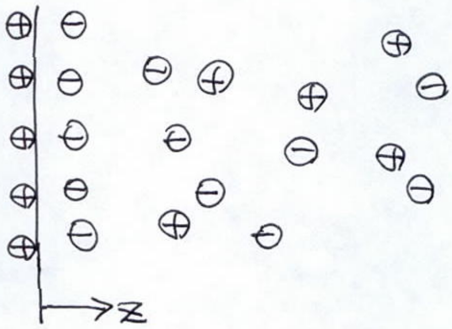
Electrokinetic Phenomena

- Electrokinetics : coupling between electric currents and fluid flow in liquids containing electrolytes

- Electric double layer



$z_+ = z_- = z$

- Rough estimation

  Poisson's eq

$$\frac{d^2\phi}{dx^2} = \frac{Fzc}{\varepsilon} . \qquad c = \text{const.}$$

- Detailed calculation

  - concentration of ions : Boltzmann distribution (probability of finding an ion at a particular point depends on the local potential)

$$\begin{cases} c_+ = c_0 \exp\left(-\frac{zF\phi}{RT}\right) \\ c_- = c_0 \exp\left(+\frac{zF\phi}{RT}\right) \end{cases} \qquad c \to c_0 \text{ as } \phi \to 0$$

  - charge density $\rho_E = F \sum z_i c_i$

$$\rho_E = F(zc_+ - zc_-)$$

$$= zFc_0 \left[\exp\left(\frac{-zF\phi}{RT}\right) - \exp\left(+\frac{zF\phi}{RT}\right) \right]$$

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

- Poisson's eq

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

$$= \frac{2zFc}{\varepsilon}\sinh\left(\frac{zF\phi}{RT}\right)$$: Poisson-Boltzmann Eq

For small potentials, $zF\phi \ll RT$

$$\sinh x = \sum_{n=0}^{\infty}\frac{1}{(2n+1)!}x^{2n+1}$$

$$= x + \frac{1}{3!}x^3 + \frac{1}{5!}x^5 + \cdots$$

$$\frac{d^2\phi}{dx^2} = \frac{2zFc}{\varepsilon}\cdot\frac{zF\phi}{RT} = \frac{2z^2F^2c}{\varepsilon RT}\cdot\phi$$

Recalling $\lambda_D \equiv \left(\frac{\varepsilon RT}{2F^2z^2c}\right)^{1/2}$

$$\frac{d^2\phi}{dx^2} = \frac{\phi}{\lambda_D^2}$$: Debye-Hückel approximation

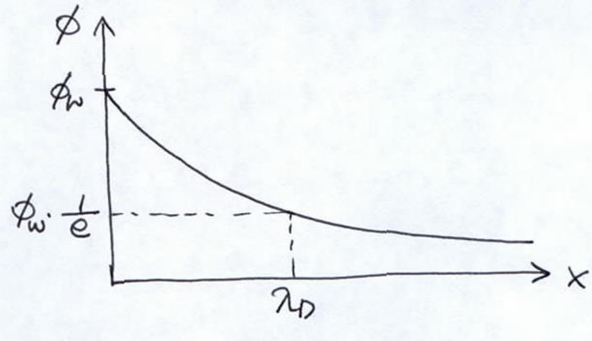
integrating,

$$\phi = a\exp\left(\frac{x}{\lambda_D}\right) + b\exp\left(-\frac{x}{\lambda_D}\right)$$

B.C. $x=0$: $\phi = \phi_w$

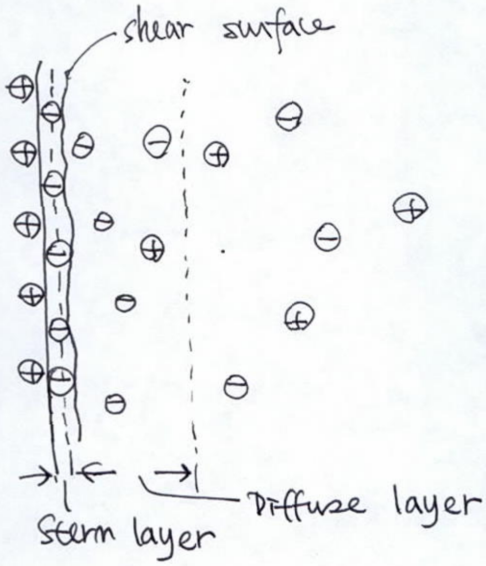
$x \to \infty$: $\phi = 0$, $\frac{d\phi}{dx} = 0$

$$\therefore \phi = \phi_w \exp\left(-\frac{x}{\lambda_D}\right)$$



: diffuse double layer (ions : point charges)

- Ions : finite size

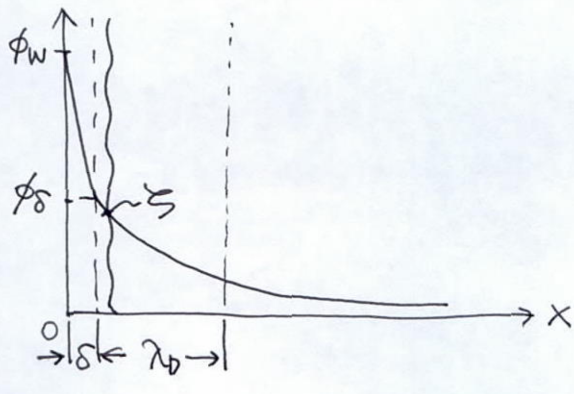


· Stern layer : Inner part of the double layer next to the surface, the outer boundary of which is approximately a hydrated ion radius from the surface

· Stern plane : the plane separating the inner layer and outer diffuse layer

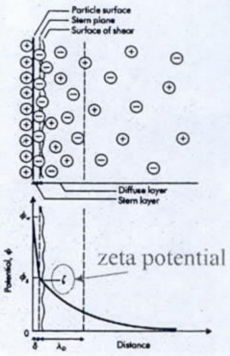
· zeta (ζ) potential = electrokinetic potential :
the potential at the shear surface between the charge surface and the electrolyte solution.

· shear surface : the plane at which the mobile portion of the diffuse layer can "slip" or flow past the charged surface

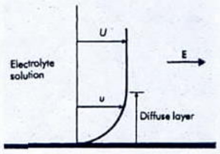


Lecture 9
Electrokinetically driven flows

- Basic concept

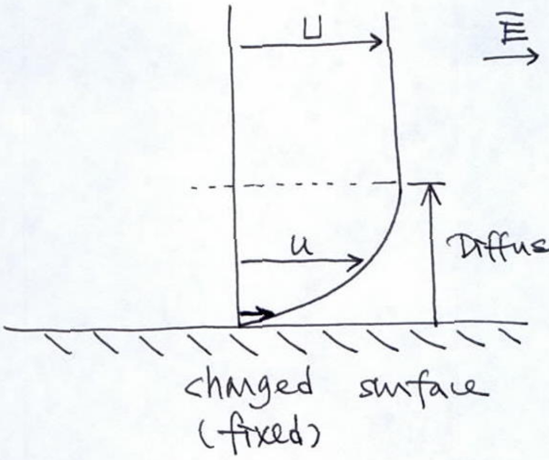


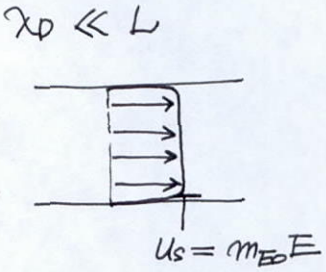
- Structure of electric double layer
- Flow produced by E-field



Four categories for electrokinetic phenomena

- Electroosmosis
  - motion of ionized *liquid* relative to the stationary *charged surface* by an applied *electric field*
- Electrophoresis
  - motion of the *charged surface* relative to the stationary *liquid* by an applied *electric field*
- Streaming potential
  - *electric field* created by the motion of ionized *liquid* along stationary *charged surfaces* ↔ electroosmosis
- Sedimentation potential
  - *electric field* created by the motion of *charged particles* relative to a stationary *liquid* ↔ electrophoresis





- Four categories of electrokinetic phenomena

	Nature of solid surface	
Potential	stationary[a]	Moving[b]
Applied	Electroosmosis	Electrophoresis
Induced	Streaming potential	Sedimentation potential

(a) e.g. microchannel surface

(b) e.g. colloidal particles, protein molecules