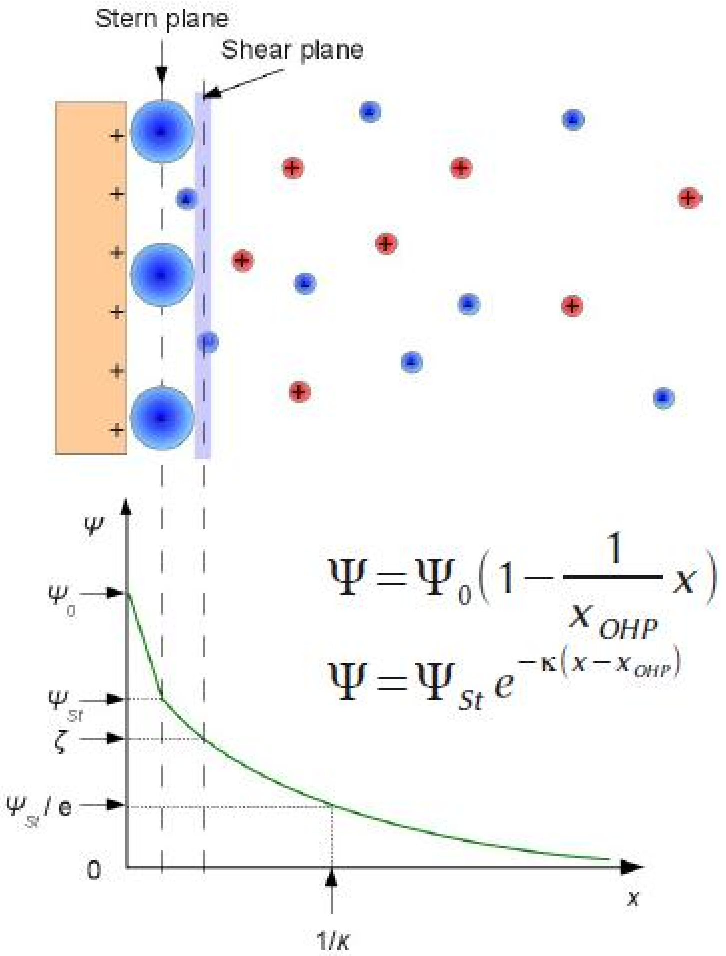
The Stern model

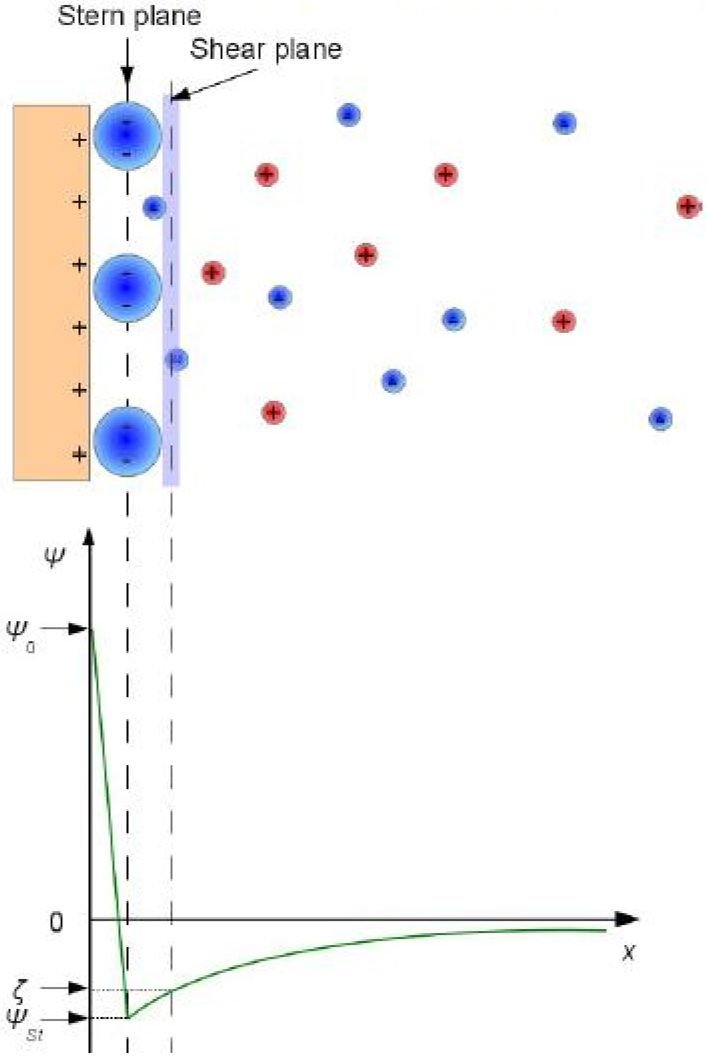


$$\Psi = \Psi_0 \left(1 - \frac{1}{x_{OHP}} x\right)$$

$$\Psi = \Psi_{St} \, e^{-\kappa (x - x_{OHP})}$$

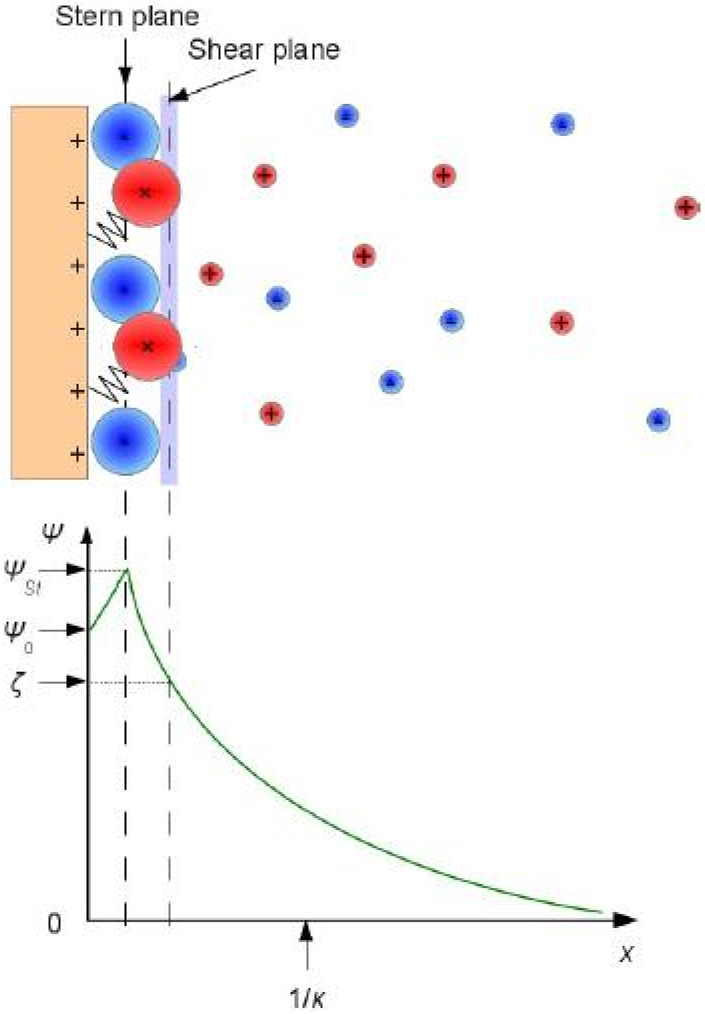
- Stern, 1924
- Combination model: Helmholtz + Gouy-Chapman
- First layer of solvated ions of finite size, tightly adsorbed onto the surface
- Subsequent layers as point charges like in the Gouy-Chapman model
- Slipping (shear) plane: at the boundary of the diffuse layer
- Potential at the shear plane: ζ or electrokinetic potential
- If shear plane and Stern-plane close enough: $\Psi_{St} \approx \zeta$
- The model can deal with specific ion sorption

The Stern model, charge reversal



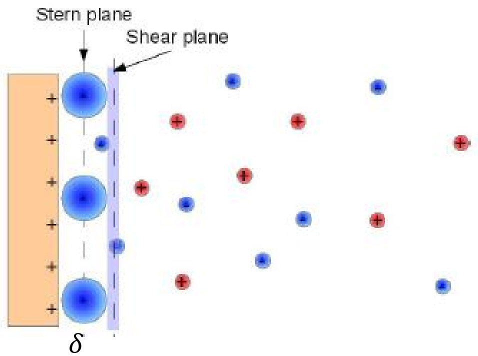
- If polyvalent or surface-active co-ions are adsorbed, charge reversal can occur
- In this case, Ψ_0 and Ψ_{St} have different sign
- The elektrokinetic potential (ζ) changes also its sign

The Stern model, overcharge



- If surfactant co-ions adsorb to the interface, Ψ_{St} can become bigger than $\Psi_0 \longrightarrow$ charge increase
- If the Stern plane and the shear planes are close enough, elektrokinetic potential also increase

Surface Charge



Stern layer   Diffuse layer

As before

$$\sigma_d = -\sigma_s$$

$$\sigma_d = \sigma_{st} + \sigma_{dl}$$

Stern layer   Diffuse layer

Langmuir adsorption can be used to describe the adsorption in the Stern layer

$$\frac{\sigma_{st}}{\sigma_m} = \frac{Kn_0}{1 + Kn_0}$$

$$\sigma_m = surface\ charge\ density\ corresponding\ to\ a\ monolyer\ of\ counter-ions$$

$$\sigma_{st} = \frac{\sigma_m K n_0}{1 + Kn_0}$$

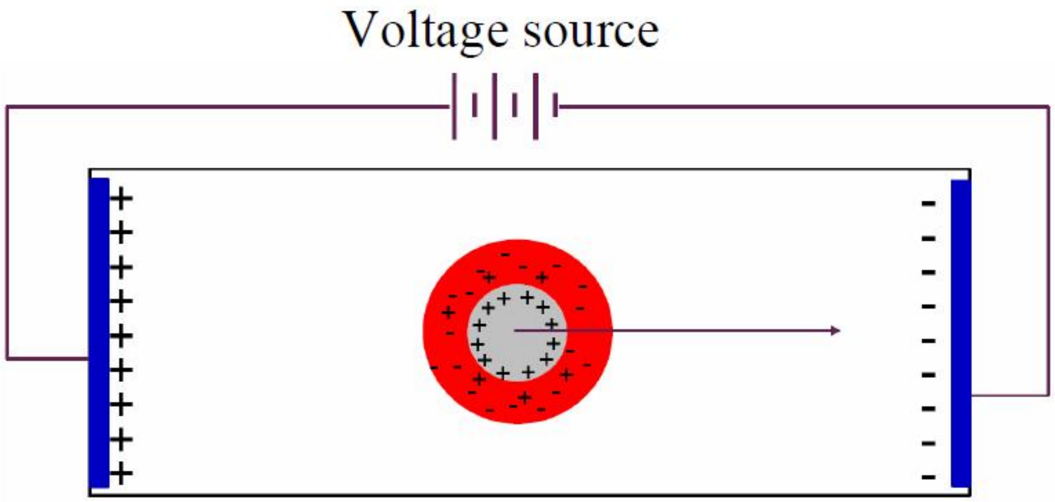
From the capacitor theory

$$\sigma_s = \frac{\epsilon}{\delta}(\Psi_0 - \Psi_{st})$$

$$\sigma_{dl} = -\sqrt{8\varepsilon kTn_0}\,\sinh\left(\frac{ze\Psi_{st}}{2kT}\right)$$

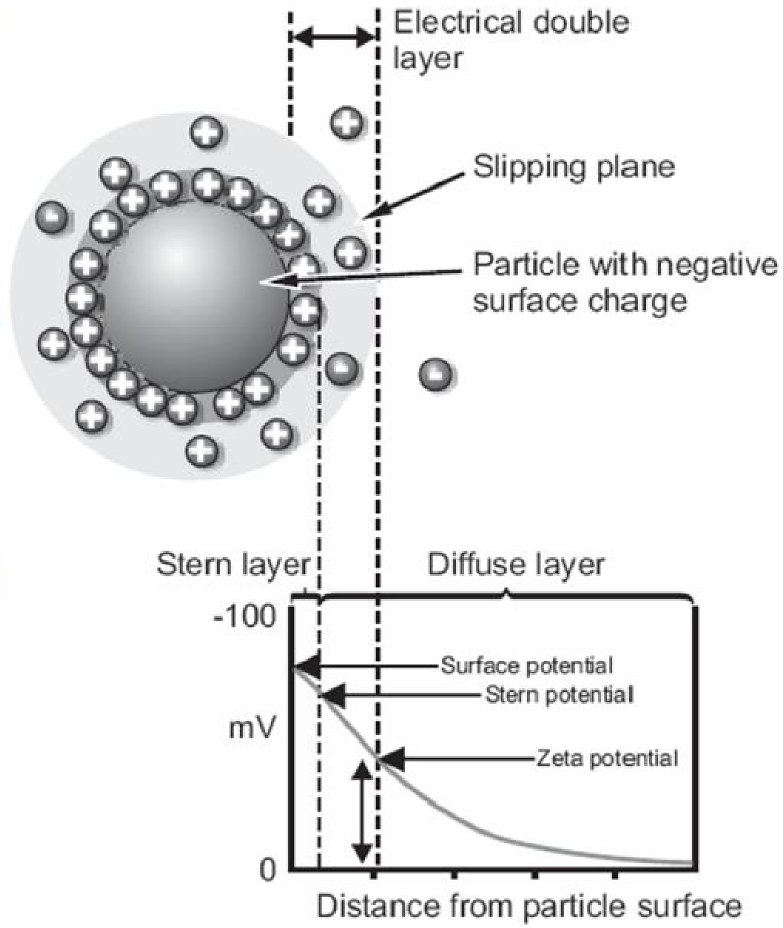
Electrokinetic Phenomena

- When an electric field is applied across an electrolyte, charged particles suspended in the electrolyte are attracted towards the electrode of opposite charge.
- Viscous forces acting on the particles tend to oppose this movement.
- When equilibrium is reached between these two opposing forces, the particles move with constant velocity.
- The velocity of a particle in an electric field is commonly referred to as its Electrophoretic mobility.



Origin of Zeta (ζ) Potential

- Charged particles in an electric field will respond to that field
- Only part of EDL moves with particle
- Movement of particle depends on particle potential at the "slipping" or "shear" plane
  - This is the zeta potential (ψ_ζ)
- Measurement of zeta potential is a method to determine PZC
  - By applying a model of the EDL, can then determine surface charge and potential

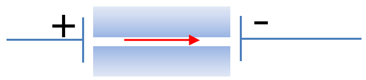


Electrokinetic phenomena

Technique	What Is measured	What Moves	What Causes Movement
Electrophoresis	Velocity	particles move	applied electric field
Electroosmosis	Velocity	liquid moves in capillary	applied electric field
Streaming Potential	Potential	liquid moves	pressure gradient
Sedimentation Potential	Potential	particles move	gravity = $g\Delta\rho$

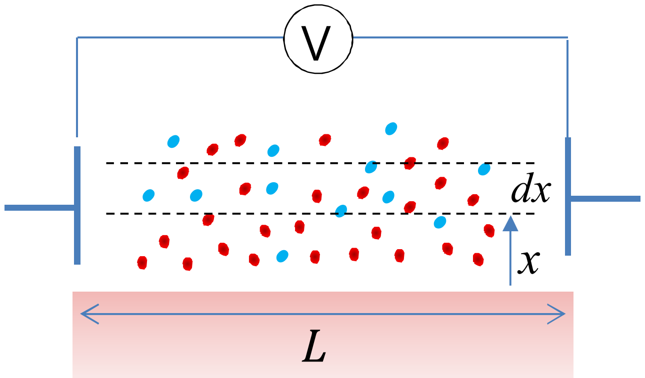
1. Electrophoresis
   Particles/molecules move in solution.

2. Electroosmosis
   Liquid moves in capillary.



3. Streaming potential
   The moving liquid generates potential (reverse of electroosmosis).
4. Sedimentation potential
   Moving particles generate potential.

Electroosmosis



Forces acting on the layer
- Electrical force
- Viscous drag

In steady state, two forces balance

$$\frac{V}{L}\rho A dx = \mu A\left[\left(\frac{dv}{dx}\right)_{x+dx} - \left(\frac{dv}{dx}\right)_{x}\right]$$

$$= \mu A \frac{d^2 v}{dx^2} dx$$

Poisson Eq. $\rho = -\varepsilon \frac{d^2\Psi}{dx^2}$

$$-\frac{\varepsilon V}{L}\frac{d^2\Psi}{dx^2} = \mu \frac{d^2 v}{dx^2}$$

Integrating $-\frac{\varepsilon V}{L}\frac{d\Psi}{dx} = \mu \frac{dv}{dx} + const$

$$x \to \infty \quad \frac{d\Psi}{dx} \to 0, \frac{dv}{dx} \to 0 \quad \therefore const. = 0$$

Integrating again

$$-\frac{\varepsilon V}{L}\Psi = \mu v + const$$

Close to the surface (x→ 0)

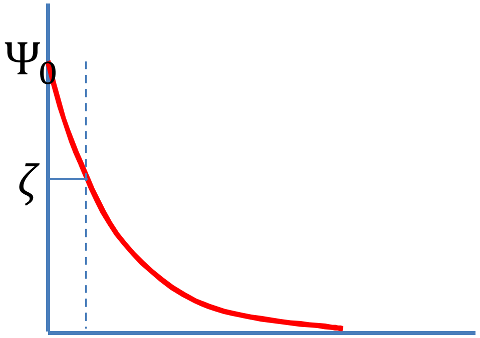
$$v = 0 \ at\ some\ plane\ close\ to\ surface$$

$$\zeta = potential\ at\ the\ shear\ place$$

zeta potential (electrokinetic potential)

Boundary Condition

$\zeta = 0 \; when \; v = 0 \; at \; shear \; plane$



$$const = -\frac{\varepsilon V}{L}\zeta$$

$$i.e. -\frac{\varepsilon V}{L}(\zeta - \Psi) = \mu v$$

Far from the surface $\quad \Psi = 0$

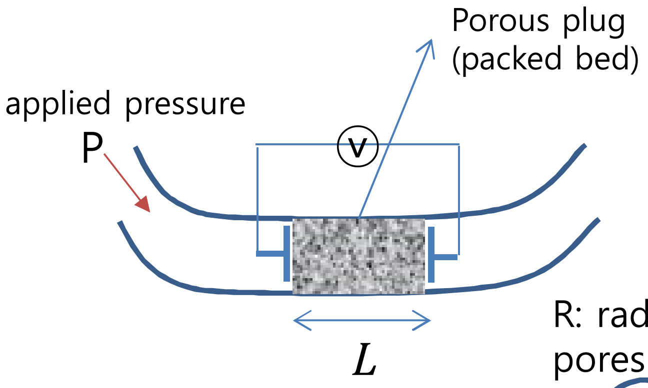
$$v = \frac{\varepsilon V}{\mu L}\zeta$$

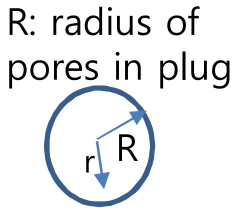
Velocity of bulk fluid relative to surface

$\varepsilon \; and \; \mu$ may have different values close to surface

$$v = \frac{V}{L}\int_0^{\zeta}\frac{\varepsilon}{\mu}d\Psi$$

Streaming Potential





Fluid flow → convection current
Potential Diff. → conduction current

} Opposite direction
Equal at steady state

Convection current

$$i = \int_A v(r)\rho(r)dA$$

$$v(r) = \frac{P}{4\mu L}(R^2 - r^2): \ \ Poiseuille\ Eq.$$

$$\rho(r) = -\varepsilon\nabla^2\Psi: \ \ Poisson\ Eq.$$

$$dA = 2\pi r dr$$

Conduction current

Ohm's Law $V = iR$

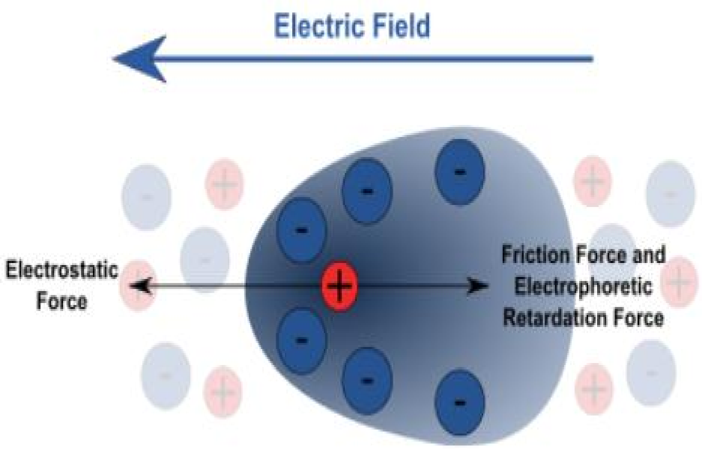
$$i = \frac{AV\lambda}{L} \qquad \lambda: \ \ specific\ conductance$$

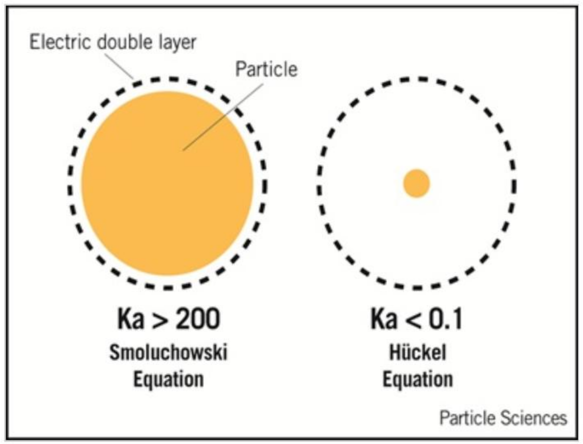
Solving $\dfrac{V}{P} = \dfrac{\varepsilon\zeta}{\mu\lambda}$

Restriction

i) laminar flow
ii) R >> double layer thickness $(\kappa R \gg 1)$
iii) surface conductance effects negligible

Electrophoresis





Charged particles under an electric field experience three forces

- Electrostatic Coulomb force
- Fluid drag force
- Retardation force due to the charges in the double layer moving in opposite direction
- Relaxation effect: distortion of double layer (center of + charge and – charge do not coincide)

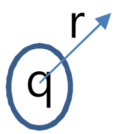
Two extreme cases:

(1) Double layer is thin compared to particle size: $(\kappa R \gg 1)$

(2) Double layer is very thick compared to particle size: $(\kappa R < 0.1)$

1) $\kappa R < 0.1$: retardation force is small
And spherical particles can be treated as a point charge
At steady state, electrostatic force=viscous drag

$$F_{elec} = qE \qquad F_{drag} = 6\pi\mu vR$$



$$\Psi = \frac{q}{4\pi\varepsilon r}$$

for $\kappa R = 0.1$

if $R = 0.01\ \mu m$

$\kappa = 10\ \mu m^{-1}$
$\rightarrow c$: 10^{-5} M for 1:1 electrolyte

May not be applicable to particle electrophoresis in aqueous media

Potential close to the surface: ζ

$$\zeta = \frac{q}{4\pi\varepsilon R} \qquad R: paticle\ radius$$

$$q = 4\pi\varepsilon R\zeta$$

$$4\pi\varepsilon R\zeta E = 6\pi\mu vR$$

$$\frac{v}{E} = \frac{4\pi\varepsilon R\zeta}{6\pi\mu R} = \frac{2\varepsilon\zeta}{3\mu} \qquad H\ddot{u}ckel\ Eq.$$

$$\frac{v}{E} = u: \ \ electrophoretic\ mobility$$

Ex) calculate ζ when $u = 10^{-4} cm^2/Vs$ in water at 20°C

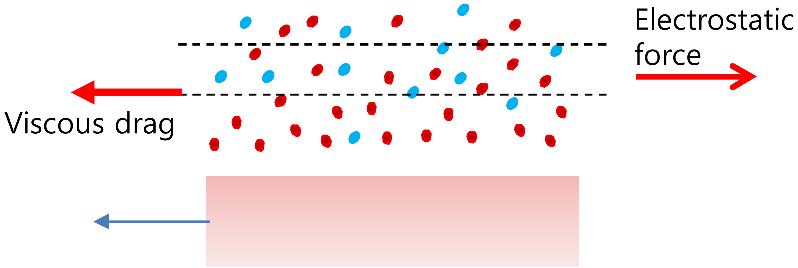
$$\mu_{water} = 0.01\ p \qquad 1\ p = 1\frac{\text{g}}{\text{cm}\cdot s} = 0.1\ \frac{kg}{m\cdot s}$$

$$\zeta = \frac{3\mu u}{2\varepsilon} = \frac{3(0.01\times 0.1)(10^{-8})}{2(80)(8.85\times 10^{-12})} \qquad \varepsilon = \varepsilon_r\varepsilon_0$$

$$= 2.11\times 10^{-2} V$$

2) $\kappa R > 200$

When κR is large, the double layer is effectively large, and may be treated as such.



Treatment is the same as electroosmosis

$$v = \frac{\varepsilon V}{\mu L}\zeta : \quad Smoluchowski\ Eq.$$

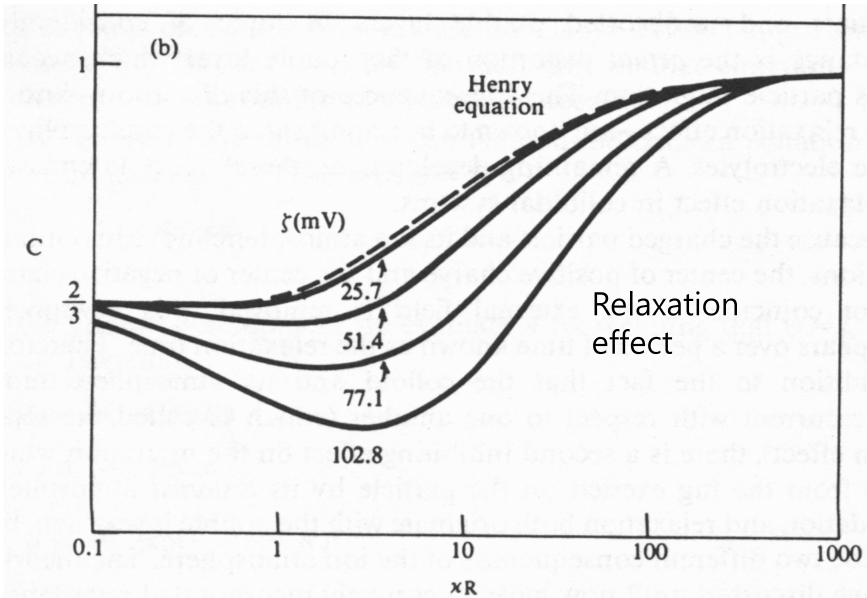
$$\frac{v}{E} = \frac{\varepsilon \zeta}{\mu}$$

Mobility is independent of size and shape

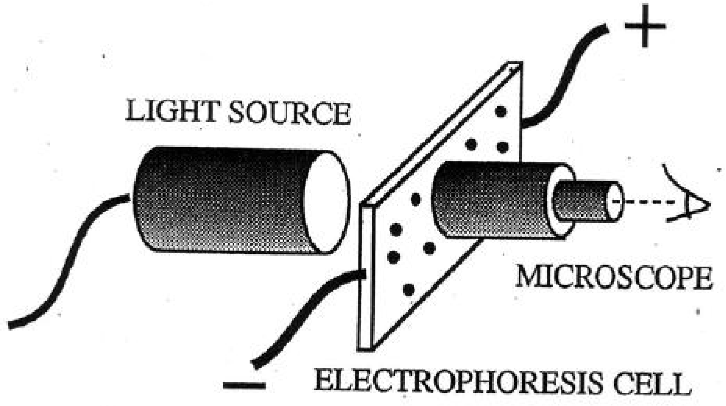
$$u = \frac{\varepsilon \zeta}{\mu}$$

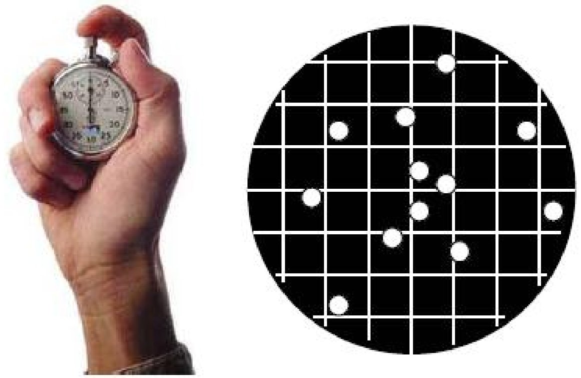
$$u = \frac{\varepsilon \zeta}{\mu} f : \quad Henry\ Eq. \qquad f = \frac{2}{3} \quad \kappa R < 0.1$$
$$= 1 \quad \kappa R > 200$$

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



Measurement of ζ potential by microelectrophoresis





$$u_{elf} = \frac{v_{elf}}{E_x} \; [=] \; \frac{(\mu m/s)}{(V/cm)}$$ electrophoretic mobility

$$v_{elf} = \frac{dx}{dt} \; [=] \; \mu m/s$$ electric drift velocity

$$E_x = \frac{U}{\ell} \; [=] \; V/cm$$ electric field strength

Smoluchowski equation

$$\zeta = u_{elf} \frac{\eta}{\varepsilon_r}$$

(big particle thin double layer)

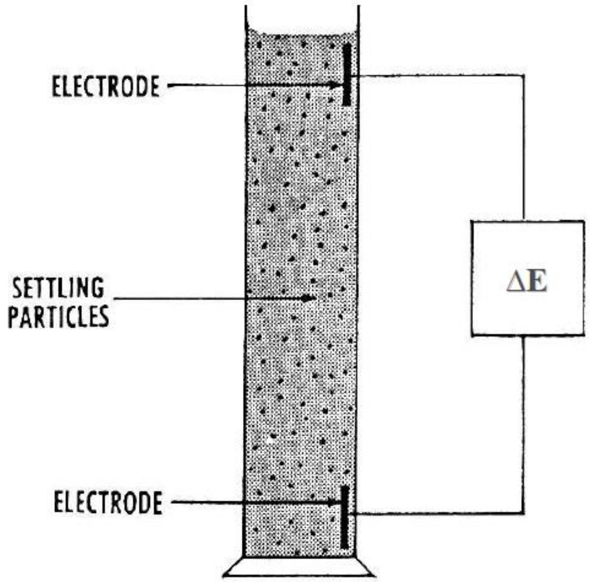
Hückel equation

$$\zeta = \frac{3}{2} u_{elf} \frac{\eta}{\varepsilon_r}$$

(small particle thick double layer)

Sedimentation potential ("Dorn-effect)

creation of an electric field when a charged particle moves relative to stationary fluid



ΔE = sedimentation potential

$$\Delta E = \frac{\varepsilon\zeta}{3\mu\lambda} R^3 (\rho_p - \rho_l) n g$$

R: *particle radius*

ρ_p: *particle density*

ρ_l: *fluid density*

n: *no conc. of particles*