Electric Double Layer

When an electrolyte is brought in contact with a solid surface, and a charge accumulation occurs near the surface within the electrolyte, the chemical potential μ is constant throughout the system.

$\Rightarrow$ For any position r, $\boxed{\nabla \mu_{\pm}(r) \equiv 0}$

where $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$ where N = No. of identical non-interacting molecules.

If μ_0 and c_0 are the chemical potential and ionic density in absence of the electric potential,

then the chemical potential in presence of electric field

$$\mu_{\pm}(r) = \mu_0 + k_B T \ln\left(\frac{c_{\pm}(r)}{c_0}\right) \pm Z e \phi(r)$$

Here $\pm Z$ refers to ionic valences

e = elementary charge $\equiv$ charge of an electron $= 1.602 \times 10^{-19}$ Coulomb

(Also, remember $1\,eV = 1.602 \times 10^{-19}$ Joule)

$k_B \equiv$ Boltzmann Constant

$T \equiv$ Absolute temperature

$$\nabla \mu_{\pm}(r) = 0 \Rightarrow \boxed{k_B T \nabla \ln\left(\frac{c_{\pm}(r)}{c_0}\right) = \mp Z e \nabla \phi(r)}$$

Electric Double layer .... contd.

The governing equation on concentration to be solved with following Boundary conditions

Governing Eqn.

$$k_B T \nabla \ln\left(\frac{c_\pm(r)}{c_0}\right) = \mp Ze \nabla \phi(r)$$

$$\left.\begin{aligned} c_\pm(\infty) &= c_0 \\ \phi(\infty) &= 0 \\ \phi(\text{surface}) &= \zeta \end{aligned}\right\}$$

Solution

$$c_\pm(r) = c_0 \exp\left[\mp \frac{Ze}{k_B T}\phi(r)\right]$$

Charge density $\rho_{el}(r) = Ze\left[c_+(r) - c_-(r)\right]$

$$= -2Zec_0 \sinh\left[\frac{Ze}{k_B T}\phi(r)\right]$$

Poisson's Eqn.

$$\left.\begin{aligned} \Rightarrow \nabla \cdot E &= \frac{\rho_{el}}{\epsilon} \\ \text{and } E &= -\nabla\phi \end{aligned}\right\} \Rightarrow \nabla^2\phi(r) = 2\frac{Zec_0}{\epsilon}\sinh\left[\frac{Ze}{k_B T}\phi(r)\right]$$

Debye Hückel Limit $\quad Ze\zeta << k_B T \quad$ (At room temperature $\zeta << 26$ mV)

for which $\sinh(u) \approx u$ (Taking Taylor Series expansion, and ignoring higher order terms)

$$\Rightarrow \nabla^2\phi(r) = 2\frac{(Ze)^2 c_0}{\epsilon k_B T}\phi(r) \equiv \frac{1}{\lambda_D^2}\phi(r)$$

Electric Double Layer ..... contd.

One dimensional problem as a special case

$$\partial_z^2 \phi(z) = \frac{1}{\lambda_D^2} \phi(z) \qquad \text{with B.C.} \quad \left.\begin{array}{l} \phi(z=\infty) = 0 \\ \phi(z=0) = \zeta \end{array}\right\} \quad \frac{\partial}{\partial z}\phi \equiv \partial_z \phi$$

z is the distance from the solid surface

Z is the valence-state

<u>Solution</u>

$$\phi(z) = \zeta \exp\left[-\frac{z}{\lambda_D}\right]$$

From Poisson equation

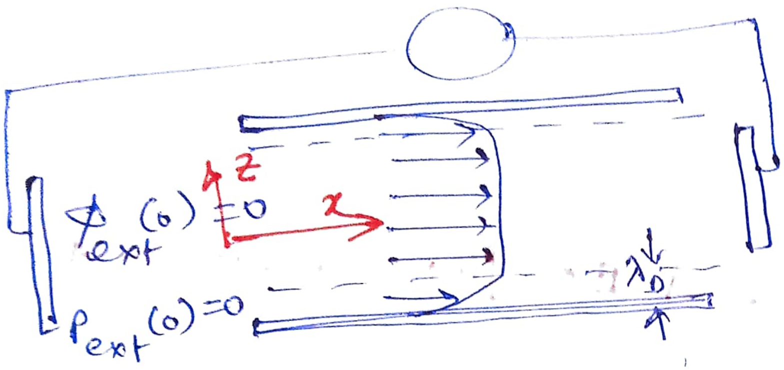
$$\rho_{el}(z) = -\epsilon\, \partial_z^2 \phi(z) = -\frac{\epsilon \zeta}{\lambda_D^2} \exp\left(-\frac{z}{\lambda_D}\right)$$

From the last slide $$c_\pm(z) = c_0 \exp\left[\mp \frac{Ze}{k_B T}\phi(z)\right]$$

and upon Taylor series expansion
and ignoring higher order terms based on Deby Hückel assumption $\boxed{\frac{Ze\zeta}{k_B T} << 1}$

$$c_\pm(z) = c_0 \exp\left[1 \mp \frac{Ze\zeta}{k_B T}\exp\left(-\frac{z}{\lambda_D}\right)\right]$$

Electroosmotic flow



Navier Stokes equation

$$\rho\left(\partial_t v + (v\cdot\nabla)v\right) = -\nabla p_{ext} + \eta\nabla^2 v - \rho_{el}^{eq}\nabla\phi_{ext}$$

For infinitely wide parallel plate channel at steady state, only x component to be considered

under electric field, which is homogeneous $(E = -\nabla\phi_{ext})$

Body force arising from Coulombic force $= qE$
Per unit volume, it becomes $\rho_{el}E$

$$E = -E\,\hat{e}_x$$

$$\nabla\phi_{ext}(r) = -E = E\,\hat{e}_x$$

$$v(r) = v_x(z)\,\hat{e}_x$$

x-component of Navier Stokes equation $0 = \eta\,\partial_z^2 v_x(z) + \left[\epsilon\,\partial_z^2\phi_{eq}(z)\right]E$

$$\Rightarrow \partial_z^2\left[v_x(z) + \frac{\epsilon E}{\eta}\phi_{eq}(z)\right] = 0$$

Boundary conditions $v_x\left(\pm\frac{h}{2}\right) = 0$ at upper and lower wall

$$\Rightarrow v_x(z) = \left[\zeta - \phi_{eq}(z)\right]\frac{\epsilon E}{\eta}$$

Electroosmotic Flow continued

For parallel plate geometry, the governing equation for potential remains same as before $\quad \dfrac{d^2\phi}{dz^2} = \dfrac{\phi}{\lambda_D^2}$

However, the boundary conditions will be different; $\phi(\pm \frac{h}{2}) = \zeta$

$\dfrac{d\phi}{dz} = 0$ at $z=0$ due to symmetry

$$\Rightarrow \phi(z) = c_1 e^{z/\lambda_D} + c_2 e^{-z/\lambda_D}$$

$$\Rightarrow \zeta = c_1 e^{\frac{h/2}{\lambda_D}} + c_2 e^{-\frac{h/2}{\lambda_D}}$$

$$= c_1 e^{-\frac{h/2}{\lambda_D}} + c_2 e^{\frac{h/2}{\lambda_D}}$$

and $\dfrac{c_1}{\lambda_D} - \dfrac{c_2}{\lambda_D} = 0$

$$\Rightarrow \phi(z) = \zeta \frac{\cosh(z/\lambda_D)}{\cosh\left(\frac{h/2}{\lambda_D}\right)}$$

$$\Rightarrow v_x(z) = \left[1 - \frac{\cosh(z/\lambda_D)}{\cosh\left(\frac{h/2}{\lambda_D}\right)}\right] \cdot \frac{\epsilon\zeta}{\eta} E$$

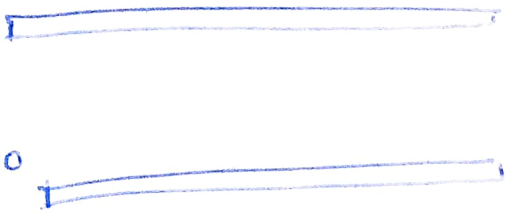
$$\boxed{v_{eo} = \frac{\epsilon\zeta}{\eta} E}$$

Electroosmotic Flow . . . contd.

Electroosmotic pumping requires flow against back pressure

$\phi_{ext}(x=0)=0$

$P_{ext}(x=0)=0$



$\phi_{ext}(x=L)=\Delta V$ $\qquad -\nabla\phi_{ext}=E=-\dfrac{\Delta V}{L}\hat{e}_x$

$P_{ext}(x=L)=\Delta P$ $\qquad -\nabla P_{ext}=-\dfrac{\Delta P}{L}\hat{e}_x$

Parabolic dent arising from superimposed EO flow and standard Poiseuille's flow.

$$v_x(z)=v_{x,eo}(z)+v_{x,p}(z)$$

$$=\left[1-\frac{\cosh(z/\lambda_D)}{\cosh\left(\frac{h/2}{\lambda_D}\right)}\right]\frac{\epsilon\zeta}{\eta}\frac{\Delta V}{L}-\underbrace{\left[\left(\frac{h}{2}\right)^2-z^2\right]\frac{1}{2\eta}\cdot\frac{\Delta P}{L}}_{\text{Responsible for back flow}}$$

For $\zeta=0.1\,V$

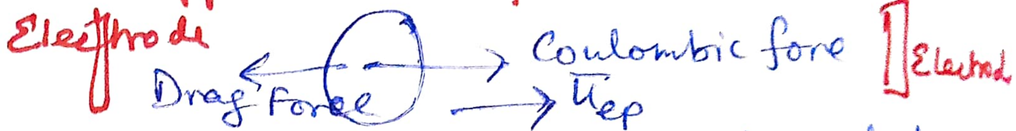
0 → Electroosmotic flow at zero back pressure

0 → Back pressure needed to exactly cancel the EO flow

Electrophoresis

Induced drift motion of charged colloidal particles or molecules, suspended in polar solution due to application of an electric field.

$$q_{surface} E = 6 \pi \eta \bar{u}_{ep} r_p$$



(Because of small size and low Re No., Stokes equation is valid

$$q_{surface} = Z_i e$$ where Z_i is integer valence number

e is elementary charge

* Within a short time scale of few μs, the charged particle reaches steady state / terminal velocity
* Low conductivity of the liquid (say deionized water) implies lack of ions that otherwise would have accumulated around the charged particle, and thereby neutralized its charge.

$$\bar{u}_{ep} = \frac{Z_i e}{6 \pi \eta r_p} E = \mu_{ion} E$$ where μ_{ion} is referred as ionic mobility.

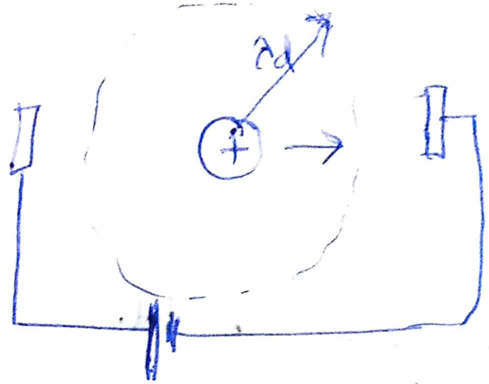
$$\bar{u}_{ep} \propto \frac{1}{r_p}$$ $\Rightarrow$ Smallest and most charged particles will attain the highest ionic mobility.

Gel Electrophoresis introduces sieving effect, and seggregates based on charge.

Electrophoresis .... contd.

Two Regimes (when suspended in ionic solution)

$d << \lambda_d$



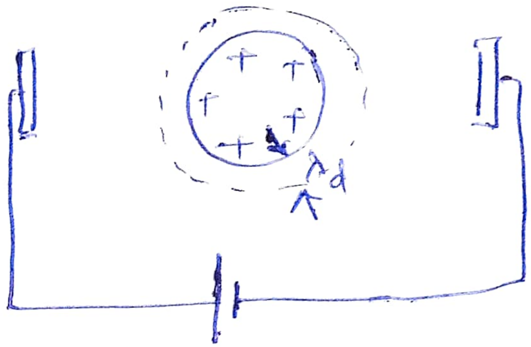
Electrophoresis of an ion

$$u = \frac{qE}{6\pi\eta r_p}$$

Here q is the total charge on the molecule

r_p is particle's Stokes radius (the radius of a sphere of equal drag).

$d >> \lambda_d$



In this case, ionic cloud near the particle surface can be approximated by the EDL relations for a flat plate

$$\Rightarrow u = \frac{\epsilon \zeta E}{\eta}$$

Electrophoresis of large solid particles of diameter 100 – 10,000 nm, polystyrene spheres, clay particles, single-celled organisms.

In the second case, the velocity does not depend on particle size

Polarization

Consider a small particle e.g., biological cell having electrical charge density ρ_{el} under electric field E.

Navier Stokes Eqn.:

$$\rho\left(\partial_t v + (v\cdot\nabla)v\right) = -\nabla P + \eta\nabla^2 v + \rho g + \rho_{el}E$$

The particle is occupying region Ω in space, centred around the point of position vector r_0.

The body force term $F_{el} = \int \rho_{el} E \, dr$

and accordingly, the i^{th} component of the body force term would be

$$F_i^{el} = \int_\Omega dr\, \rho_{el}(r_0 + r)\, E_i(r_0 + r)$$

$r_0 + r$ defines a general position inside the particle.

$$= \int_\Omega dr\, \rho_{el}(r_0 + r)\left[E_i(r_0) + r_j \partial_j E_i(r_0)\right]$$

This term arises due to Taylor Series expansion (first order terms)

$$r_i \frac{\partial E_i}{\partial x} + r_j \frac{\partial E_i}{\partial y} + r_k \frac{\partial E_i}{\partial z}$$

$$= Q E_i(r_0) + p_j \partial_j E_i(r_0)$$

Here,

$Q \equiv \int_\Omega dr\, \rho_{el}(r_0 + r)$ = Charge of particle

$p \equiv \int_\Omega dr\, \rho_{el}(r_0 + r)\, r$ = Electric dipole moment of the particle.

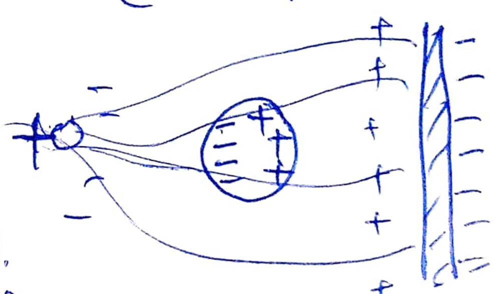
Polarization .... contd.

If the net charge of the particle is zero, $Q = 0$.

However, F_i^{el} can still exist if both dipole moment p and ∇E are non-zero.

Thus, force on charge neutral particle due to nonzero p and ∇E is refered as $F_{DEP} = (p \cdot \nabla) E$

Non-zero ∇E is generated by non-uniform electric field (Point electrode and planar electrode. Electric field becomes stronger when electrical field lines come close to each other (near point electrode).



(*) when $\epsilon_{particle} > \epsilon_{fluid}$

particle is more polizable than fluid medium

particle will have more surface charge than fluid medium.

$\Rightarrow$ particle will be pulled preferentially towards region of stronger electric field (LEFT)

when $\epsilon_{particle} < \epsilon_{fluid}$

$\Rightarrow$ fluid will be pulled preferentially towards region of stronger electric field

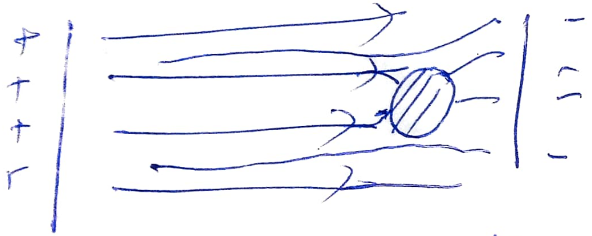
$\Rightarrow$ Particle will be pushed towards (RIGHT)

Inhomogeneous electric field is created by applying $\phi = \sigma V$ to a spherical electrode of radius r_0 situated at the floor at $r=0$, and $\phi = 0$ to planar electrode covering the ceiling at plane $r = h\, e_z$

For understanding this part go through NPTEL lec-24 (From Two issues part) and lec-25 upto(31:10)

Trapping takes place close to the spherical electrode $(|r| << h)$

$$F_{DEP}(r_0) = [p(r_0)\cdot\nabla]\, E_0(r_0).$$



Unperturbed lines of force (without sphere)

Unperturbed potential ϕ_0 is given by 2-D system

$$\phi_0(r,\theta) = -E_0\, r \cos\theta.$$

The electric field polarizes the dielectric sphere of radius a and dielectric constant ϵ_2. Distortion of ~~lines~~ electric field. Since

$$\phi(r,\theta) = \begin{cases} \phi_1(r,\theta) & \text{for } r > a \\ \phi_2(r,\theta) & \text{for } r < a. \end{cases}$$

Four boundary conditions are

$\phi_2(0,\theta)$ is finite

$\phi_1(a,\theta) = \phi_2(a,\theta)$

$\epsilon_1 \partial_r \phi_1(a,\theta) = \epsilon_2 \partial_r \phi_2(a,\theta)$

$\phi_1(r,\theta) \xrightarrow[r\to\infty]{} -E_0\, r\cos\theta$

Governing eqn. for both fluid and sphere

$$\nabla^2\phi(r) = 0$$

The solution of this ~~set of~~ governing with B.C.s listed

$$p = 4\pi\epsilon_1 \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}\right) a^3 E_0.$$

Clausius - Mossoti factor

Clausius - Mossotti factor

$$F_{DEP}(r_0) = \left[p(r_0)\cdot\nabla\right] E_0(r_0) + \cdots \text{ neglected}$$

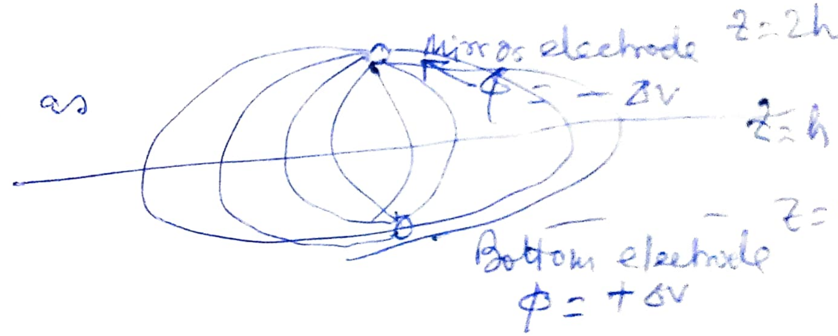
$$= 4\pi\epsilon_1 \frac{\epsilon_2-\epsilon_1}{\epsilon_2+2\epsilon_1} a^3 \left[E_0(r_0)\cdot\nabla\right] E_0(r_0)$$

$$= 2\pi\epsilon_1 \frac{\epsilon_2-\epsilon_1}{\epsilon_2+2\epsilon_1} a^3 \nabla\left[E_0(r_0)^2\right]$$

Since $2E\cdot\nabla E = \nabla\left[E^2\right]$

Because $\nabla(E^2) = \partial_i E_j E_j$

$\nabla\times E = 0 \Rightarrow \partial_i E_j = \partial_j E_i$ for $i\neq j$



Inhomogeneous electric field can be conceptualized as

$$\phi(r) = \frac{r_0}{|r|}\Delta V - \frac{r_0}{|r-2he_z|}\Delta V$$

which shows

$$\phi(r = he_z) = 0.$$

The trapping of particle takes place close to the spherical electrode; i.e., $|r| << h$.

In this region, $E(r) = -\nabla\phi(r) \approx \frac{r_0\Delta V}{r^2} e_r$ for $r_0 < |r| << h$

(i.e. the derivative of second term is neglected as it ~~as denominator~~ $\to 0$ becomes const. $= \frac{r_0}{2he_z}\Delta V$.

$$F_{DEP}(r) = 2\pi\epsilon_1 \frac{\epsilon_2-\epsilon_1}{\epsilon_2+2\epsilon_1} a^3 \nabla\left[\frac{(\Delta V)^2 r_0^2}{r^4}\right]$$

$$= -8\pi \frac{\epsilon_2-\epsilon_1}{\epsilon_2+2\epsilon_1} \frac{a^3 r_0^2}{r^5} \epsilon_1 (\Delta V)^2 e_r$$