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

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

Governing Eqn.

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

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 $\quad Ze\zeta \ll k_B T \quad$ (At room temperature $\zeta \ll 26$ 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

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

Solution

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

z is the distance from the solid surface

Z is the valence-state

From Poisson equation

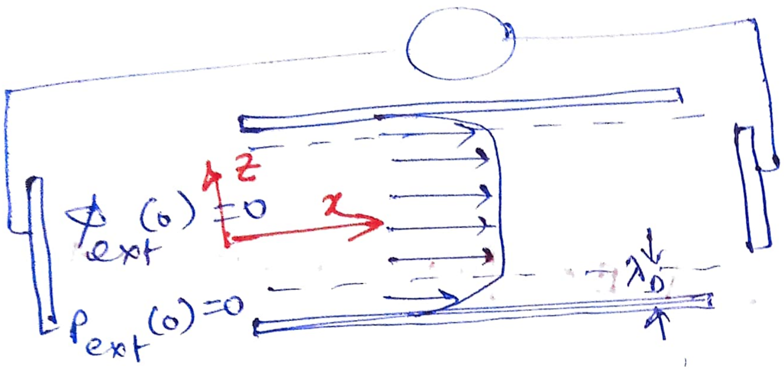
$$\rho_{el}(z) = -\epsilon\, \partial_z^2 \phi(z) = -\frac{\epsilon \zeta}{\lambda_D^2} \exp\left(-\frac{z}{\lambda_D}\right)$$

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



$\phi_{ext}(L) = \Delta V$

$p_{ext}(L) = 0$

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 $= q E$

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 $\dfrac{d^2\phi}{dz^2} = \dfrac{\phi}{\lambda_D^2}$

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

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

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

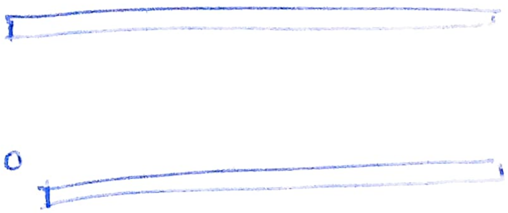
$$\boxed{v_{eo} = \frac{\epsilon \zeta}{\eta} E}$$

Electroosmotic Flow ... contd.

Electroosmotic pumping requires flow against back pressure

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

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



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

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

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 $\zeta=0.1\,V$

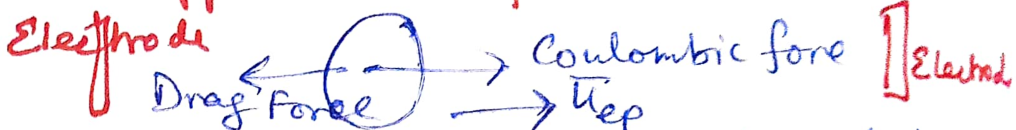
0 → Electroosmotic flow at zero back pressure

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.

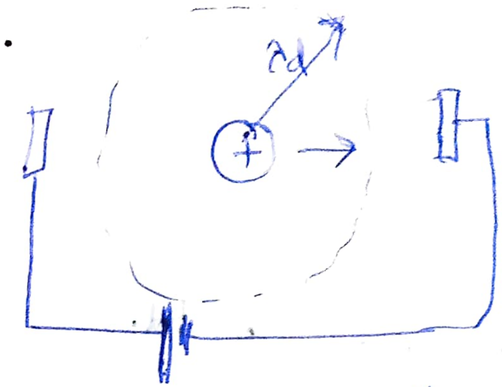
$$\bar{u}_{ep} \propto \frac{1}{r_p}$$ $\Rightarrow$ Smallest and most charged particles will attain the highest ionic mobility.

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

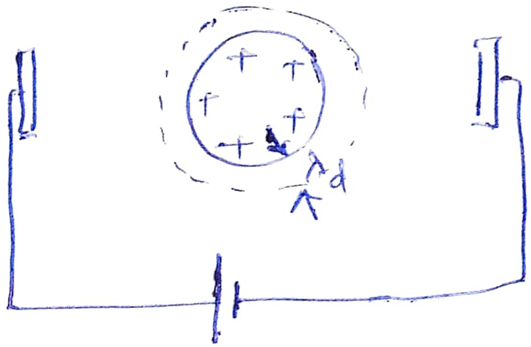
Electrophoresis . . . . contd.

Two Regimes (when suspended in ionic solution)

$d << \lambda_d$



$d >> \lambda_d$



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).

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

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

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

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.

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

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.

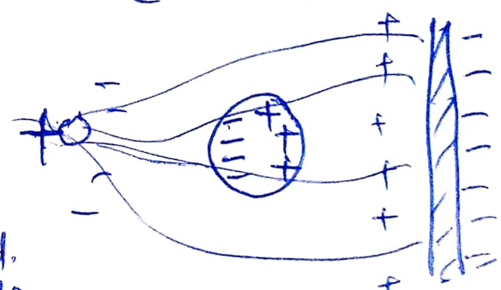
Polarization ..... contd.

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 referred 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

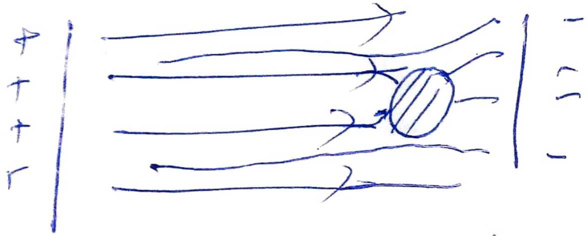
$\Longrightarrow$ Particle will be pushed towards (RIGHT)

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 $r = h e_z$

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

$$\left.\begin{aligned} &\phi_2(0, \theta) \text{ is finite} \\ &\phi_1(a, \theta) = \phi_2(a, \theta) \\ &\epsilon_1 \partial_r \phi_1(a, \theta) = \epsilon_2 \partial_r \phi_2(a, \theta) \\ &\phi_1(r, \theta) \xrightarrow[r \to \infty]{} -E_0 r \cos\theta \end{aligned}\right\}$$

Governing eqn. for both fluid and sphere

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

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

$$p = 4\pi\epsilon_1 \boxed{\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1}} a^3 E_0$$

Clausius - Mossotti factor

$[\quad\quad]\quad(\quad)$

Clausius - Mossotti factor

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

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

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

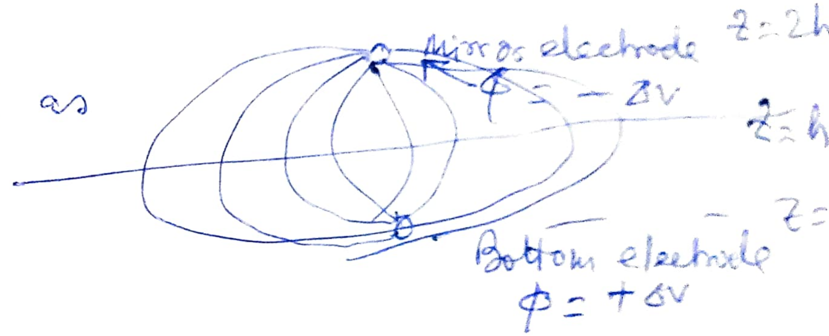
Since $2E\cdot\nabla E = \nabla\left[E^2\right]$

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 → 0~~ becomes const. $= \frac{r_0}{2he_z}\Delta V$.)

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

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