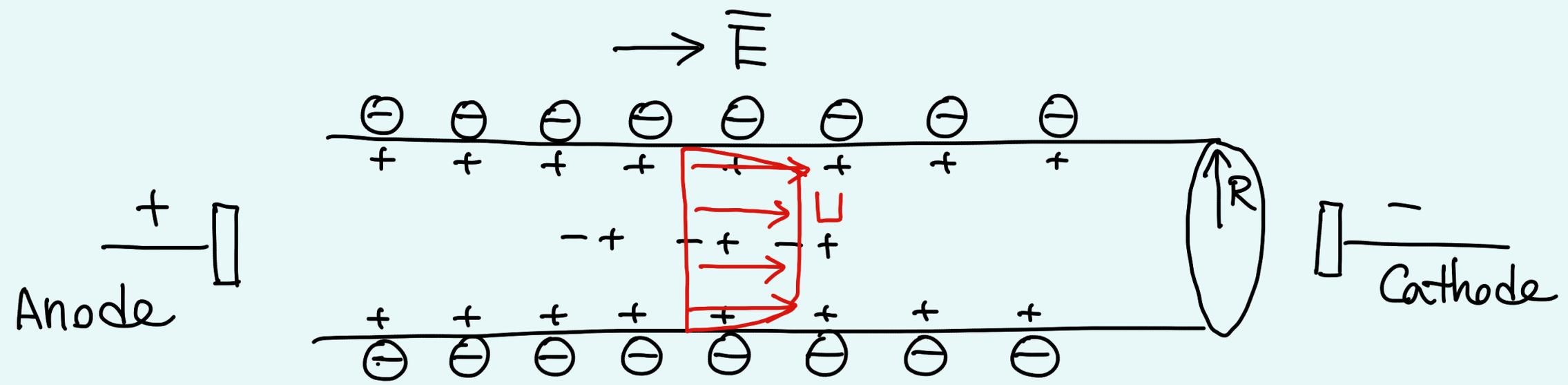


# Electroosmosis

Basic concept

$$\frac{\bar{u}}{V} = \frac{\rho \bar{E}}{V}$$



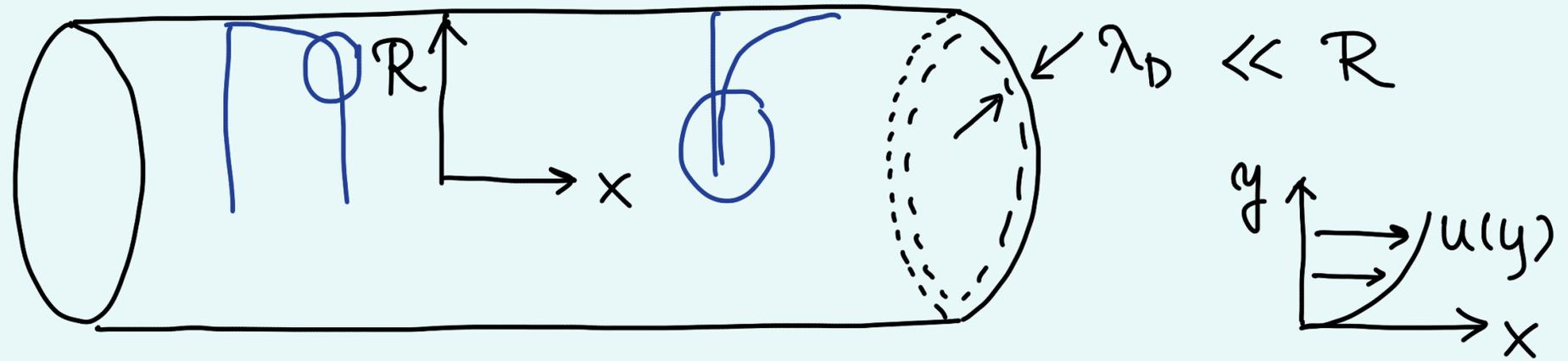
momentum equation

$$\rho \frac{D\bar{u}}{Dt} = -\nabla p + \mu \nabla^2 \bar{u} + \rho g + \underbrace{\rho_E \bar{E}}_{\text{electric body force per unit volume}}$$

no pressure gradient  
inertia free

$$\mu \nabla^2 \bar{u} = -\rho_E \bar{E}$$

electric body force per unit volume



in diffuse layer,

$$\mu \frac{\partial u}{\partial y^2} = - \underbrace{\int_E \rho}_{\text{Poisson's eq.}} E_x = \underbrace{\epsilon \frac{\partial^2 \phi}{\partial y^2}}_{\substack{= \\ \frac{\partial^2 \phi}{\partial x^2} \ll \frac{\partial^2 \phi}{\partial y^2}}} E_x$$

$$\mu \frac{\partial u}{\partial y} = \epsilon \frac{\partial \phi}{\partial y} E_x + \text{circled arrow}$$

at the edge of diffuse layer ( $y \rightarrow \infty$ )  
 $\frac{\partial u}{\partial y} = \frac{\partial \phi}{\partial y} = 0$

$$\mu \int_0^{\infty} \frac{\partial u}{\partial y} dy = \epsilon E_x \int_0^{\infty} \frac{\partial \phi}{\partial y} dy$$

$$\mu [\underline{u(y \rightarrow \infty)} - u(y=0)] = \epsilon E_x [\underline{\phi(y \rightarrow \infty)} - \underline{\phi(y=0)}]$$

$$\mu (U - 0) = \epsilon E_x (0 - \xi)$$

$$U = - \frac{\epsilon \xi}{\mu} E_x$$

Helmholtz - Smoluchowski eq.

Outside the diffuse layer

$$\frac{\mu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) = \cancel{\rho_E} E_x = 0$$

$$r \frac{\partial u}{\partial r} = \text{const.} = a$$

$$\frac{\partial u}{\partial r} = \frac{a}{r}$$

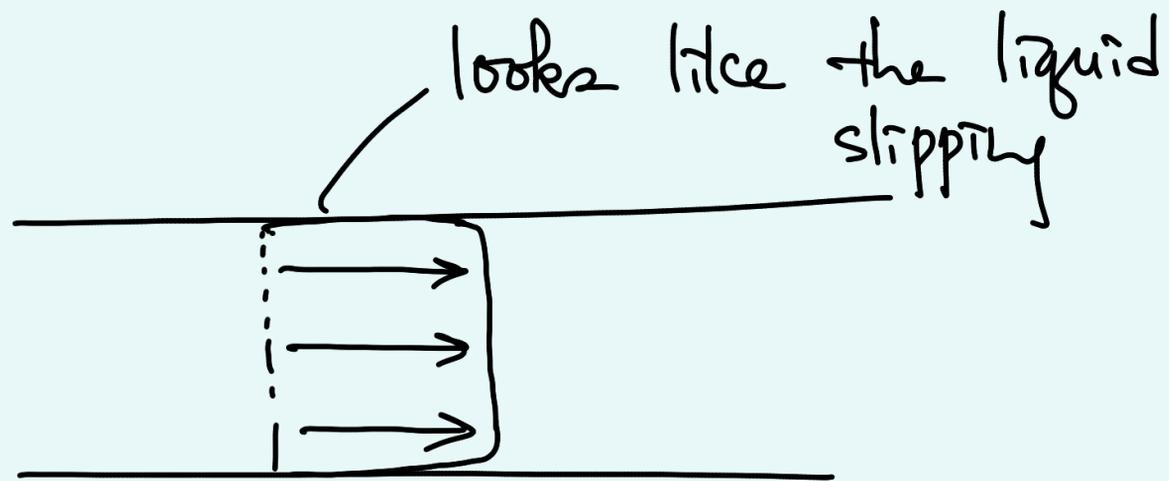
$$\left[ \begin{array}{l} \rho = 10^3 \text{ kg/m}^3 \\ \mu = 10^{-3} \text{ Pa}\cdot\text{s} \\ \sigma = 0.072 \text{ N/m} \\ \nu = 10^{-6} \text{ m}^2/\text{s} \\ \frac{\mu}{\rho} \end{array} \right]$$

$$u = a \ln r + \underline{b}$$

$$u(r=0) = \text{finite} \quad : \quad a = 0$$

$$u = \text{const.} = U$$

$\therefore$  plug flow



$U$  independent of  $R$

e.g.  $\zeta_{\text{typical}} \approx 0.1 \text{ V}$ ,  $E_x \approx 10^3 \text{ V/m}$

$$U = ?$$

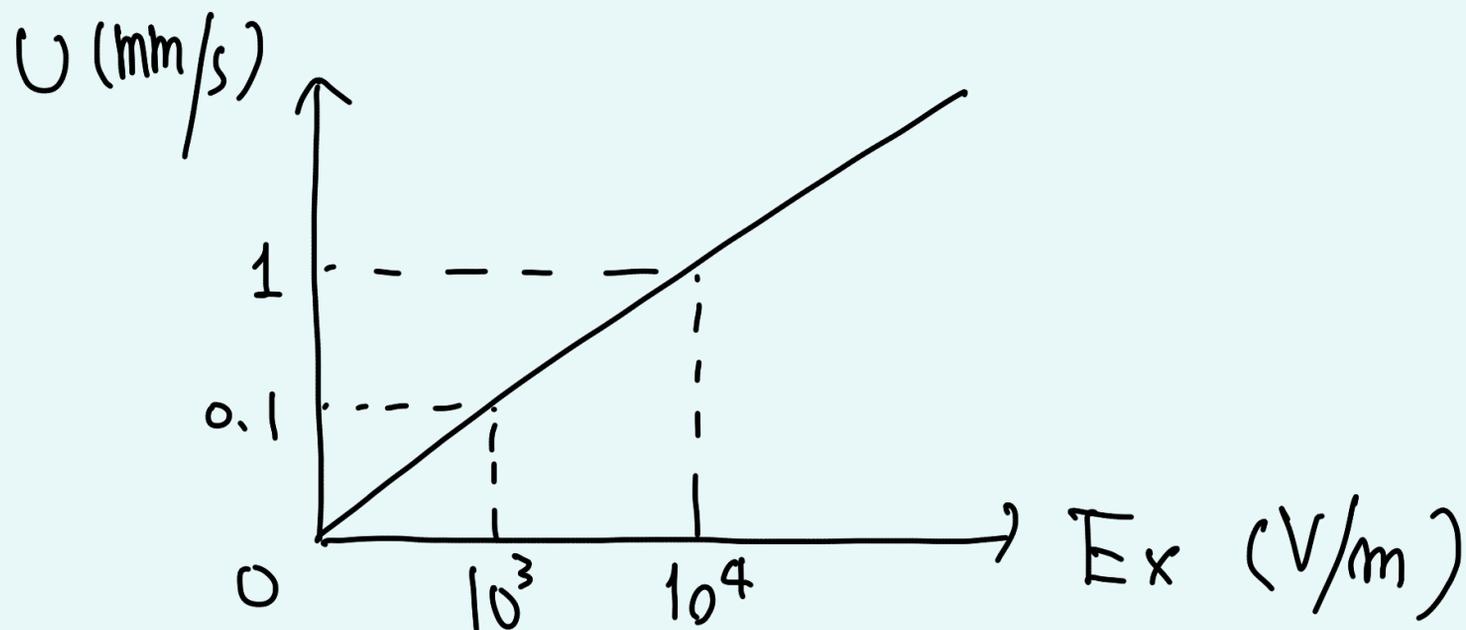
$$\epsilon_{\text{water}} = \epsilon_0 (1 + 79.1) = 7.08 \times 10^{-10} \text{ F/m}$$

$$\mu_{\text{water}} = 10^{-3} \text{ Pa}\cdot\text{s}$$

$$\frac{10 \text{ V}}{10^{-2} \text{ m}}$$

$$U = \frac{(17.08 \times 10^{-10}) (0.1) (10^3)}{10^{-3}}$$

$$\approx 10^{-4} \text{ m/s} \approx 100 \mu\text{m/s}$$



• Comparison with pressure-driven flow

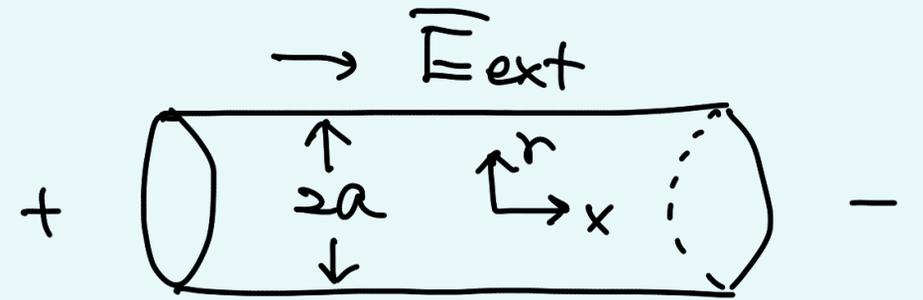
$$Q_{\Delta p} = \frac{\pi}{8\mu} R^4 \left( \frac{\Delta p}{L} \right) \sim R^4 \quad \checkmark$$

$$Q_{\text{EOF}} = U \pi R^2 \sim R^2 \quad \left( \frac{\lambda_D}{R} \ll 1 \right)$$

as  $R \downarrow$  : electroosmosis increasingly effective

# Effects of $\frac{\lambda_0}{R}$

- pressure gradient exists
- binary dilute soln.



momentum eq.

$$0 = -\nabla p + \mu \nabla^2 \bar{u} + \underbrace{\int_{\vec{E}} \rho_i \vec{E}}_{=}$$

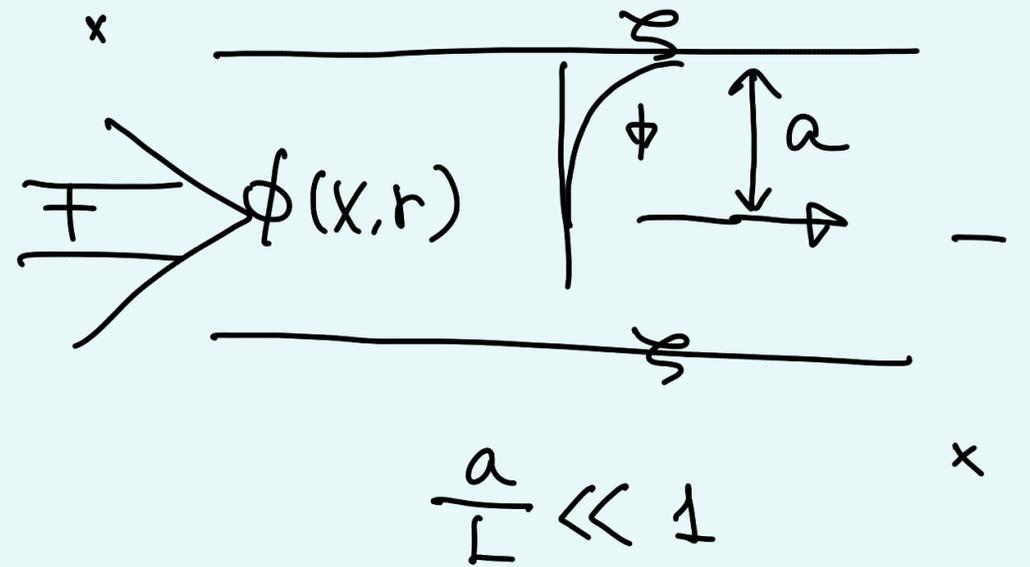
$$- F(z_+ c_+ - z_- c_-) (\nabla \phi)$$

symmetrical salt:  $z_+ = z_- = z$

$$\frac{\mu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) = \frac{\partial p}{\partial x} + F z (c_+ - c_-) \frac{\partial \phi}{\partial x}$$

ion concentration  $\sim$  electric field

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



$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) + \frac{\partial^2 \phi}{\partial x^2} = - \frac{Fz}{\epsilon} (C_+ - C_-)$$

long capillary

$$\phi(x, r) = \underline{\Phi(x)} + \underline{\psi(x, r)}$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) = - \frac{Fz}{\epsilon} (C_+ - C_-)$$

Nernst-Planck equation

Boltzmann distribution

$$C_{\pm}(x, r) = C(x) \exp \left( \mp \frac{zF\psi}{RT} \right)$$

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right) = - \frac{Fz}{\epsilon} C \left[ \exp \left( - \frac{zF\psi}{RT} \right) - \exp \left( \frac{zF\psi}{RT} \right) \right]$$

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

# Nondimensionalization

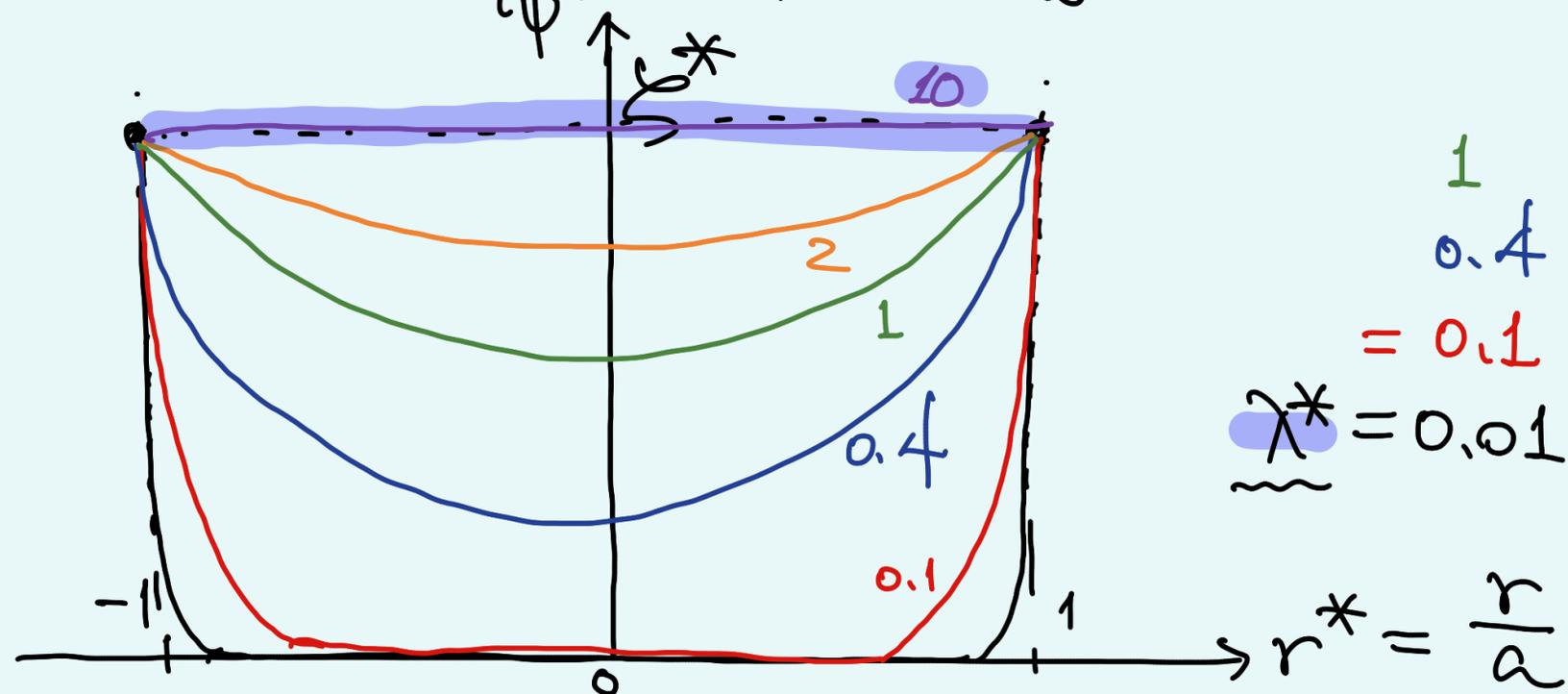
$$r^* = \frac{r}{a} \quad \boxed{\lambda^* = \frac{\lambda_D}{a}}, \quad \psi^* = \frac{zF\psi}{RT}$$

$$\lambda_D = \left( \frac{\epsilon RT}{2F^2 z^2 c} \right)^{1/2}$$

$$\lambda^{*2} = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left( r^* \frac{\partial \psi^*}{\partial r^*} \right) = \sinh \psi^*$$

B.C.  $\left[ \begin{array}{l} r^* = 0 : \frac{\partial \psi^*}{\partial r^*} = 0 \\ r^* = 1 : \psi^* = \psi_w^* = \zeta^* \end{array} \right.$

Numerical  
solution



N.-S.

$$\frac{\mu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) = - \underbrace{\frac{\epsilon}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \psi}{\partial r} \right)}_{\int \mathbb{E}} \underbrace{\frac{d\Phi}{dx}}_{\mathbb{E}_x} + \frac{dp}{dx}$$

B.C.  $\frac{\partial u}{\partial r} = 0$  and  $\frac{\partial \psi}{\partial r} = 0$  at  $r=0$

$u = 0$ ,  $\psi = \xi$  at  $r=a$ .

integrating w.r.t.  $r$  twice

$$u = - \frac{\epsilon (\psi(r) - \xi)}{\mu} \frac{d\Phi}{dx} + \frac{r^2 - a^2}{4\mu} \frac{dp}{dx} \quad \checkmark$$

$$Q = \int_0^a u(2\pi r) dr = - \int_0^a \frac{\epsilon (\psi - \xi)}{\mu} \frac{d\Phi}{dx} (2\pi r) dr \quad \checkmark$$

$$- \frac{\pi a^4}{8\mu} \frac{dp}{dx}$$

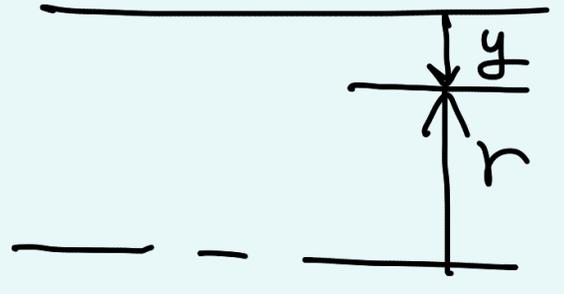
$$\psi(r) = ?$$

(1) Limiting case  $\frac{\lambda_D}{a} \ll 1$ .

neglect curvature effect.

$$\frac{\partial^2 \psi^*}{\partial y^{*2}} = \sinh \psi^*$$

$$y^* = \frac{y}{\lambda_D}$$



$y = a - r$ .

$$\psi^* = \frac{zF\psi}{RT} \ll 1$$

$$\frac{\partial^2 \psi^*}{\partial y^{*2}} - \psi^* = 0$$

$$\psi^* = C_1 e^{y^*} + C_2 e^{-y^*}$$

B.C.  $\left[ \begin{array}{l} y^* = 0 : \psi^* = \psi^* \\ y^* \rightarrow \infty : \psi^* \rightarrow 0 \end{array} \right.$

$$\psi^* = \zeta^* e^{-y^*}$$

$$\psi = \zeta e^{-(a-r)/\lambda_0} //$$

$$\therefore u = \frac{\epsilon \zeta}{\mu} \left[ 1 - e^{-(a-r)/\lambda_0} \right] \frac{d\Phi}{dx} + \frac{r^2 - a^2}{4\mu} \frac{dp}{dx}$$

$$Q = \frac{\epsilon \zeta}{\mu} \frac{d\Phi}{dx} \pi a^2 \left[ 1 - \frac{2\lambda_0}{a} + \frac{2\lambda_0^2}{a^2} - \frac{2\lambda_0^2}{a^2} e^{-a/\lambda_0} \right]$$

H.O.T.
H.O.T.

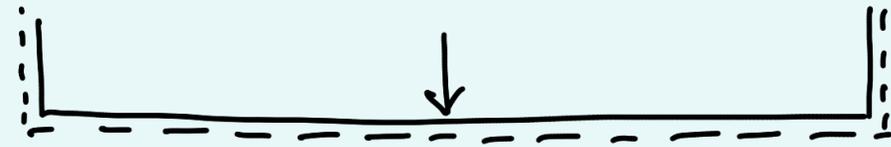
$$- \frac{\pi a^4}{8\mu} \frac{dp}{dx}$$

for  $\frac{dp}{dx} = 0$ ,  $\frac{a}{\lambda_0} \rightarrow \infty$  ( $\gg 100$ )

$$u \approx \frac{\epsilon \zeta}{\mu} \frac{d\Phi}{dx} \quad \therefore \text{Helmholtz-Smoluchowski eq.}$$

$$\lambda^* \ll 1$$

$$\lambda_D \ll a$$

 $C_0$ 
 $C_0$ 
 $C_0$ 


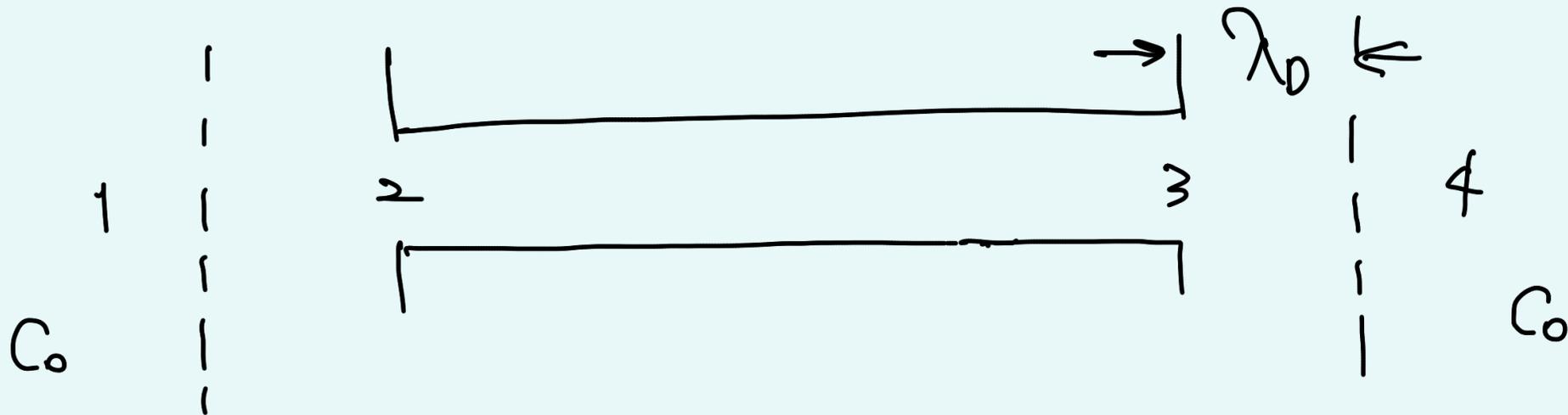
$\psi = 0$  in most region

$$C_+ = C_- = C_0$$

(2)  $\lambda^*$  large

$$\lambda_D \geq 10a$$

$\psi = \zeta$  throughout



At equilibrium with no flow ( $u=0$ ) & no flux ( $j_i=0$ )

$$\psi_1 = \psi_4 = 0, \quad \psi_2 = \psi_3 = \zeta$$

Boltzmann distribution

$$C_{\pm 2} = C_{\pm 3} = C \exp\left(\mp \frac{zF\psi}{RT}\right)$$

Momentum eq.

$$\frac{\mu}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) = \frac{\partial p}{\partial x} + \overbrace{Fz(C_+ - C_-)}^{\int_{\xi}^{\rho} E_x} \frac{\partial \phi}{\partial x}$$

$$C_+ - C_- = -C \sinh\left(\frac{zF\psi}{RT}\right)$$

B.C.  $u = 0$  at  $r = a$

$\frac{\partial u}{\partial r} = 0$  at  $r = 0$

$$\left\{ \begin{array}{l} u = -\frac{a^2 - r^2}{4\mu} \frac{d}{dx} \left[ p - 2zF C \sinh\left(\frac{zF\psi}{RT}\right) \right] \\ Q = -\frac{\pi a^4}{8\mu} \frac{d}{dx} \left[ \text{''} \right] \end{array} \right.$$