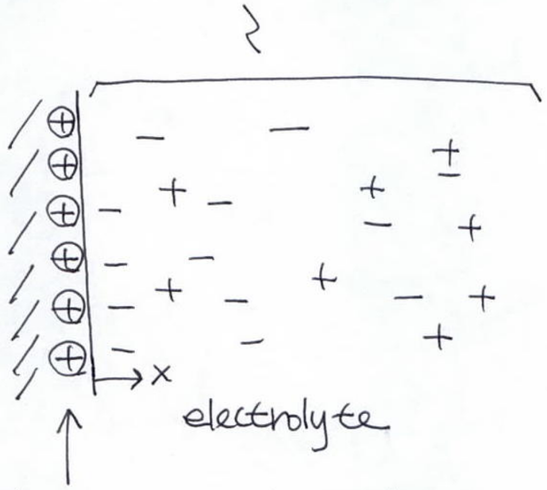
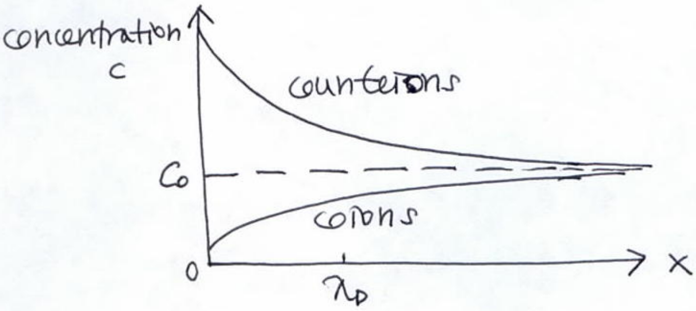
Electrical Double Layer



Acquired surface charge

: ionization, ion adsorption, ion dissolution



Thickness of the double layer

· assume ① symmetrical salt in solution

$$z_+ = -z_- = z$$

② $\bar{E} = E\hat{i}_x$

③ no coions in the layer

* Balancing : electric potential energy $\sim kT$ (thermal motion)

Poisson's eq

$$\nabla^2 \phi = -\frac{\rho_E}{\varepsilon} \sim \text{permittivity}$$

$$\rho_E = F z c$$

· F = Faraday's constant (charge of 1 mole of singly ionized molecules)

$= N_A e = 9.65 \times 10^4$ C/mol

$\left[\begin{array}{l} N_A = 6.022 \times 10^{23} \text{ /mole} \\ e = 1.602 \times 10^{-19} \text{ C} \end{array} \right.$

· z = charge number

$$\frac{d^2\phi}{dx^2} = \frac{Fzc}{\varepsilon}$$

· Electric potential energy $W = -Fz\phi$

$$\frac{d\phi}{dx} = \frac{Fzc}{\varepsilon}x \qquad \Delta\phi = \frac{Fzc}{2\varepsilon}x^2$$

$$\therefore \Delta W = -\frac{F^2 z^2 c x^2}{2\varepsilon} \qquad [\text{J/mole}]$$

$$\Delta W = RT$$

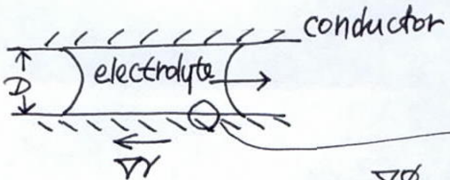
$$x \equiv \lambda_D = \left(\frac{\varepsilon RT}{2F^2 z^2 c}\right)^{1/2} \quad : \text{Debye length}$$

For an aqueous sol. of a symmetric electrolyte at 25°C

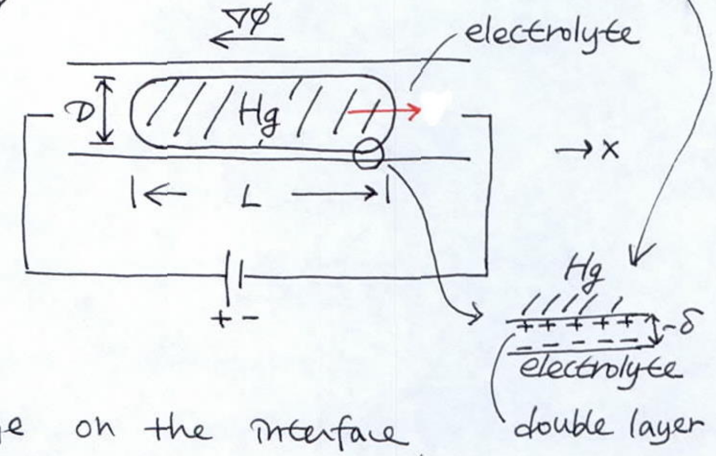
$$\lambda_D = \frac{9.61 \times 10^{-9}}{(z^2 c)^{1/2}} \quad [\text{m}]$$

$z = 1$ (univalent) : $c = 10^2$ mol/m³ $\Rightarrow \lambda_D = 1$ nm

$c = 1$ mol/m³ $\Rightarrow \lambda_D = 10$ nm



Electrocapillarity



- Lippman eq

$$\left(\frac{\partial \gamma_{SL}}{\partial V}\right)_\mu = +\sigma$$

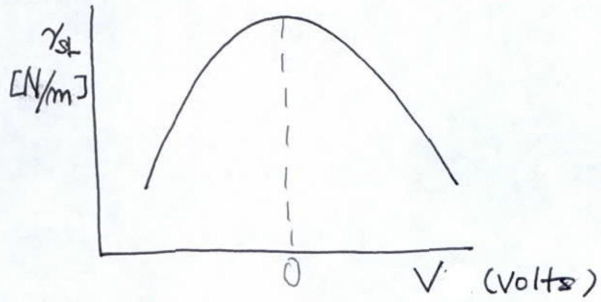
E: potential

σ: amount of charge on the interface

$$\left(\frac{\partial^2 \gamma_{SL}}{\partial V^2}\right)_\mu = +\frac{\partial \sigma}{\partial V} = -c$$

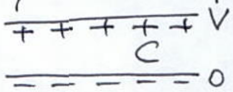
c: capacity of the double layer

$\mu = const.$: solution composition held const. (μ: chemical potential).



- $\gamma_{SL} = \gamma_0 - \frac{1}{2} c V^2$

· parallel capacitor



V related to $\nabla\phi$.

$$V(x) = \phi(x) - \langle\phi\rangle - \phi_q$$

$\langle\phi\rangle = \frac{1}{L}\int_0^L \phi(x)\,dx$: avg potential on the solid surface

- $\phi_q = \frac{q}{c}$, q : charge per unit area present at the interface in the absence of the applied potential $\phi(x)$

Flow field

$$\frac{dp}{dx} = \mu \frac{\partial^2 u}{\partial y^2}$$

$$u(y=0) = 0, \quad \left.\frac{\partial u}{\partial y}\right|_{y=D/2} = 0$$

$$\mu u' = \frac{dp}{dx}\left(y - \frac{D}{2}\right)$$

$$\mu u = \frac{dp}{dx}\left(\frac{1}{2}y^2 - \frac{D}{2}y\right)$$

$$\Delta p = \frac{2}{D}\Delta\gamma$$

$$-\frac{dp}{dx} = \frac{2}{D}\left(\frac{d\gamma}{dx}\right) = \frac{2}{D}\frac{\Delta\gamma}{L}$$

$$u = \frac{1}{\mu}\frac{dp}{dx}\left(\frac{1}{2}y^2 - \frac{D}{2}y\right)$$

$$U = \frac{1}{D}\int_0^D u\,dy = \frac{1}{D}\int_0^D \frac{1}{\mu}\frac{dp}{dx}\left(\frac{1}{2}y^2 - \frac{D}{2}y\right)dy$$

$$= \frac{1}{\mu D}\frac{dp}{dx}\underbrace{\left(\frac{1}{6}D^3 - \frac{1}{4}D^3\right)}_{\frac{2-3}{12}D^3 = -\frac{1}{12}D^3}$$

$$= -\frac{1}{12}\frac{1}{\mu}\frac{dp}{dx}D^2$$

see the next page

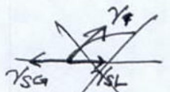
$$= -\frac{D}{6\mu}\frac{\Delta\gamma}{L}$$

$$\cancel{\Delta\gamma = \frac{d\gamma}{dx}L = -cV\frac{dV}{dx}L}$$

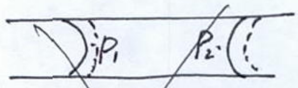
$$\cancel{= -cV\left(\frac{d\phi}{dx}\right)L}$$

$$\cancel{= -c(\phi - \langle\phi\rangle - \phi_q)\frac{d\phi}{dx}L}$$

$$\cancel{U = -\frac{cD}{6\mu}(\phi - \langle\phi\rangle - \phi_q)\frac{d\phi}{dx}}$$



$$\gamma_{SG} = \gamma\cos\theta + \gamma_{SL}$$



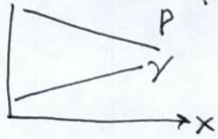
$$\cancel{P_1 = P_a - \gamma_1 \cdot K}$$

$$\cancel{-)\ P_2 = P_a - \gamma_2 K}$$

$$\cancel{P_1 - P_2 = \gamma_2 - \gamma_1}$$

$$\cancel{\Delta E = (\gamma_{SL} - \gamma_{SG})_2\Delta X - (\gamma_{SL} - \gamma_{SG})_1\Delta X = (-\gamma_2 + \gamma_1)\Delta X < 0}$$

$$\cancel{\gamma_2 > \gamma_1}$$



$$\cancel{\tau = -\frac{dP}{dx} = \gamma_2 - \gamma_1}$$

$$\Delta\gamma = -\frac{1}{2}C\,(V_2^2 - V_1^2)$$

$$U = -\frac{D}{6\mu L}\left(-\frac{C}{2}\right)(V_2^2 - V_1^2)$$

Assuming linear $\phi(x)$

$$\Delta\gamma = \int_0^L \frac{d\gamma}{dx}dx = \int_0^L -CV\frac{dV}{dx}dx$$

$$= \int_{\phi(0)}^{\phi(L)} -C\,(\phi - \langle\phi\rangle - \phi_q)\,d\phi$$

$$= -C\left[\underbrace{\int_{\phi(0)}^{\phi(L)} \phi\,d\phi}_{\substack{= \frac{1}{2}[\phi^2(L)-\phi^2(0)] \\ = \frac{1}{2}[\phi(L)+\phi(0)][\phi(L)-\phi(0)]}} - \underbrace{\int_{\phi(0)}^{\phi(L)} (\langle\phi\rangle + \phi_q)\,d\phi}_{= (\langle\phi\rangle+\phi_q)[\phi(L)-\phi(0)]}\right]$$

let $\phi(L) - \phi(0) = \Delta\phi$

$\frac{1}{2}[\phi(L)+\phi(0)] = \bar{\phi}$

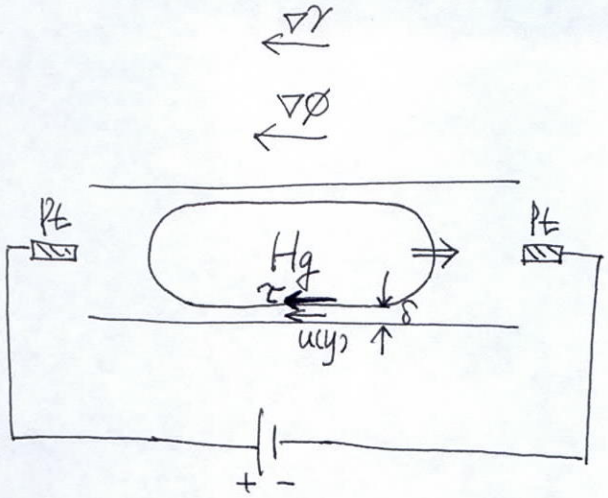
$$\Delta\gamma = -C\,(\bar{\phi} - \langle\phi\rangle - \phi_q)\,\Delta\phi$$

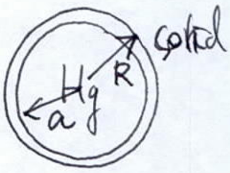
$$\therefore\ U = +\frac{C}{6\mu}\frac{D}{L}\left[\bar{\phi} - \langle\phi\rangle - \phi_q\right]\Delta\phi.$$

$$U \approx +\frac{1}{6\mu}\frac{D}{L}\,q\,\Delta\phi.$$

$$q \approx C\,(\bar{\phi} - \langle\phi\rangle - \phi_q)$$

$\approx 5\,\mu C/cm^2$: typical charge in the EDL for mercury in most aqueous electrolytes





$\cancel{U = \frac{1}{2\mu}\left(\frac{dp}{dx}\right)\delta^2}$

$$\frac{dp}{dx} = \mu \frac{\partial^2 u}{\partial y^2}$$

$$u(y=0) = 0$$

$$\mu \frac{\partial u}{\partial y}(y=\delta) = \tau = \frac{d\gamma}{dx}$$

$$\mu \frac{\partial u}{\partial y} = \frac{dp}{dx} y + c_1 \qquad \frac{dp}{dx}\delta + c_1 = \frac{d\gamma}{dx} \qquad c_1 = -\frac{dp}{dx}\delta + \frac{d\gamma}{dx}$$

$$\mu u = \frac{1}{2}\frac{dp}{dx} y^2 + c_1 y + \cancelto{0}{c_2}$$

$$= \frac{1}{2}\frac{dp}{dx} y^2 + \left(-\frac{dp}{dx}\delta + \frac{d\gamma}{dx}\right) y$$

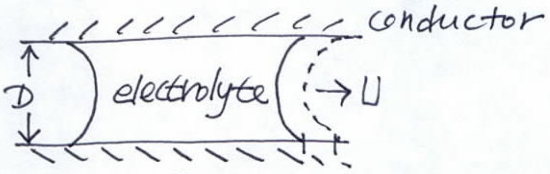
$$= \frac{dp}{dx}\left(\frac{y^2}{2} - \delta y\right) + \frac{d\gamma}{dx} y$$

$$u = \frac{1}{\mu}\left[\frac{dp}{dx}\left(\frac{y^2}{2} - \delta y\right) + \frac{d\gamma}{dx} y\right]$$

$$Q_{liquid} = 2\pi R \int_0^\delta u\,dy = \pi a^2 U_{Hg}$$

$$U_{Hg} = \frac{2R}{a^2}\int_0^\delta u\,dy \simeq \frac{2}{R}\int_0^\delta u\,dy$$

Continuous electrowetting



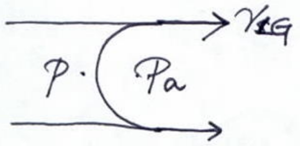
$\nabla\gamma > 0.$

$$\Delta E = \left[(\gamma_{SL}-\gamma_{SG})_A - (\gamma_{SL}-\gamma_{SG})_R\right] dx < 0.$$

$$\therefore \gamma_{SL,A} < \gamma_{SL,R}$$

Inertia-free flow $\qquad \frac{D}{L} \ll 1$

$$U = \left(-\frac{dp}{dx}\right)\frac{1}{12\mu}D^2$$



$$P = P_a - \frac{\gamma_{LG}}{(D/2)}$$

$$\gamma_{LG} = \gamma_{SG} - \gamma_{SL} \qquad (\text{assuming } \theta \approx 0)$$

$$\frac{dp}{dx} = -\frac{2}{D}\frac{d\gamma_{LG}}{dx}$$

$$= \frac{2}{D}\frac{d\gamma_{SL}}{dx}$$

$$\therefore U = -\frac{D}{6\mu}\frac{\Delta\gamma_{SL}}{L}$$

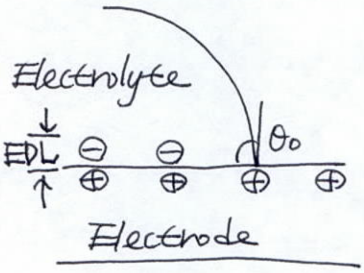
$$\Delta\gamma_{SL} = -\frac{1}{2}C(V_2^2 - V_1^2)$$

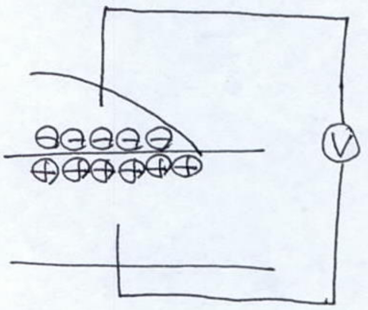
$$U = -\frac{D}{6\mu}\left(-\frac{C}{2}\right)(V_2^2 - V_1^2)$$

$$= \frac{DC}{12\mu}(V_2^2 - V_1^2)$$

Electrowetting

$\gamma_{SL}(V)$
$= \gamma_{SL}(V=0) - \frac{c}{2}V^2$





· Young's eq $\quad \gamma_{LG}\cos\theta = \gamma_{SG} - \gamma_{SL}$

$$\gamma_{LG}\cos\theta = \gamma_{SG} - \gamma_{SL,0} + \frac{c}{2}V^2$$

$$= \gamma_{LG}\cos\theta_0 + \frac{c}{2}V^2$$

$$\gamma_{LG}(\cos\theta - \cos\theta_0) = \frac{c}{2}V^2$$

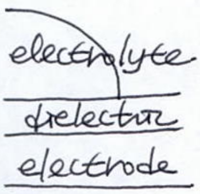
$$\cos\theta = \cos\theta_0 + \frac{c}{2\gamma_{LG}}V^2$$

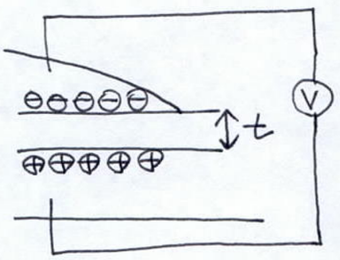
$$\theta < \theta_0$$

$c =$ specific capacitance of the layer

V across EDL : too low. $\Delta\theta$: small.

* Electrowetting on dielectric (EWOD)





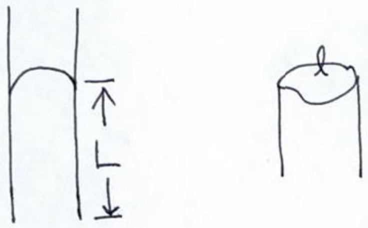
$$c = \frac{\epsilon_0 \epsilon}{t}$$

(ϵ_0 : vacuum permittivity
ϵ : dielectric constant

$$\cos\theta - \cos\theta_0 = \frac{\epsilon_0\epsilon}{2\gamma_{LG}t}V^2$$

To get the same $\Delta\theta$: $t\uparrow \sim V\uparrow$: Fig. 6. JAP CJ Kim

* Electrocapillary pressure



$$E = (\gamma_{SL} - \gamma_{SG})\, l L$$

$$\gamma_{SL} = \gamma_0 - \Delta\gamma$$

$$\Delta E = (-\Delta\gamma_{SL})\, l L + (\gamma_{SL} - \gamma_{SG})\, l \Delta L$$

$$F_d = -\frac{dE}{dx} = \underbrace{\Delta\gamma\, l}_{\text{electrocapillary force}} + \underbrace{(\gamma_{SG} - \gamma_{SL})}_{= \gamma_{LG}\cos\theta}\, l$$

ECP (ElectroCapillary Pressure)

$$= \frac{\text{force}}{\text{area}} = \frac{l\Delta\gamma}{A}$$

$$\Delta\gamma = \frac{1}{2} C V^2 = \frac{1}{2}\frac{\varepsilon_0 \varepsilon_r}{t} V^2$$