

LECTURE 14: THE ELECTRICAL DOUBLE LAYER (EDL)

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Objectives: To understand the qualitative origins and mathematical foundations for the electrical double layer

Readings: Course Reader Documents 24 and 25

Multimedia : Boundary Lubrication Podcast, Briscoe, et al. *Nature* **2006** 444, (191 - 194)

REVIEW LECTURE #11 : INTRODUCTION TO THE ELECTRICAL DOUBLE LAYER

$$W(D) = W(D)_{VDW} + W(D)_{ELECTROSTATIC} + W(D)_{STERIC} + W(D)_{STRUCTURAL} - W(D)_{DEPLETION}$$

"Electrostatic Double Layer Repulsion" : for charged particles, this force arises from a diffuse, highly mobile surface layer of counterions; an exponential repulsion exists on compression since which is entropic in origin since the counterions want to retain their translational mobility

$$W(D) = W(D)_{VDW} + W(D)_{ELECTROSTATIC}$$

"DLVO Theory"-Derjaguin, Landau, Verwey and Overbeek

- 1. Colloidal /Nanoparticle Stability Dispersion
- 2. Biocompatibility
- 3. Tissue Nanomechanics: Cartilage

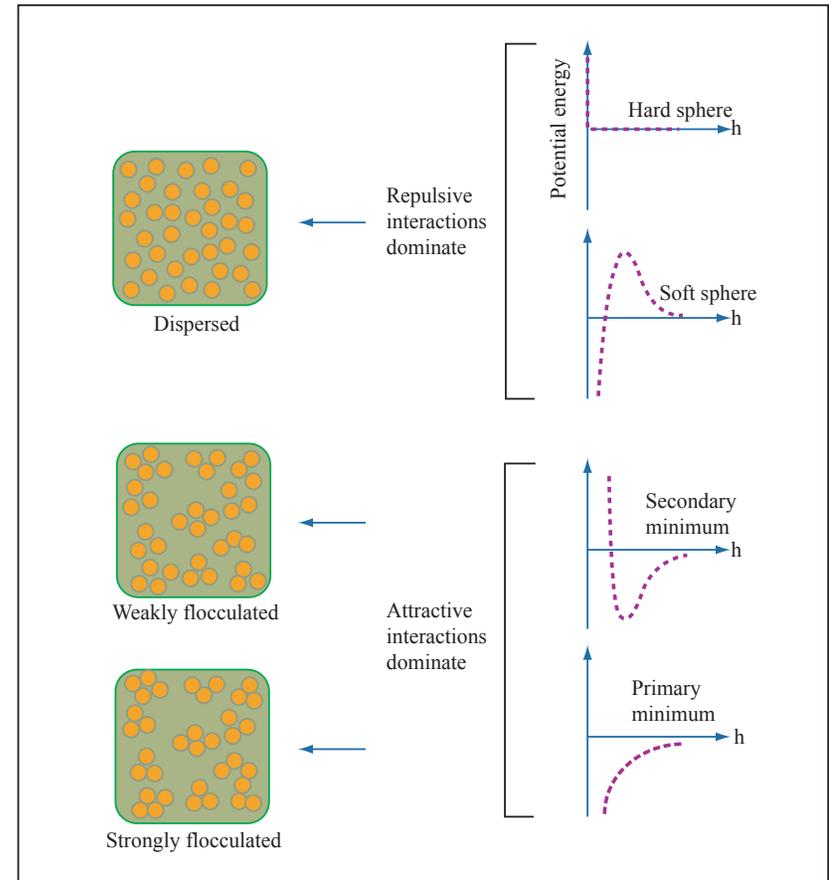
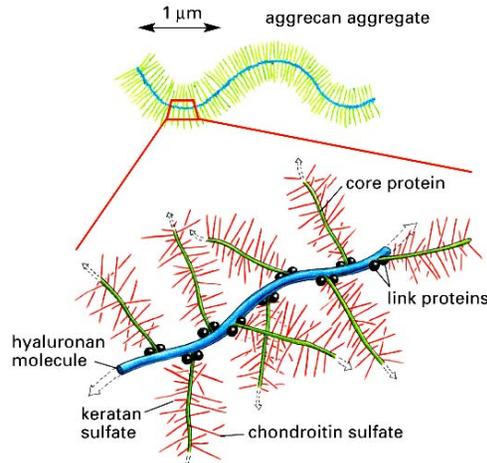
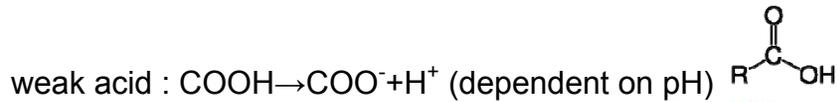


Figure by MIT OCW. □□
 After Lewis. *J Am Ceram Soc* 83, no. 10 (2000): 2341-59.

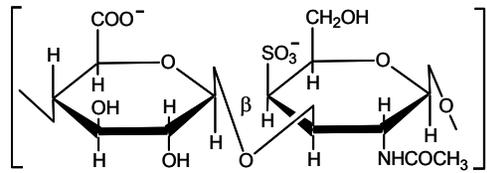
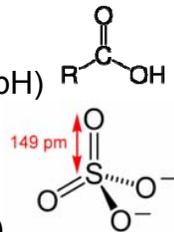
SURFACE CHARGE : WHERE DOES IT COME FROM?

Net Surface Charge (Fixed Charge Groups on Surface) :

1. Direct ionization or dissociation of surface chemical groups, e.g.

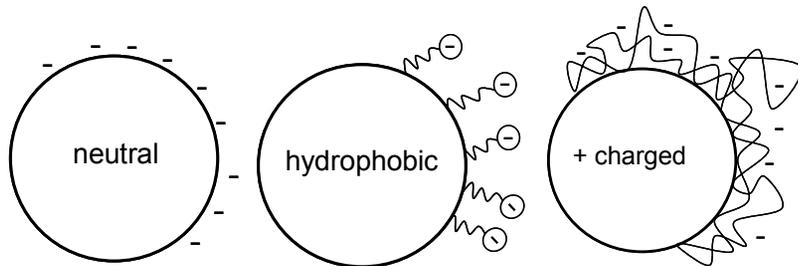


strong acid : sulfate SO_4^{2-} (independent of pH)



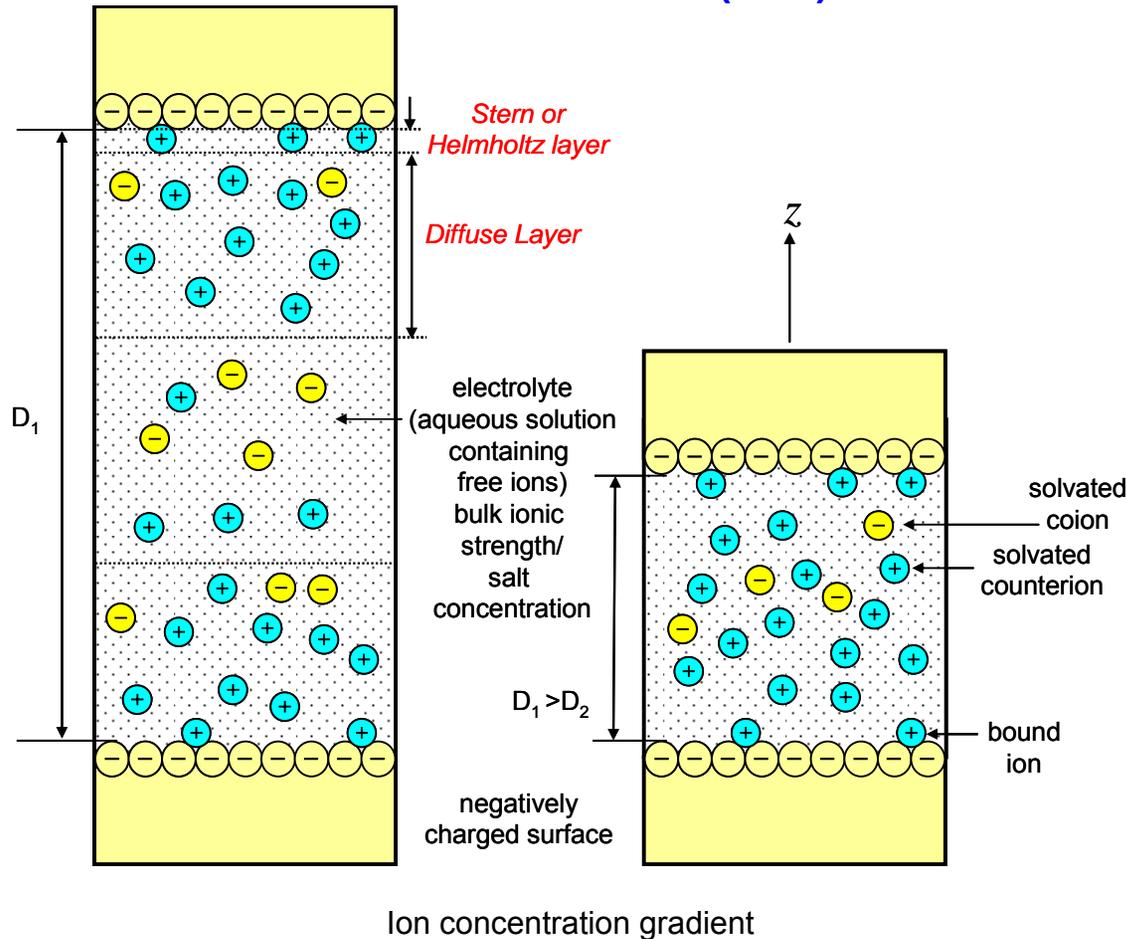
cartilage glycoaminoglycan (chondroitin-6-sulfate)

2. Adsorption (binding of ions) via van der Waals, hydrophobic, or ionic interactions, e.g. lipids, polyelectrolytes (charged polymers)



Group	Acid \rightleftharpoons Base + H^+	pK _a
Terminal carboxyl		3.1
aspartic acid or glutamic acid		4.4
Histidine		6.5
Terminal Amino		8.0
Cysteine		8.5
Tyrosine		10.0
Lysine		10.0
Arginine		12.0

THE ELECTRICAL DOUBLE LAYER (EDL): GENERAL DEFINITION



-Electroneutrality maintained; # of counterions = # of surface charge groups + # of bulk coions

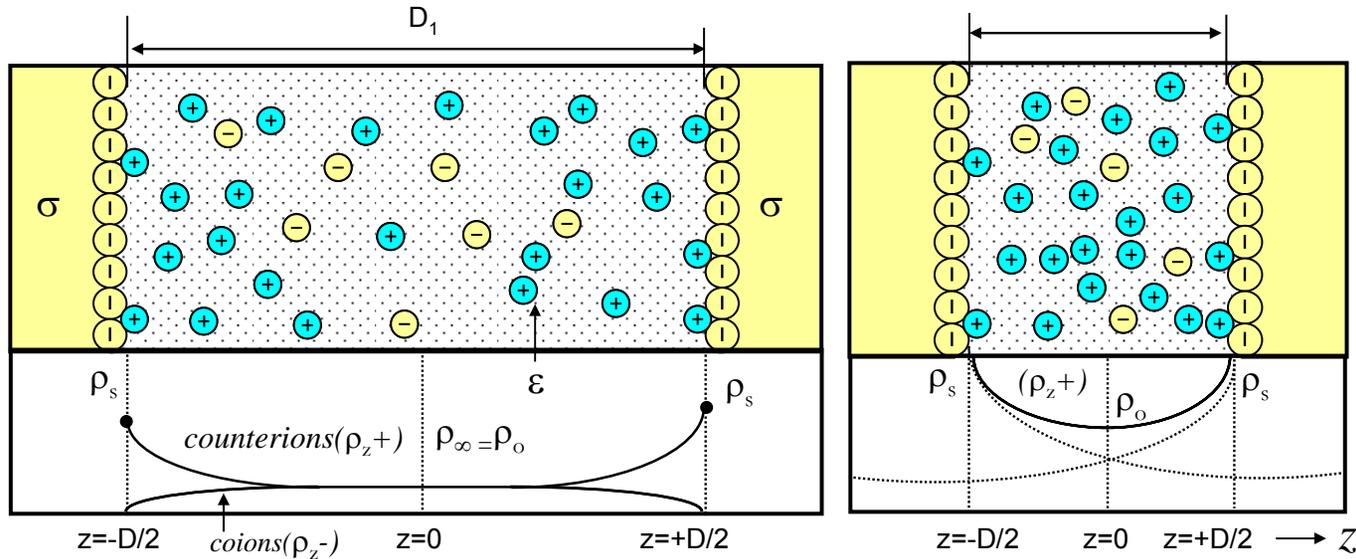
Diffuse Layer : atmosphere of mobile counterions in rapid motion, attractive ionic forces pulling them to surface (electrical migration force) causes concentration gradient, gain translational /rotational entropy by moving away from surface (diffusion down the concentration gradient)→these effects are balanced so there is no net flux of any ionic species

Stern or Helmholtz Layer : bound, usually transiently, thickness is a few Å, reflects the size of the charged surface groups and bound counterions→ do not completely neutralize the surface charges

When two similarly charged electrical double layers are compressed together and overlap ($D_1 < D_2$), repulsive force→entropic/osmotic, deviating the system from its minimum

THE ELECTRICAL DOUBLE LAYER : GENERAL MATHEMATICAL FORMULATION

Concentration gradient $\rightarrow \rho =$ volume density of ions (C/m^3)



Generally; $W(D)_{ELECTROSTATIC} = C_{ES} e^{-\kappa D}$

C_{ES} = electrostatic prefactor analogous to the Hamaker constant for VDW interactions

κ^{-1} = Electrical Debye Length (characteristic decay length of the interaction)- will be defined more rigorously later on \rightarrow rule of thumb : range of the electrostatic interaction $\sim 5\kappa^{-1}$

THE ELECTRICAL DOUBLE LAYER : POISSON-BOLTZMANN (P-B) FORMULATION

Assumptions; ions are point charges (don't take up any volume, continuum approximation), they do not interact with each other, uniform dielectric; permittivity independent of electrical field, electroquasistatics (time varying magnetic fields are negligibly small)

Start with Poisson's Law, relation between electrical potential, ψ (Volts), at any point within a diffuse space charge region of volume charge density, ρ (C/m³), is ;

$$\nabla^2 \psi = -\frac{\rho}{\epsilon}; \epsilon = \text{permittivity}, \nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$$

1D Case, $z \perp$ to charged surface:

$$\frac{d^2 \psi(z)}{dz^2} = -\frac{1}{\epsilon} \sum_i^n z_i F c_{i0} \exp \frac{-z_i F \psi(z)}{RT}$$

Boltzmann Ion Distribution; thermodynamic equilibrium, describes variation of ion concentration in electric field

1D General P - B Equation, describes EDL, defines potential as a function of z in a spatial charge distribution

R = Universal Gas Constant = 8.314 J/K mole

T = Temperature (K)

F = Faraday Constant (96,500 Coulombs/mole of electronic charge)

c_{i0} (moles/cm³ or mole/L = [M]; 1 ml = 1 cm³) = electrolyte ionic strength (IS) =

bulk concentration of the i^{th} species, ideally for $x \rightarrow \infty$, but practically just far enough away from surface charge region, several Debye lengths away

z_i = electrolyte valence of i^{th} ion

THE ELECTRICAL DOUBLE LAYER : POISSON-BOLTZMANN (P-B) FORMULATION FOR A MONOVALENT ELECTROLYTE

For Na⁺, Cl⁻ (monovalent 1:1 electrolyte solution)

$$\sinh(x) = \frac{e^x - e^{-x}}{2}; \frac{d^2\psi(z)}{dz^2} = \frac{2Fc_o}{\epsilon} \sinh \frac{F\psi(z)}{RT}$$

2nd order nonlinear differential eq.;

Linearize when $\frac{F\psi(z)}{RT} \ll 1$ or $\psi \ll \sim 60$ mV

"Debye-Huckel Approximation"

$$\frac{d^2\psi(z)}{dz^2} \approx \frac{2F^2c_o\psi(z)}{\epsilon RT} = \kappa^2\psi(z) \text{ (*) linear differential equation}$$

$$\text{where: } \kappa^{-1} = \sqrt{\frac{\epsilon RT}{2z^2 F^2 c_o}}$$

κ^{-1} (nm) = Debye Length = is more specifically defined as the distance over which the electric field and potential decay to (1/e) of their value at x = 0

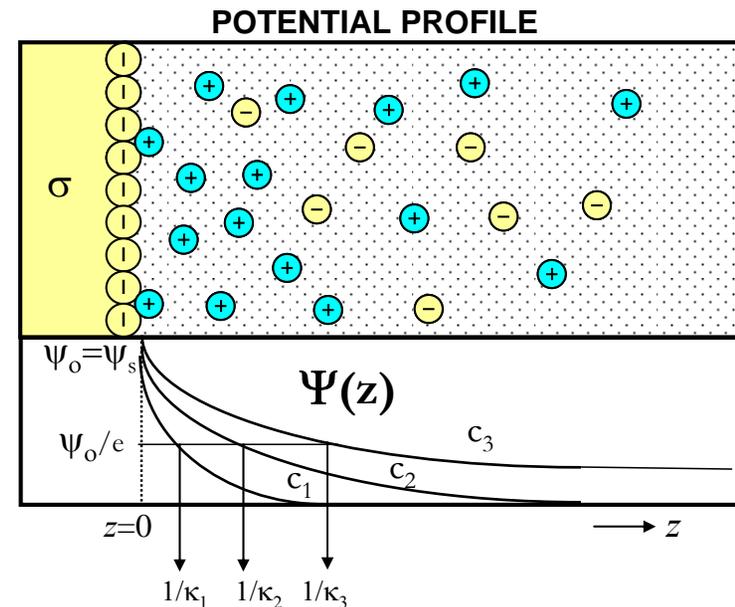
Solution to (*): $\psi(z) = \psi(0)e^{-\kappa z} + K$

$\psi(z)$ = electrical potential

$\psi(0) = \psi_s$ = surface potential (x = 0) = constant

K = integration constant, Boundary Conditions; $\psi(\infty) = 0, K = 0$

rule of thumb : range of the electrostatic interaction $\sim 5\kappa^{-1}$

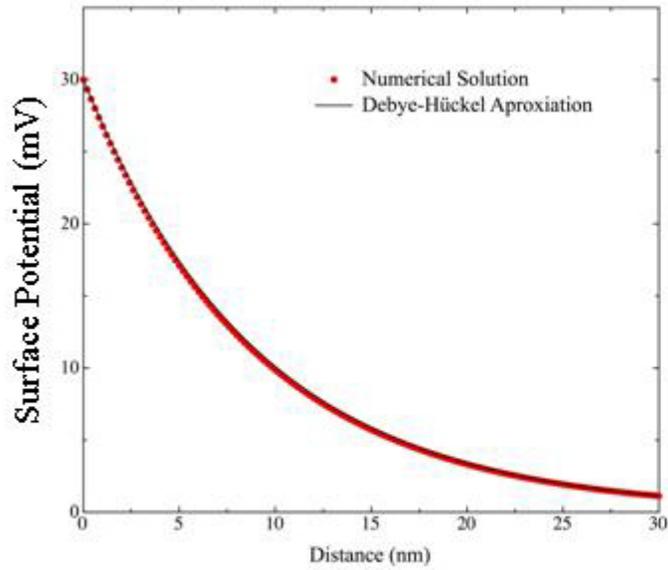


IS [M]	κ^{-1} (nm)
10^{-7} (pure water) [H ⁺]=[OH ⁻]	950
0.0001 [NaCl]	30
0.001 [NaCl]	9.5
0.01 [NaCl]	3.0
0.15* [NaCl]	0.8
1 [NaCl]	0.3 (not physical!)

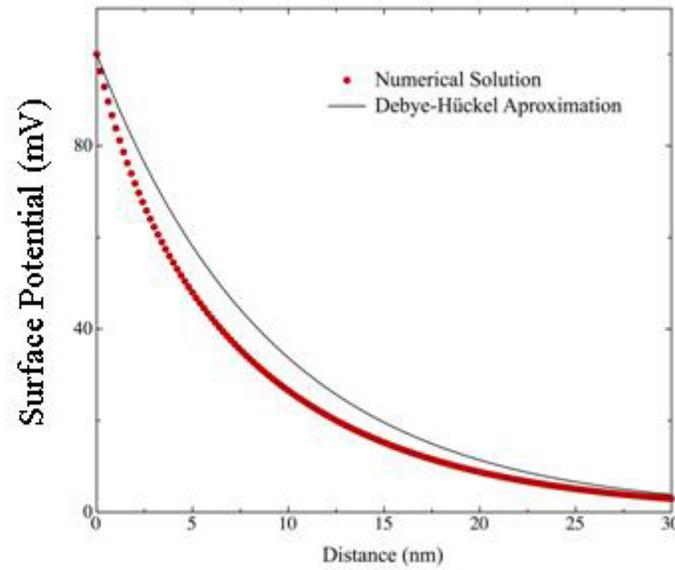
*physiological conditions

COMPARISON OF NONLINEAR AND LINEAR P-B SOLUTIONS

For 0.001 M 1-1 electrolyte

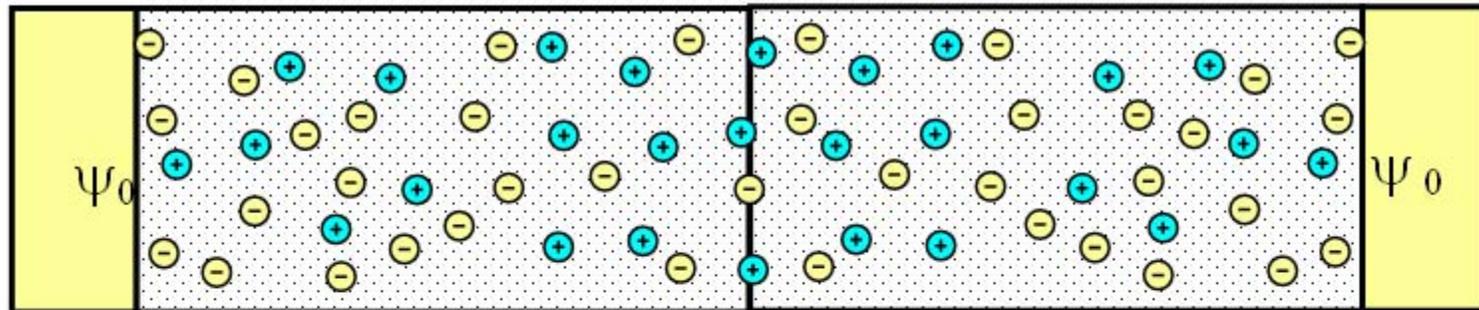


$$\frac{Ze\Psi}{kT} < 1$$

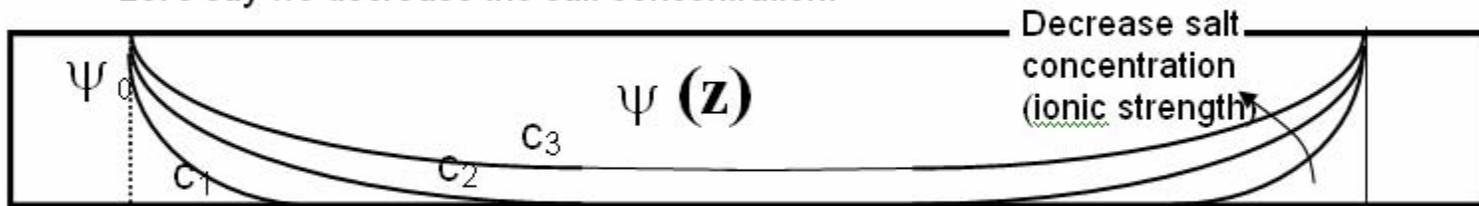


$$\frac{Ze\Psi}{kT} > 1$$

ELECTRICAL POTENTIAL PROFILE FOR TWO INTERACTING EDLs



Let's say we decrease the salt concentration:



Now let's say we move the two surfaces close to each other:

