

Module 7: "Electrostatic Interaction"

Lecture 36: "Potential Energy"

The Lecture Contains:

- ☰ Potential Energy
- ☰ Debye-Huckel Approximation when potential on the surfaces are not same
- ☰ References

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Potential Energy

In many cases it is desirable to calculate potential energy due to repulsion per unit area. By definition potential energy may be given as the product of force and distance, thus we may write energy as

$$dG^{EL} = -F_R d(D) \quad (9.35)$$

where D is a dummy variable. Substituting F_R from equation (9.34) in equation (9.35) we get

$$dG^{EL} = 64n_0kT\gamma_0^2 \exp(-kd) d(D)$$

Integrating with boundary conditions ($d \rightarrow \infty, G^{EL} \rightarrow 0$) we get:

$$G^{EL} = \frac{64n_0kT\gamma_0^2}{k} \exp(-kd) \quad (9.36)$$

Total energy between 2 plates then can be evaluated as a summation of energy due to acid base interaction, van der Waal interaction and electrostatic interaction. Thus,

$$G^{Total} = G^{EL} + G^{LW} + G^{AB}$$

For spherical particle potential energy can be calculated by Deryaguin's approximation.

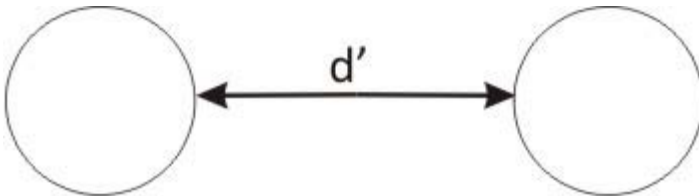


Fig. 9.3: ΔG^{EL} for spherical particles.

$$\phi^{EL} = \pi R \int_d^\infty G^{EL} d(D)$$

$$\phi^{EL} = \frac{64\pi R n_0 k T \gamma_0^2}{k^2} \exp(-kd) \quad (9.37)$$

Note that if radius of two spheres is different, then instead of using R in the above equation we would

have used $\frac{2R_1 R_2}{R_1 + R_2}$. Again we see that the total energy is equal to

$$\phi^{TOTAL} = \phi^{EL} + \phi^{LW} + \phi^{AB}$$

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Debye-Huckel Approximation when potential on the surfaces are not same

Now we consider a more general case when potential on the surfaces are not same. For this case we take Debye-Huckel approximation to be valid that is taking surface potential to be low. For this Poisson Boltzman equation becomes

$$\frac{d^2\Psi}{dx^2} = k^2\Psi$$

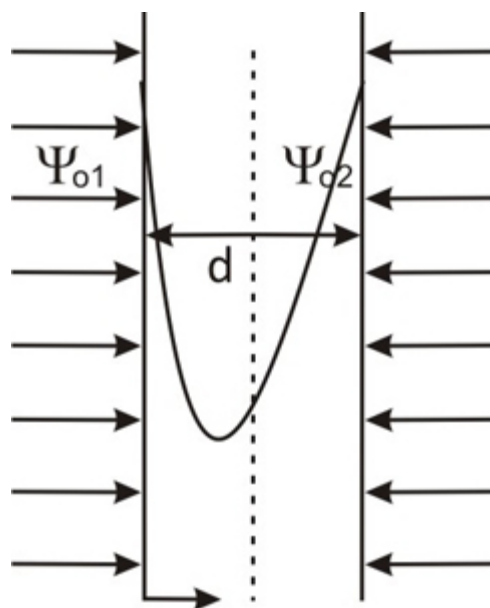


Fig. 9.4: Distribution of potential between two charged particles.

General solution of above equation is

$$\Psi = A\cosh(kx) + B\sinh(kx) \quad (9.38)$$

By applying the appropriate boundary conditions we can determine the constants in the above equation. Let us assume that the potential at two surfaces are ψ_{o1} and ψ_{o2} as shown in the figure.

Thus the boundary conditions we have are

- 1) $\psi = \psi_{o1}$ at $x = 0$;
- 2) $\psi = \psi_{o2}$ at $x = d$

Substituting these boundary conditions in equation (9.38) we have

$$A = \Psi_{01}$$

and

$$B = \left[\frac{\Psi_{02} - \Psi_{01} \cosh(kd)}{\sinh(kd)} \right]$$

Thus

$$\Psi = \cosh(kx) + \left[\frac{\Psi_{02} - \Psi_{01} \cosh(kd)}{\sinh(kd)} \right] \sinh(kx) \quad (9.39)$$

Since the potential at surfaces are different so the minimum of potential (ψ_m) will lie somewhere in between 2 plates but not at the centre. If we take $\psi_{01} = \psi_{02} = \psi_0$ then we get ψ_m at the middle point as:

$$\Psi_m = \frac{\Psi_0}{\cosh\left(\frac{kd}{2}\right)}$$

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When the potential on the surfaces are different then we can calculate the point where potential is minimum by differentiation. So we would like to find out x_m at which $d\psi/dx = 0$. On differentiating equation (9.39) and put it equal to 0. We get:

$$\frac{1}{k} \frac{d\Psi}{dx} = \Psi_{01} \sinh(kx) + \left(\frac{\Psi_{02} - \Psi_{01} \cosh(kd)}{\sinh(kd)} \right) \cosh(kx) = 0$$

From this we get a relationship for x_m as

$$\tan(kx_m) = -\frac{B}{\Psi_{01}} = \coth(kd) - \frac{\Psi_{02}}{\Psi_{01} \sinh(kd)} \quad (9.40)$$

Then ψ_m can be calculated as:

$$\Psi_m = \Psi_{01} \cosh(kx_m) + \left(\frac{\Psi_{02} - \Psi_{01} \cosh(kd)}{\sinh(kd)} \right) \sinh(kx_m) \quad (9.41)$$

$$\Psi_m = \Psi_{01} \cosh(kx_m) \left(\Psi_{01} + \frac{B^2}{\Psi_{01}} \right)^2 \quad (9.42)$$

Now if we recall from equation (9.33) we have the expression for force as

$$F_n \approx n_0 kT \left(\frac{ze\Psi_m}{kT} \right)^2$$

so we need to calculate ψ_{m2} to get the value of FR.

$$\Psi_m^2 = [\cosh(kx_m)]^2 \left(\Psi_{01} + \frac{B^2}{\Psi_{01}} \right)^2$$

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using

$$\cosh^2 y = \frac{1}{2} (1 + \cosh (2y)) \quad (9.43)$$

$$\tanh^2 y = \frac{\cosh 2y - 1}{\cosh 2y + 1}$$

$$\cosh(2y) = \frac{\tanh^2 y + 1}{1 - \tanh^2 y} \quad (9.44)$$

Combining equations (9.43) and (9.44) we get,

$$\cosh^2 y = \frac{1}{1 - \tanh^2 y}$$

From equation (9.40) we have

$$\tanh(kx_m) = -\frac{B}{\Psi_{01}} \quad (9.45)$$

Thus we get ψ_{m2} as

$$\Psi_m^2 = \left(\Psi_{01} - \frac{B^2}{\Psi_{01}} \right)^2 \left(\frac{1}{1 - \frac{B^2}{\Psi_{01}^2}} \right)$$

Substituting this value of ψ_{m2} in (9.32), we get

$$F_R = \frac{k^2 \epsilon}{2 \sinh(kd)} \left[\frac{\Psi_{01}^2 - \Psi_{02}^2}{\sinh(kd)} - 2 \Psi_{01} \Psi_{02} \coth(kx_m) \right] \quad (9.46)$$

This equation is valid only for small potentials. It must be noted that value of F_R could be positive or negative for same type of potential. Thus F_R could be attractive or repulsive same type of potential, depending upon the values of ψ_{01} and ψ_{02} . However F_R will always be attractive for different type of potential on the surfaces. Energy per unit area when 2 charged surfaces are brought from infinity to separation distance can be calculated as:

$$G^{EL} = - \int_{\infty}^d F_R d(d)$$

$$G^{EL} = \frac{\epsilon k}{2} [(\Psi_{01}^2 + \Psi_{02}^2)(1 - \coth(kd)) + 2 \Psi_{01} \Psi_{02} \operatorname{cosech}(kd)] \quad (9.47)$$

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If $\psi_{o1} = \psi_{o2} = \psi_o$ we get:

$$G^{EL} = \epsilon k \psi_o^2 \left(1 - \tanh\left(\frac{kd}{2}\right) \right) \quad (9.48)$$

Under Deryaguin approximation electrical potential energy of spherical particle can be written as

$$\phi(\text{sphere}) = \pi R \int_0^\infty G^{EL} d(d) \quad (9.49)$$

From equation (9.47) substituting value of GEL in equation (9.49) we have

$$\phi^{EL} = \frac{\pi \epsilon R_1 R_2}{R_1 + R_2} (\psi_{o1}^2 + \psi_{o2}^2) \left[\frac{2 \psi_{o1}^2 \psi_{o2}^2}{\psi_{o1}^2 + \psi_{o2}^2} \ln \left(\frac{1 + e^{-kd}}{1 - e^{-kd}} \right) + \ln(1 - e^{-2kd}) \right]$$

where R is replaced by $\frac{2R_1 R_2}{R_1 + R_2}$ for particles of different diameter. If $\psi_{o1} = \psi_{o2} = \psi_o$ we get:

$$\phi^{EL}(\text{sphere}) = 2\pi R \epsilon \psi_o^2 \ln(1 + \exp(-kd)) \quad (9.50)$$

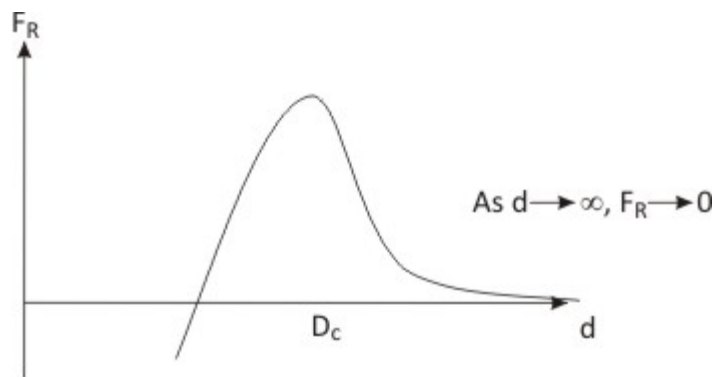


Fig. 9.5: Electric force between two particles with distance.

From above figure we see that for same type of potential on the two surface, F_R will be repulsive for $d > D_c$ but will be attractive for $d < D_c$. To avoid the distortion of potential field, 2nd plate is kept where the potential of 1st plate is equal to that of 2nd plate.

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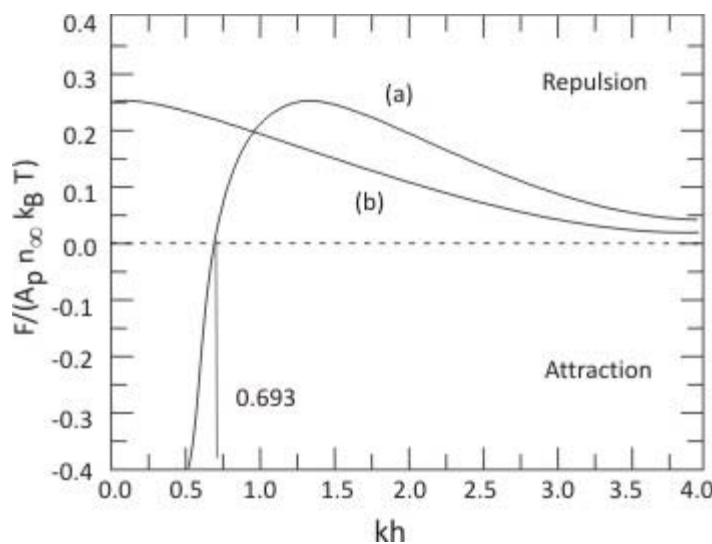


Fig 9.6: Electrostatic double layer force between two constant potential surfaces.

Case (a) $\Psi_a = 0.5$ and $\Psi_b = 1.0$ and Case (b) $\Psi_a = \Psi_b = 1.0$

Reference: pg. 144 Electrokinetic and colloid transport phenomenon, Masliyah J. H. and Bhattacharjee S. ; John Wiley & Sons Inc. , 2006

Surfaces of same sign but of dissimilar potentials can encounter attractive forces on close approach has a major impact in the area of coagulation. This behavior at close separation is because of change in sign of the surface charges on one of the surface due to the overlapping double layer. In case (a) with dissimilar surface potential the electrostatic force becomes attractive at some distance whereas in case (b) with similar potential the force remains repulsive all the time.

If the two plates have charge density s_1 and s_2 , then by electric neutrality of the system we can write

$$\sigma_1 + \sigma_2 + \int_0^D \rho dx = 0$$

Substituting ρ from Poisson equation we have

$$\sigma_1 + \sigma_2 = \epsilon \int_0^D \frac{d^2 \Psi}{dx^2} dx$$

$$\sigma_1 + \sigma_2 = \epsilon \left(\frac{d\Psi}{dx} \right)_0^D$$

$$\sigma_1 + \sigma_2 = \epsilon \left(\frac{d\Psi}{dx} \right) \Big|_{x=D} - \epsilon \left(\frac{d\Psi}{dx} \right) \Big|_{x=0}$$

As we have calculated earlier $\psi(x)$ can be calculated either by Gouy Chapman equation or under

Debye-Huckel approximation.

Surface potential application in biology: It has wide range of applications at biological membranes and proteins. The ions in solution will be capable of concentrating or depleting at the surface depending on the potential sign and valence of the ion. The effect for membrane is comparatively larger than for proteins, as potentials are generally higher.

In biotechnology, the purification of proteins are done with salting-in and salting-out mechanism which can be evaluated with Debye Huckel approximation. Diseases such as gout (characterized by deposition of sodium urate crystals) and kidney stones (deposition of calcium oxalate crystals) are studied to determine the various affects leading to deposition of salts and inducing their dissolution in biological buffer. Protein folding mechanisms and diseases caused due to protein aggregation such as Alzheimer's are being investigated using this approximation.

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References:

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