STREAMING POTENTIAL AND STREAMING CURRENT OF A PARTICLE COVERED SURFACE

Part 1

Krzysztof Sadlej

ZMiFP IPPT PAN

OVERVIEW

- Introduction
- Electrical Double Layer (EDL)
- *Gouy-Chapman-Stern* model
- Electrokinetics
  - Electro-osmosis
  - Electrophoresis
  - Streaming current/Streaming potential
- Measuring the Streaming Potential
- Particles adsorbed at the interface – what changes?

INSPIRERS, CO-WORKERS

- Prof. Zbigniew Adamczyk (IKiFP PAN)

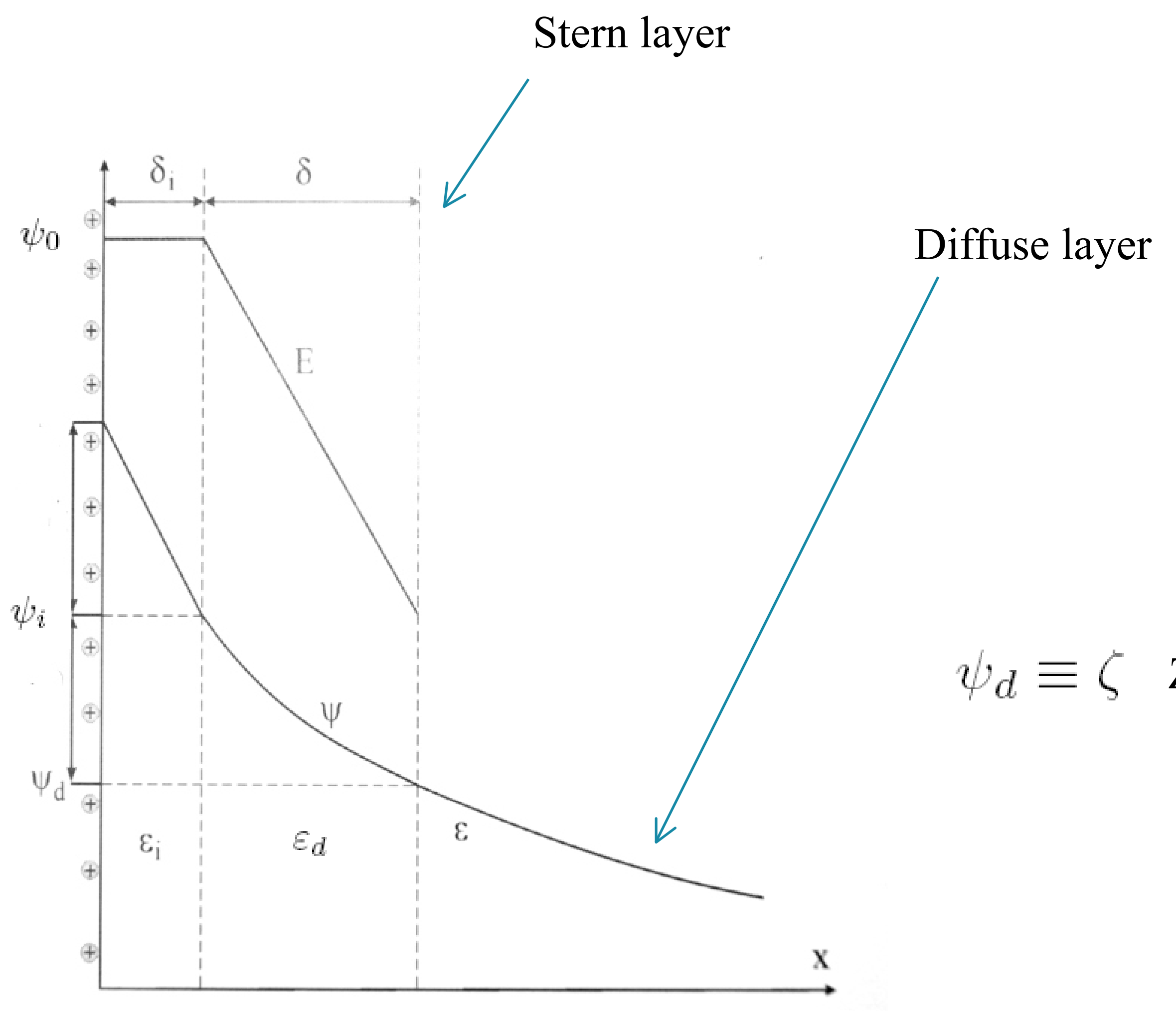
- Eligiusz Wajnryb (IPPT PAN)
- Maria Ekiel-Jeżewska (IPPT PAN)
- Jerzy Bławzdziewicz (Yale University)

INTRODUCTION

- Charge…

Surface charge [C m^{-2}]	a=10^{-6} m		a=10^{-4} m	
	ψ[V]	E[V m^{-1}]	ψ[V]	E[V m^{-1}]
0.16	1.8×10^4	1.8×10^{10}	1.8×10^6	1.8×10^{10}
	2.31×10^2	2.31×10^8	2.31×10^4	2.31×10^8
1.6×10^{-3}	1.8×10^2	1.8×10^8	1.8×10^4	1.8×10^8
	2.31	2.31×10^6	2.31×10^2	2.31×10^6

ELECTRICAL DOUBLE LAYER (EDL)



$\psi_d \equiv \zeta$ Zeta-potential

GOUY-CHAPMAN-STERN MODEL

$$\nabla \cdot (\varepsilon \nabla \psi) = -\rho$$

$$\rho = \sum_i n_i z_i e$$

Bulk concentration of ions

Concentration of ions

$$n_i = n_i^0 \exp(-w_i/kT)$$

$$w_i = z_i e \psi$$

Poisson-Boltzmann equation:

$$\nabla^2 \psi = -\frac{1}{\varepsilon} \sum_i n_i^0 z_i e \exp(-z_i e \psi / kT)$$

GOUY-CHAPMAN-STERN MODEL

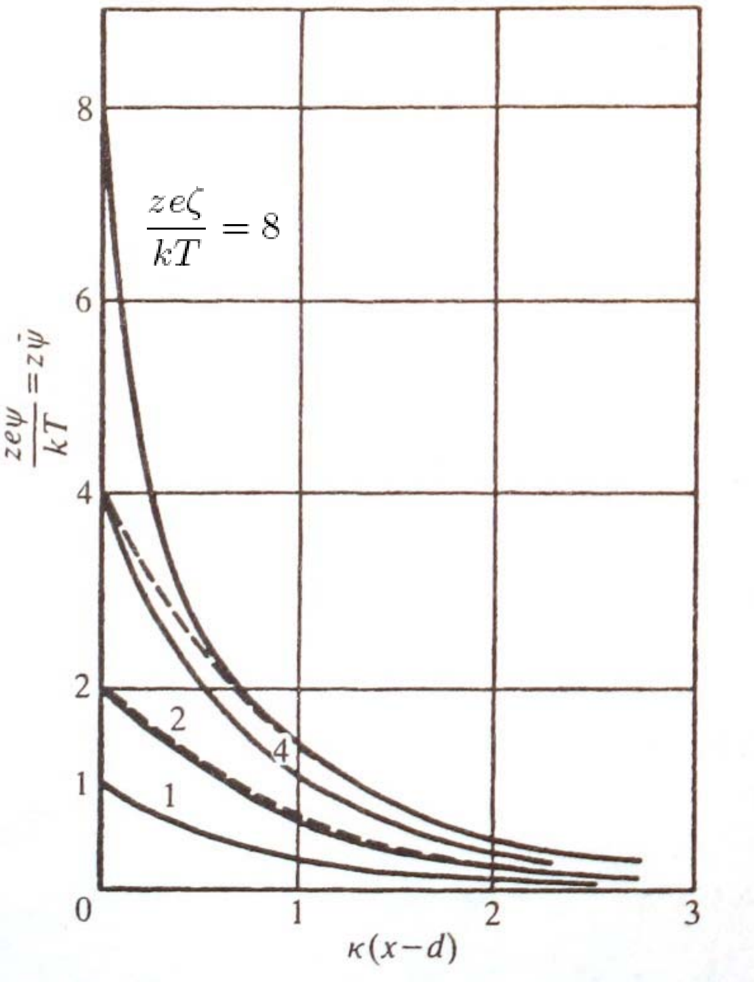
- Solution method od the Poisson-Boltzmann eq.
  - Debye-Hückel approx. Works only for $|z_i e\psi| \ll kT$
  - Gouy-Chapman model:
    - Flat surface
    - Symmetric electrolite $z_i = z_+ = z_- = z$

$$\frac{d^2\psi}{dx^2} = \frac{2n^0 ze}{\varepsilon} \sinh \frac{ze\psi}{kT}$$

$$\tanh(ze\psi/4kT) = \tanh(ze\zeta/4kT)\exp[-\kappa(x-d)]$$

Debye-Hückel parameter $\kappa = \sqrt{\frac{2z^2e^2n^0}{\varepsilon kT}}$

GOUY-CHAPMAN-STERN MODEL



$$\frac{ze\psi}{kT} \ll 1$$

$$\tanh(ze\psi/4kT) \simeq ze\psi/4kT$$

$$\psi = \zeta \exp[-\kappa(x-d)]$$

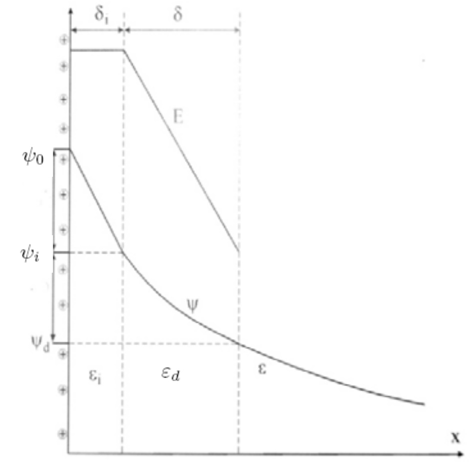
GOUY-CHAPMAN-STERN MODEL

- Diffuse layer charge

$$\sigma_d = \int_d^\infty \rho dx \quad \Rightarrow \quad \sigma_d = -\frac{4n^0 ze}{\kappa} \sinh \frac{ze\zeta}{2kT}$$

- Adsorbed charge in the inner region (Stern layer, Stern 1924, Graham 1947)
    - No charge within the layer of thickness δ_i

$$\nabla \cdot (\varepsilon_i \nabla \psi) = 0 \qquad \Delta\psi^0 = \frac{\sigma_0 \delta_i}{\varepsilon_i}$$



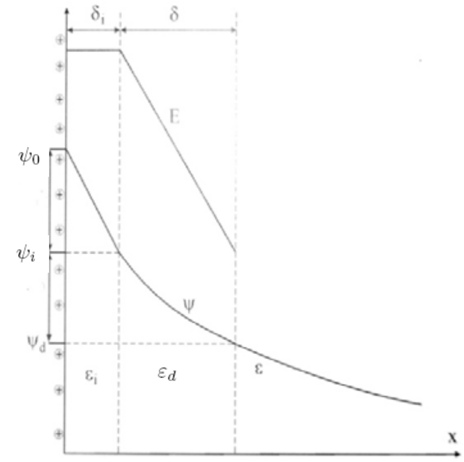
GOUY-CHAPMAN-STERN MODEL

- What is the charge distribution in the layer δ?
  - Uniform space charge distribution, distant-dependent permittivity

Or

  - All ions are assumed to be confined to a layer and are treated as point charges.

$$
\begin{aligned}
\psi_0 - \psi_i &= \sigma_0 \delta_i / \varepsilon_i \\
\psi_i - \psi_d &= -\sigma_d \delta / \varepsilon_d
\end{aligned}
$$



ELECTRO-OSMOSIS

- Motion of liquid induced by an applied electric field

$$\begin{aligned} \eta \nabla^2 \boldsymbol{v} - \nabla p &= -\rho_e \boldsymbol{E} \\ \nabla \cdot \boldsymbol{v} &= 0 \end{aligned}$$

Stokes equations

$$\boldsymbol{F} = \rho_e \boldsymbol{E} = -\varepsilon_0 \varepsilon_r \nabla^2 \psi \boldsymbol{E}$$

Slip velocity

$$v = \varepsilon_0 \varepsilon_r (\psi - \zeta) E / \eta$$

Smoluchowski 1903

ELECTROPHORESIS

- Motion of suspended particles in an applied electric field

$$\boldsymbol{v} = \mu_E \boldsymbol{E}$$

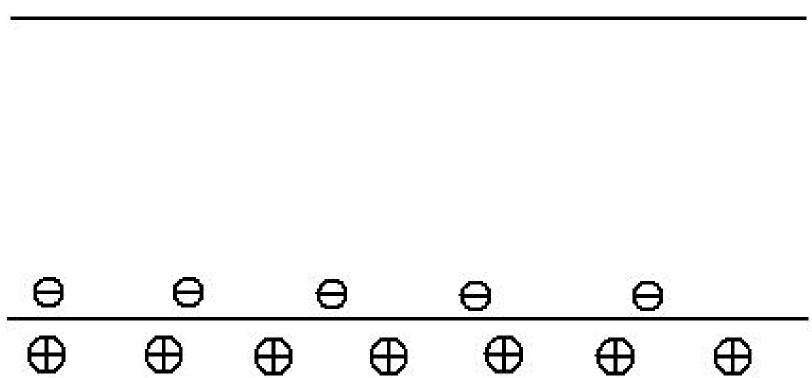
Electrophoretic mobility

$$\mu_E = \varepsilon_0 \varepsilon_r \zeta / \eta$$

Smoluchowski 1921

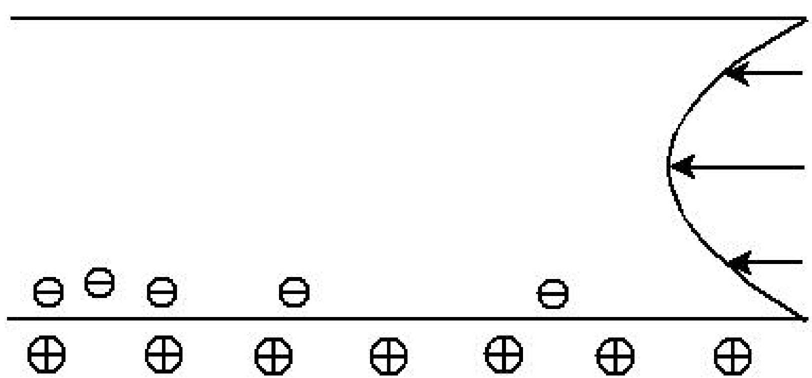
STREAMING CURRENT AND STREAMING POTENTIAL

- Current appearing due to double-layer charge movement with the fluid
- Transfer of charge downstream (due to pressure gradient) is balanced by current due to electric field
- Potential drop associated with this field: STREAMING POTENTIAL



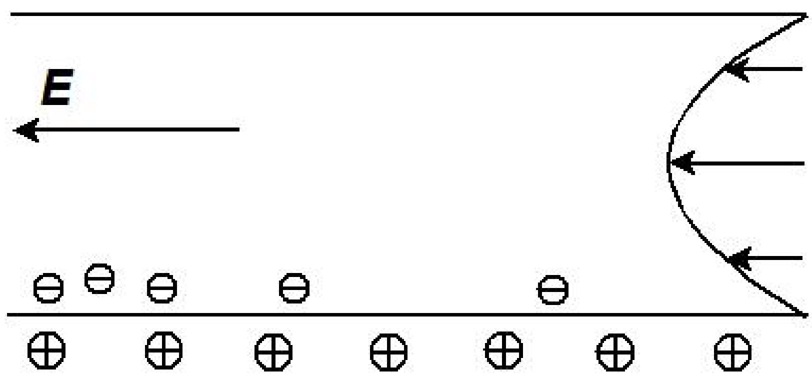
STREAMING CURRENT AND STREAMING POTENTIAL

- Current appearing due to double-layer charge movement with the fluid
- Transfer of charge downstream (due to pressure gradient) is balanced by current due to electric field
- Potential drop associated with this field: STREAMING POTENTIAL



STREAMING CURRENT AND STREAMING POTENTIAL

- Current appearing due to double-layer charge movement with the fluid
- Transfer of charge downstream (due to pressure gradient) is balanced by current due to electric field
- Potential drop associated with this field: STREAMING POTENTIAL



STREAMING CURRENT AND STREAMING POTENTIAL

Poiseuille flow in a tube:

Pressure difference

$$v = \frac{\Delta p}{4\eta L}(a^2 - r^2)$$

Tube length

Electric current due to convection:

$$I_1 = \int_0^a 2\pi r \rho_e(r) v(r) dr$$

Dominant contribution from the double layer:

$$v \simeq [\Delta p a / 2\eta L](a - r) \qquad \rho_e(y) = -\varepsilon \frac{d^2\psi}{dy^2}$$

$$y = a - r$$

STREAMING CURRENT AND STREAMING POTENTIAL

$$I_1 = -\frac{\Delta p a^2 \pi}{\eta L} \int_0^a \rho_e(y) y dy$$

$$\rho_e(y) = -\varepsilon \frac{d^2\psi}{dy^2} \qquad y = a - r$$

Balance of currents:

$$I_1 = -\frac{e\zeta}{\eta} \frac{\pi a^2}{L} \Delta p$$

$$I_2 = K \pi a^2 E$$

$$E = \frac{\varepsilon \zeta}{\eta K} \frac{\Delta p}{L}$$

$$\Delta \psi = \frac{\varepsilon \zeta}{\eta K} \Delta p$$

Streaming potential

Electrolite conductivity

MEASURING THE STREAMING POTENTIAL

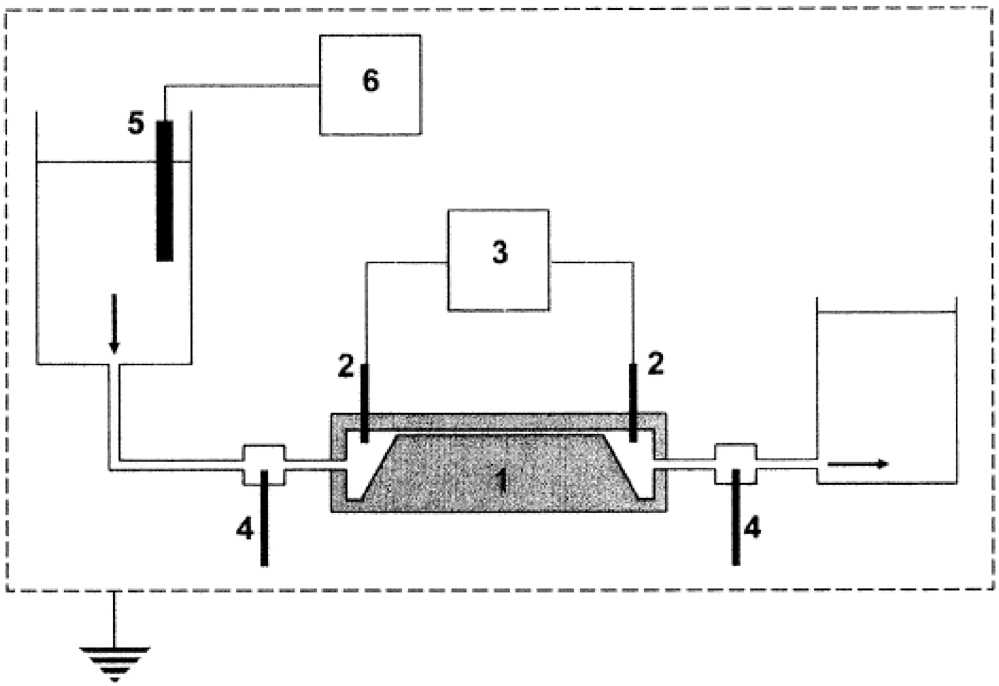
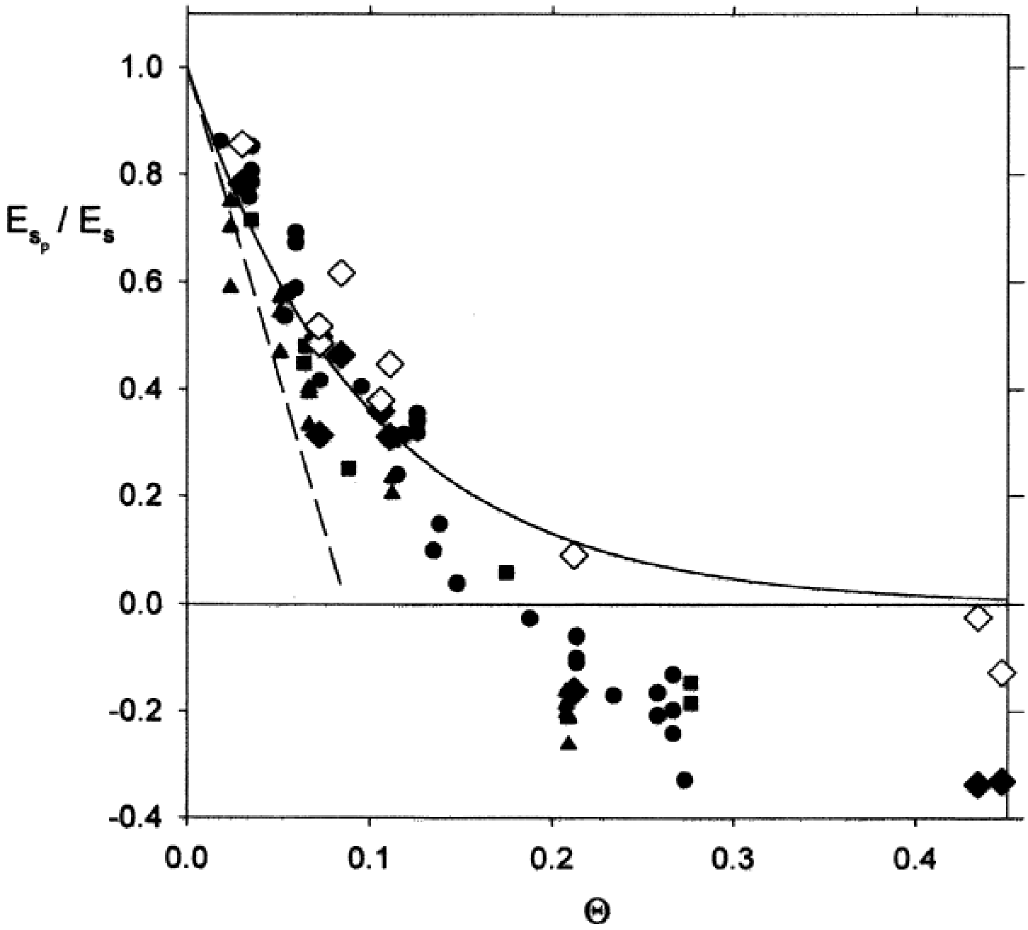


Fig. 4. A schematic view of the set up used for the streaming potential measurement: (1) the cell; (2) electrodes for streaming potential measurements; (3) electrometer; (4) electrodes for cell resistance measurements; (5) conductivity cell; (6) conductometer.

M. Zembala et al. Colloids and Surfaces A **195** (2001), 3-15

PARTICLES ADSORBED AT THE INTERFACE – WHAT CHANGES?



Rapid decrease of the streaming current/potential with particle concentration θ

TO BE CONTINUED…

- Can this dependence be explained theoretically??
  - Hydrodynamics
  - Statistical Physics

↓

- Virial expansion, Simulations