Colloids and Surfaces
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Lecture – 34
Comparison of Capacitor model and Diffuse double layer model

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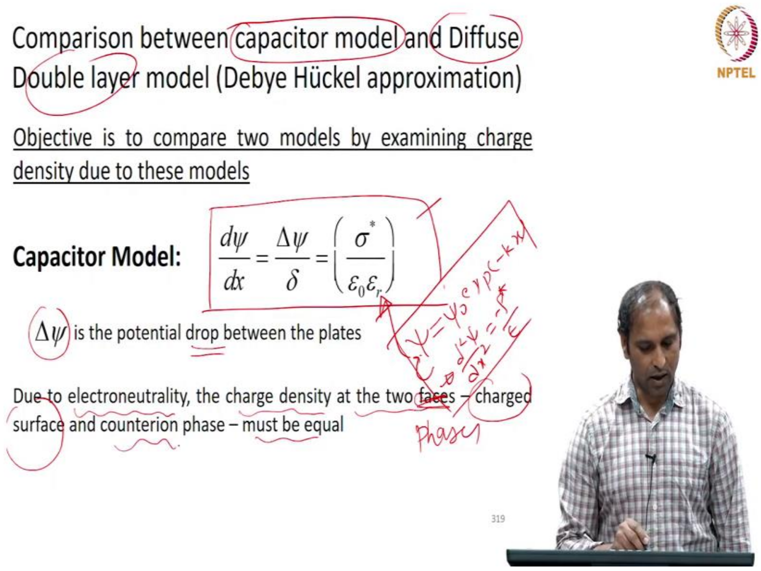

Comparison between capacitor model and Diffuse Double layer model (Debye Hückel approximation)

Objective is to compare two models by examining charge density due to these models

Capacitor Model: $\frac{d\psi}{dx} = \frac{\Delta\psi}{\delta} = \left(\frac{\sigma^*}{\varepsilon_0 \varepsilon_r}\right)$

$\psi = \psi_0 \exp(-\kappa x)$

$\frac{d^2\psi}{dx^2} = -\frac{\rho^*}{\varepsilon}$

$\Delta\psi$ is the potential drop between the plates

Due to electroneutrality, the charge density at the two ~~faces~~ phases – charged surface and counterion phase – must be equal

Now, what I want to do is a simple exercise where we would like to compare the capacitor model and the diffuse double layer model. So, this is what we derived earlier that is d psi / dx = delta psi divided by delta is equal to sigma star / epsilon not epsilon r where delta psi is the potential drop between the plates. Now, I would like to take you know the psi = Psi 0 exponent - kappa x and d square psi / dx square - rho star / epsilon.

These are the this was a basic equation that we use for obtaining how the potential varies with separation distance that is the now, I would like to use these expressions and then express this in a way I can compare with the capacitor model.

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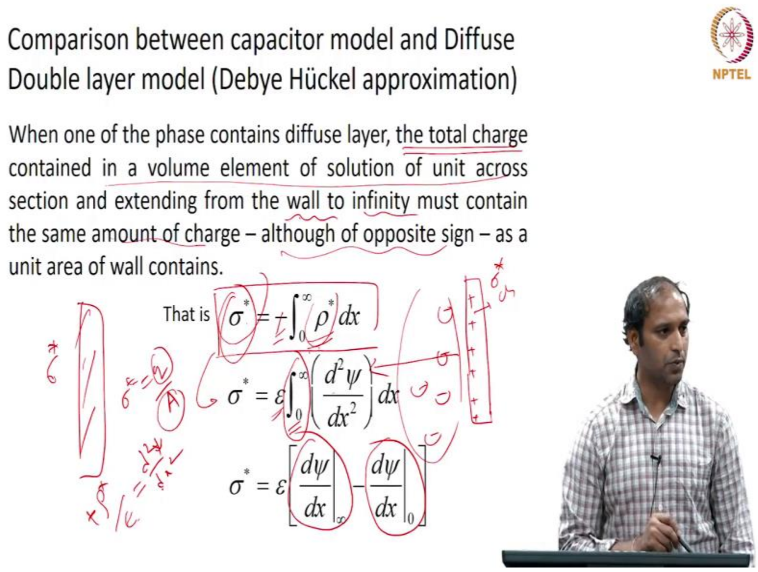

Comparison between capacitor model and Diffuse Double layer model (Debye Hückel approximation)

When one of the phase contains diffuse layer, the total charge contained in a volume element of solution of unit across section and extending from the wall to infinity must contain the same amount of charge – although of opposite sign – as a unit area of wall contains.

That is $\sigma^* = \pm\int_0^\infty \rho^* dx$

$$\sigma^* = \varepsilon\int_0^\infty \left(\frac{d^2\psi}{dx^2}\right) dx$$

$$\sigma^* = \varepsilon\left[\left.\frac{d\psi}{dx}\right|_\infty - \left.\frac{d\psi}{dx}\right|_0\right]$$

So, for that what we will do is so, I have written a expression here which tells you the sigma star which is the surface charge density that we had in the capacitor model this rho star is the charge density but that is charged per unit volume in this case. Now, if you assume that I do not have any other added electrolyte I only have the charges because of I only have the counter ions that come because of the dissociation of charges on the particle surface.

Then what I can do is I can say that because of the electro neutrality I can say that the charge density at the 2 phases must be equal when I say 2 phases one I am talking about the charged surface at the 2 phases, this was not 2 phases 2 phases, because of the electron neutrality the charge density in the 2 phases must be equal when I say 2 phases one is the charge surface and the counter ion sub phase. The other way of saying the same thing would be.

So, the total charges contained in a volume element of a solution across you know so I can put this way let us say this. So, I can define sigma star. Then what you do is I consider the total charge that is contained in a volume element. And I am going to count all the ions that are present from the wall to infinite distance away from the wall. The total charge that is contained, determined in that way must be exactly equal to the charges on the particle surface.

However, they should be opposite in sign. Is it okay? So we are talking about in this case. So, imagine that I have a diffused double layer now. We will come back. When one other phase contains diffuse layer that means this is a charged surface. And I have a diffuse layer when one of the phases contained diffuse layer. The total charge contained in a volume element of a solution across the cross section extending from wall to infinity must contain the same amount of charge, although opposite in sign as the unit area of the wall contains.

So that is what this expression essentially says. You have a question. So, that is a good point. So, sigma star corresponds to the charge density of the surface, if I have a charged surface. So, we what we defined is sigma star was q /A. The total charge on the particle surface divided by area that is how it was defined and in this case, rho star is a charge in the solution.

So, we are talking about equating the charges on the particle surface and the charges in solution. And because of the fact that the electro neutrality you know must be preserved, the total charges that are in the solution on the particle surface should be same as the charges in the solution, however, they should be of opposite sign. Think a little bit about this, you know, we can discuss this further as well.

So, now, I have rho star I can instead of sigma star is a rho star, what I can do is I know that rho star / epsilon, is minus d square psi / dx square, so, we will replace with that instead of rho star and we could have d psi / dx, and I would have epsilon that comes here and there is a – 1 minus here minus here it becomes plus. So, therefore, sigma star is epsilon 0 to infinity d square psi by dx square into dx.

And I would have to sum up all the charges all the way from distance is equal to 0 to infinity. Therefore, sigma star if I integrate this I can write this as sigma star is equal to epsilon into d psi / dx at infinity - d psi / dx at 0 that is at the surface of the charged body and that is at a distance very far away from the charge surface.

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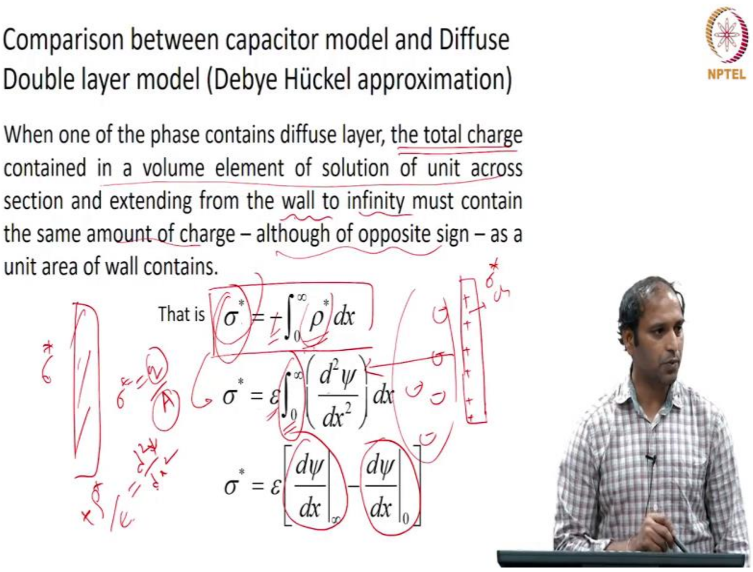

Comparison between capacitor model and Diffuse Double layer model (Debye Hückel approximation)

When one of the phase contains diffuse layer, the total charge contained in a volume element of solution of unit across section and extending from the wall to infinity must contain the same amount of charge – although of opposite sign – as a unit area of wall contains.

That is $\sigma^* = -\int_0^\infty \rho^* dx$

$$\sigma^* = \varepsilon \int_0^\infty \left(\frac{d^2\psi}{dx^2}\right) dx$$

$$\sigma^* = \varepsilon \left[\left.\frac{d\psi}{dx}\right|_\infty - \left.\frac{d\psi}{dx}\right|_0 \right]$$

And we know that we know that d psi / dx at infinity is going to be 0 because we know that psi itself is 0 at you know x is equal to infinity therefore, the first term is going to be 0 then you are left with epsilon times 0 - d psi / dx at 0 therefore, sigma star is - epsilon d psi / dx 0 and because we know that the potential varies in a false and you know in an exponential way I can get what is d psi / dx at 0.

Therefore, d psi / dx = 0 will be psi not exponent - kappa x times - k and because for extending to 0 this term becomes 1. So, I have - k times Psi 0. Therefore, sigma star which is equal to - epsilon d psi/ dx at 0 will be equal to epsilon kappa Psi 0.

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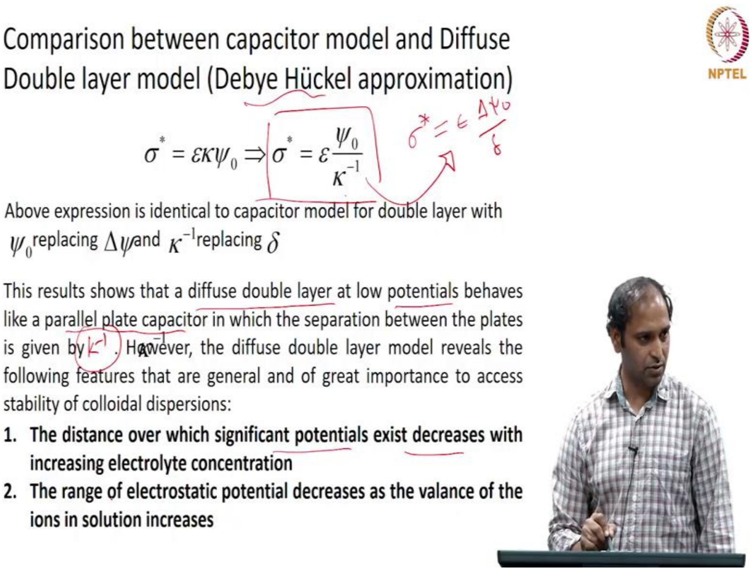

Comparison between capacitor model and Diffuse Double layer model (Debye Hückel approximation)

$$\sigma^* = \varepsilon\kappa\psi_0 \Rightarrow \sigma^* = \varepsilon\frac{\psi_0}{\kappa^{-1}}$$

$\sigma^* = \varepsilon \frac{\Delta\psi_0}{\delta}$

Above expression is identical to capacitor model for double layer with ψ_0 replacing $\Delta\psi$ and κ^{-1} replacing δ

This results shows that a diffuse double layer at low potentials behaves like a parallel plate capacitor in which the separation between the plates is given by κ^{-1}. However, the diffuse double layer model reveals the following features that are general and of great importance to access stability of colloidal dispersions:

1. **The distance over which significant potentials exist decreases with increasing electrolyte concentration**
2. **The range of electrostatic potential decreases as the valance of the ions in solution increases**

And therefore, I can rearrange this to get sigma star is equal to epsilon into Psi 0 divided by kappa inverse and if you look at the capacitor model the expression was sigma star is equal to epsilon delta Psi 0/ delta. So, we are able to express sigma star you know obtained from the

Debye Huckel approximation in a you know is an equation which is analogous to the capacitor model.

So, what you can infer from this is that these results they essentially show that the diffuse double layer at low potential you know you can think about it behaves like you know capacitor model however, the separation distance is replaced by k inverse. Instead of delta you have kappa inverse. But of course it this model captures the you know some really important features for example, the distance over which significant potential exist decrease with increasing electrolyte concentration.

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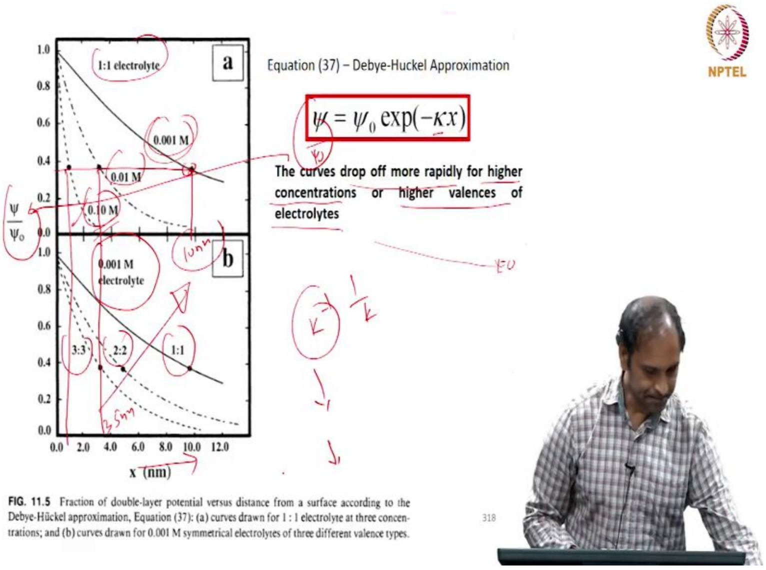

Equation (37) – Debye-Huckel Approximation

$$\boxed{\psi = \psi_0 \exp(-\kappa x)}$$

The curves drop off more rapidly for higher concentrations or higher valences of electrolytes

FIG. 11.5 Fraction of double-layer potential versus distance from a surface according to the Debye-Hückel approximation, Equation (37): (a) curves drawn for 1 : 1 electrolyte at three concentrations; and (b) curves drawn for 0.001 M symmetrical electrolytes of three different valence types.

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What I mean by that if I look at this expression what do you understand by the statement the distance at which the significant potential exists decrease with electrolyte concentration. So, if I look at these expressions of course, if I go to a very far away distance potential is going to be 0. Now, what is important when you worry about electrical double layer interaction is that when the 2 surfaces charged surfaces come closer if the potential when they approach if the potential is very, very high that means the repulsion is also going to be high.

So, if I look at a particular let us look at this potential which is this prediction rate it occurs at may be separation distance of 10 nanometer, let's go back and look at a same potential occurs at a much lower separation distance the same potential occurs at whatever 3.5 nanometers something like that. Now, if I go here, the same potential occurs at even lesser separation distance. That is what the first statement essentially means, the distance over which significant potential exist decreases with increase in the electrolyte concentration.

That was actually demonstrated by here. Because this is a case where the electrolyte concentration is changing, the electrolyte concentration is changing when the electrolyte concentration is 0.001 this particular potential occurs at 10 nanometer, but the same potential occurs at a lower distance, when I have a higher concentration of salt, if I go for even higher concentration of salt, the distance at which the same potential exists even decreases.

That is the first statement the distance or which significant potential exists decreases with increasing electrolyte concentration. And the second point, the range of electrostatic potential decreases as the valency of the ions in the solution increases. This is right that we can draw from the second point. Can I make this so I am going read that again .The range of electrostatic potential decreases as the valence of the ions in the solution increases.

So, there I mean, now you have a statement about the range of interaction. Now, the range of interaction electrical double layer interaction essentially depends on how does this potential vary with distance, if the potential falls off steeply, the range over which the electrical double layer interactions become important is smaller. However, if you have a case, where the potential decreases more gradually.

That means, the range over which the electrical double layer interactions are important or the electrostatic interactions become important over a larger range of separation distance. Do you get that point? Or do you have to explain? So, you can think about it, you can in a way, think about k inverse or 1 over k as a distance over which the electrical double layer interactions are become important. If you go by that so the more the kappa inverses, more will be the range.

Now, because I am able to decrease kappa inverse by adding a higher concentration of salt or by increasing the valency of the ions I have put in. Therefore kappa inverse is going to go down. Therefore, the range of over which the electrical double layer interactions become important is also going to go down, that is the point. I think a little bit about it.

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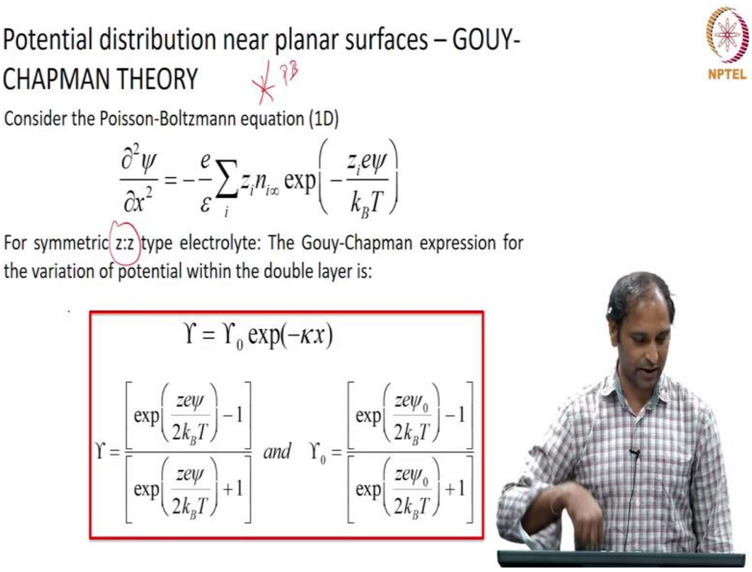

Potential distribution near planar surfaces – GOUY-CHAPMAN THEORY κ^{PB}

Consider the Poisson-Boltzmann equation (1D)

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{e}{\varepsilon}\sum_i z_i n_{i\infty} \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$

For symmetric z:z type electrolyte: The Gouy-Chapman expression for the variation of potential within the double layer is:

$$\Upsilon = \Upsilon_0 \exp(-\kappa x)$$

$$\Upsilon = \frac{\left[\exp\left(\frac{ze\psi}{2k_B T}\right) - 1\right]}{\left[\exp\left(\frac{ze\psi}{2k_B T}\right) + 1\right]} \quad and \quad \Upsilon_0 = \frac{\left[\exp\left(\frac{ze\psi_0}{2k_B T}\right) - 1\right]}{\left[\exp\left(\frac{ze\psi_0}{2k_B T}\right) + 1\right]}$$

So that is about what I want to speak today. So we will what we will do the next class is to look at more general solution. Instead of looking at linearized Poisson Boltzmann equation, we will just look at a more general case for a symmetric electrolyte and then we will try and look at it how does a potential vary with separation distance and then discuss again, the implications.