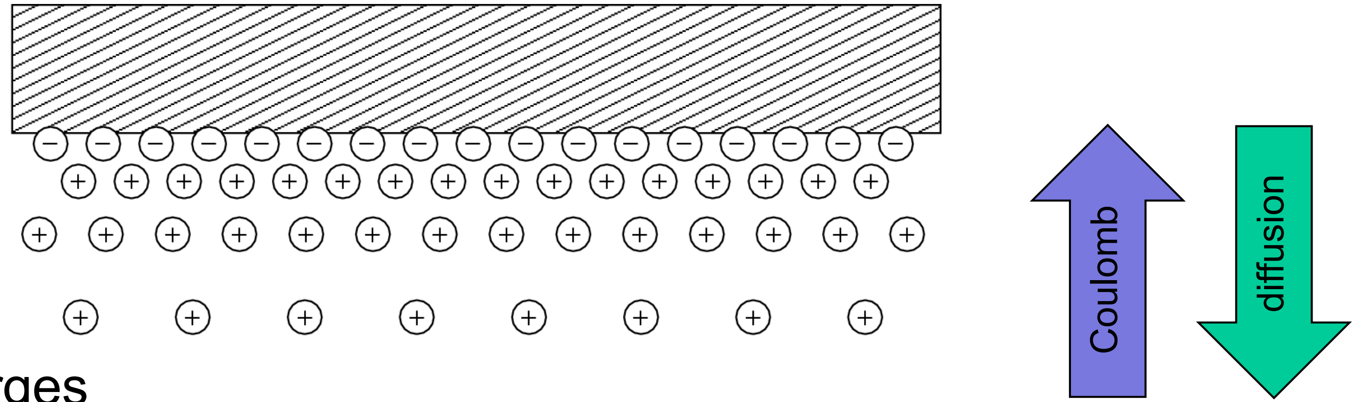
- Microfluidic devices
  - Often controlled by EK

3.7. Electrokinetics

1. **Electric Double Layers**
2. Electroosmotic Flow
3. Electrophoresis
4. Dielectrophoresis



3.7.1. Electric Double Layers (EDLs)

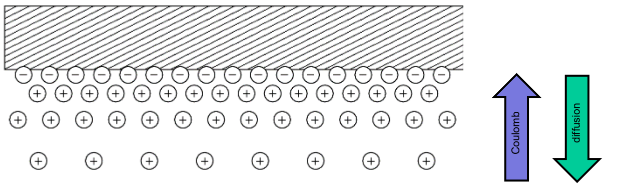


- Surface charges
  - Dissociation of ions or ionic groups from surface
  - Deprotonation of silanol group

$$\mathrm{SiOH(s)} \rightleftharpoons \mathrm{SiO^-(s)} + \mathrm{H^+(aq)}$$

  - Governed by
    - Surface **charge density** σ_q
    - pH-value
- Release of **free energy** $G = H - TS$ at interface
  - Enthalpy H: Binding energy
  - Entropy S: Diffusion
- Layer of immobilized charges: Coulomb attraction

3.7.1. EDL-Structure and Surface Potential

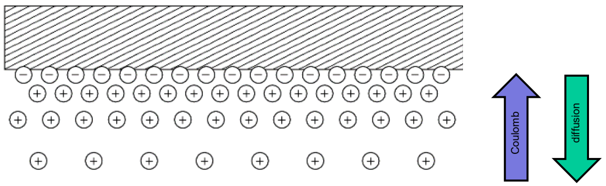


- Reaction of liquid
  - Screening of immobilized charges
  - Surplus of oppositely charged mobile molecules in liquid at interface
  - Capacitive coupling
  - Counteracting Brownian motion (diffusion)
- Potential in EDL
  - Poisson equation
    - Source: Charge density ρ_q

$$\Delta \psi = \frac{\varrho_q}{\varepsilon \varepsilon_0}$$

- Helmholtz-model for EDL
  - Rigid double layer of atomic dimension
  - One-by-one matching of charges
  - Linear decrease of potential in intermediate region

3.1.1. Gouy-Chapman Model



- Diffusion counteracts rigid „Helmholtz“-alignment
- Poisson-Boltzmann equation

$$\varrho_q(x) = \varrho_{q,0} \exp\left[-\frac{ze\psi(x)}{k_\mathrm{B}T}\right]$$

  - ➢ Assumption
    - Point-like ions
    - Undisturbed dielectric constant ε of solvent
  - ➢ Radial charge-density distribution
    - Debye length $r_\mathrm{D} = \sqrt{\frac{\varepsilon\varepsilon_0 k_\mathrm{B}T}{e^2 \sum_i c_i z_i^2}}$

$$\varrho_q(r) = -\frac{\varepsilon\varepsilon_0}{r_\mathrm{D}^2}\zeta\frac{I_0(r/r_\mathrm{D})}{I_0(r_0/r_\mathrm{D})}$$

modified Bessel function

  - ➢ Charge density σ_q at surface
    - ζ - potential ~ 0.1 V

$$\sigma_q = \frac{\varepsilon\varepsilon_0\zeta}{r_\mathrm{D}}$$

3.1.1. Stern Model

- Helmholtz model (Coulomb)
  - ➢ High concentration limit
- Gouy-Chapman model (diffusion)
  - ➢ High dilution limit
- Interpolation
  - ➢ Stern plane at $x = \delta$
  - ➢ Reflecting finite size of ions
    - Thickness on nanometer-scale
  - ➢ Molecular condenser
    - Stern layer
    - Bulk liquid

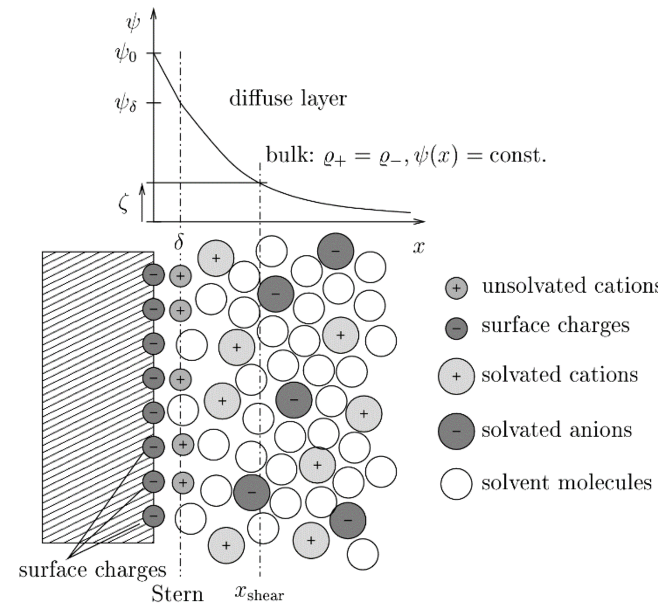
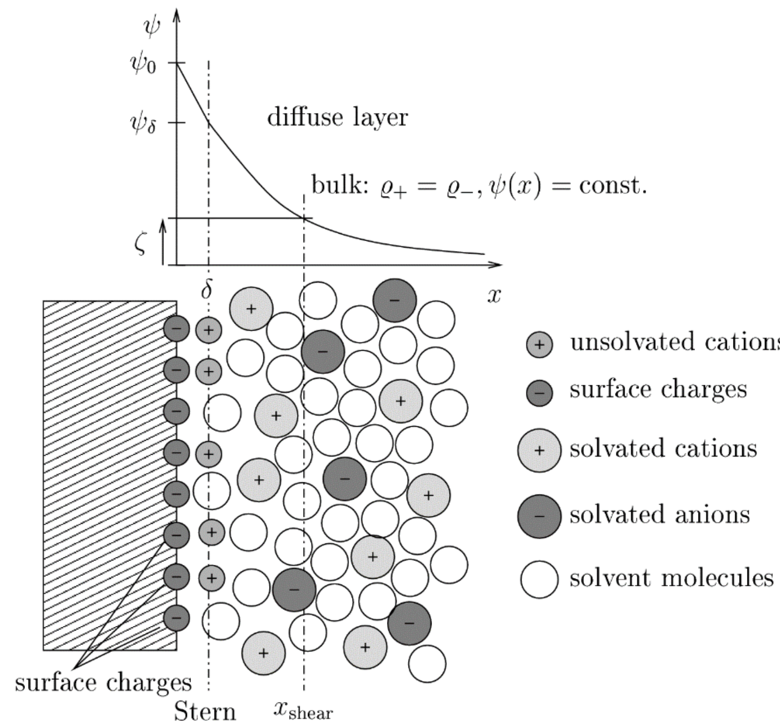


Fig. 3.40. Structure of the first fluid layers next to a (negatively) charged surface. The curve of the surface potential $\psi(x)$ reflects the transition from the surface over the immobilized Stern plane at $x = \delta$ and the diffuse layer to the bulk solution with $\psi(x \mapsto \infty) = 0$

- Thermodynamic equilibrium
  - ➢ Surface potential attracts ions from bulk
  - ➢ Energy required for dehydration process near surface
  - ➢ Brownian motion

3.7.1. Stern Model

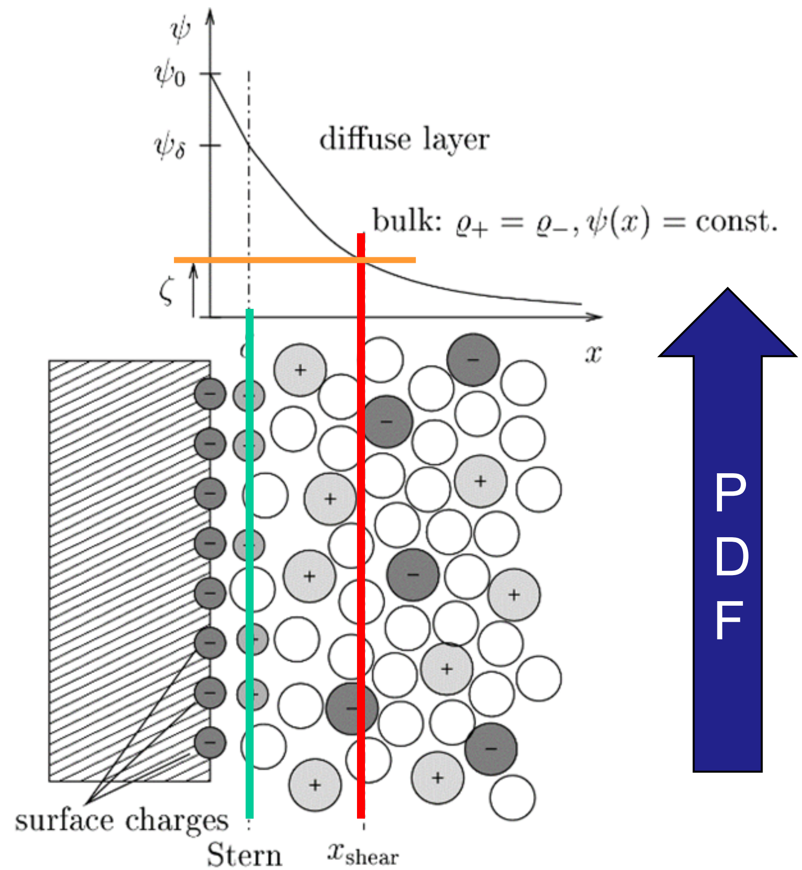
- Stern layer
  - Specifically bound molecules
  - Inner Helmholtz layer
    - Partially solvated ions
  - Outer Helmholtz layer
    - Completely solvated ions
  - Both layers very narrow
    - On range of atomic dimensions



- Diffuse layer
  - Kinetic energy of same magnitude as electrostatic potential
  - Approximation of point charges justified
  - Brownian motion
  - Exponential decay of potential

3.7.1. Zeta-Potential

- Pressure-driven flow (PDF)
  - Shear "dragging" mobile charges
- Formation of Stern layer at δ
- Formation of shear plane at x_{shear}
- Zeta potential ζ



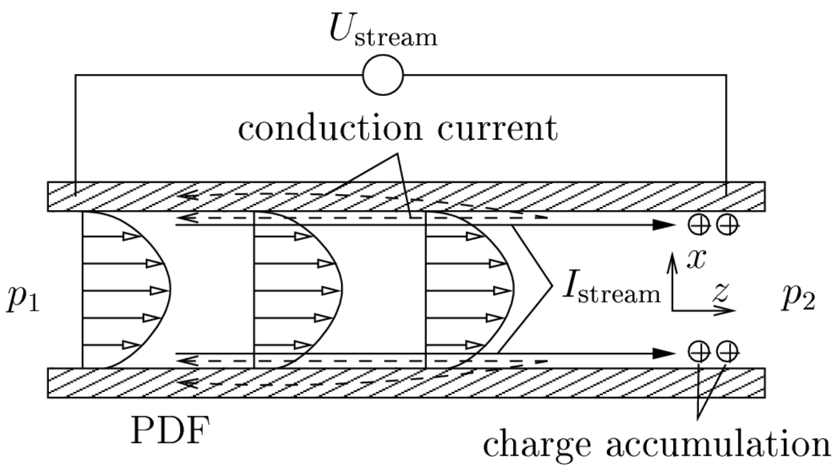
$$\zeta = \psi(x_{\text{shear}}) - \psi(x \mapsto \infty)$$

3.7.1. Electric Double Layers

optional

- Heat transfer
  - Pinning of liquid molecules in EDL
  - Blocking of diffusive Transport of Heat
  - Nu increases with decreasing ζ-potential

3.7.1. Streaming Current



Hydrodynamic → Electric

$$I_{\text{stream}} = \int_A \boldsymbol{v}(\boldsymbol{r})\varrho_q(\boldsymbol{r})\mathbf{d}\boldsymbol{A}$$

$$v_z(r) = \frac{\Delta p}{4\eta l}(r_0^2 - r^2)$$

- PDF
  - Axial displacement of charges in shear plane
- Streaming current
  - Counteracting flow through
    - Liquid (ions)
    - Wall (electrons)
  - Wetted perimeter w

$$v_{\text{shear}} = v(x_{\text{shear}} - r_{\text{D}} < x < x_{\text{shear}} + r_{\text{D}}) \simeq \left.\frac{\partial v_z}{\partial x}\right|_{x_{\text{shear}}} r_{\text{D}}$$

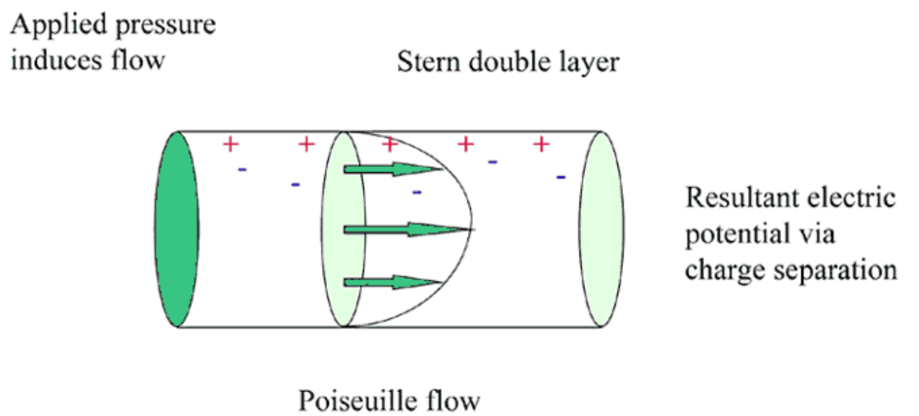
$$v_{\text{shear}} = \frac{d r_{\text{D}} \Delta p}{\eta l}$$

$$I_{\text{stream}} = \sigma_{q,\text{shear}} w v_{\text{shear}} = \frac{w \sigma_{q,\text{shear}} d r_{\text{D}} \Delta p}{\eta l}$$

3.7.1. Streaming Potential

- Streaming current I_{stream}
  - ➢ Charge displacement
  - ➢ Counteracting potential
- Streaming potential U_{stream}
  - ➢ Conversion
    - Mechanical force Δp
    - Electric potential U
    - Powering I_{stream}
  - ➢ Helmholtz-Smoluchowski
    - Between parallel plates
    - Gap distance d
    - Electric resistance R
      - ➢ Electrolyte
      - ➢ Channel wall

Hydrodynamic → Electric

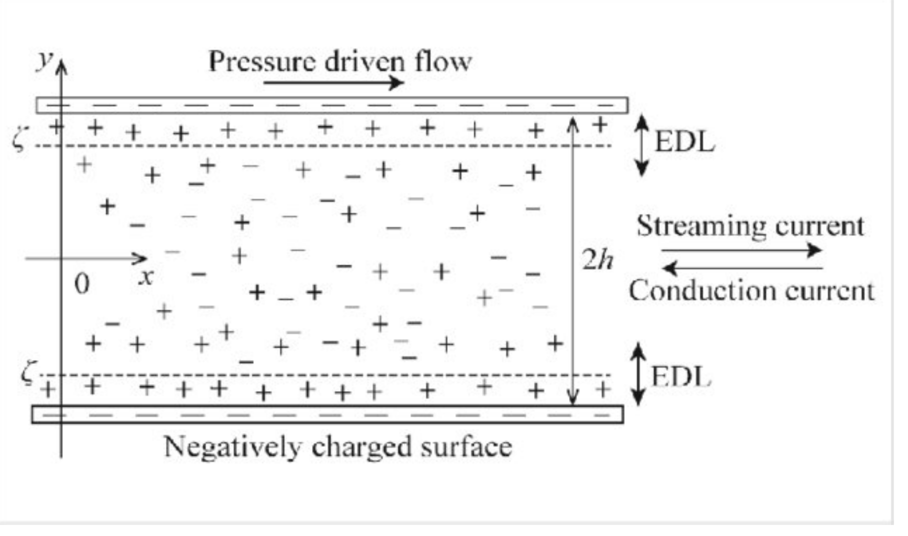


$$U_{\text{stream}} = \frac{\zeta \varepsilon \varepsilon_0 w d R \Delta p}{\eta l}$$

3.7.1. Electroviscous Effect

optional

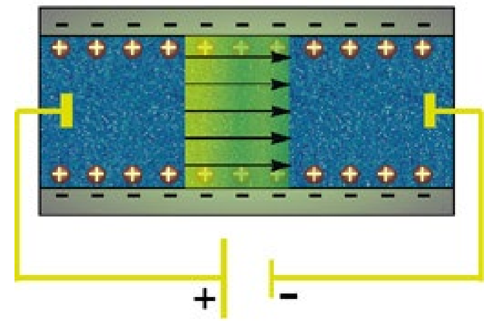
- Electric double layers
  - Streaming current powered by mechanical force
  - Hydrodynamic effect similar to viscosity
  - Apparent viscosity > bulk viscosity
  - Thickness of EDL however small (nm to µm)
  - Effect only important for small-diameter tubes



3.7. Electrokinetics

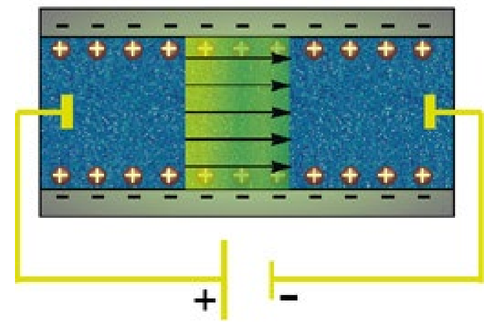
1. Electric Double Layers
2. **Electroosmotic Flow**
3. Electrophoresis
4. Dielectrophoresis

Electric → Hydrodynamic



3.7.2. Electroosmotic Flow

- Mechanism
  - „Reversed streaming“
  - EDL
  - Axial electric field, tangential to surface
  - Force on net charge in diffuse mobile layer
  - Bulk fluid dragged by mobile layer like „chains“
  - Negative surface charges
    - EOF towards cathode



$$\boldsymbol{f}_q(\boldsymbol{x}) = \varrho_q(\boldsymbol{x})\boldsymbol{E}(\boldsymbol{x})$$

- Electroosmotic mobility
  - Electric field $E = U / l$
  - Equation of motion (NS)
    - Steady flow of incompressible fluid at low Re
    - Vanishing material derivative
  - Helmholtz-Smoluchowski relation
    - Limit of small Debye length
  - EO mobility μ_ζ
    - Not EP mobility
    - ζ-potential
    - Viscosity η

$$-\nabla p + \eta \nabla^2 \boldsymbol{v} - \varrho_q \boldsymbol{E} = 0$$

$$v_\zeta = \mu_\zeta |\boldsymbol{E}|$$

$$\mu_\zeta = \frac{\varepsilon \varepsilon_0 \zeta}{\eta}$$

3.7.2. Flow Profile

- Velocity field
  - Assumption: $v \sim E$
  - v-profile directly from Poisson
  - v-profile roughly follows potential ψ across capillary
    - Strong variation only near wall
      - Immobilized Stern layer: $v = 0$
      - V_{max} reached at shear layer
    - Flat profile in center at value $v = v_\zeta$
      - Plug-like shape

$$\nabla \cdot \boldsymbol{E} = \frac{1}{\varepsilon_0} \varrho_q(\boldsymbol{r}, t)$$

$$v = \mu_\zeta |\boldsymbol{E}| \left(1 - \frac{\psi(r)}{\zeta}\right)$$

$$\psi(0) = 0, \psi(r) \mapsto 0 \text{ at } r \gg r_D$$

- Dependency ψ / ζ mostly negligible

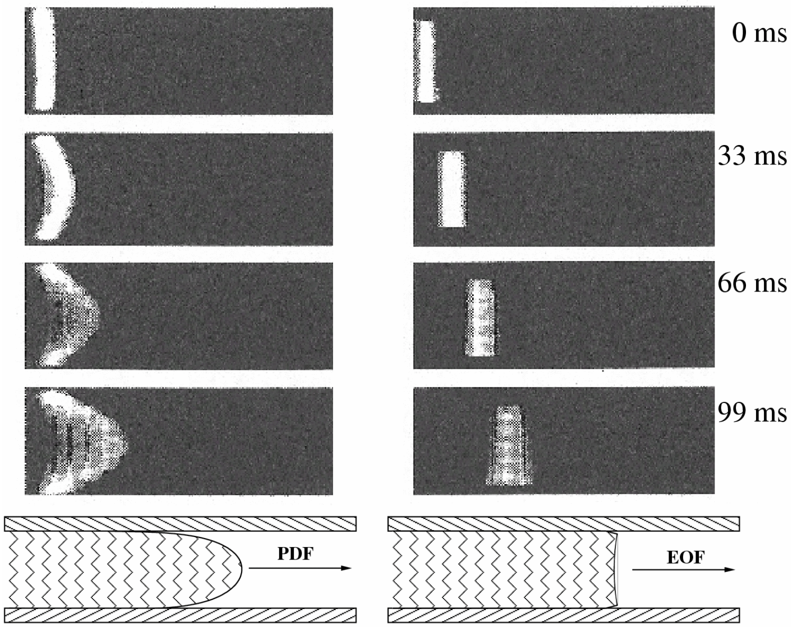


Fig. 3.42. Velocity profiles in pressure-driven and electroosmotic flow and experimental observations recorded in 33-ms time frames

3.7.2. Pressure Gradient

optional

- Pressure difference counteracting EOF
- Superposition of PDF and EOF profile
  - Cylindrical channel
    - Length l

$$v_z(r) = \frac{p}{4\eta l}(r_0^2 - r^2) - \frac{\varepsilon\varepsilon_0\zeta U}{\eta l}$$

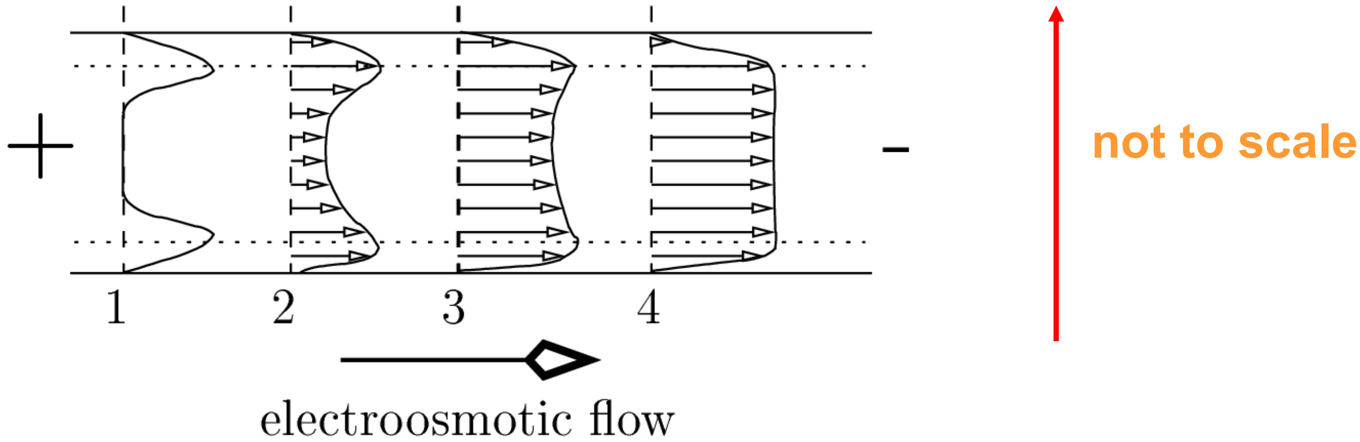
  - Parallel plates
    - Gap distance d

parabolic — flat

$$v_z(r) = \frac{p}{2\eta l}\left(\frac{d^2}{4} - y^2\right) - \frac{\varepsilon\varepsilon_0\zeta U}{\eta l}$$

3.7.2. Temporal Evolution of EOF

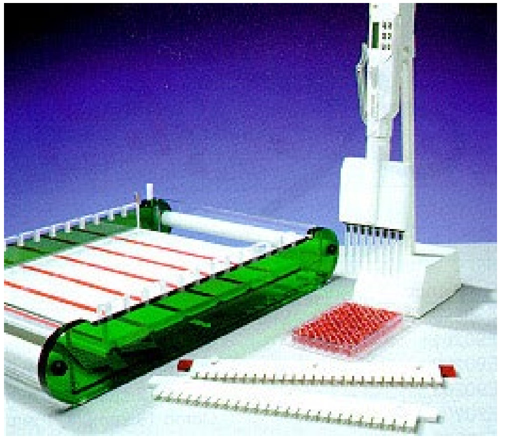
optional



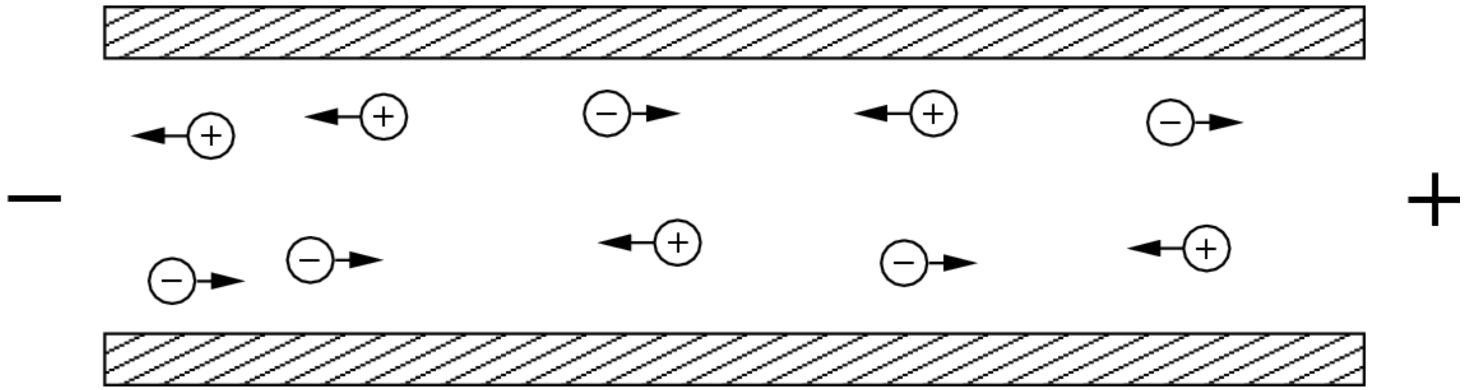
- No „dispersion“ of EOF plug
  - Broadening widely suppressed
- Charged layer pulled by electric field
  - Bulk liquid dragged along

3.7. Electrokinetics

1. Electric Double Layers
2. Electroosmotic Flow
3. **Electrophoresis**
4. Dielectrophoresis



3.7.3. Electrophoresis



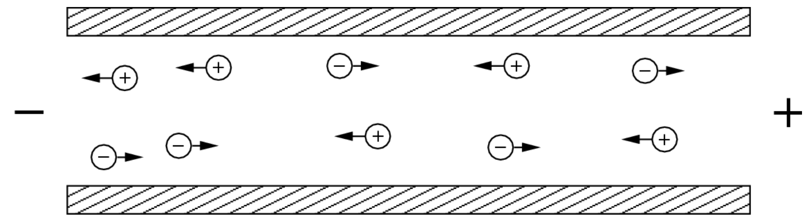
- Ionic mobility μ_i
  - Electric field strength $|\boldsymbol{E}|$
  - Velocity of ions v_i
- Electrophoresis
  - Method in analytical chemistry
  - Separation according to μ_i
- Kohlrausch‘s law
  - Limit of high dilution
  - Independent migration of ions

$$v_+ = \mu_+ |\boldsymbol{E}|$$
$$v_- = -\mu_- |\boldsymbol{E}|$$

$$\mu = \frac{e l_{\mathrm{mfp}}}{2 m v_T}$$

3.7.3. Electrophoresis

- Electrophoretic (ionic) mobility
  - ➢ Governed by charge-to-size ratio
  - ➢ Charge
    - Electric “pull” force
  - ➢ Size
    - Frictional drag with bulk molecules

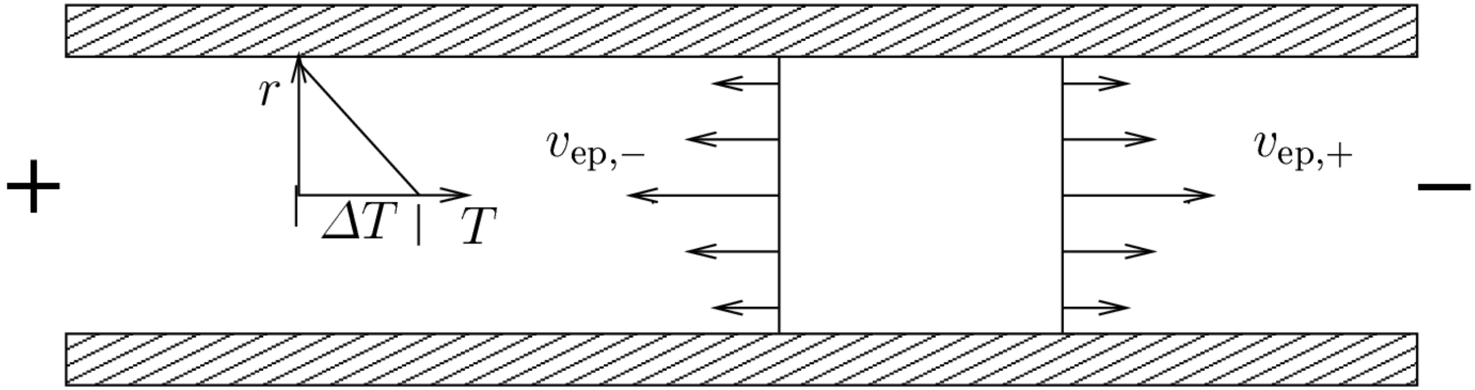


- Electrophoretic mobility μ_i
  - ➢ Molecular structure approximated by sphere
    - Radius r_i
    - Charge q_i
  - ➢ Stokes drag: $F_{\text{Stokes}} = q\,|\boldsymbol{E}|$
    - Balanced by electric field
  - ➢ Viscosity η
    - Background electrolyte

$$\mu_i = \frac{v_i}{|\boldsymbol{E}|} = \frac{q_i}{6\pi\eta r_i}$$

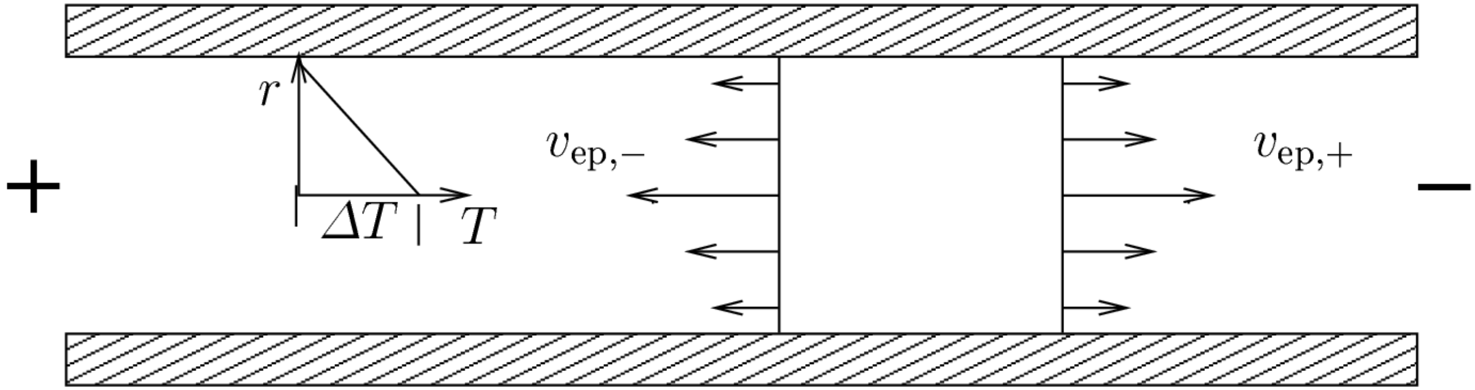
- Electrophoretic speed usually much smaller than EOF!

3.7.3. Joule Heating



- Speed of electrophoretic motion / separation
  - Grows with field strength $E = U / l$
- Electrolyte
  - Ohmic resistor
  - Dissipation of energy
  - Heating of liquid
  - Temperature gradient

3.7.3. Joule Heating



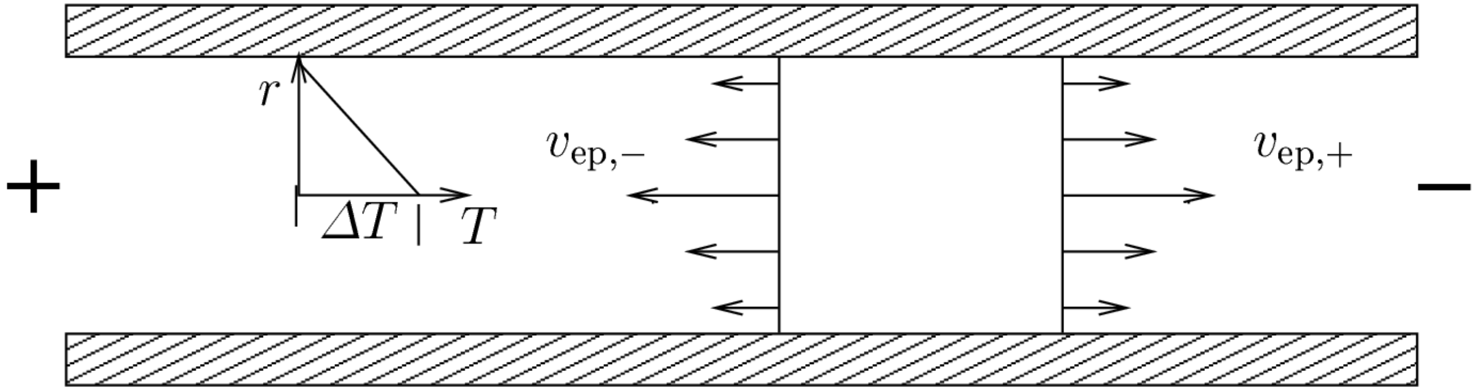
- Rate of heat generation P_Q

$$P_Q = \frac{\mathrm{d}E}{\mathrm{d}t} = \frac{U^2}{R} = \frac{\sigma_E A U^2}{l} = \sigma_E A l |\boldsymbol{E}|^2$$

  - Square of field strength $|\boldsymbol{E}|$
  - Capillary length l
- Temperature drop ΔT
  - Power of heat generation P_Q
  - Cylindrical capillary of **radius** r_{cap}

$$\Delta T \propto \frac{P_Q r_{cap}^2}{\lambda}$$

3.7.3. Joule Heating – Band Broadening

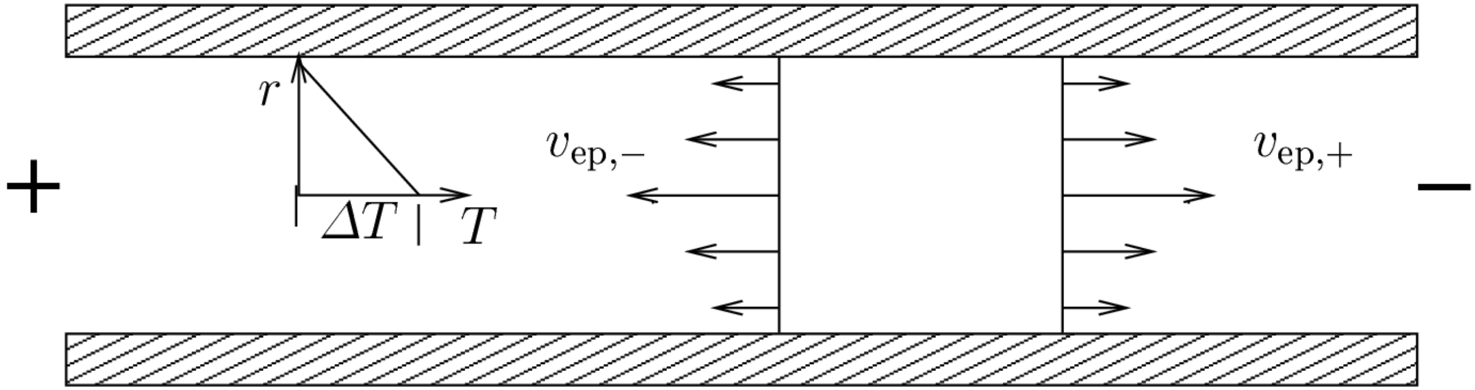


- Increased T in centre of channel
  - Slower dissipation of heat
- Enhanced EP mobility in hot areas
  - Viscosity η decreases with T
  - Effective ion radius r (hydration) shrinks
    - Approx. 2%-increase per Kelvin
  - Flow profile resembles PDF profile
    - Solutions

$$\eta = \frac{k_\mathrm{B} T}{a^3 \nu_0} \exp\left(\frac{E_0}{k_\mathrm{B} T}\right)$$

$$\mu_i = \frac{v_i}{|\boldsymbol{E}|} = \frac{q_i}{6\pi\eta r_i}$$

3.7.3. Joule Heating – Temperature Gradient



- Band broadening by buoyancy
  - Temperature gradient
  - Free convection

$$\Delta T \propto \frac{P_Q r_{\mathrm{cap}}^2}{\lambda}$$

- Counter measures
  - Small-diameter capillaries
    - Fast transport of heat from liquid to wall
  - Cooled walls

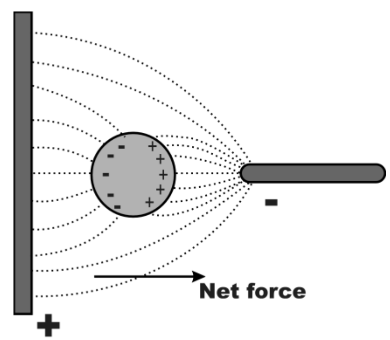
3.7. History of Electrokinetics

- Reuss in 1808
  - DC applied to clay-water mixture
  - First observation of electrokinetic (EK) effect
- Napier in 1846
  - Distinction between EO and EP
- Quincke in 1861
- Helmholtz in 1879
  - Analytical model
- Pellat (1904) and Smoluchowski (1921)
  - Extension of Helmholtz model to derive EK velocity
- Leo Casagrande (1941)
  - EK phenomena in porous media like soils

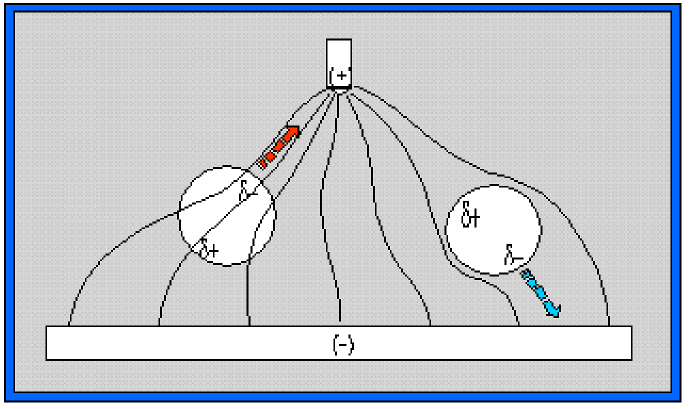
H. Helmholtz

3.7. Electrokinetics

1. Electric Double Layers
2. Electroosmotic Flow
3. Electrophoresis
4. **Dielectrophoresis**



Dielectrophoresis (DEP)



- Polarizable particles in non-uniform electric field
- Positive DEP
  - Particle more polarizable than surrounding medium
  - Attraction towards strong field at pin electrode
- Negative DEP
  - Particle of low polarizability
  - Repulsion away from strong field region

3.7.4. Dielectrophoresis

- Electric field E
  - Monopole force
    - Charge q
  - Dipole term
    - Electric dipole moment $\boldsymbol{p}_q = q\,\boldsymbol{r}$
    - Inhomogeneous field grad $\boldsymbol{E} \neq 0$

$$\boldsymbol{F}_E = [q + (\boldsymbol{p}_q \cdot \nabla)]\,\boldsymbol{E}$$

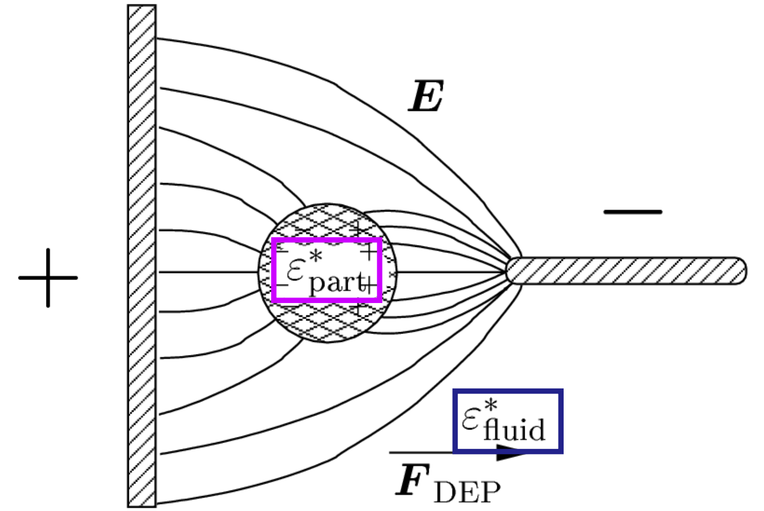
- AC dielectrophoretic (DEP) force F_{DEP}
  - Oscillating external field
  - Induced dipole moment
  - Phase lag
    - Particle motion
    - E-field

$$\boldsymbol{F}_{\mathrm{DEP}} = \frac{\mathrm{Re}[\boldsymbol{p}_q]}{2|\boldsymbol{E}|}\nabla\left(|\boldsymbol{E}|^2\right)$$

- Application in microfluidics
  - Separation / manipulation of large particles
    - Cells
    - Beads

3.7.4. Induced Dipole Moments

- Dielectric permittivity ε
  - Material
    - Particle $\varepsilon_{\text{part}}$
    - Surrounding medium $\varepsilon_{\text{fluid}}$
  - Frequency of external field $\boldsymbol{E}$: $\varepsilon = \varepsilon(\nu)$



- Example: Dipole moment $\boldsymbol{p}$ of sphere
  - Radius r_0
  - Clausius-Mossotti factor f_ε

$$\boldsymbol{p}_q(\nu) = 4\pi\varepsilon_0\varepsilon_{\text{fluid}} f_\varepsilon(\varepsilon^*_{\text{part}}, \varepsilon^*_{\text{fluid}}) r_0^3 \boldsymbol{E} = \alpha_\varepsilon(\nu)\boldsymbol{E}$$

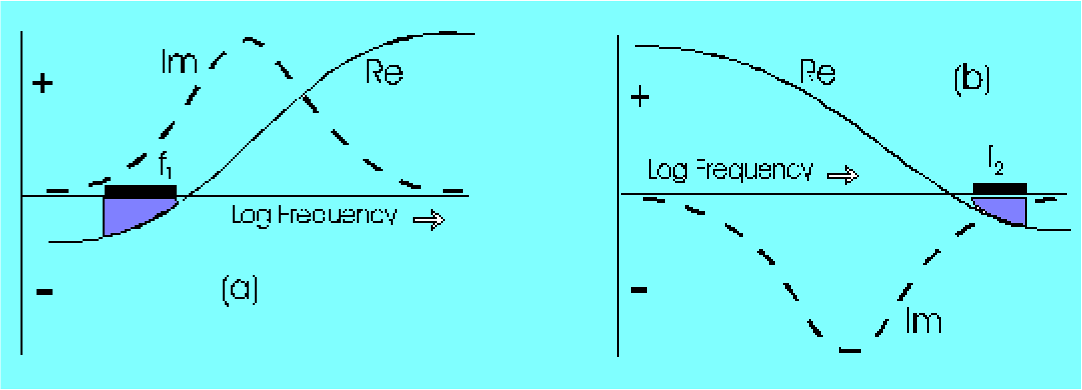
$$f_\varepsilon(\varepsilon^*_{\text{part}}(\nu), \varepsilon^*_{\text{fluid}}(\nu)) = \frac{\varepsilon^*_{\text{part}}(\nu) - \varepsilon^*_{\text{fluid}}(\nu)}{\varepsilon^*_{\text{part}}(\nu) + 2\varepsilon^*_{\text{fluid}}(\nu)}$$

  - Induced force

$$\boldsymbol{F}_{\text{DEP}} = 2\pi\varepsilon_0\varepsilon_{\text{fluid}} \text{Re}[f_\varepsilon(\varepsilon^*_{\text{part}}(\nu), \varepsilon^*_{\text{fluid}}(\nu))] r_0^3 \nabla\left(|\boldsymbol{E}|^2\right)$$

3.7.4. Induced Dipole Moments

optional

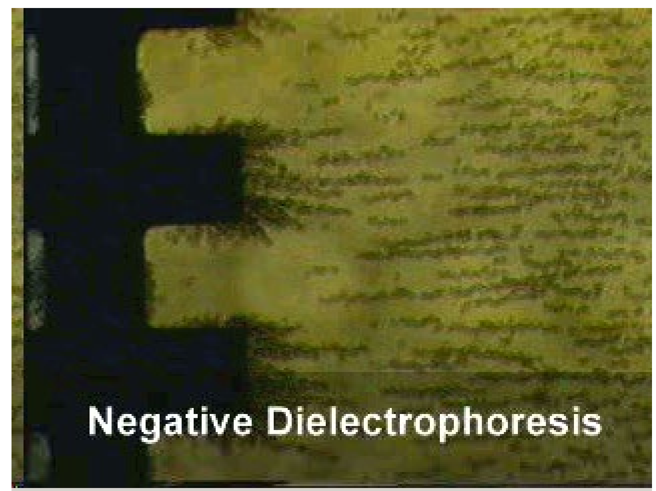


- Frequency dependence of real and imaginary components of induced dipole moment for model cases
  a) viable cell with intact membrane
  b) cell with a porous membrane
- Translational motion under influence of traveling fields can occur in frequency ranges f_1 and f_2

3.7.3. Positive & Negative DEP

optional

pdep



ndep

3.7.4. Cell Separation

optional

- Array of interdigitated electrodes
- Force depends on
  - Permittivities
  - RMS voltage U
  - Geometry / setup (inhomogeneous field)

$$F_{\mathrm{DEP}} = 1.5 V \varepsilon_{\mathrm{fluid}} \alpha_{\mathrm{DEP}}(\nu) U^2 \beta^2(\nu) A e^{-2\pi h/d}$$

  - Field-induced dielectrophoretic polarizability

$$\alpha_{\mathrm{DEP}} = \mathrm{Re}\left[\frac{\varepsilon^*_{\mathrm{cell}}(\nu) - \varepsilon^*_{\mathrm{fluid}}(\nu)}{3(\varepsilon^*_{\mathrm{cell}}(\nu) - \varepsilon^*_{\mathrm{fluid}}(\nu))A_i + 3\varepsilon^*_{\mathrm{fluid}}(\nu)}\right]$$

    - Eccentricity A_i
    - Permittivity of cell
      - Internal
      - Membrane

$$\varepsilon^*_{\mathrm{cell}} = \varepsilon^*_{\mathrm{mem}} \frac{\varepsilon^*_{\mathrm{mem}} + \frac{\varepsilon^*_{\mathrm{int}} - \varepsilon^*_{\mathrm{mem}}}{A_i + \hat{V}(1-A_i)}}{\varepsilon^*_{\mathrm{mem}} + \frac{\varepsilon^*_{\mathrm{int}} - \varepsilon^*_{\mathrm{mem}}}{A_i - \hat{V} A_i}}$$

3.7.4. Traveling-Wave DEP

optional

- Linear analogue of electrorotation
  - Linear arrangement of electrodes
  - 90° phase shift between electrodes

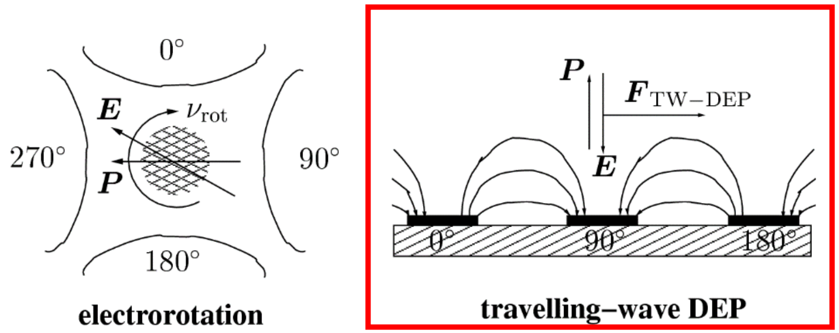


Fig. 3.47. Electrorotation (left) and travelling wave DEP (right)

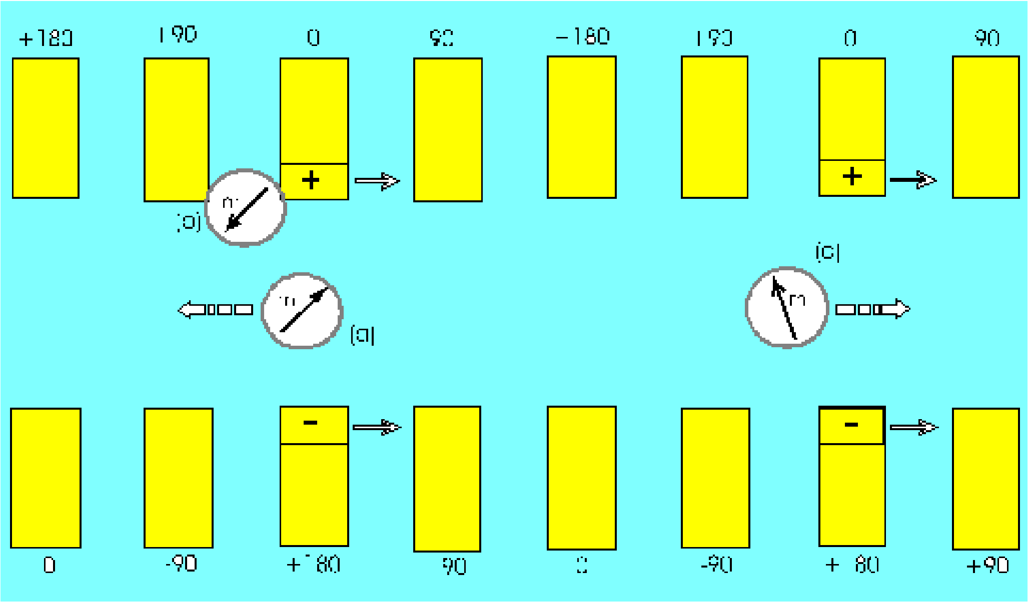
- Force on particle

$$\boldsymbol{F}_{\text{TW-DEP}} = -\frac{4\pi\varepsilon_0\varepsilon_{\text{fluid}}\varepsilon r_0^3 \operatorname{Im}[f_\varepsilon(\nu)]|\boldsymbol{E}|^2}{\lambda}$$

  - Wave length of traveling field λ

3.7.4. Traveling-Wave DEP

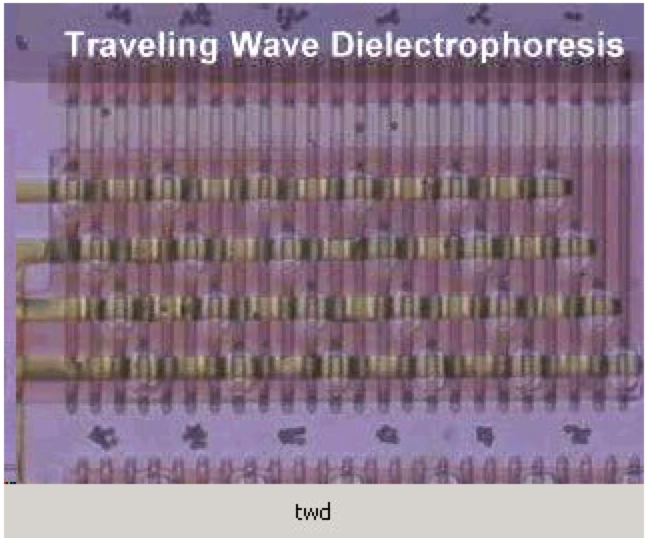
optional



- Produced by electrodes energized by cosine voltages of indicated phase relationships
  - a) Motion expected for viable cell (f_1 in Figure 2)
  - b) Cell trapped by positive dielectrophoresis
  - c) Motion of a non-viable cell

3.7.4. Traveling-Wave DEP

optional



3.7.4. Electrorotation

- DEP in rotating dipole field
  - Polarizable particle suspended in rotating field

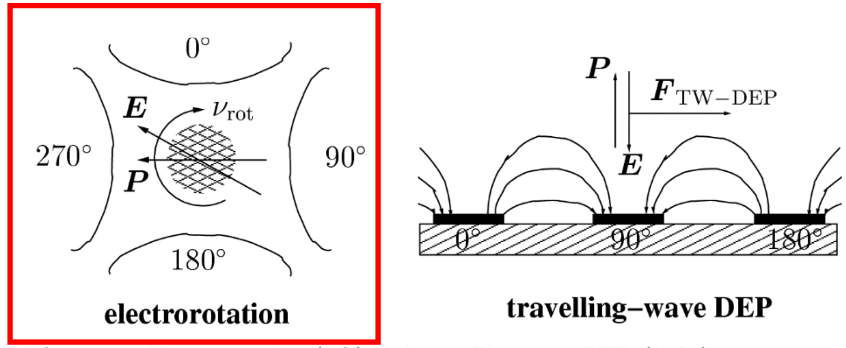


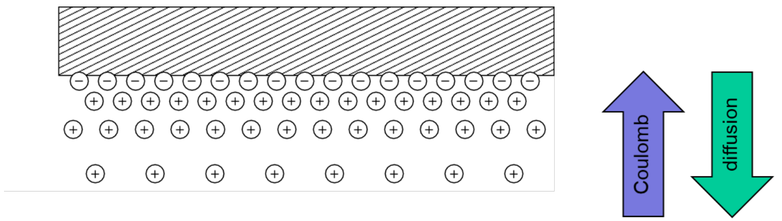
Fig. 3.47. Electrorotation (left) and travelling wave DEP (right)

- Torque on particle
  - Sufficient angular velocities
  - Rotation of dipole lags field
    - Frequency-dependent phase shift
  - Geometrical angle between ***E*** and $\boldsymbol{p}_q$

$$|\boldsymbol{\tau}] = -4\pi\varepsilon_0\varepsilon_{\text{fluid}}\varepsilon r_0^3 \,\mathrm{Im}[f_\varepsilon(\nu)]|\boldsymbol{E}|^2$$

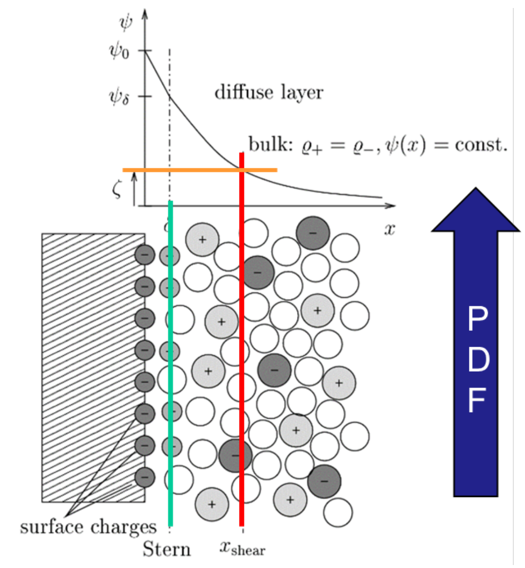
Summary

$$\mathrm{SiOH(s)} \rightleftharpoons \mathrm{SiO^-(s)} + \mathrm{H^+(aq)}$$



Zeta-potential & EOF

$$\zeta = \psi(x_{\text{shear}}) - \psi(x \mapsto \infty)$$



$$v_\zeta = \mu_\zeta |\boldsymbol{E}|$$

$$\mu_\zeta = \frac{\varepsilon\varepsilon_0\zeta}{\eta}$$

Electrophoretic mobility

$$\mu_i = \frac{v_i}{|\boldsymbol{E}|} = \frac{q_i}{6\pi\eta r_i}$$