Electrokinetic Phenomena in Micro- and Nanochannels

II. Transport of Fluid Relative to a Solid Wall in a Single Double Layer:

Electroosmosis and Electrophoresis and Electric Current

CBE/NE/BME 525

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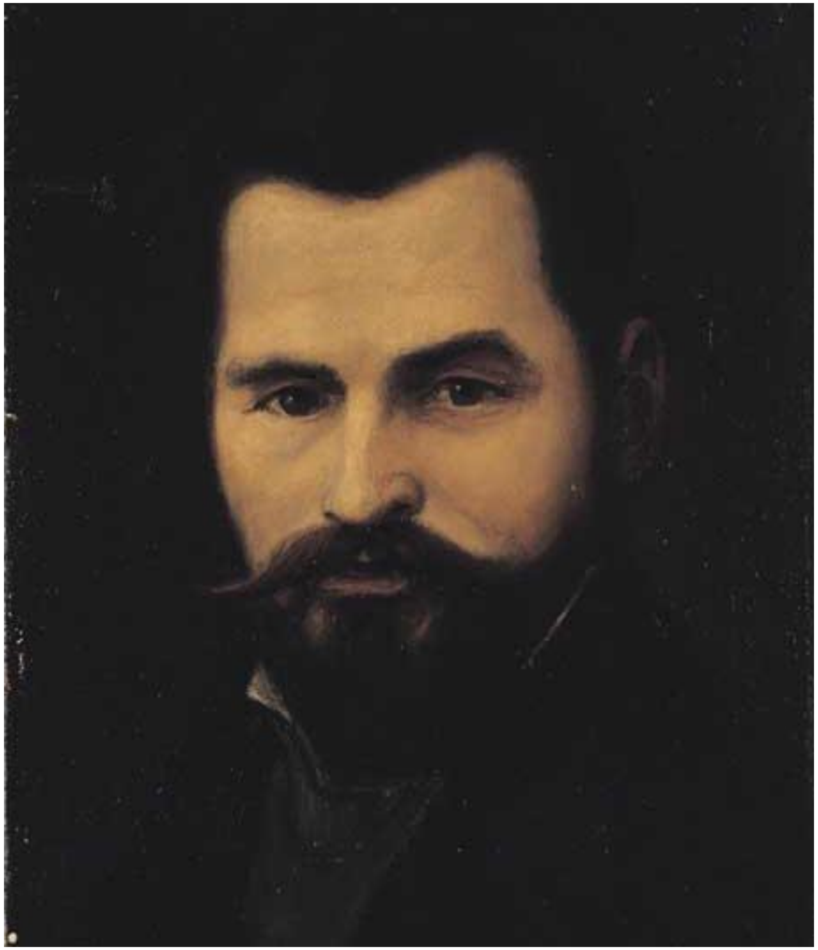
Outline

1. Fluid Flow in the Double Layer Driven by External Electric Field. Concept of Electroosmosis and Electrophoresis
2. Smoluchowski Theory. Thin Double Layer Approximation.
3. Huckel Theory for Electrophoresis: Thick Double Layer.
4. Henry Theory: Intermediate Case $\kappa R \sim 1$. Ohshima Approximation.
5. Current Transport
6. Double Layer Polarization and Relaxation.

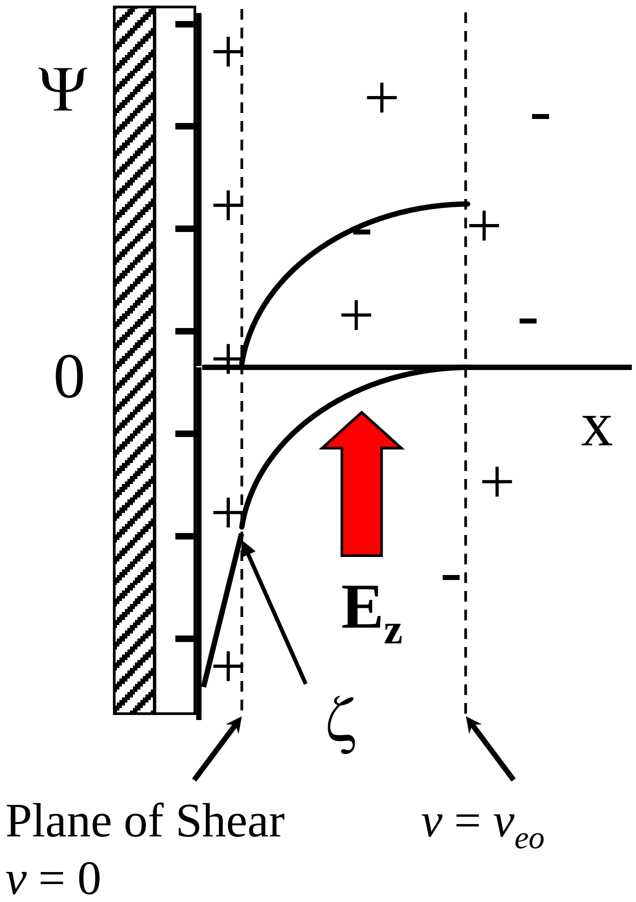
Electrokinetic Phenomena

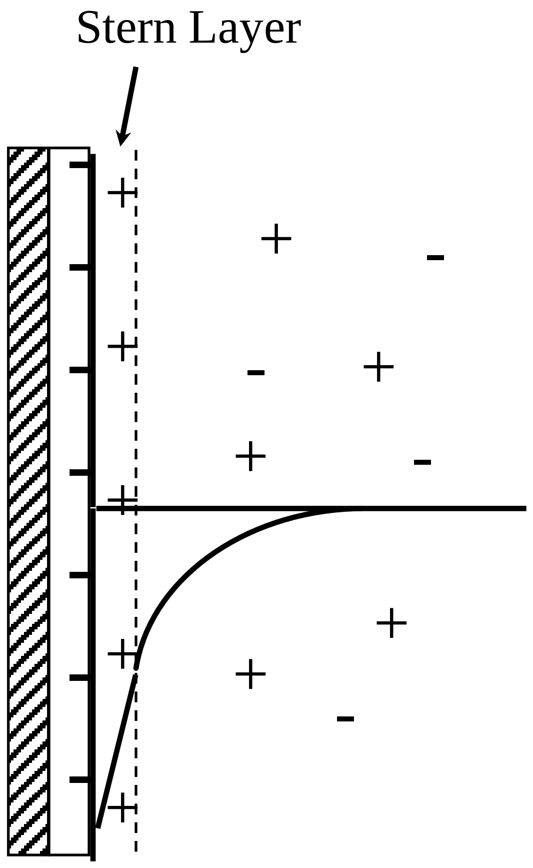


Marian Ritter von Smolan Smoluchowski

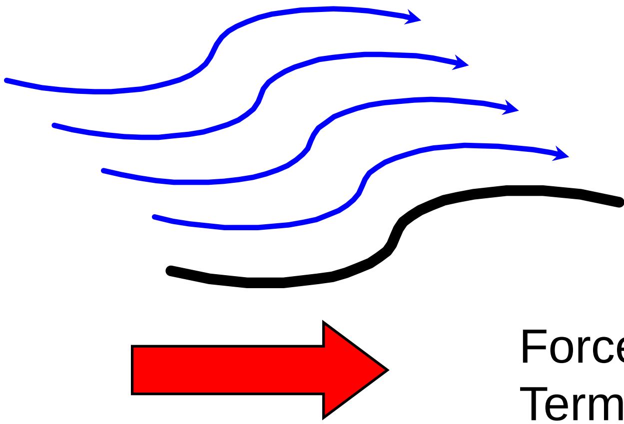
1872-1917

Solid Liquid Interface and Characteristic Lengths





Basic Equations and Force Balance



$\mathbf{E_z}$

Poisson Equation

$$\nabla\cdot\ \varepsilon\varepsilon_0\nabla\Psi\ = -\rho_e$$

ρ_e – charge density
$\varepsilon\varepsilon_0$–dielectric permitivity
Ψ – potential

Force balance: Stokes Equation with Body Force Term

$$\boxed{\nabla\cdot\ \eta\nabla\mathbf{v}\ = \rho\mathbf{E_z} = -\nabla\cdot\ \varepsilon\varepsilon_0\nabla\Psi\ \mathbf{E_z}}$$

If, ε and η (viscosity) are constants and $\mathbf{E_z}$ and Ψ are independent, then

$$\boxed{\eta\nabla^2\mathbf{v} = -\varepsilon\varepsilon_0\ \nabla^2\Psi\ \mathbf{E_z}\ \text{ or }\ \nabla\cdot\left[\eta\nabla\mathbf{v} + \varepsilon\varepsilon_0\ \nabla\Psi\ \mathbf{E_z}\right] = \mathbf{0}}$$

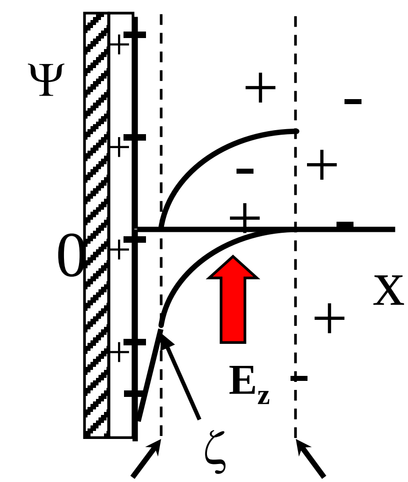
Boundary Conditions

$$\eta\nabla\mathbf{v}+\varepsilon\varepsilon_0\ \ \nabla\Psi\ \ \mathbf{E_z}=\mathbf{Const}$$ – tensor of the linear momentum flux

Far from the solid surface all gradients are zero, hence the momentum flux is also zero

$$\nabla\mathbf{v}=\mathbf{0}\ \text{ and } \nabla\Psi=\mathbf{0},\ \text{ hence } \ \nabla\ \ \eta\mathbf{v}+\varepsilon\varepsilon_0\Psi\mathbf{E_z}\ \ =\mathbf{0}$$

$$\eta\mathbf{v}+\varepsilon\varepsilon_0\Psi\mathbf{E_z}=\mathbf{B}=\mathbf{const},\ \text{ or } \ \mathbf{v}=\frac{1}{\eta}\ \ \mathbf{B}-\varepsilon\varepsilon_0\Psi\mathbf{E_z}$$



The constant vector $\mathbf{B}$ has to be determined using the boundary condition at the surface of shear where

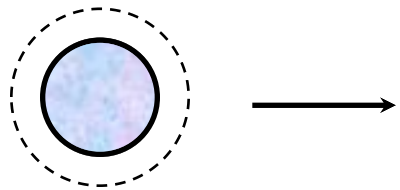
$\mathbf{v}=\mathbf{0},\ \ \Psi=\zeta$ Electrokinetic (ζ) potential

Hence $\mathbf{B}=\varepsilon\varepsilon_0\zeta\mathbf{E_z}$ and $\boxed{\mathbf{v}\ \ \mathbf{r}\ \ =\frac{\varepsilon\varepsilon_0\mathbf{E_z}}{\eta}\left[\zeta-\Psi\ \ \mathbf{r}\ \ \right]}$

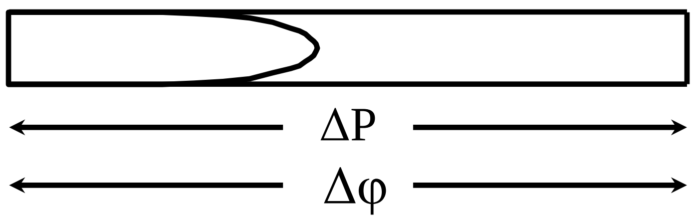
Types of Electrokinetic Phenomena

- Electroosmosis → Electroosmotic Pressure

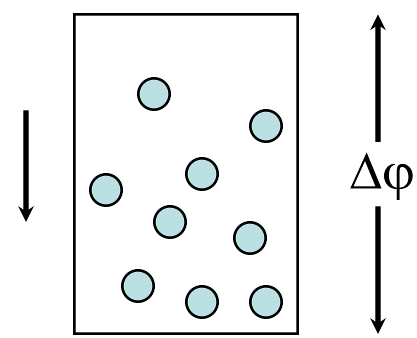
- Electrophoresis



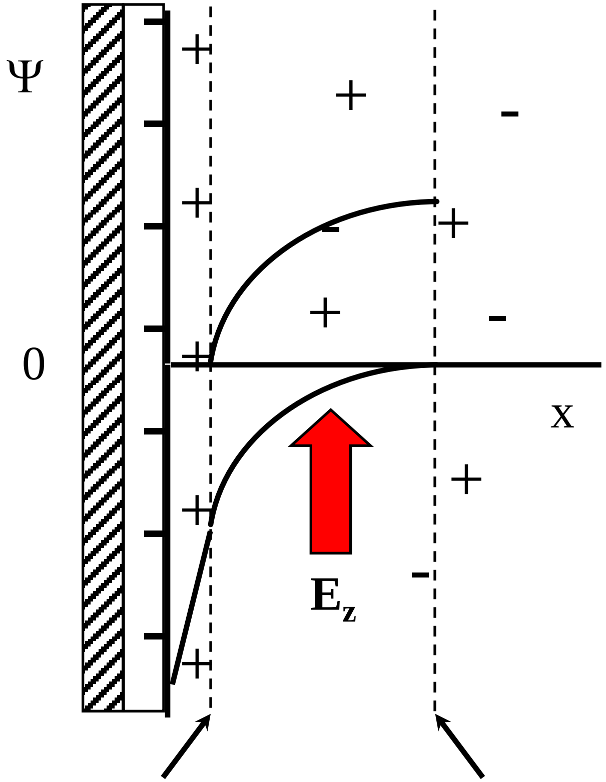
- Streaming Potential and Streaming Current



- Sedimentation Potential



Smoluchowski Theory for Electroosmosis



Plane of Shear
$v = 0$

$v = v_{eo}$

Force Balance

$$\eta \frac{d^2 v}{dx^2} = E_z \varepsilon \varepsilon_0 \frac{d^2 \Psi}{dx^2}$$

Boundary Conditions:

Far from the surface (in the bulk)

$$\frac{d\Psi}{dx} = \frac{dv_z}{dx} = 0,\ v_z = v_{eo},\ \Psi = 0$$

At the plane of shear

$$v_z = 0,\ \Psi = \zeta$$

$$\int_{\frac{dv}{dx}}^{0} d\,\frac{dv}{dx} = \frac{E_z \varepsilon \varepsilon_0}{\eta} \int_{\frac{d\Psi}{dx}}^{0} d\,\frac{d\Psi}{dx} \quad \Rightarrow \quad \frac{dv}{dx} = \frac{E_z \varepsilon \varepsilon_0}{\eta} \frac{d\Psi}{dx}$$

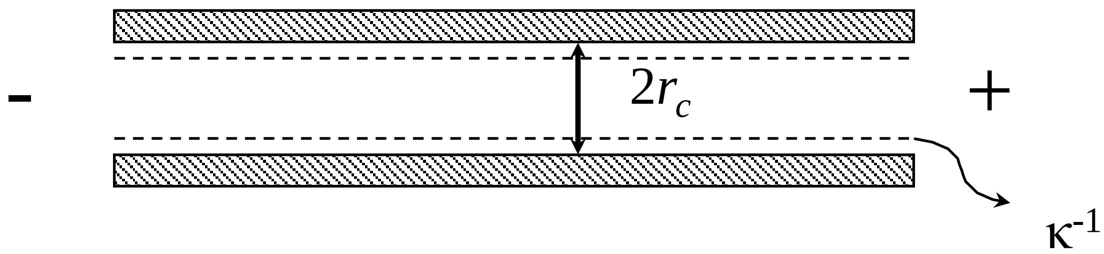
$$\int_{0}^{v_{eo}} dv = \frac{E_z \varepsilon \varepsilon_0}{\eta} \int_{\zeta}^{0} d\Psi \quad \Rightarrow \quad v_{eo} = -\frac{\varepsilon \varepsilon_0 \zeta}{\eta} E_z$$

Electroosmotic Velocity

$$\boxed{v_{\mathrm{eo}} = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}E_z}$$

M. von Smoluchowski

Exact for flat single double layers. In all other cases it is an approximation, valid for thin double layers when they can be considered locally flat.

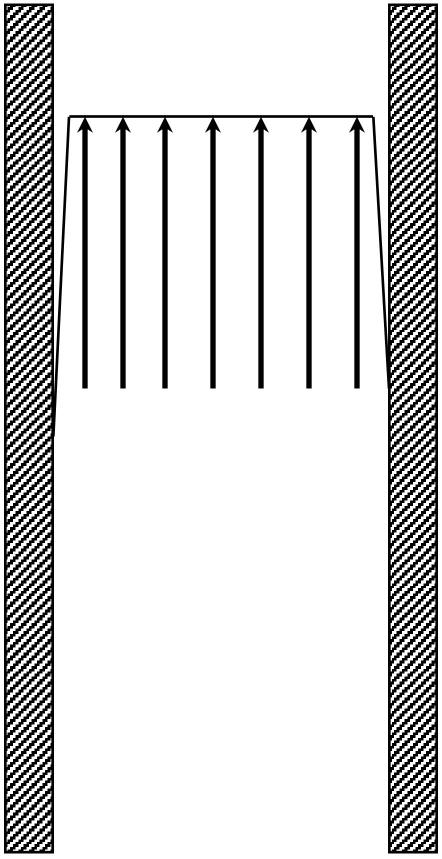


$\kappa r_{\mathrm{c}} >> 1$

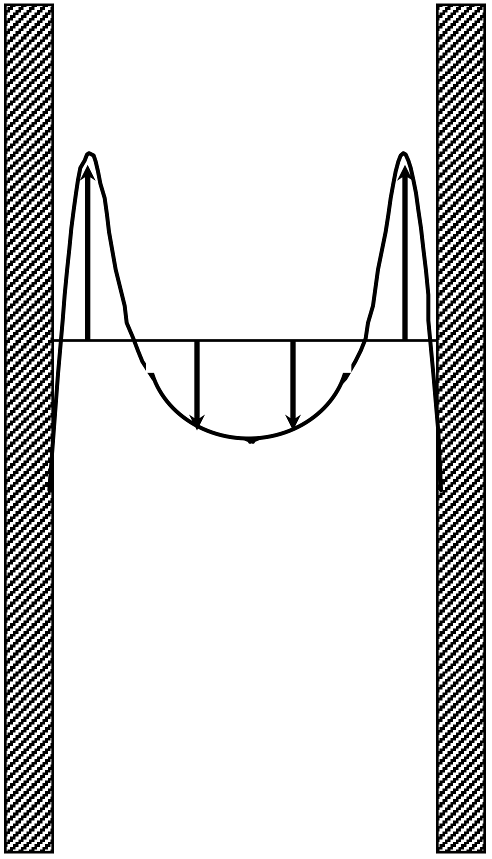
$$\boxed{\frac{v_{\mathrm{eo}}}{E_z} = \mu_{\mathrm{e}}}$$

Electroosmotic mobility

Types of EO Cells



Open cell – Plug Flow



Closed cell – Back Flow

Open Cell

Bulk fluid transport

$\kappa r_c >> 1$

$$V = 2\pi \int_0^R v_{eo} r dr = \pi R^2 v_{eo} = \pm \pi R^2 \frac{\varepsilon \varepsilon_0 \zeta}{\eta} E_z$$

Electric current (no surface conductivity)

$$I = \pi r_c^2 \lambda_0 E$$

K_0 – specific bulk conductivity

$$\boxed{\frac{V}{I} = \frac{\varepsilon \varepsilon_0 \zeta}{\eta K_0}}$$

– important ratio, depends only on the material constants

Surface Conductivity Contribution

$$\frac{I}{E_z} = \pi r_c^2 K_0 + 2\pi r_c K_s$$

K_s – surface conductivity

Surface conductivity is important at low electrolyte concentrations and for narrow channels and capillaries

$$\frac{V}{I} = \frac{\varepsilon\varepsilon_0\zeta}{\eta\left(K_0 + \frac{2}{r_c}K_s\right)}$$

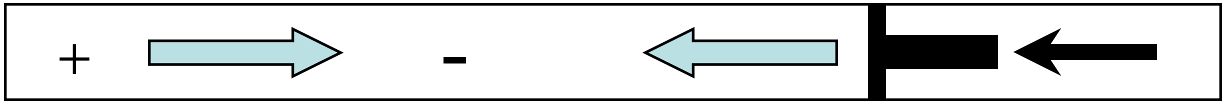
– this ratio depends on r_c

For arbitrarily shaped capillaries

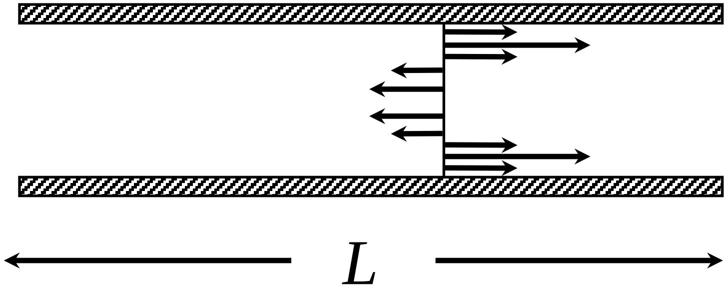
$$K_0 + \frac{2}{r_c}K_s \rightarrow K_0 + fK_s$$

f – form factor

Closed Cell



Pressure balance



Flow balance

$$U = \frac{\pi R^4 \Delta p}{8\eta l}, \quad U = \frac{\pi R^2 \varepsilon\varepsilon_0 \zeta E_z}{\eta}, \quad \frac{I}{E_z} = \pi R^2 K_0$$

$$\frac{\pi R^4 \Delta p}{8\eta l} = \frac{\pi R^2 \varepsilon\varepsilon_0 \zeta E}{\eta} = \frac{\varepsilon\varepsilon_0 \zeta I}{\eta K_0},$$

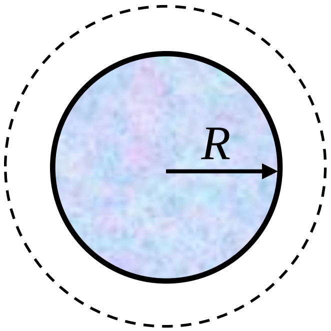
Pressure drop

$$\frac{\Delta p}{l} = \frac{8\varepsilon\varepsilon_0 \zeta E}{R^2} = \frac{8\varepsilon\varepsilon_0 \zeta}{\pi R^4 K_0} I$$

Important: $\Delta p/l \sim I$

The surface conductance is ignored.

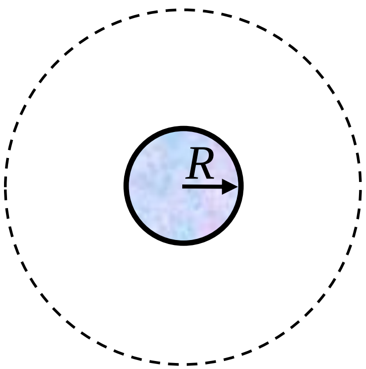
Electrophoresis



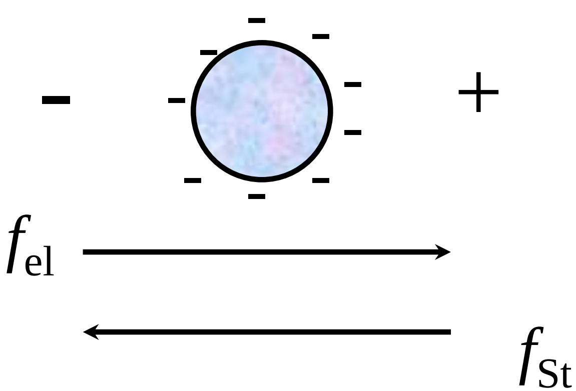
Smoluchowski, $\kappa R >> 1$. Shape is unimportant.

$$\boxed{\frac{v_{\mathrm{ep}}}{E_z} = \mu_{\mathrm{ep}} = \frac{\varepsilon\varepsilon_0\zeta}{\eta}}$$

Same as μ_{eo} but with opposite sign



Huckel, $\kappa R << 1$.



$f_{\mathrm{el}} = QE_z$ electric force

$f_{\mathrm{St}} = 6\pi\eta R v_{\mathrm{ep}}$ friction force

Q – particle charge

Electrophoresis

Force balance

$$QE_z = 6\pi\eta R v_{\mathrm{ep}}$$

Electrophoretic Mobility

$$\frac{v_{\mathrm{ep}}}{E_z} = \mu_{\mathrm{ep}} = \frac{Q}{6\pi\eta R}$$

Linear electrostatic theory

$$Q = 4\pi\varepsilon\varepsilon_0 R\zeta\ 1+\kappa R$$

$$\mu_{\mathrm{ep}} = \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta}\ 1+\kappa R \ \xrightarrow[\kappa R\to 0]{} \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta}$$

Intermediate Case

Henry

$$\boxed{\mu_{ep} = \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta} f_1(\kappa a)}$$

$\kappa R \sim 1$

$\kappa R < 100$

$$f_1(\kappa R) = 1 + \frac{(\kappa R)^2}{16} - \frac{5(\kappa R)^3}{48} - \frac{(\kappa R)^4}{96} + \frac{(\kappa R)^5}{96} - \left[\frac{(\kappa R)^4}{8} - \frac{(\kappa R)^6}{96}\right]\exp(\kappa R)\int_{\infty}^{\kappa R}\frac{\exp(-t)}{t}dt$$

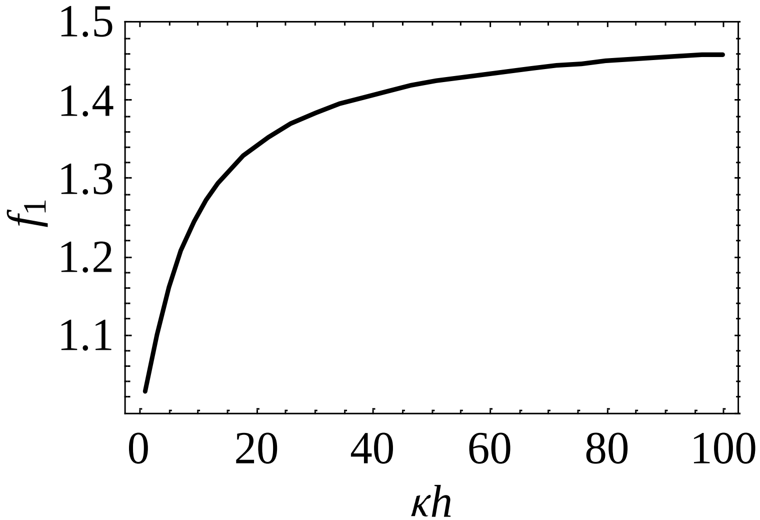
Far Asymptotics
$\kappa R > 100$

$$f_1(\kappa R) = \frac{3}{2} - \frac{9}{2\kappa R} + \frac{75}{2(\kappa R)^2} - \frac{330}{(\kappa R)^3}$$

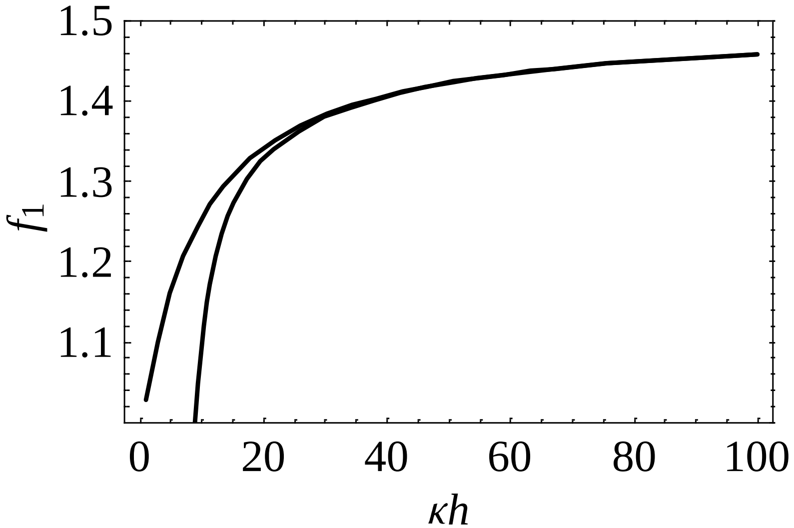
Ohshima

$$f_1(\kappa R) = 1 + \frac{1}{2\left[1 + \frac{5}{2\kappa R\left(1 + 2e^{-\kappa R}\right)}\right]^3}$$

Comparison



1.5
1.4
1.3
1.2
1.1
f_1
0
20
40
60
80
100
κh



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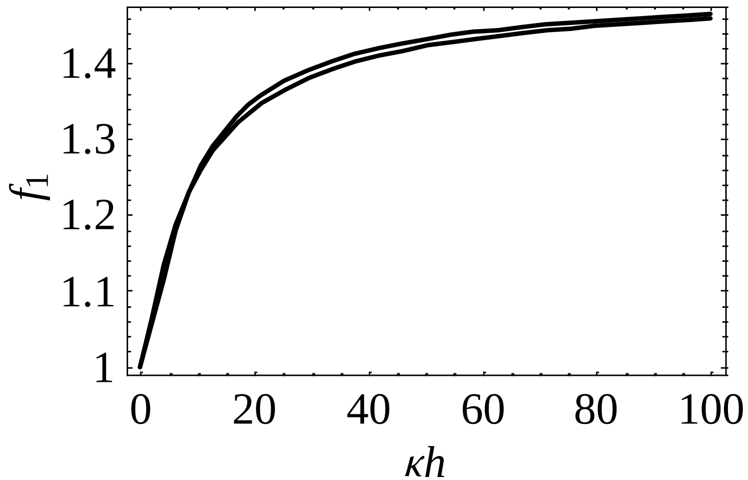


1.4
1.3
1.2
1.1
1
f_1
0
20
40
60
80
100
κh

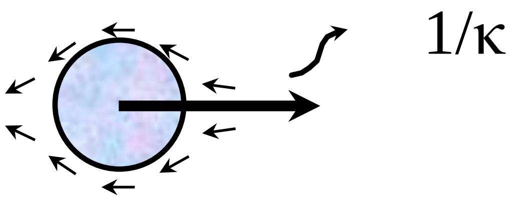
Comparison between the Two Approaches

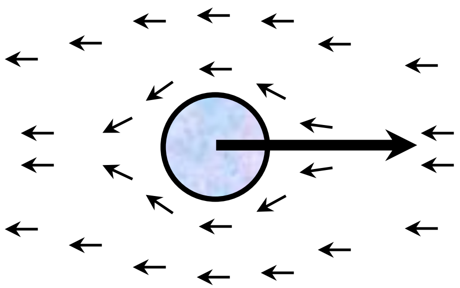
Smoluchowski: the applied field is uniform everywhere and parallel to the particle surface

Huckel: the particle has no effect on the applied field

Two types of opposing forces to the particle motion

- retardation (Smoluchowski, $\kappa R >> 1$)
- viscous friction (Huckel, $\kappa R << 1$)

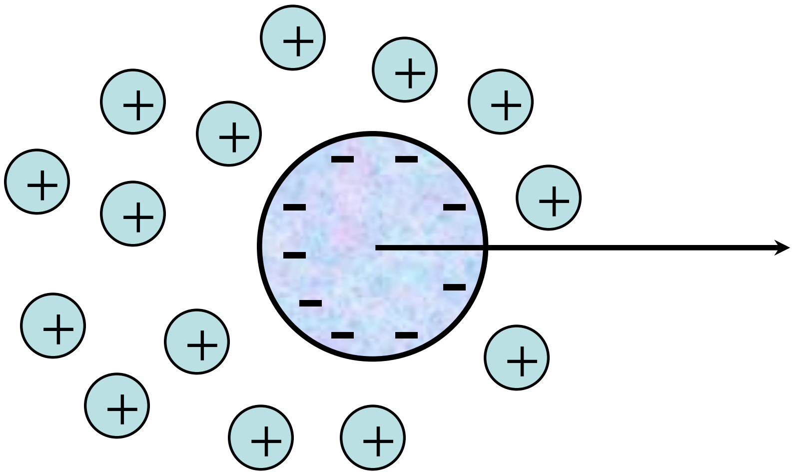




$$\frac{f_{\text{retardation}}}{f_{\text{friction}}} \sim \kappa R$$

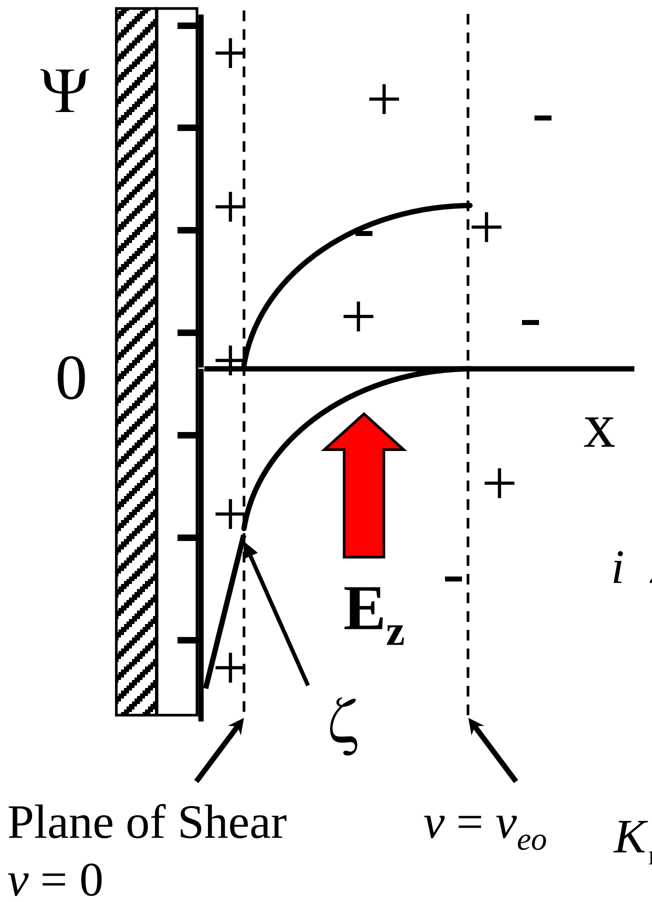
Other Possible Complications

- particle and surface conductance
- electrophoresis of droplets (interfacial mobility)
- relaxation effects, $\kappa R \sim 1$



- Electrophoresis
- Brownian motion
- Primary electrviscous effect

Transport of Current in a Single Flat Double Layer: Theory of Bikerman



Total current in a single double layer

$$I_{\text{tot}} = L\int_0^\infty i(x)\,dx$$

$$i(x) = \underbrace{K_{\text{mig}}(x)}_{\text{Migration}} - \underbrace{\frac{\rho_{\text{e}}\varepsilon\varepsilon_0\left[\zeta - \Psi(x)\right]}{\eta}}_{\text{EO Convection}}, \quad \rho_{\text{e}} = e\sum_i z_i n_i^0 \exp\left(-\frac{z_i e\Psi}{kT}\right)$$

$$K_{\text{mig}}(x) = \frac{e^2}{kT}\left(z_1^2 D_1 n_1^0 \exp\left[-z_i\tilde{\Psi}(x)\right] + z_2^2 D_2 n_2^0 \exp\left[-z_i\tilde{\Psi}(x)\right]\right)$$

Double Layer Contribution to the Conductivity

Far from the Double Layer

(Bulk)

$$I_\mathrm{b} = \frac{e^2 z_1 z_2 n_0}{kT} \; z_1 D_1 + z_2 D_2 \; LE$$

$$z_1 n_1^0 = z_2 n_2^0 \quad \Rightarrow \quad \frac{n_1^0}{z_1} = \frac{n_2^0}{z_2} = n_0$$

The contribution form the Double Layer only will be

$$I_\mathrm{tot} - I_\mathrm{b} = LE \left\{ \frac{e^2}{kT} \; z_1^2 D_1 \int_0^\infty \left[n_1 \; x \; - n_1^0 \right] dx + z_2^2 D_2 \int_0^\infty \left[n_2 \; x \; - n_2^0 \right] dx \; + \right.$$

$$\left. \frac{\varepsilon \varepsilon_0}{\eta} \int_0^\infty \rho_\mathrm{e} \; x \; \left[\zeta - \Psi \; x \; \right] dx \right\}$$

Surface Conductivity

Symmetric *z*:*z* electrolyte

Integration variable substitution

$$dx = -\frac{d\tilde{\Psi}}{2\kappa \sinh\left(\frac{\tilde{\Psi}}{2}\right)}$$

$$K_s = \frac{e^2 z^2 n_0}{kT\kappa}\left[D_1 \int_0^{\tilde{\zeta}} \frac{\exp\left(-\tilde{\Psi}\right) - 1}{2\sinh\left(\tilde{\Psi}/2\right)} d\tilde{\Psi} + D_2 \int_0^{\tilde{\zeta}} \frac{\exp\left(\tilde{\Psi}\right) - 1}{2\sinh\left(\tilde{\Psi}/2\right)} d\tilde{\Psi} + \right.$$

$$\left. \frac{\varepsilon\varepsilon_0}{\eta}\frac{kT}{ze}\int_0^{\tilde{\zeta}} \frac{\left[\exp\left(\tilde{\Psi}\right) - \exp\left(-\tilde{\Psi}\right)\right]\left(\tilde{\zeta} - \tilde{\Psi}\right)}{2\sinh\left(\tilde{\Psi}/2\right)} d\tilde{\Psi} \right]$$

Bikerman Formula for z = 1

$$K_s = \frac{2e^2 n_0}{kT\kappa}\left\{D_1\left[\exp\left(-\frac{\tilde{\zeta}}{2}\right)-1\right] 1+3m_1 \; + D_2\left[\exp\left(\frac{\tilde{\zeta}}{2}\right)-1\right] 1+3m_2 \;\right\}$$

$$m_{1,2} = \left(\frac{kT}{e}\right)^2 \frac{\varepsilon\varepsilon_0}{6\pi\eta D_{1,2}}$$

For KCl $\quad m_{1,2} = 0.186$

Summary

1. The fluid flow velocity profile in the double layer follows the shape of the potential distribution for straight channels and capillaries.
2. Smoluchowski method is valid for particles/channels much larger than the double layer thickness. The shape of the particle is unimportant.
3. Huckel theory is valid for spherical particles that are much smaller than the double layer thickness.
4. In the intermediate region one can use Henry or Ohshima expressions.
5. Theory of Bikerman for the current transport in the double layer.