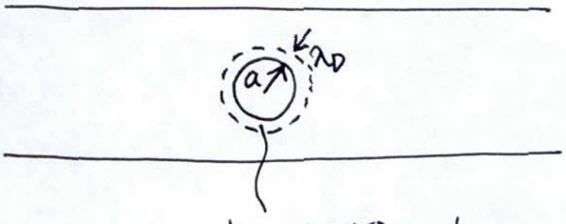
when $\lambda_D \gg a$

$Q \sim a^4$: same as pressure-driven flow

ELECTROPHORESIS

· The charge of macromolecules and particles



$$dq = 4\pi r^2 \rho_E \, dr$$

Poisson eq in spherical coordinates

$$\nabla^2 \phi = -\frac{\rho_E}{\epsilon}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial^2}{\partial \phi^2}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) = -\frac{\rho_E}{\epsilon}$$

$$q = \int dq = -\int_a^\infty 4\pi r^2 \epsilon \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) dr$$

$$= -\int_a^\infty 4\pi\epsilon \frac{\partial}{\partial r}\left(r^2 \frac{\partial \phi}{\partial r}\right) dr$$

$$= -4\pi\epsilon \left(r^2 \frac{\partial \phi}{\partial r}\Big|_{r\to\infty} - r^2 \frac{\partial \phi}{\partial r}\Big|_{r=a} \right)$$

$$= 4\pi\epsilon a^2 \left(\frac{\partial \phi}{\partial r}\right)_{r=a} \quad [C]$$: charge in the double layer

Surface charge density $q_s = -\frac{q}{4\pi a^2} = -\epsilon\left(\frac{\partial \phi}{\partial r}\right)_{r=a}$ [C/m^2]

$\frac{\partial \phi}{\partial r}\Big|_{r=a} \sim q_s$

$$\left(\frac{\partial \phi}{\partial r}\right)_{r=a} = ?$$

Poisson eq $\quad \nabla^2\phi = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right) = -\frac{\rho_E}{\epsilon}$

Boltzmann distribution $\quad \rho_E = zF c_0 \left[\exp\left(-\frac{zF\phi}{RT}\right) - \exp\left(\frac{zF\phi}{RT}\right)\right]$

$$= -2Fz c_0 \sinh\left(\frac{zF\phi}{RT}\right)$$

Debye-Hückel approximation for small potentials,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right) = \frac{\phi}{\lambda_D^2}$$

Set $\xi = r\phi$

$$\frac{d\phi}{dr} = \frac{1}{r}\frac{d\xi}{dr} - \frac{1}{r^2}\xi$$

$$LHS = \frac{1}{r^2}\frac{d}{dr}\left(r\frac{d\xi}{dr} - \xi\right) = \frac{1}{r^2}\left(\frac{d\xi}{dr} + r\frac{d^2\xi}{dr^2} - \frac{d\xi}{dr}\right) = \frac{1}{r}\frac{d^2\xi}{dr^2}$$

$$\therefore \frac{d^2\xi}{dr^2} = \frac{\xi}{\lambda_D^2}$$

: the same form as for the plane wall problem.

$$\xi = A\exp\left(-\frac{r}{\lambda_D}\right) + B\exp\left(\frac{r}{\lambda_D}\right)$$

$$\phi = \frac{A}{r}\exp\left(-\frac{r}{\lambda_D}\right) + \cancelto{0}{\frac{B}{r}}\exp\left(\frac{r}{\lambda_D}\right)$$

$\phi \to 0$ as $r \to \infty$

$$\phi = \frac{A}{r}\exp\left(-\frac{r}{\lambda_D}\right)$$

$A = ?$

At $r = a$ (particle surface) : $\phi = \zeta$

$$\zeta = \frac{A}{a}\exp\left(-\frac{a}{\lambda_D}\right)$$

$$A = \zeta a \exp\left(\frac{a}{\lambda_D}\right)$$

$$\phi = \zeta\frac{a}{r}\exp\left(\frac{a-r}{\lambda_D}\right)$$

$$\frac{\partial\phi}{\partial r} = -\xi\frac{a}{r^2}\exp\left(\frac{a-r}{\lambda_D}\right) + \frac{\xi a}{r}\left(-\frac{1}{\lambda_D}\right)\exp\left(\frac{a-r}{\lambda_D}\right)$$

$$\left(\frac{\partial\phi}{\partial r}\right)_{r=a} = -\xi\frac{1}{a} - \xi\frac{1}{\lambda_D}$$

$$= -\xi\left(\frac{1}{a}+\frac{1}{\lambda_D}\right)$$

$$= q_s\left(-\frac{1}{\epsilon}\right)$$

$$\therefore q_s = \epsilon\xi\left(\frac{1}{a}+\frac{1}{\lambda_D}\right) \qquad \cdots \quad (8)$$

By the way, $q_s = \dfrac{q}{4\pi a^2}$

$$q = \epsilon\xi 4\pi a\left(1+\frac{a}{\lambda_D}\right)$$

$$\xi = \frac{q}{4\pi\epsilon a(1+a/\lambda_D)}.$$

or

$$\xi = \frac{q}{4\pi\epsilon a} - \frac{q}{4\pi\epsilon(a+\lambda_D)}$$

* Electric potential ϕ due to a particle of charge, q, at a radial distance r from the particle :

$$\phi = \frac{q}{4\pi\epsilon r}$$

pf) $\dfrac{1}{r^2}\dfrac{d}{dr}\left(r^2\dfrac{d\phi}{dr}\right) = -\dfrac{\rho_E}{\epsilon}$

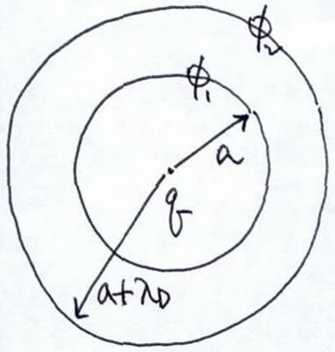
$$\int_0^r \frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right)dr = -\frac{1}{\epsilon}\int \rho_E r^2 dr = -\frac{1}{4\pi\epsilon}\int_0^r \rho_E(4\pi r^2)\,dr$$

$$r^2\frac{d\phi}{dr} = -\frac{q}{4\pi\epsilon}$$

$$\frac{d\phi}{dr} = -\frac{q}{4\pi\epsilon}r^{-2}$$

$$\int_\phi^0 d\phi = -\frac{q}{4\pi\epsilon}\int_r^\infty r^{-2}dr$$

$$0-\phi = -\frac{q}{4\pi\epsilon}\left[-\frac{1}{r}\right]_r^\infty = -\frac{q}{4\pi\epsilon}\left(0+\frac{1}{r}\right) \qquad \therefore \phi = \frac{q}{4\pi\epsilon r}$$

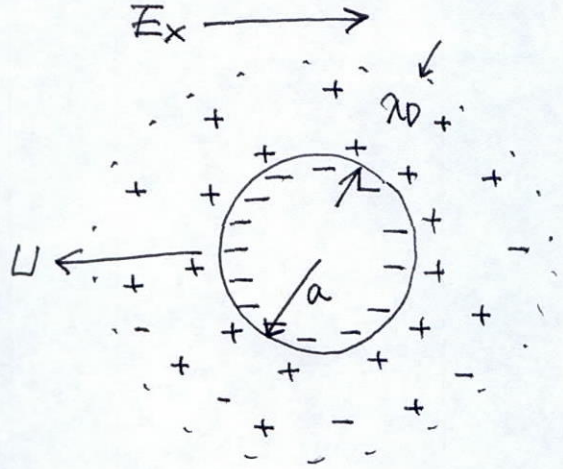


$\zeta = \phi_1 - \phi_2$

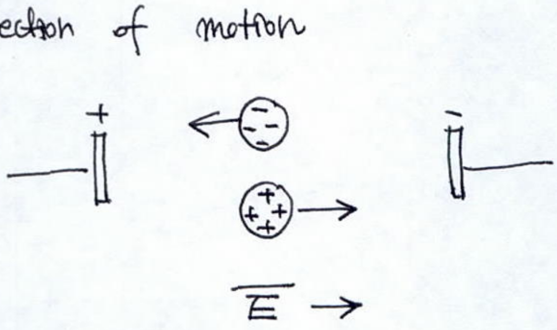
Coming back to Eq (8).

* small Debye length: $\lambda_D \ll a \rightarrow q_s = \dfrac{\epsilon\zeta}{\lambda_D}$

Electrophoretic motion of spherical particle



- Direction of motion



- For both small and large Debye length
  - no retardation

* Large Debye length ($\lambda_D \gg a$)

· particle ~ point charge

· force balance

$$qE_x = 6\pi\mu U a$$

q: net charge between the charged sphere and the concentric spherical double layer of predominantly opposite charge

$$U = \frac{E_x}{6\pi\mu a} \cdot 4\pi\epsilon a \left(1 + \frac{a}{\lambda_D}\right)\zeta$$

$$= \frac{2}{3}\frac{\epsilon\zeta E_x}{\mu} \qquad \left(\frac{a}{\lambda_D} \ll 1\right).$$

└ Hückel approximation

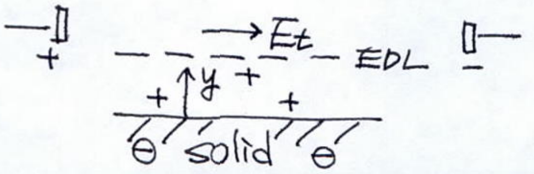
$$U = \left(\frac{2}{3}\frac{\epsilon\zeta}{\mu}\right) E_x$$

↓

electrophoretic mobility $= \frac{U}{E_x}$ $\left[\frac{Cs}{kg}\right]$

* Small Debye length ($\lambda_D \ll a$)

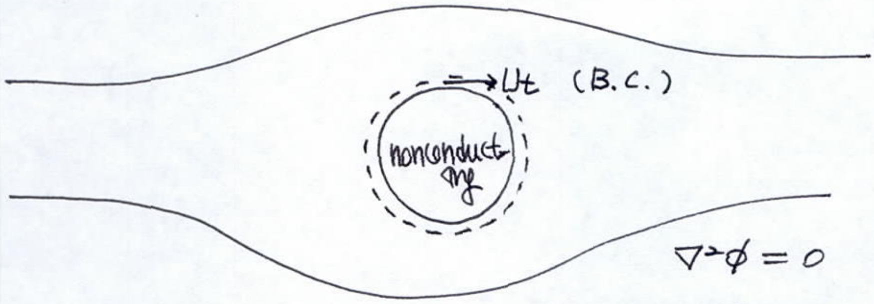
– neglect curvature effects in the double layer



(stationary) → same as electroosmosis

$$U_t = -\frac{\epsilon\zeta}{\mu} E_t$$

(t : tangential to the solid surface)



$\nabla^2 \phi = 0$ (electric field)

$\nabla^2 \Phi = 0$ (fluid flow)

$\because$ slip B.C.

B.C. normal to the surface

$\sigma_a \ll \sigma_b$

Ohm's law : $\hat{n}\cdot(\sigma_a \overline{E}^a - \sigma_b \overline{E}^b) = 0$ (a) insulating

$\hat{n}\cdot\overline{E}^b = 0.$

$\hat{n}\cdot\nabla\phi = 0$ in conducting region (b) conducting

continuity (mass conservation) : $\hat{n}\cdot\nabla\Phi = 0$

B.C. tangential to the surface

$$\begin{cases} \hat{t}\cdot\overline{E} = E_t \\ \hat{t}\cdot\overline{u} = U_t = -\dfrac{\epsilon\zeta}{\mu}E_t \end{cases}$$

Free stream condition

$$\begin{cases} \overline{E} = E_x \hat{i}_x \\ \overline{U} = U \hat{i}_x \end{cases}$$

$$\therefore \quad \Phi = -\frac{\epsilon\zeta}{\mu}\phi$$

Velocity of a particle moving relative to a stationary liquid:

$$U = \frac{\epsilon\zeta E_x}{\mu}$$

: compare with $\left(\frac{2}{3}\frac{\epsilon\zeta}{\mu}\right)E_x$ $\lambda_D \gg a$

$\rightarrow$ Helmholtz - Smoluchowski eq

$\because$ electrophoresis $\xleftrightarrow{\text{complementary}}$ electroosmosis

· electrophoretic velocity of a nonconducting particle ($\lambda_D \ll L$)

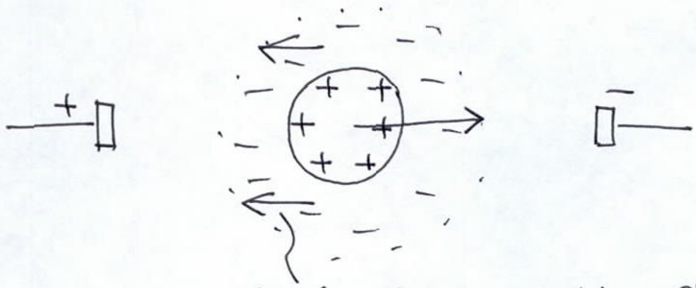
→ independent of particle size and shape

* Finite-thickness double layer

Three effects

- electrophoretic retardation
- surface conductance
- relaxation

① Electrophoretic retardation



local electroosmotic flow opposing the motion of particle

Henry's analysis (Proc. Roy. Soc. A 133, 106-129, 1931)

· assumptions

i) double layer is undistorted.

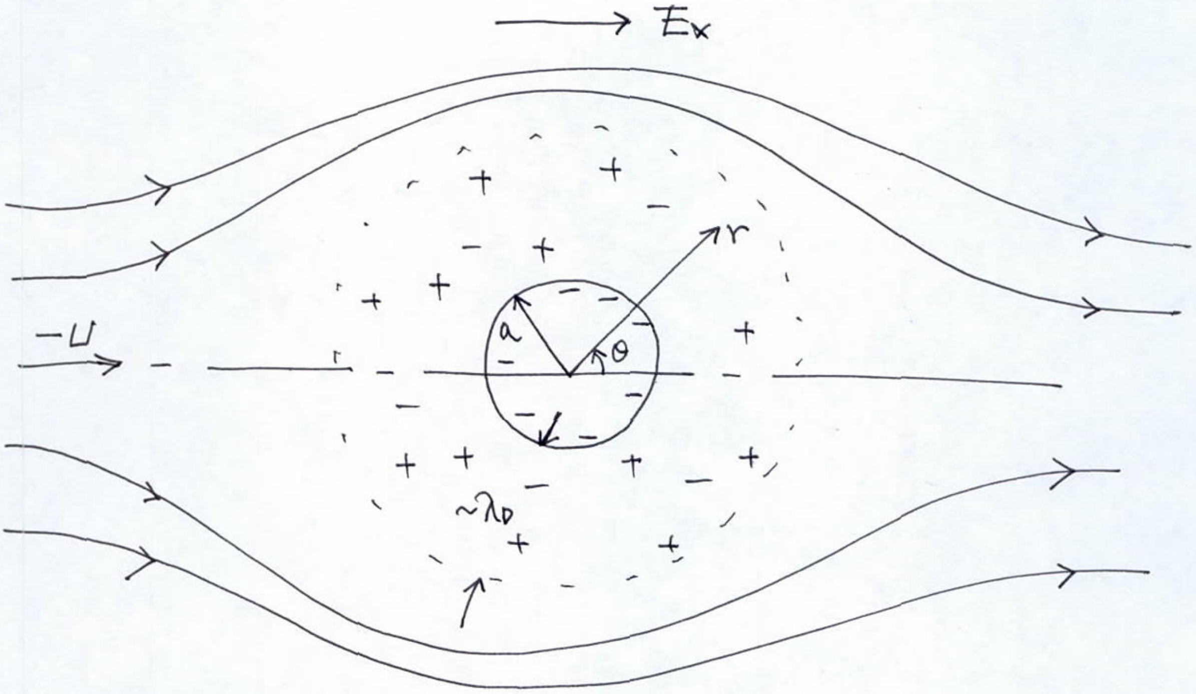
superposition of potentials possible

ψ (from particle charge ~~in double layer~~)

$+ \phi$ (application of E-field // direction of motion)

ii) low surface potential ~ Debye-Hückel approximation

iii) inertia-free flow



reference frame on the particle

Navier-Stokes equation

$$0 = -\nabla p + \mu \nabla^2 \overline{u} + \underbrace{\rho_E \overline{E}}_{\substack{\parallel \\ -\rho_E \nabla(\phi + \psi)}}$$

ϕ due to applied electric field : $\nabla^2 \phi = 0.$

B.C. $r \to \infty$ $\quad \nabla\phi = -E_x \hat{i}_x$

$\phi = -E_x r \cos\theta$

$r = a$ $\quad \hat{n}\cdot\nabla\phi = \frac{\partial\phi}{\partial r} = 0.$

$$\phi = -E_x \left(r + \frac{1}{2}\frac{a^3}{r^2}\right)\cos\theta$$

ψ in the double layer : $\nabla^2\psi = -\frac{\rho_E}{\epsilon}$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) = -\frac{1}{\epsilon} zF(c_+ - c_-)$$

Boltzmann distribution

$$= \frac{2Fzc}{\epsilon}\sinh\left(\frac{zF\psi}{RT}\right)$$

Debye-Hückel

$$= \frac{\psi}{\lambda_D^2}$$

set $\xi = r\psi$

$$\frac{d^2\xi}{dr^2} = \frac{\xi}{\lambda_D^2}$$

$$\psi = \frac{A}{r}\exp\left(-\frac{r}{\lambda_D}\right)$$

$$\begin{cases} r = a: & \psi = \zeta \\ r \to \infty: & \psi \to 0 \end{cases}$$

$$\psi = \zeta\left(\frac{a}{r}\right)e^{-(r-a)/\lambda_D}$$

N.S. : $-\mu\nabla^2\bar{u} + \nabla p = -\rho_E\nabla(\phi+\psi)$

continuity : $\nabla\cdot\bar{u} = 0.$

B.C. : as $r\to\infty$, $u_r = -U\cos\theta$, $u_\theta = U\sin\theta$, $\psi = 0$

at $r = a$, $u_r = u_\theta = 0.$ $\psi = \zeta$

Force balance : steady-state

$\leftarrow \Sigma f_i = -$ Drag force $+$ Electrical force

Drag force $= 6\pi\mu a U$

Elec. force (force due to the fixed surface charge)

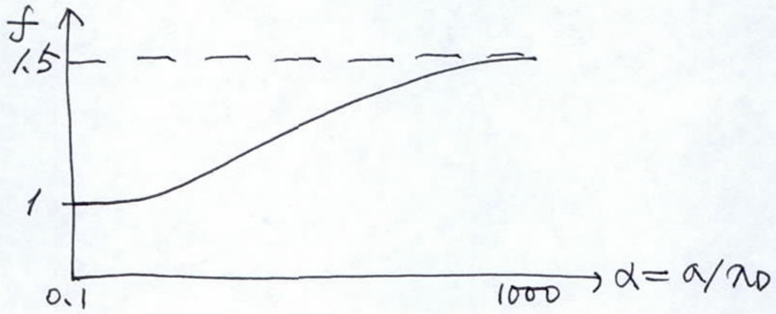
$= q E_x = 4\pi\epsilon a^2\left(\frac{\partial\psi}{\partial r}\right)_{r=a} E_x$

$= 4\pi\epsilon a\zeta E_x f(\alpha)$, $\alpha = \frac{a}{\lambda_D}$

$$6\pi\mu a U = 4\pi\epsilon a\zeta E_x f(\alpha)$$

$$U = \frac{2}{3}\frac{\epsilon\zeta E_x}{\mu}f(\alpha)$$: Henry eq

$$f(\alpha) = 1 + \frac{1}{16}\alpha^2 - \frac{5}{48}\alpha^3 - \frac{1}{96}\alpha^4 + \frac{1}{96}\alpha^5 + \frac{1}{8}\alpha^4 e^{\alpha}\left(1 - \frac{\alpha^2}{12}\right)\int_{\infty}^{\alpha} \frac{e^{-t}}{t}\,dt$$



② Surface conductance

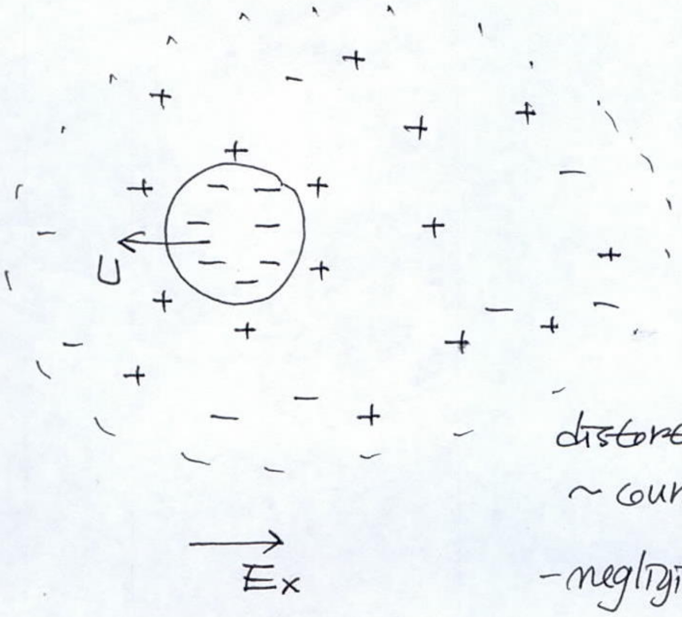
finite-thickness double layer

→ region of higher conductivity

→ applied electric field is reduced

→ decrease in electrophoretic velocity

③ Relaxation



distorted double layer

~ counter emf

- negligible for $\frac{a}{\lambda_D} \gg 1$

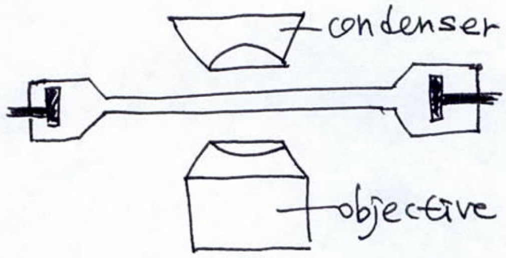
$\frac{a}{\lambda_D} \ll 1$

Electrophoretic Separations : colloids, proteins, nucleic acids

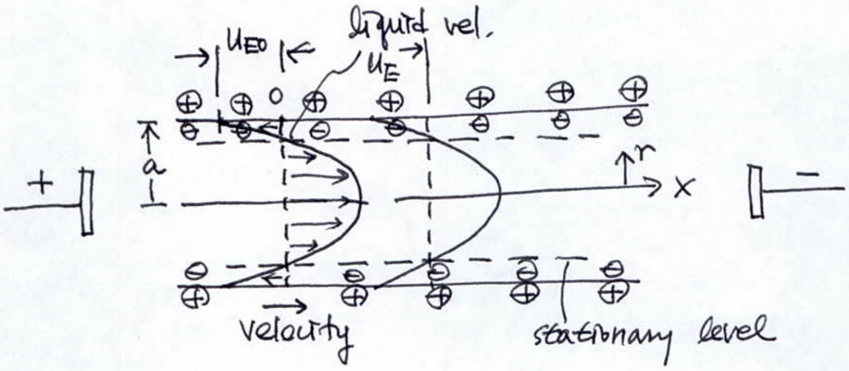
- Three principal techniques
  - · microelectrophoresis
  - · moving boundary electrophoresis
  - · zone electrophoresis

* Microelectrophoresis

= electrophoresis cell + microscope



- Flow field in cylindrical electrophoresis cell (closed)



$$u_L = u_{E0} - c(a^2 - r^2) \quad \leftarrow \quad 0 = -\frac{dp}{dx} + \frac{\mu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right)$$

B.C. $\left.\frac{\partial u}{\partial r}\right|_{r=0} = 0$

$u|_{r=a} = u_{E0} \quad : (\lambda_D \ll a)$

$$Q = \int_0^a 2\pi r u \, dr = 0$$

- $$2\pi \int_0^a [u_{E0} r - c(a^2 r - r^3)] \, dr$$

$$= 2\pi \left(u_{E0}\frac{a^2}{2} - ca^2\frac{a^2}{2} + c\frac{a^4}{4}\right) = 0$$

$$u_{E0}\frac{a^2}{2} - \frac{1}{4}ca^4 = 0 \quad : \quad \frac{c}{4}a^2 = \frac{u_{E0}}{2}$$

$$c = \frac{2u_{E0}}{a^2}$$

$$\frac{u_L}{u_{E0}} = \frac{2r^2}{a^2} - 1$$

$u_L = 0 \rightarrow$ stationary level

$$r_{stat} = \frac{a}{\sqrt{2}}$$

distance from the wall :

$$y_{stat} = a - r_{stat} = \left(1 - \frac{1}{\sqrt{2}}\right) a \quad . \quad \frac{y_{stat}}{a} = 1 - \frac{1}{\sqrt{2}} \approx 0.292$$

· Observed velocity of a particle in the cell

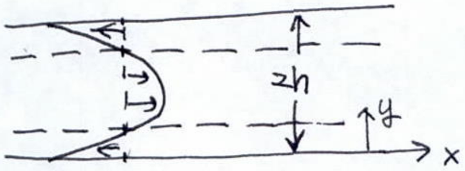
$$u_{obs} = \underbrace{u_E}_{\text{true electrophoretic velocity}} + u_L = u_E + u_{E0}\left(\frac{2r^2}{a^2} - 1\right)$$

· If $\zeta_{particle} = \zeta_{cell\ wall}$

$$u_E = -u_{E0} \qquad : \text{Helmholtz- Smoluchowski eq} \quad \left(U = \frac{\epsilon\zeta}{\mu} E_x\right)$$

$$u_{obs}(r=0) = 2u_E$$

* Plane cell



$$\frac{dp}{dx} = \mu \frac{d^2u}{dy^2}$$

$$\frac{1}{\mu}\frac{dp}{dx} y \underset{+c_1}{} = \frac{du}{dy}$$

$$u = \frac{1}{\mu}\frac{dp}{dx}\frac{y^2}{2} + c_1 y + \cancel{c_2}^{\,u_{E0}} = \frac{1}{2\mu}\frac{dp}{dx}(y^2 - 2hy) + u_{E0}$$

$$\therefore \ u_L = u_{E0} - c(2yh - y^2)$$

$$Q = \int_0^{2h} u\,dy = 0.$$

$$u_{E0}(2h) - c\left[h(2h)^2 - \frac{1}{3}(2h)^3\right]$$

$$= u_{E0}(2h) - c\left(4h^3 - \frac{8}{3}h^3\right) = 0$$

$$c\left(\frac{4}{3}h^3\right) = u_{E0}(2h)$$

$$c = \frac{3}{2}\frac{u_{E0}}{h^2}$$

$$\frac{u_L}{u_{E0}} = 1 - \frac{3}{2}\left(\frac{2y}{h} - \frac{y^2}{h^2}\right)$$

· stationary level : $u_L = 0$:

$$\frac{2y}{h} - \frac{y^2}{h^2} = \frac{2}{3}$$

$$\left(\frac{y}{h}\right)^2 - 2\left(\frac{y}{h}\right) + \frac{2}{3} = 0$$

$$3\alpha^2 - 6\alpha + 2 = 0$$

$$\alpha = \frac{1}{3}\left[3 \pm \sqrt{9-6}\right] = \frac{1}{3}(3 \pm \sqrt{3})$$

$$\frac{y}{h} = 1 - \frac{\sqrt{3}}{3} = 0.422$$

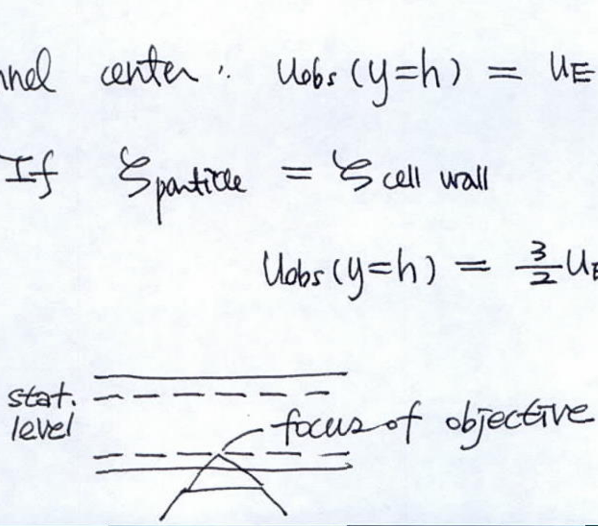
$$y_{stat} = \left(1 - \frac{\sqrt{3}}{3}\right)h \approx 0.422\,h$$

$$u_{obs} = u_E + u_L = u_E + u_{E0}\left[1 - \frac{3}{2}\left(\frac{2y}{h} - \frac{y^2}{h^2}\right)\right]$$

channel center : $u_{obs}(y=h) = u_E - \dfrac{u_{E0}}{2}$

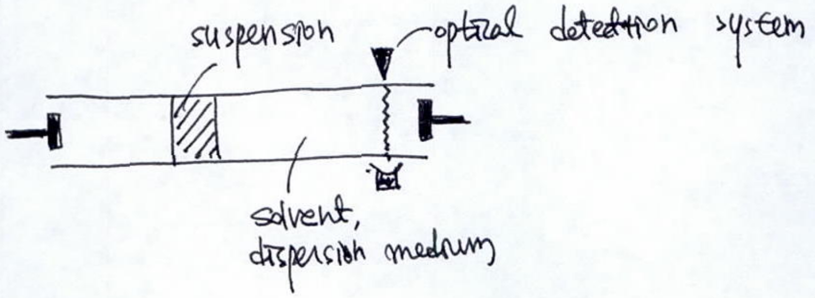
If $\zeta_{particle} = \zeta_{cell\ wall}$: $u_{E0} = -u_E$

$$u_{obs}(y=h) = \frac{3}{2}u_E$$



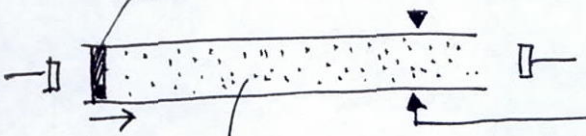
Moving boundary electrophoresis

· particles too small, e.g. macromolecules. proteins



Zone electrophoresis

macromolecular solution



optical detection / developing

support (solid, gel) : saturated with buffer solution

↓

"gel electrophoresis"

- to minimize convectional effects arising from temperature gradients due to Joule heating
- support materials
  - noninteracting : filter paper, cellulose, cellulose acetate membrane
  - molecular sieving (size) : polyacrylamide, agarose gel
  - charge retardation : ion-exchange paper
- principal analytical procedure used for protein and amino acid analysis in biochemistry labs

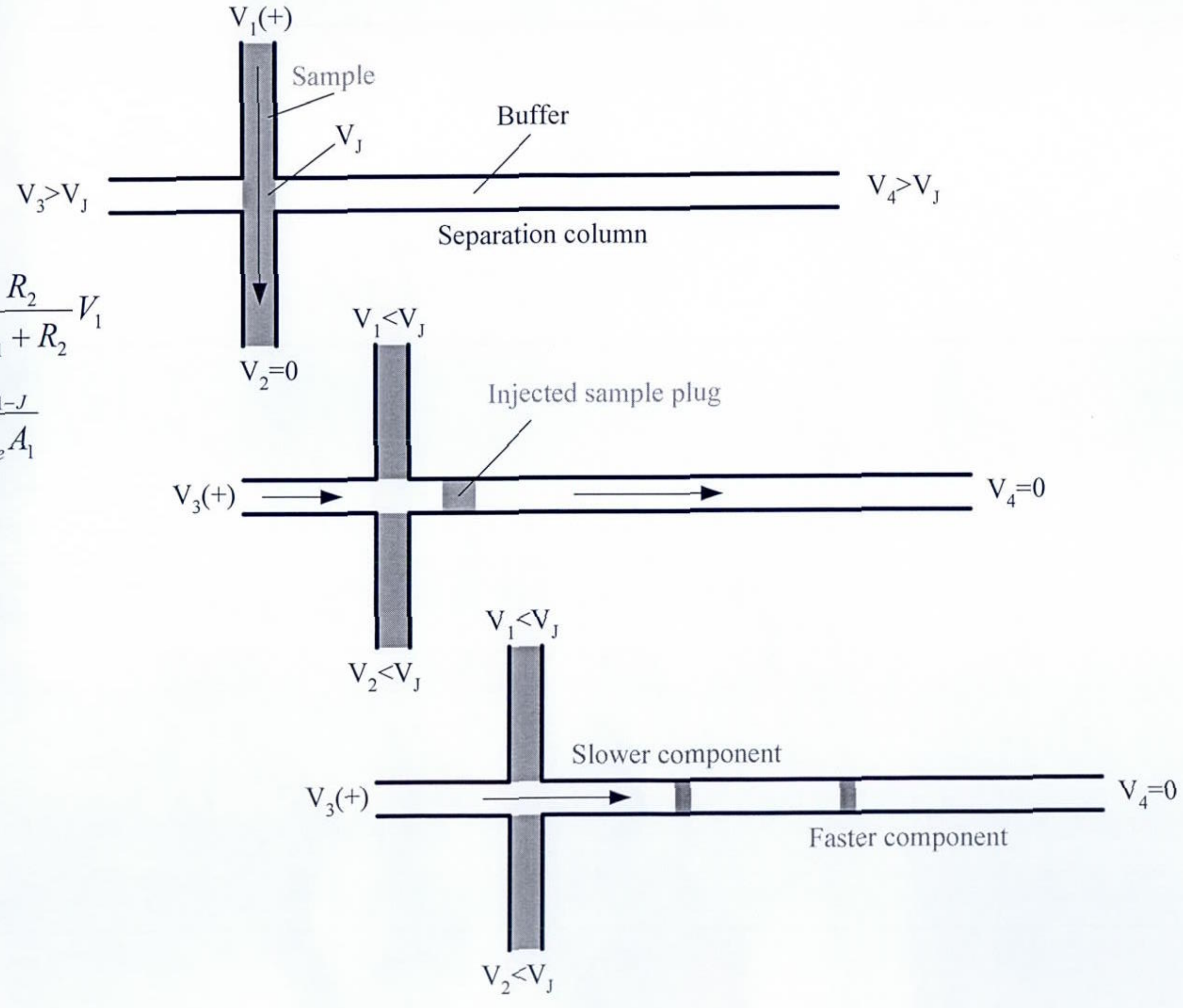
  ∵ simple, cheap, complete separation of all electrophoretically different components

  small samples

Electrophoretic separation with electroosmotic flow

$$V_J = \frac{R_2}{R_1 + R_2} V_1$$

$$R_1 = \frac{L_{1-J}}{\sigma_e A_1}$$



Prof. Ho-Young Kim