

when $\lambda_0 \gg a$

$$Q \sim a^4$$

: same as pressure - driven flow



Electrophoresis

The charge of macromolecules and particles



Poisson eq in spherical coordinates

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

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

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

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

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

\downarrow_0

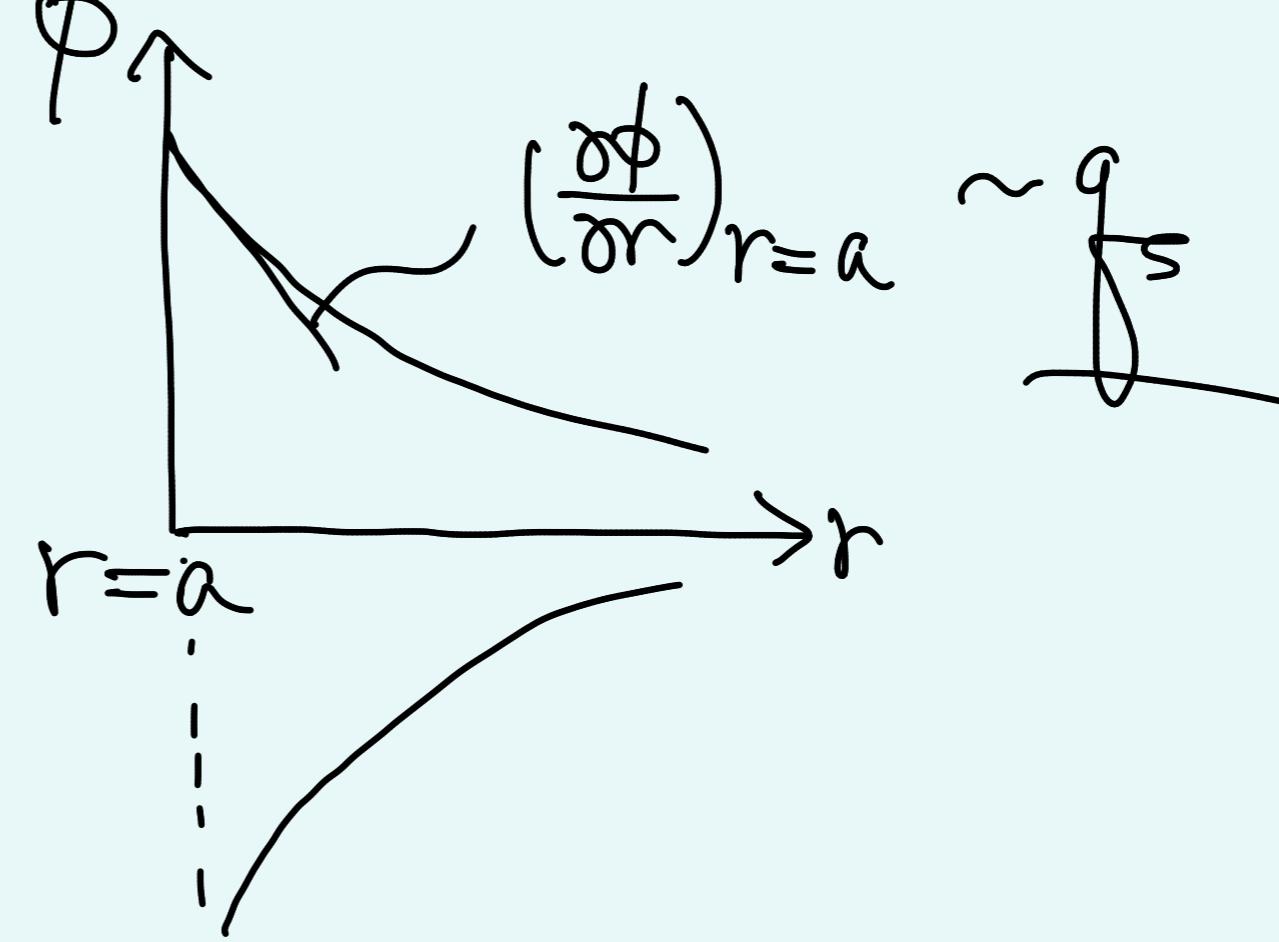
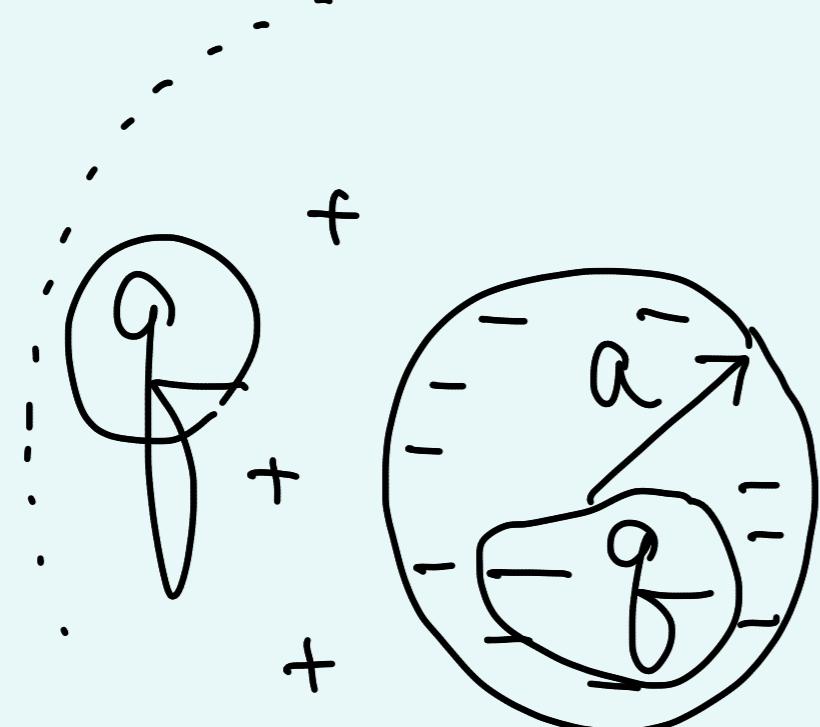
$$= 4\pi\epsilon a^2 \left(\frac{\partial \phi}{\partial r} \right)_{r=a}$$

[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/m²]



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

Poisson eq.

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

Boltzmann distribution

$$\begin{aligned} \rho_E &= zFC_0 \left[\exp \left(-\frac{2F\phi}{RT} \right) - \exp \left(\frac{2F\phi}{RT} \right) \right] \\ &= -2zFC_0 \sinh \left(\frac{2F\phi}{RT} \right) \end{aligned}$$

Debye - Hückel approximation for small potentials,

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

$$\text{set } \xi = r\phi$$

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

Σ

$[x_i]$

$$\text{LHS} = \frac{1}{r} \frac{d^2 \xi}{dr^2}$$

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

: the same form as for the plane wall prob.

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

° $\phi \rightarrow 0$ as $r \rightarrow \infty$

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

$$\text{at } r = a, \quad \phi = \xi \quad : \quad A = \xi a \exp\left(\frac{a}{\lambda_D}\right)$$

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

$$\frac{\partial \phi}{\partial r} = \dots$$

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

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

$$g_s = \epsilon \Sigma \left(\frac{1}{a} + \frac{1}{\lambda_D}\right).$$

w

OR

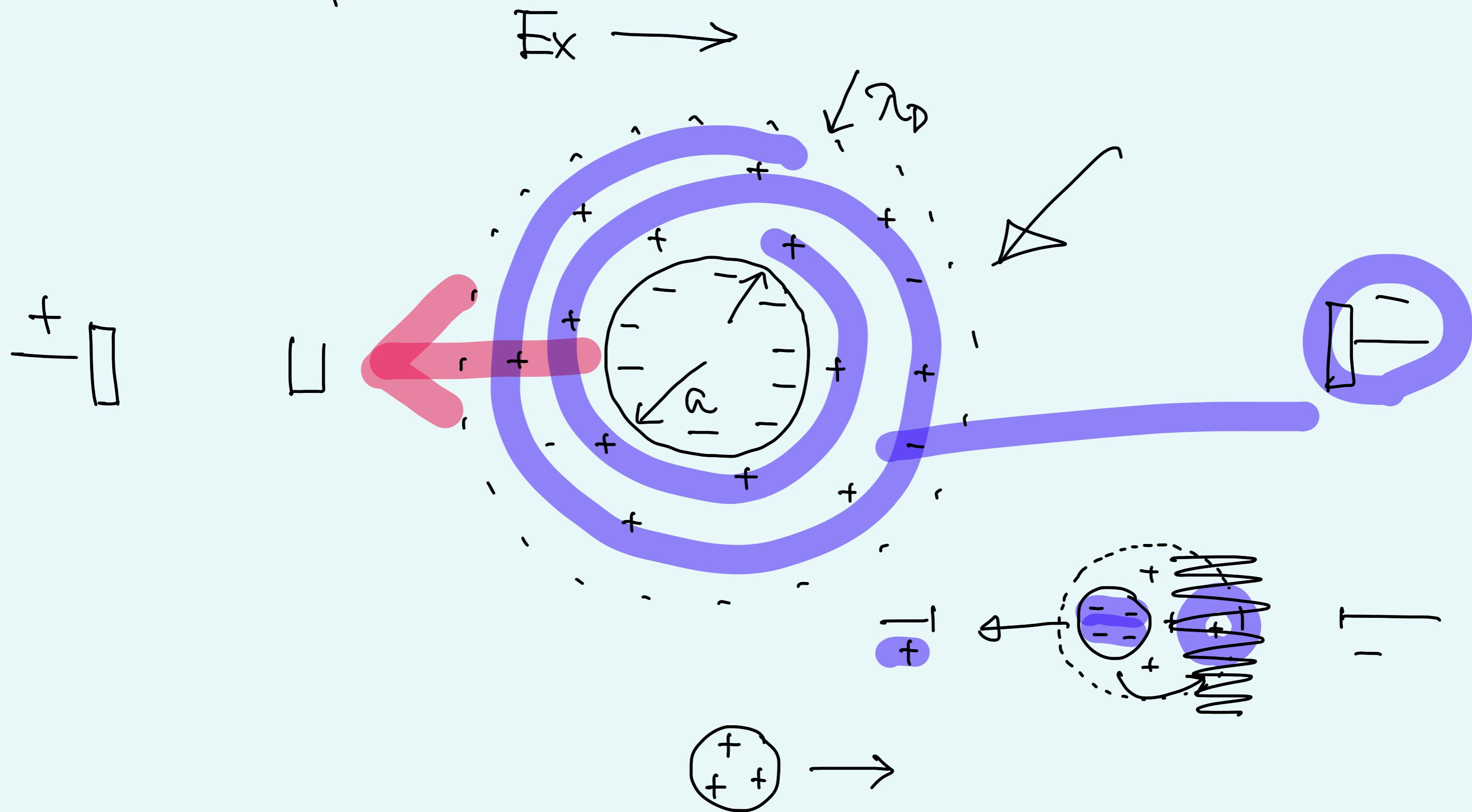
$$g_s = \frac{q}{4\pi a^2}$$

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

"

if $\lambda_D \ll a \rightarrow g_s = \frac{\epsilon \Sigma}{\lambda_D}$

Electrophoretic motion of spherical particle



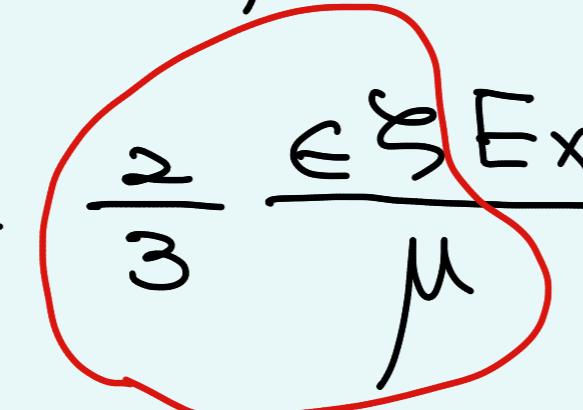
- For both small and large Debye length
 - no retardation

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

- particle \sim point charge
- force balance

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

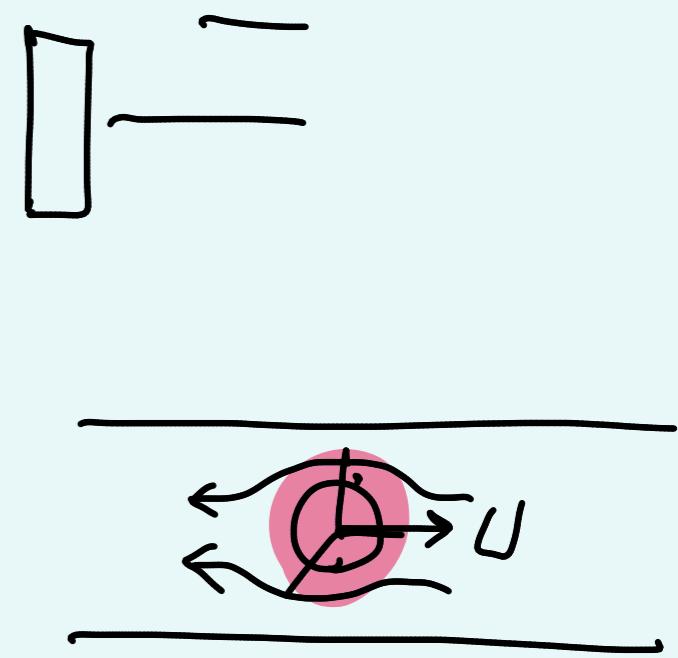
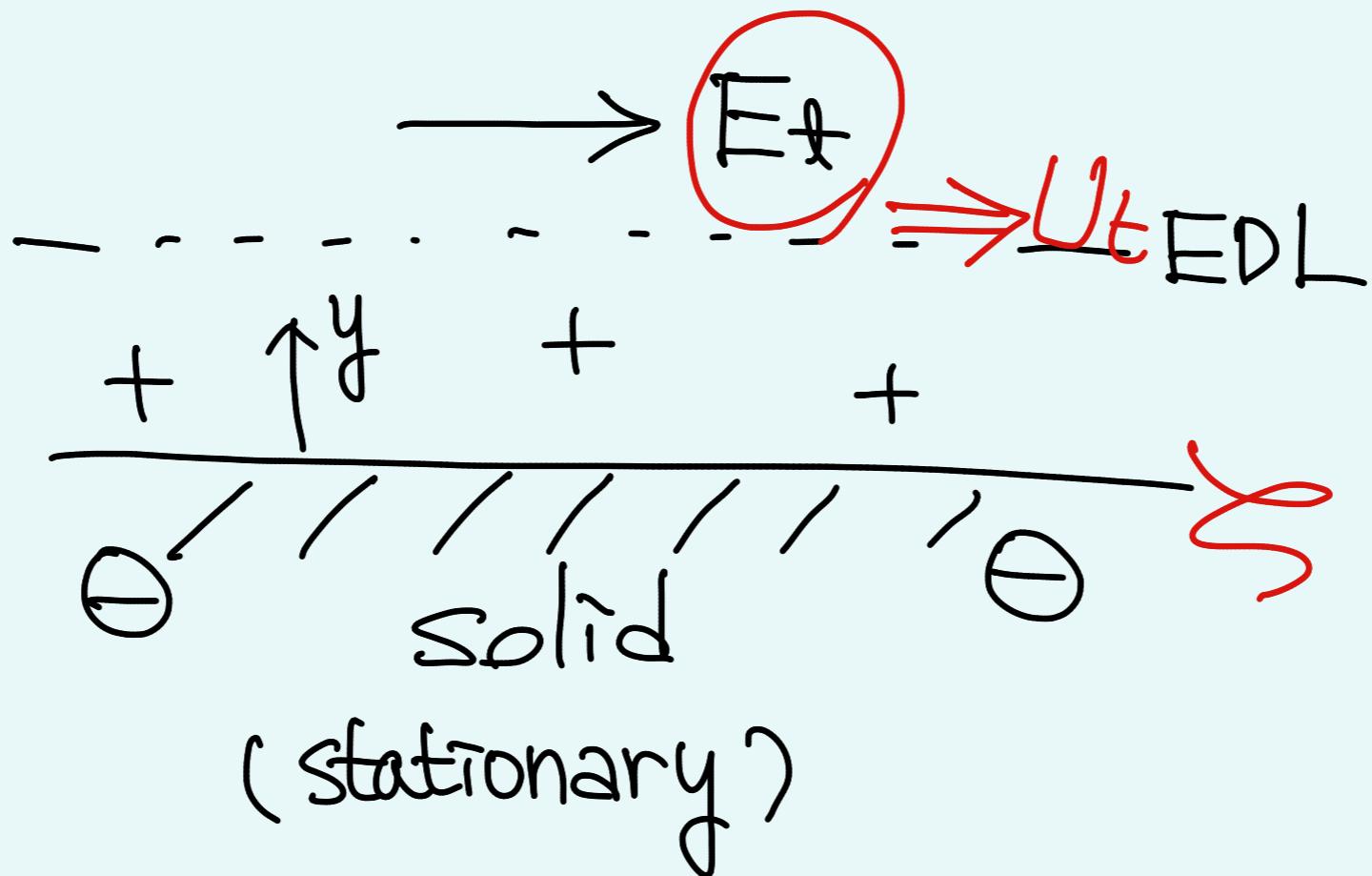
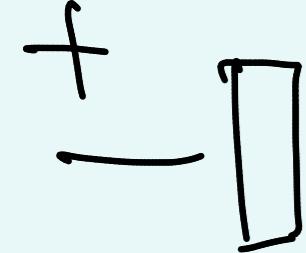
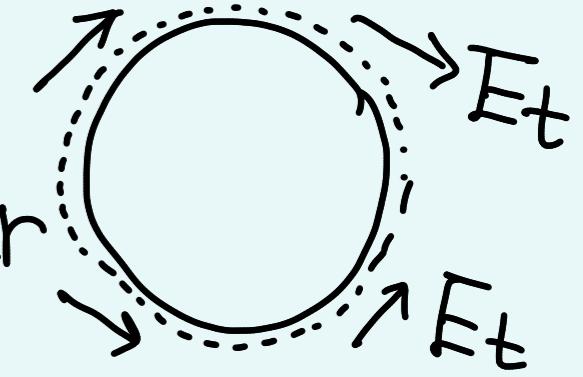
$$U = \frac{qE_x}{6\pi\mu a} = \frac{E_x}{6\pi\mu a} 4\pi\epsilon a \left(1 + \frac{a}{\lambda_D}\right) \underbrace{\ll 1}_{\text{for } a \gg \lambda_D}$$

$$= \frac{2}{3} \frac{\epsilon E_x}{\mu}$$


$\frac{U}{E_x}$: electrophoretic mobility

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

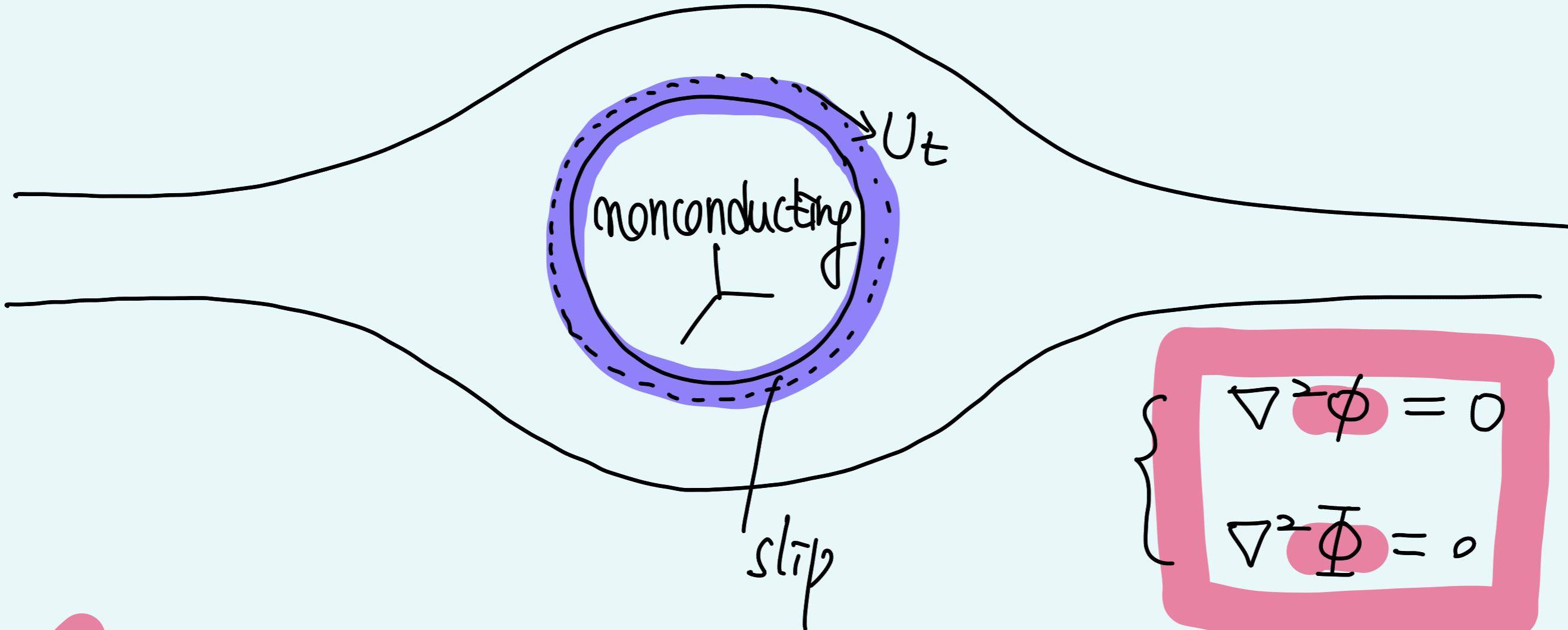
- neglect curvature effects in the double layer



: same as electrophoresis

$$U_f = - \frac{\epsilon s}{\mu} E_t$$

tangential to the solid surface



$$\left. \begin{array}{l} \nabla^2 \phi = 0 \\ \nabla^2 \Phi = 0 \end{array} \right\}$$

$$I = \frac{V}{R}$$

$$= \sigma V$$

$$E \cdot l$$

(electric field)

(fluid flow)

\therefore slip B.C.

B.C. normal to the surface

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

(a)

insulating
(glass bead)

$$\downarrow 0$$

$$\hat{n} \cdot \bar{E}^b = 0 \quad \text{in conducting medium}$$

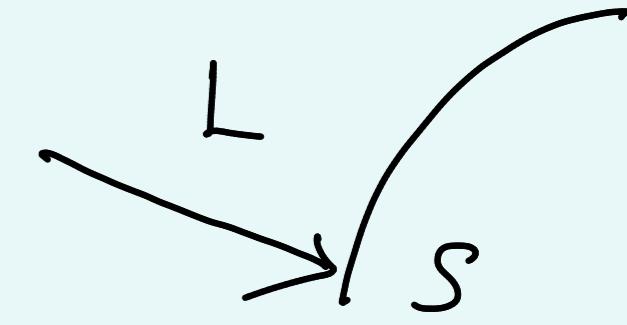
conducting
(electrolyte soln)

$$\sigma_a \ll \sigma_b$$

$$\hat{n} \cdot \nabla \phi = 0$$

in liquid

Continuity : $\hat{n} \cdot \bar{U} = 0 \mid_{\text{body}}$



$$\hat{n} \cdot \nabla \bar{\phi} = 0 //$$

B.C. tangential to the surface

$$\left\{ \begin{array}{l} \hat{t} \cdot \bar{E} = E_t \\ \hat{t} \cdot \hat{u} = U_t = - \frac{\epsilon \varsigma}{\mu} E_t \end{array} \right.$$



Free stream condition

$$\left\{ \begin{array}{l} \bar{E} = E_x \hat{i}_x \\ \bar{U} = U \hat{i}_x \end{array} \right.$$

Q. 10

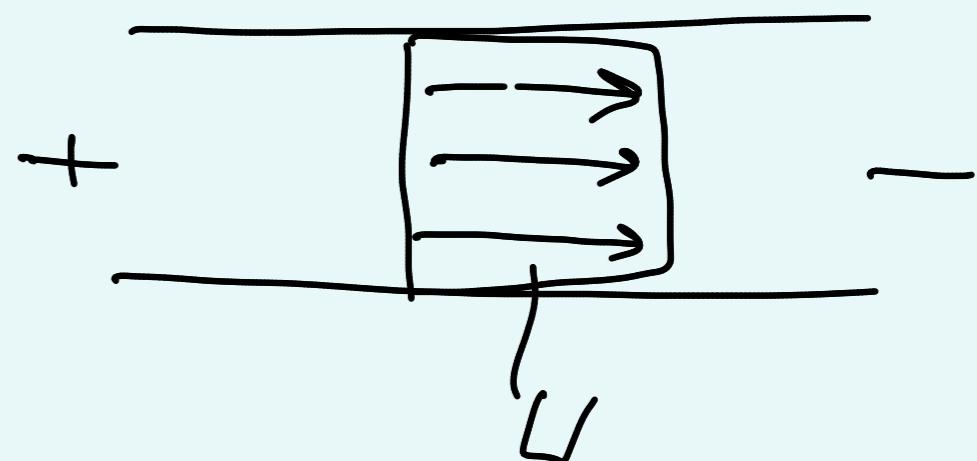
$$10 \downarrow \quad \bar{\phi} = - \frac{\epsilon \varsigma}{\mu} \phi \quad 2V \quad 1V$$

Velocity of a particle moving relative to a stationary liquid :

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

: Helmholtz - Smoluchowski eq.

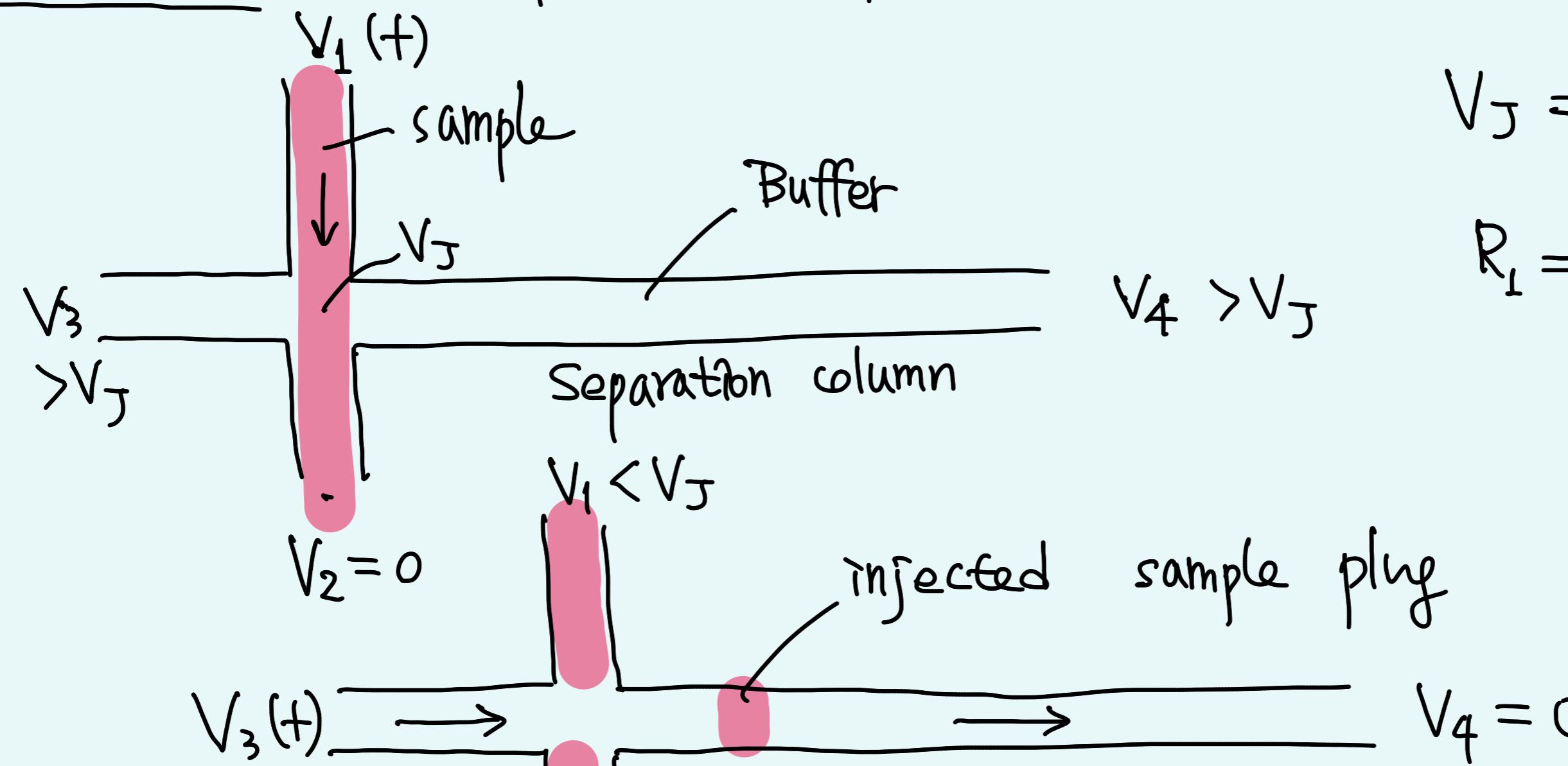
∴ electrophoresis $\xleftrightarrow[\text{complementary}]{}$ electroosmosis



Zone electrophoresis

- to minimize convectional effects arising from temperature gradients due to Joule heating.
- Support materials
 - [moninteracting : 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

Micromscale electrophoretic separation with electroosmotic flow



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

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

