LECTURE 15: THE ELECTRICAL DOUBLE LAYER (EDL) 2

Outline :

Objectives: To understand the mathematical formulation for the repulsive EDL Interaction between two charged surfaces

Readings: Course Reader Documents 24 and 25

Multimedia : Cartilage Podcast, Dean, et al. *J. Biomech.* **2006** 39, 14 2555

Acknowledgement : These lecture notes were prepared with the assistance of Prof. Delphine Dean (Clemson University)

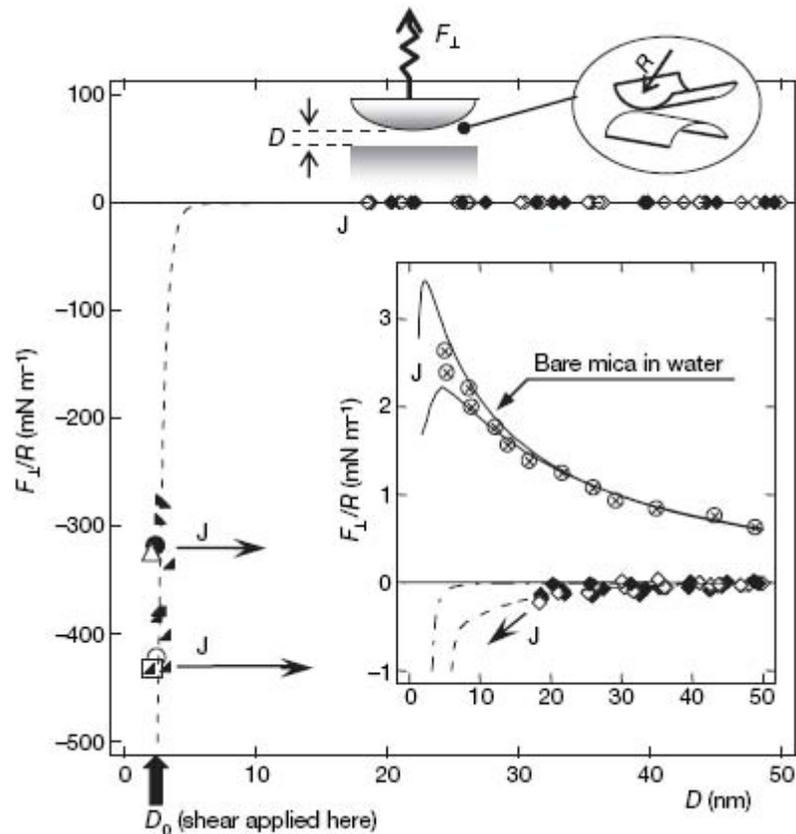# THE ELECTRICAL DOUBLE LAYER (EDL) IN BOUNDARY LUBRICATION PODCAST

Figure 1 | Normal interactions $F_{\perp}/R$ between DDunAB-coated crossed-cylindrical mica surfaces (radius of curvature R is ~1 cm), as a function of closest separation D. Forces $F_{\perp}$ were measured with a surface force balance[11] (cartoon). Different symbols indicate separate experiments (10-min or 120-min layers, see Methods). The open triangle and closed circle represent adhesive contact in dry air (mean of several measurements). The closed and open diamonds represent interaction profiles across water with no added salt, up to jumps (J) into adhesive contact. The open square and circle indicate adhesive contact following first approach in water. The adhesion in water on subsequent approaches following shear is similar or slightly decreased (◢ is 120 min, and ◤ is 10 min). The inset shows interactions on an enlarged scale: crossed circles represent interactions between the bare mica surfaces (solid curves show expected DLVO double-layer forces[13]. Upper solid curve, constant surface charge density of $0.0048\,\mathrm{C\,m^{-2}}$; lower solid curve, constant surface potential of 155 mV; both with 1.5×10^{-5} M 1:1 background electrolyte concentration). Other symbols as in the main figure. The lowest curves are van der Waals attraction (dot-dashed curve) and an empirical double exponential function (dashed curve) characteristic of hydrophobic attraction[14]. All measurements are at $25 \pm 0.5\,^{\circ}\mathrm{C}$.

Courtesy of Jacob Klein. Used with permission.
Source: Briscoe, W. H., et al. "Boundary Lubrication Under Water." *Nature* 444 (November 9, 2006): 191-194.

# REVIEW LECTURE #14 : THE ELECTRICAL DOUBLE LAYER (EDL) 1

● Applications, Origins of Surface Charge, Definitions : EDL, Stern layer→ balance between attractive ionic forces (electrical migration force) driving counterions to surface and entropy/diffusion/osmotic down the concentration gradient

General Mathematical Form : $W(D)_{ELECTROSTATIC} = C_{ES}e^{-\kappa D}$

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 today

Poisson-Boltmann (P-B) Formulation : 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)
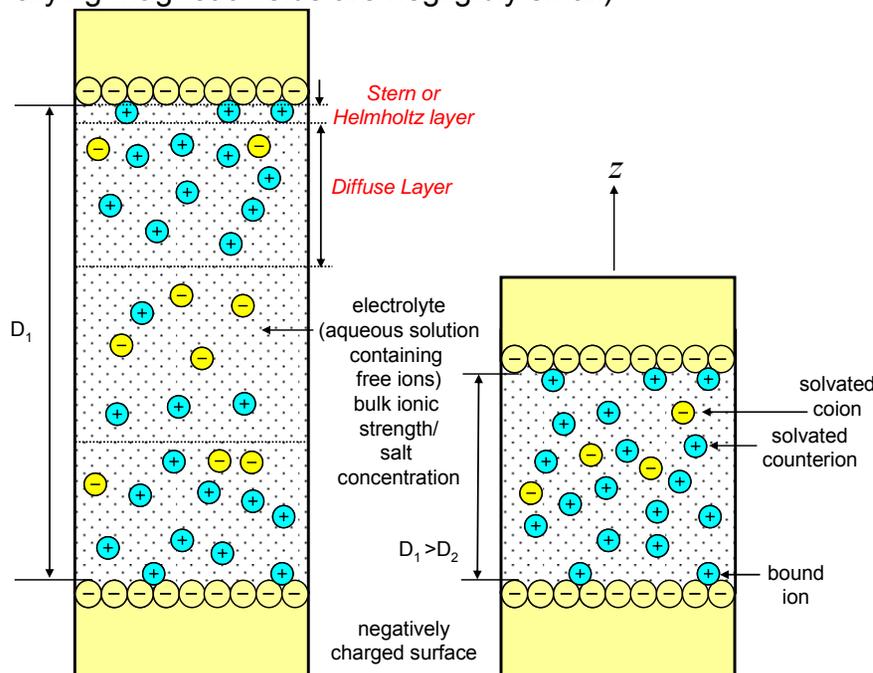
Derived 1D P-B Equation for a 1:1 monovalent electrolyte (e.g. Na^+, Cl^-)

$$\frac{d^2\psi(z)}{dz^2} = \frac{2Fc_o}{\varepsilon} sinh\frac{F\psi(z)}{RT}$$

$\psi(z) =$ electrical potential
R=Universal Gas Constant = 8.314 J/mole K
T= Temperature (K)
F= Faraday Constant (96,500 Coulombs/mole electronic charge)
c_o (moles/cm^3 or mole/L=[M], 1 ml=1 cm^3)=electrolyte ionic strength (IS) = bulk salt concentration, ideally for z→∞, but practically just far enough away from surface charge region, several Debye lengths away
ε (C^{2}J^{-1}m^{-1})=permittivity

Figure labels (left diagram):
Stern or Helmholtz layer
Diffuse Layer
z
D_1
electrolyte (aqueous solution containing free ions) bulk ionic strength/ salt concentration
negatively charged surface

Figure labels (right diagram):
solvated coion
solvated counterion
$D_1 > D_2$
bound ion

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SOLUTION TO 1D LINEARIZED P-B EQUATION FOR A 1:1 MONOVALENT ELECTROLYTE

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

$$\frac{d^2\psi(z)}{dz^2} = \frac{2Fc_o}{\varepsilon} sinh \frac{F\psi(z)}{RT}$$

2nd order nonlinear differential eq. $\rightarrow$ solve numerically

Linearize when $\frac{F\psi(z)}{RT} << 1$ or ψ <~ 60 mV

"Debye - Huckel Approximation" - Linearized P - B Equation

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

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

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

$\psi(z)$ = electrical potential, K = integration constant

Boundary Conditions (1Layer or $D > 5\kappa^{-1}$); $\psi(z = \infty) = 0$, K = 0
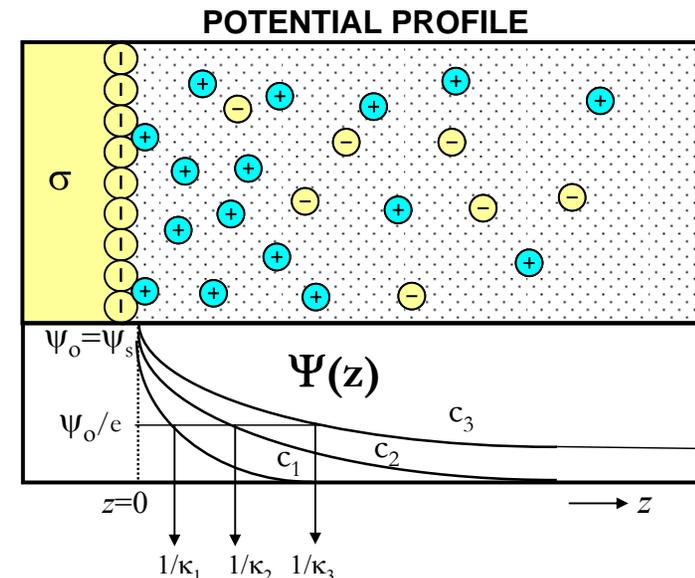
1) Constant Surface Potential

$\psi(0) = \psi_o = \psi_s$ = surface potential (z = 0) = constant

κ^{-1} (nm) = Debye Length = the distance over which the potential

decays to $(1/e)$ of its value at z = 0, depends solely on the

properties of the solution and not on the surface charge or potential

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

POTENTIAL PROFILE

$c_3 < c_2 < c_1 \rightarrow$ "salt screening"

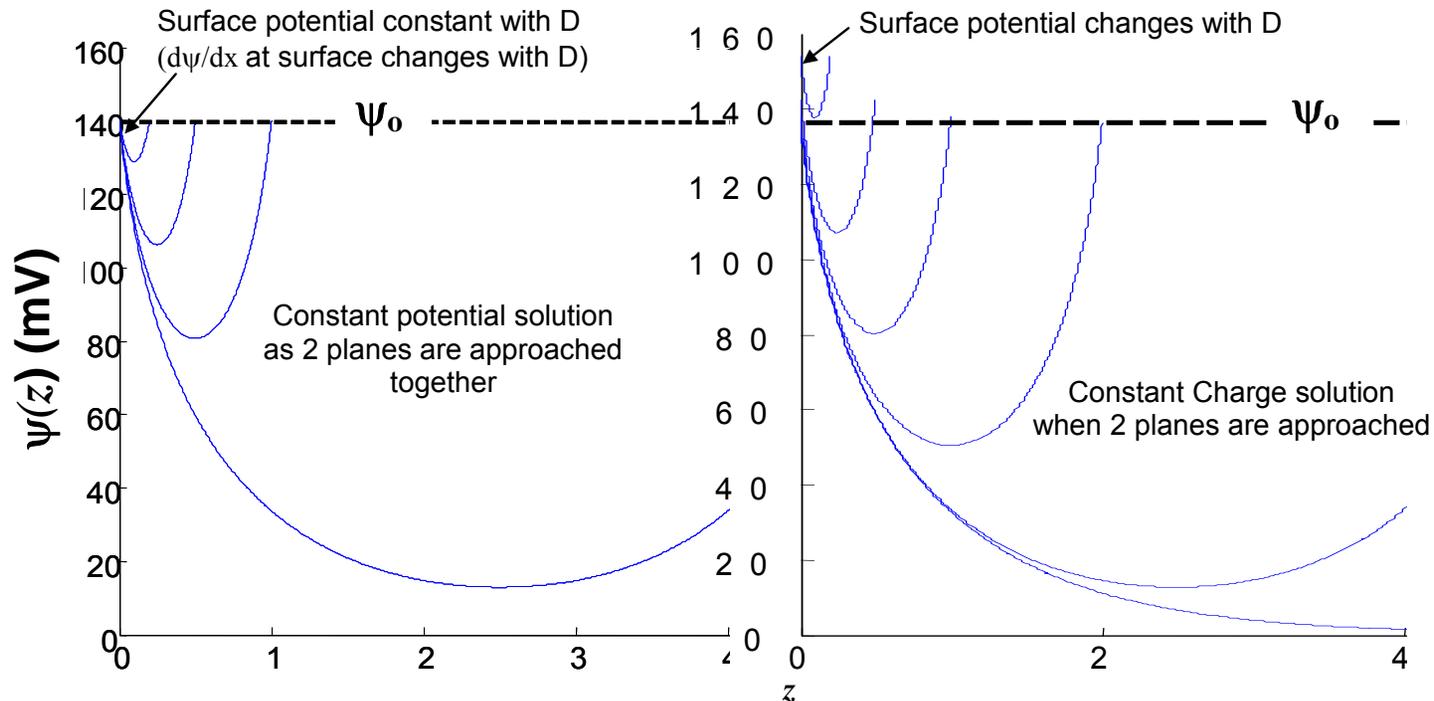| IS [M]	k^{-1} (nm)
10^{-7} (pure water) $[H^+]=[OH^-]$	950
0.0001 [NaCl]	30
0.001 [NaCl]	9.5
0.01 [NaCl]	3.0
0.15* [NaCl]	0.8
1 [NaCl]	0.3 (not physical!)

*physiological conditions

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ELECTRICAL POTENTIAL PROFILE FOR TWO INTERACTING EDLs

2) Constant Surface Charge $\dfrac{d\psi}{dz}\Big|_{z=0} = \dfrac{\sigma}{\varepsilon}$

σ = surface charge density (C/m^2), ρ = volume charge density of entire electrolyte phase (C/m^3)

comes from electroneutrality : $\sigma = -\displaystyle\int_0^\infty \rho\,dz = -\int_0^\infty \underbrace{-\varepsilon\dfrac{d^2\psi}{dz^2}}_{\text{Poisson's Law}}\,dz = \varepsilon\dfrac{d\psi}{dz}\Big|_{z=0} = \psi_0\varepsilon\kappa$

Boundary Conditions for Two Interacting Plane Parallel Layers : $\dfrac{d\psi}{dz} = 0, \psi = \psi_m \, for \, z = D/2$

Surface potential constant with D
($d\psi/dx$ at surface changes with D)

Constant potential solution
as 2 planes are approached
together

Surface potential changes with D

Constant Charge solution
when 2 planes are approached

EDL : FORCE CALCULATION (1)

-So now that we can solve the P-B equation and get $\psi(z)$ and $\rho(z)$ in space, how do we calculate a **force**?

-We can calculate a pressure (**P = force per unit area**) on these infinite charged surfaces if we know the potential. Using a control box, the pressure on the surface at x = D is the pressure calculated at any point between the surfaces relative to a ground state: $P(z = z_j) - P(\infty)$
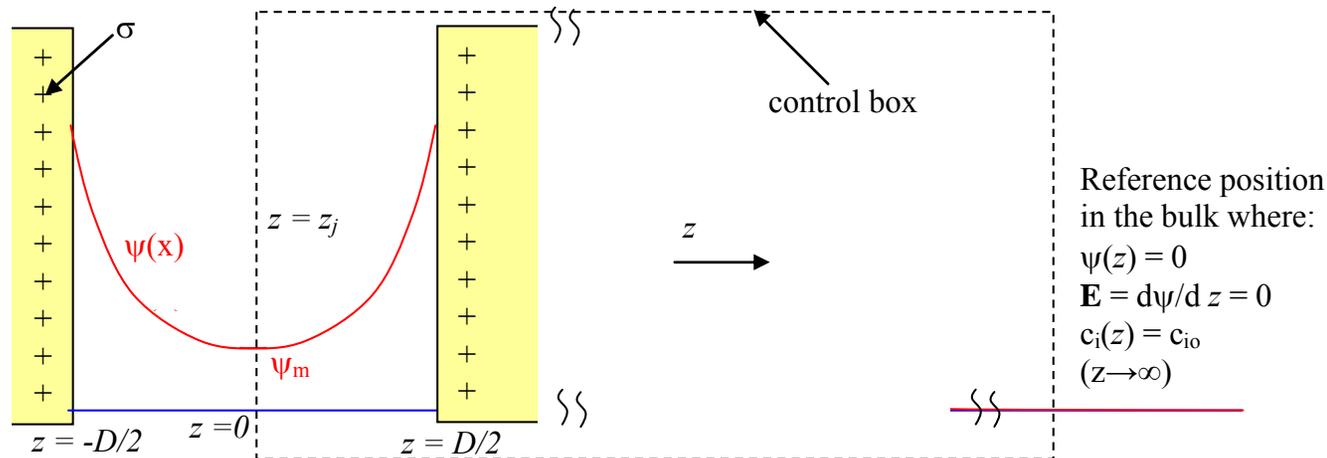
Now at any point the pressure is going to be the sum of two terms:

$P(z = z_j) - P(\infty) = "electrical" + "osmotic"$

The "electrical" contribution (a.k.a. Maxwell stress) is due to the electric field:

$$P(z = z_j) - P(\infty) = \frac{\varepsilon}{2}(E^2(z = z_i) - E^2(\infty)) + "osmotic"$$

The "osmotic" contribution is due to the ion concentrations (van't Hoff's Law, chemical equation of state):

$$P(z = z_j) - P(\infty) = \frac{\varepsilon}{2}(E^2(z = z_i) - E^2(\infty)) + RT \sum_{all\ ions} (c_i(z = z_i) - c_i(\infty))$$

Now some things simplify because at $z \rightarrow \infty$, E $\rightarrow$ 0 and $c_i(\infty) \rightarrow c_{io}$

EDL : FORCE CALCULATION (2-CONT'D)

-If we can simplify things if we pick z_j to be the point between the surfaces where **E** = 0 (i.e. if the surface charges are the same then this is the mid point between the two surfaces, $z = 0$), only have an osmotic component:

$$P(z = 0) - P(\infty) = RT \sum_{all\ ions} (c_i(0) - c_{io})$$

Note: we can pick any point z_j because the sum of the "osmotic" and "electrical" terms is a constant. We chose $z = 0$ because it's less messy since we don't have to calculate **E**.

If it's a monovalent salt solution we can plug in the formula for the concentration for Boltzmann Statistics:

$$P = RT \left(c_0 e^{-\frac{F\psi_m}{RT}} + c_0 e^{\frac{F\psi_m}{RT}} \right) - RTc_o = 2RTc_0 \left(cosh\left(\frac{F\psi_m}{RT} \right) - 1 \right)$$

where : ψ_m is the potential at z=0 and P is the net force/area on the surface.

If ψ_m<< RT/F ~60mV, then we can actually solve this equation further:

$$P \approx 2RTC_0 \left(\left(1 - \left(\frac{F\psi_m}{RT}\right)^2 \right) - 1 \right) = \left(\frac{2c_0 F^2 \psi_m^2}{RT} \right) = \varepsilon \kappa^2 \psi_m^2$$

and we can solve for ψ_m if we wanted using the linearized PB equation (it's a little messy). If you plug in the value for ψ_m you get:

$$P \approx 4\varepsilon\kappa^2\psi_o^2 e^{-\kappa D}$$ (constant surface potential)

$$P \approx \frac{4\sigma^2}{\varepsilon} e^{-\kappa D}$$ (constant surface charge)

Exponential in this case so you can think of the Debye length, κ^{-1}, as being the length scale over which electrostatic forces occur.

APPENDIX : MATHEMATICAL POTENTIALS FOR ELECTRICAL DOUBLE LAYER FOR DIFFERENT GEOMETRIES *(From Leckband, Israelachvili, Quarterly Reviews of Biophysics, 34, 2, 2001)*

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Table 2 in Leckband and Israelachvili, Quarterly Reviews of Biophysics, 34, 2, 2001

$Z = \left(9.38 \times 10^{-11}\right) tanh^2(\psi_o/107)$ J m^{-1} (monovalent electrolyte)

$\sigma = 0.116 sinh(\psi_o/53.4)\sqrt{c_o}$ Cm^{-2} (monovalent electrolyte)