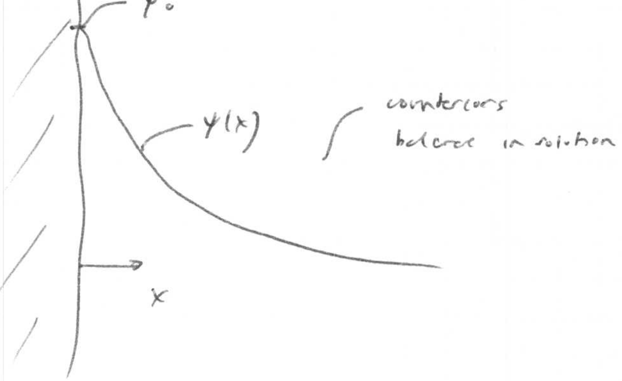
modeling the electrical double layer ~ requirement of <u>total</u> electrical neutrality

assume a planar, isolated, constant potential surface



variation in potential from a surface: poisson eqn.

$$\nabla^2\psi = -\rho^e/\varepsilon$$

charge density $[\mathrm{C/m^3}]$

$\rho^e(x,y,z)$

$$\varepsilon = \varepsilon_r\varepsilon_0$$

in 1D, $\dfrac{d^2\psi}{dx^2} = -\rho^e(x)/\varepsilon$ ~ constant

BCs: $\psi(0) = \psi_0, \quad \psi(\infty) = 0$

now we need to relate ρ to ψ

consider the ions obey a Boltzmann distribution

$$n_i/n_{i\infty} = \exp\left\{-z_i e\psi/k_B T\right\}$$ = probability of finding an ion at a potential ψ

\# ions/vol

at ∞

$$\rho^e = z_i e n_i = (\text{charge})(\text{valence})(\#/\text{vol})$$

if we have multiple ions in solution, then

$$\rho^e = \sum z_i e n_i = \sum z_i e n_{i,\infty} \exp\left\{-z_i e\psi/k_B T\right\}$$

$\hookrightarrow$ poisson-boltzmann equation can now be written ("ρ/ε" eqn)

P/B eqn $\Rightarrow$ $$\frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon}\underbrace{\sum_i z_i n_{i\infty} \exp\left(-z_i e\psi / k_b T\right)}_{\text{implies superposition of charges}}$$

no general solution: need to make assumptions.

first, assume $z_i e\psi < k_bT$: $\underbrace{\frac{k_bT}{e} \text{ @ } 298\text{ K} = 25.7\text{ mV}}_{\text{rule of comparing potentials}}$

given this assumption we can expand the exponential term (power series)

keep first-order terms

$$\rho^* = \underbrace{\sum_i z_i e n_{i\infty}}_{= 0 \text{ because of electroneutrality}}\left(1 - (z_i e\psi / k_bT)\right)$$

$$\Rightarrow \rho^+ = -\sum_i z_i^2 e^2 \psi n_{i\infty} / k_bT$$

now the linearized P/B eqn is

$$\frac{d^2\psi}{dx^2} = \left(\left(\frac{e^2}{\varepsilon k_bT}\right)\sum z_i^2 n_{i\infty}\right)\psi$$

define $$\kappa^2 = \left(\frac{e^2}{\varepsilon k_bT}\right)\sum z_i^2 n_{i\infty}$$

then $$\frac{d^2\psi}{dx^2} = \kappa^2\psi \Rightarrow \psi = \psi_0 e^{-\kappa x} \quad \text{or} \quad \psi = \psi_0 e^{-x/\kappa^{-1}}$$

κ^{-1} = "double layer thickness"

"Debye length"

example, 0.1 M solution of 1:1 electrolyte, e.g. KOH, NaCl

$\Rightarrow \kappa^{-1} = 3.04 \text{ nm}$

M = molarity

useful conversion: $n_i = 1000 M_i N_A$

$$(\text{ions}/m^3) = (L/m^3)(\text{mol}/L)(\text{ions}/\text{mol})$$

$$\kappa = \left[\left(1000 e^2 N_A / k_b T \right) \sum z_i^2 \underset{\nwarrow \text{ molarity of } i}{M_i} \right]^{1/2}$$

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gouy-chapman solution; if we don't make the D-H approximation

$$\Phi = \Phi_0 e^{-\kappa x}$$

$$\Phi_0 = \Phi(\psi_0)$$

$$\Phi = (\Delta - 1)/(\Delta + 1), \quad \Delta = \exp\left(ze\psi / 2k_bT \right)$$

for a symmetrical 1:1 electrolyte.

if we expand with $(ze\psi)/ \ll k_bT \Rightarrow$ D/H approx $\Rightarrow$ previous solution

2 more cases:

(i) large x, where $\psi \ll \psi_0$

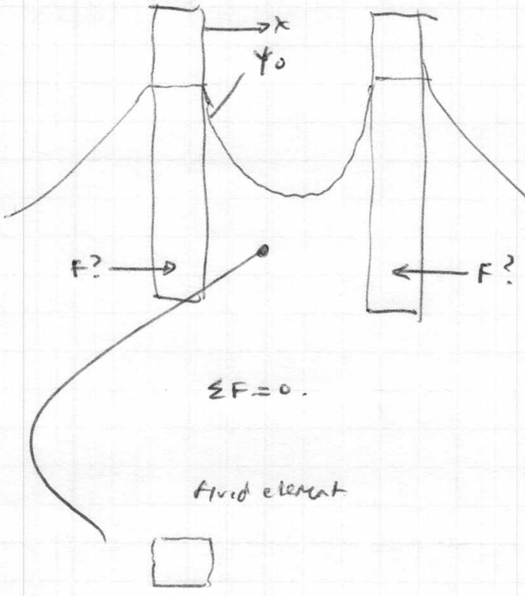
$$\frac{ze\psi}{4k_bT} = \Phi_0 \exp(-\kappa x) \Rightarrow \psi = \frac{4k_bT}{ze} \Phi_0 \exp(-\kappa x)$$

large ψ_0, so $\Phi_0 \Rightarrow 1$

$$\Rightarrow \psi = \frac{4k_bT}{ze}\exp(-\kappa x)$$

In a typical dispersion $ze\chi \approx 1$

consider overlapping double layers: electrostatics = repulsive force.



$$F_x + F_{el} = 0.$$

$$F_x = -\frac{dp}{dx}$$

$$F_{el} = -\rho^+\frac{d\psi}{dx}$$

$$\Sigma F = 0 : \quad \frac{dp}{dx} + \rho^+\frac{d\psi}{dx} = 0$$

ΣF=0 : $F_x + F_{el}$.

$$\frac{dp}{dx} + \underbrace{\varepsilon\left(\frac{d\psi}{dx}\right)\left(\frac{d^2\psi}{dx^2}\right)}_{=\frac{1}{2}\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2} = 0$$

$$\Rightarrow \frac{d}{dx}\left(p - \frac{\varepsilon}{2}\left(\frac{dp}{dx}\right)^2\right) = 0$$

$$\text{so,} \quad \underbrace{p}_{\text{pressure}} - \underbrace{\frac{\varepsilon}{2}\left(\frac{d\psi}{dx}\right)^2}_{\text{electric field contribution "Maxwell pressure"}} = \text{constant.}$$

assume potentials from 2 surfaces are additive, and κ is large

$(h >> \kappa)$

then solve $F_R = 64 k_b T n_\infty \bar{\Phi}_0^2 \exp(-\kappa h)$

h = seperation

Φ_0 = defined previously

$\kappa \propto n_\infty^{-1/2}$, so

$$F_R = c_1 n_\infty \exp\left(-c_2 n_\infty^{1/2}\right)$$

this term dominates.

$\uparrow n_\infty \Rightarrow \downarrow F$ = adding salt = coagulation of a colloid

example: thickness of soap bubbles: pressure/repulsive force balance

molecules are charged on surface

this is a force, how do we get potential energy as we had before?

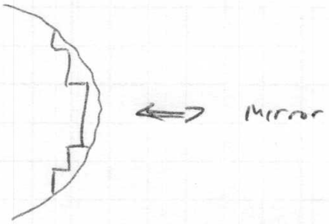
integrate, $V = \int_0^V dV = \int_\infty^h -F_R \, dh$

$$\Rightarrow V(h) = 64 k_b T n_\infty \bar{\Phi}_0^2 \kappa^{-1} \exp(-h\kappa)$$

DLVO theory: add VDW and electrostatic interaction potentials

recall Derjaguin approximation: sphere-sphere interaction = collection of plates, if $(R_1, R_2) >> h$

integrate:



Derjaguin: $F(D)_{curved} = 2\pi\left(\frac{R_1 R_2}{R_1+R_2}\right) W(D)$ plates.

if $R_1 = R_2$, $F(D) = \pi R W_{pl}$

so, $F(D)_{curved} = \pi R\left(64 k_b T n_\infty \Gamma_0^2 \kappa^{-1} \exp(-h\kappa)\right)$ ⇒ electrostatic.

integrate to get $W(D)_{curved} = \kappa^{-1} F(D)_{curved}$

recall VDW energy

$$W(D) = \frac{-A}{6D}\left(\frac{R_1 R_2}{R_1+R_2}\right) = \frac{-AR}{3D}$$

⇒ $V_{DLVO} = V_{ES} + V_{VDW}$ = electrostatic + VDW.

$$= 64\pi R k_b T n_\infty \Gamma_0^2 \kappa^{-2} \exp(-D\kappa) - \frac{AR}{3D}.$$

Maximum / Minima at $\frac{dV}{dD} = 0.$ ⇒ see curves.