Determination of Zeta Potential by Microelectrophoresis

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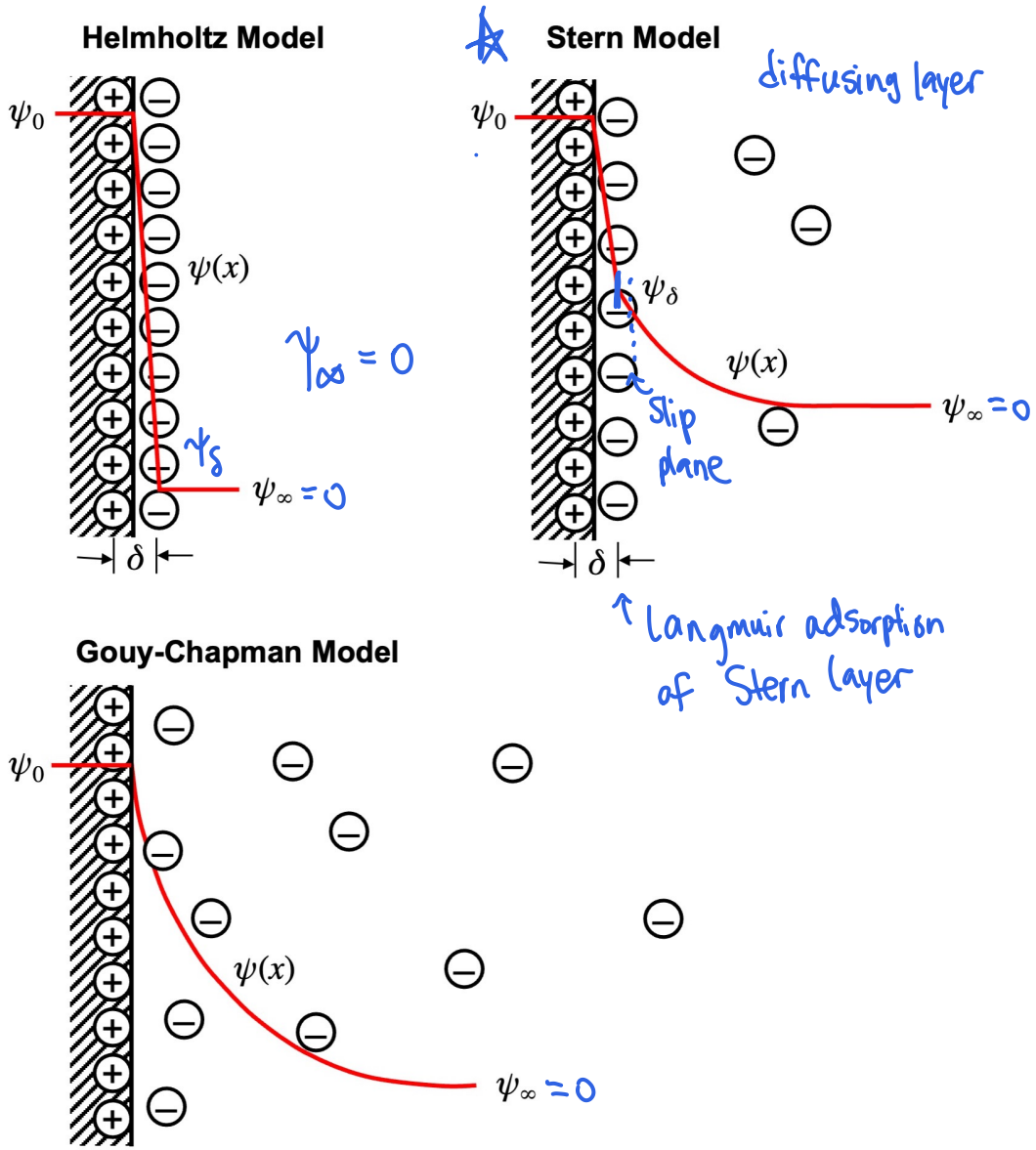
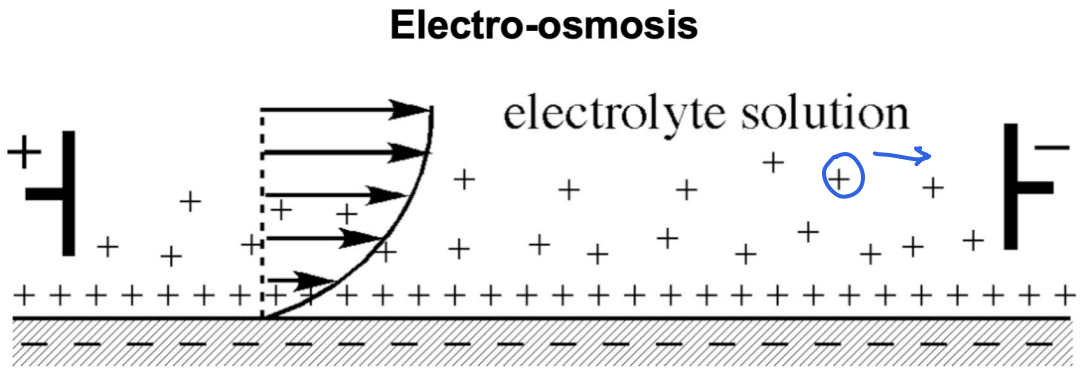
Zeta potential is the electrical potential at the slip plane of the electric double layer

- ψ - electrical potential difference between dispersing medium and ...
  - $\psi_\infty \equiv 0$ - the dispersing medium
  - ψ_0 - the surface of colloidal particle
    - True surface potential
  - ψ_δ - the outer first layer of counterions
    - Effective (Stern) surface potential
  - ζ - the slip plane (medium velocity = 0)
    - Zeta potential, electrokinetic potential
- The slip plane may be slightly further out into the solution than Stern layer
  - $\psi_\delta \approx \zeta$ ✓

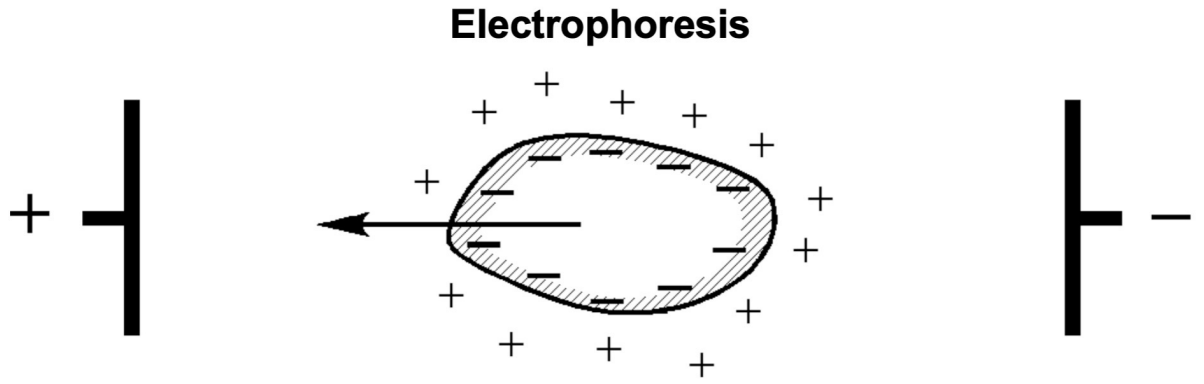


Electro-osmosis and electrophoresis give the same zeta potential

- **Electro-osmosis** - diffuse layer of ions beside a charged immobile surface move under *E* field, which sets the liquid into motion by the action of viscosity
  - *Liquid* moves, *solid* at rest



- **Electrophoresis** - diffuse layer of ions beside a charged particle surface move under *E* field, which sets the particle into motion
  - *Solid* moves, *liquid* at rest



Electrophoretic mobility allows determination of zeta potential

- **Electrophoretic mobility** - $u_E[(\mu m/s)/(V/cm)]$
  - $u_E = \frac{V_p}{E_x} = \begin{cases} \frac{\varepsilon\varepsilon_0\zeta}{\mu} & (\kappa a > 200) \\ \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\mu} & (\kappa a < 0.1) \end{cases}$ Helmholtz-Smoluchowski limit; Huckel limit

$$\zeta = \frac{V_p\ \mu}{E_x\ \varepsilon\varepsilon_0}$$ measure; V_p ✓, μ ✓, E_x ✓, ε ✓, ε_0 ✓

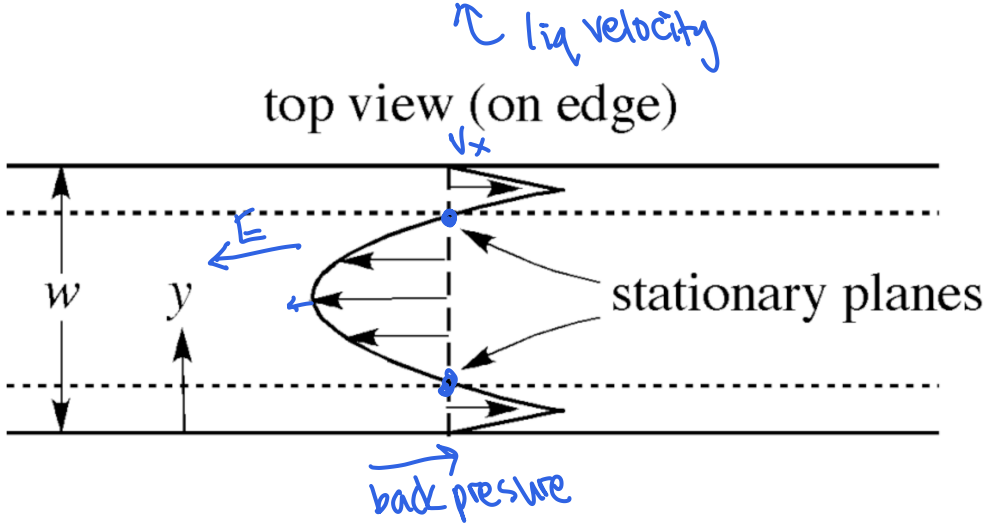
- u_E - Electrophoretic mobility
- V_p - Particle velocity — Measure
- E_x - Electric field strength — Known
- ε - Dielectric constant of the medium — Known - H_2O
- ε_0 - Permittivity of free space — Known
- ζ - Zeta potential — Want
- μ - Viscosity of the medium — Known - H_2O
- κ^{-1} - Debye length
- a - Particle radius

Point of zero charge and isoelectric point define pH at which potentials are zero

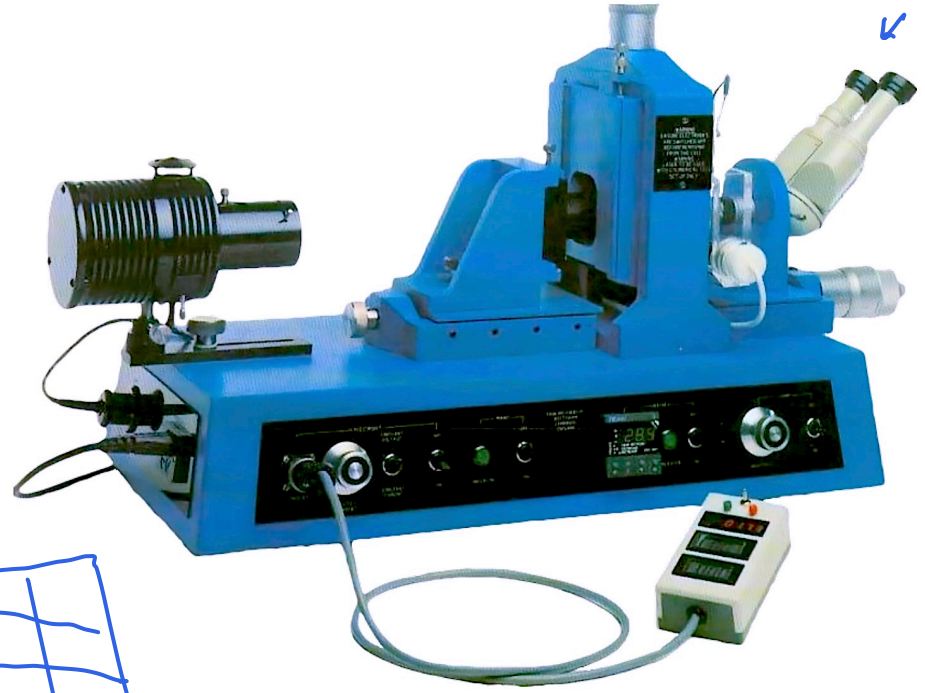
- **Potential determining ions** - ions whose concentration determines surface potential
  - Crystalline solid - lattice ions
  - Oxides - $\mathrm{H_3O^+}$, $\mathrm{OH^-}$ (pH)
- **Point of zero charge (PZC)** - pH at which $\psi_0 = 0$
  - pH < PZC: $\psi_0 > 0$
  - pH > PZC: $\psi_0 < 0$
- **Isoelectric point (IEP, pI)** - pH at which $\zeta \approx \psi_\delta = 0$
  - $u_E = 0 \Rightarrow V_p = 0$

Darkfield illumination microscopy visualizes colloidal particles under *E* field

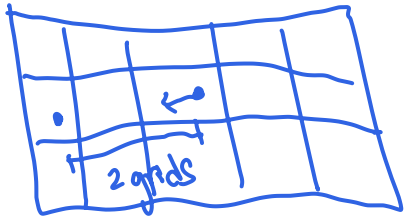
- $u_E = \dfrac{V_p}{E_x} = \dfrac{\varepsilon\varepsilon_0\zeta}{\mu} \qquad (\kappa a > 200)$
  - $\boxed{\zeta = \dfrac{\mu V_p}{\varepsilon\varepsilon_0 E_x}}$ particle velocity
- Electrophoresis has solid particles moving when liquid is at rest ($v_x = 0$)

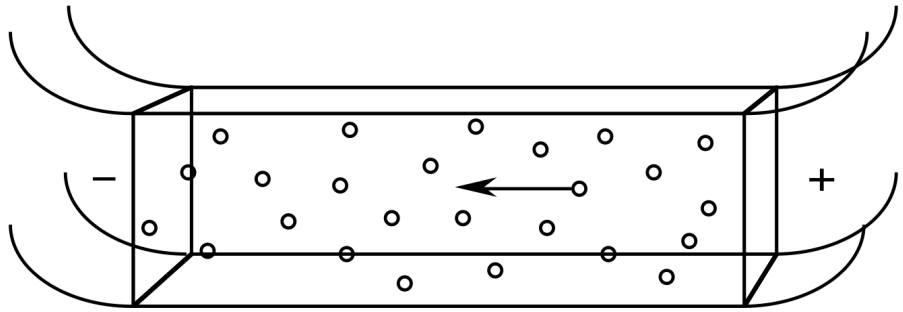


  - $v_x = 0$ when $y = \begin{cases} 0.205w & \checkmark \\ 0.795w & \checkmark \end{cases}$



$E_x = 5\,mV$





Laser Doppler electrophoresis determines zeta potential with more sensitivity