Gouy-Chapman EDL Model

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Lecture-33

Diffuse double layer model; linearized Poisson-Boltzmann equation; potential distribution around the charged plate as a function of distance and electrolyte concentration

So, in this video lecture, we will look at some of the shortcomings of the capacitor model proposed by Helmholtz equation. And we will also look at the importance of , you know, looking at incorporating ,you know ,other aspects right so that the results that we get is you know pretty accurate right so in this video lecture we will also look at Gouy-Chapman electrode electrical double layer model which is improved version of the electrical double layer model okay so we will look at the the shortcomings first and then we will see the Gouy-Chapman model right in this video lecture okay let's begin

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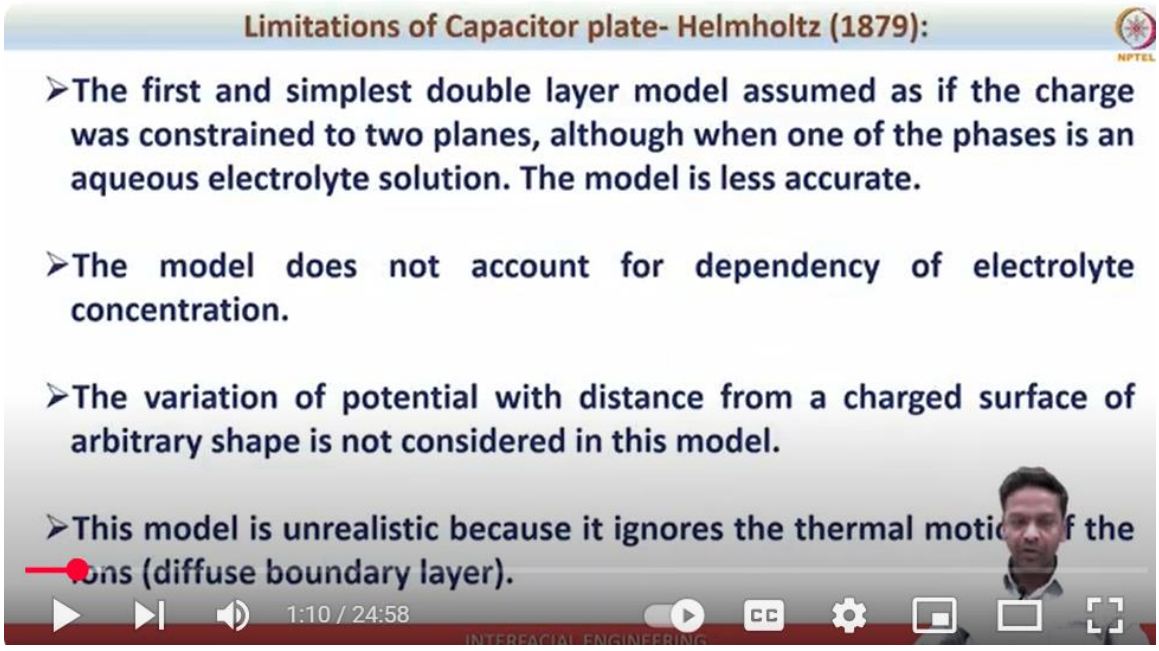

Yeah, so as we have just now described, you know that the limitations of Capacitor plate model, which was proposed by Helmholtz in 1879, right, are listed here, okay? so the first and foremost uh shortcoming that if you want to uh you know present is the uh the the parallel plate assumption right so if you look at there are two plates two parallel plate

right we considered uh both plate carries with it equal and opposite charge right with it okay Now, the problem here is one of the plate is solid and rigid plate, okay? And the other one is the electrolyte, right? So, we consider the strongly bound counter ions as the rigid, you know, solid boundary itself, which is actually not very accurate, okay? And the consequence of that will be on the one hand, you will not get very accurate results. On the other hand, it also leaves aside the dependency of electrolyte concentration, right, which is very much crucial, right? So, because, as you know, when the electrolyte concentration goes up, when the strength of the electrolyte concentration goes up, it affects the distribution of the ions. So, the counter ions and co-ions present in the solution also vary as a function of concentration, but these details are not presented by this model, that is the capacitor model. So that is actually a major drawback and the other drawback is, we considered parallel plate assumption, right?

What if we have to deal with a situation where instead of parallel plate, we encounter cylindrical shape, right, or spherical shape or any arbitrary, for such situation, this model does not provide any, you know, accurate results. because it considers basically parallel plate assumptions, which is not true always in all cases. So that is another drawback of the model. The last but not least is that it ignores the, you know, the thermal motion of the ions. So, you know that in the solution, due to, you know, bombardment of solvent ions, there will be thermal motion, right? Because of the thermal energy, right? Which is nothing but k_BT, okay? But because there will be thermal motion, ions will not be distributed, you know, in a linear fashion. It can be distributed in a random fashion. So that aspect's not covered by the model. So, these are the shortcomings. Now, as a remedy to this, Gouy and Chapman have proposed another electrical double layer model that actually kind of incorporates or addresses these shortcomings or gaps. We will see them in detail.

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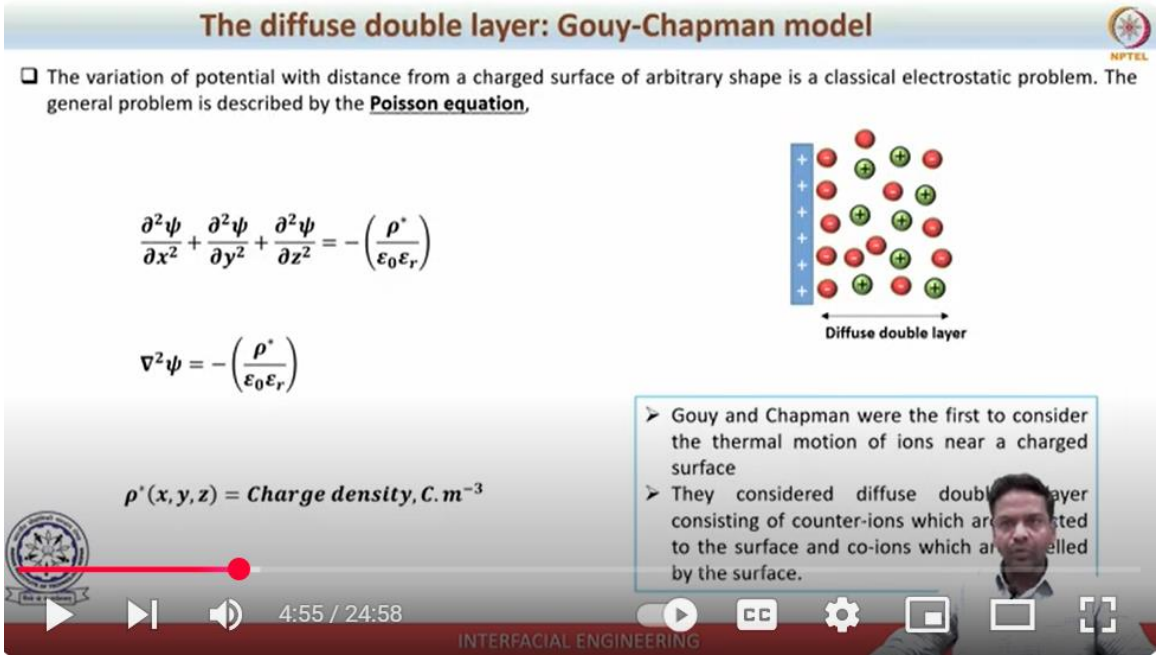

So, this is nothing but the diffuse double layer because it considers the diffuse double layer, right? And it is predicted by the, proposed by the Gouy and Chapman, right? That's why it is called Gouy-Chapman model, okay? And because it considers diffuse double layer, it means that they, you know, take the thermal motion of ions near the charged surface into consideration. That is very, you know, a very good thing considering the situation. realistic situation and the next one is that in the Capacitor model unlike the Capacitor model here in the solution you also consider both counter ions which are attracted by the you know the charged surface and the co-ions which are repelled by the surface so both counter ions and co-ions you know coexist in the solution which is also considered by this model OK, so remember when we talked about the electrical double layer theory, in the beginning, we said whenever you introduce a charged surface into the solution, you can expect three possibilities, right? One is strongly bound counter ion. weakly bound counter ion, diffuse counter ions you may be asking like why these aspects are not taken into consideration in the first place itself, remember ,you know one would not get this much clarity in the first place itself right as we understand about the the difficulties okay as we face the challenges we try to ask questions and get answer so with the time we get more clarity and with the time we evolve right that's how these different models you know came into existence okay you may be wondering why in the Helmholtz model itself uh this diffuse double layer thing was not incorporated because at the time this much clarity was not provided that's why this was not included with the time we understand better and we also evolved right so that's why different at different point of time you get different model okay um come into existence okay so this particular model remember i mean we just now described that there are three you know, types of counter ions that we always encounter. One is strongly bound. So, the Capacitor model

considered only the strongly bound counter ions, whereas the weakly bound and diffuse boundary layer was not considered. So, this Gouy-Chapman model, Gouy and Chapman, they consider not only the strongly bound, but they also consider the diffuse double layer. So, if you incorporate along with the parallel plate, if you incorporate this diffuse double layer, that means it is Gouy-Chapman model. So, the variation of the potential with the distance from a charged surface of... So now we are going to talk about any arbitrary shape. We are not only going to deal with the parallel plate. For any arbitrary shape, but We also know from a classical electrostatic problem, there is something called Poisson equation, which describes the variation of potential with the distance, right? So, this is going to be our starting point, okay?

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho^*}{\varepsilon_0 \varepsilon_r}$$

$$\nabla^2 \psi = -\frac{\rho^*}{\varepsilon_0 \varepsilon_r}$$

- Ψ - Potential
- ρ* - Charge density per unit volume

When you take into consideration the region of space of interest, if you include the total volume, then you will get the potential for, I mean, the total charge, right, for a given problem, okay? And you can also see in denominator, we actually considered not just a vacuum, which is ε_0, we consider $\varepsilon_0\varepsilon_r$. So, when I say $\varepsilon_0\varepsilon_r$, this is simply nothing but ε_m. So, we take the advantage of the relative permittivity, which doesn't have any dimension unit whereas the ε_0 is vacuum permittivity. So, for different materials, we have already listed what is ε_r. So, if you simply multiply ε_r with ε_0, what you will be getting is the ε_m which is the permittivity of any given material, right? Or medium, sorry, medium in this case, right?

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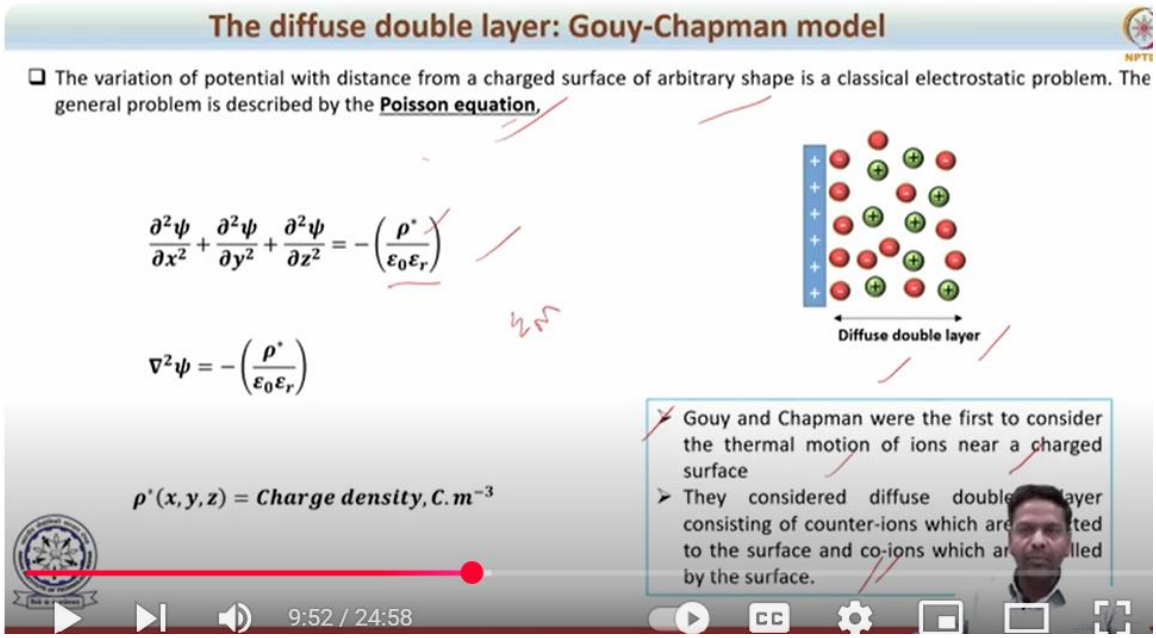

So, since we are dealing with electrolyte, we have to include the medium, right? That's why we have taken ε_0 ε_r instead of just ε_0, okay? Yeah, so. .. Here, we will try to obtain, you know, the potential variation across the surface, right, across the interface, right? So as a function of distance, as well as as a function of electrolyte concentration, okay? Our starting point is going to be the Poisson equation.

$$\nabla^2\psi=-\frac{\rho^*}{\varepsilon_0\varepsilon_r} \qquad \ldots (1)$$

Our first step will be to incorporate the random distribution of ions, a function that will describe the random distribution of ions, right? And then we have to get the equation, you know, of... Ψ, right, equation for Ψ as a function of, you know, distance as well as the electrolyte concentration, right?

$$\Psi = f(x, c)$$

So that is exactly what we are going to look at, okay? All right. So, our first step will be the Poisson distribution equation. So, we have written that here. So, when we say that we are talking about the diffuse nature of ions, thermal diffusion, and the distribution of ions will be random. Let's say we have a surface. So, what is the probability that any ions, you know, will exist? It could be counter ion or co-ion will exist, okay? Here is, you know, that needs to be specified using a function, right? So, we are going to borrow this random, you know, the distribution of ion, which is a random which is a function in a random fashion. So, then we are going to incorporate. So, we are going to look at what is

known as the Boltzmann distribution function. Okay. We are going to borrow this from the Boltzmann distribution function, okay? And then we are going to use this in our equation here, plug it here, and then get the relevant, the equation as a function of x and the electrolyte concentration. So what this Boltzmann distribution function says is that the number of ions, which can be defined as

$$n_i = n_{i\infty} \exp\left(-\frac{z_i e \psi}{k_B T}\right)$$

So, this is our equation, okay, what it says is that this

- $n_i\infty$ - Concentration, the bulk concentration
- z_i - Valence coulomb
- e - Electron constant, coulomb
- Ψ -Potential, volt

$$n_i = n_{i\infty} \exp\left(-\frac{z_i e \psi}{k_B T}\right) \qquad \frac{C\frac{J}{C}}{J} \rightarrow \text{dimensionless}$$

This part will be dimensionless and so we are talking about the number number of ion distribution so what it describes is that when far away from the surface, which is the bulk concentration we're talking about, far away from the surface, Ψ will be zero because it will not have any influence. So, which means that when you move, far away from the surface Ψ will be no longer valid, Ψ = zero in such cases this exponential term will be one and you will be nothing you will have

$$n_i = n_i\infty$$

As you come you know as you move towards the surface right when you approach when you move close to the surface, Ψ ≠0. Ψ will be uh you know varying right as a function of distance

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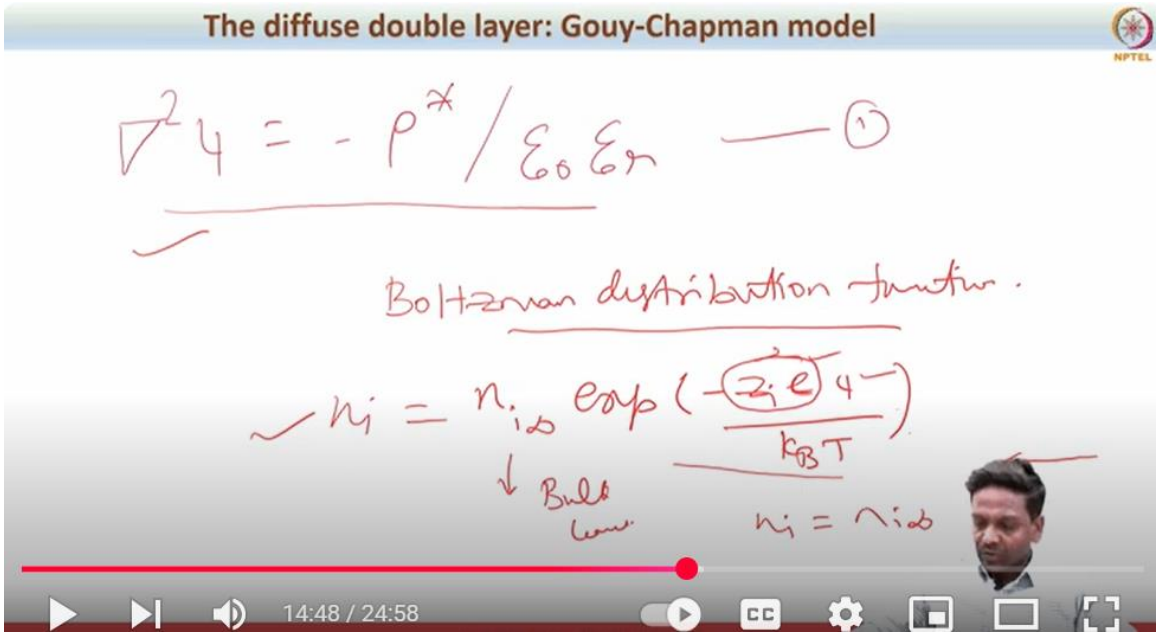

So, then you will have uh you will have this function will be like exponential decay for example if I have to specify this as a function of you know distance right distance as n_i this will be varying something like this okay, so this one is $n_{i\infty}$, right? This is the exponential decay. And this part will be, the potential correspond to this part will be Ψ_o, which is the Ψ surface potential, potential of the surface itself, right?

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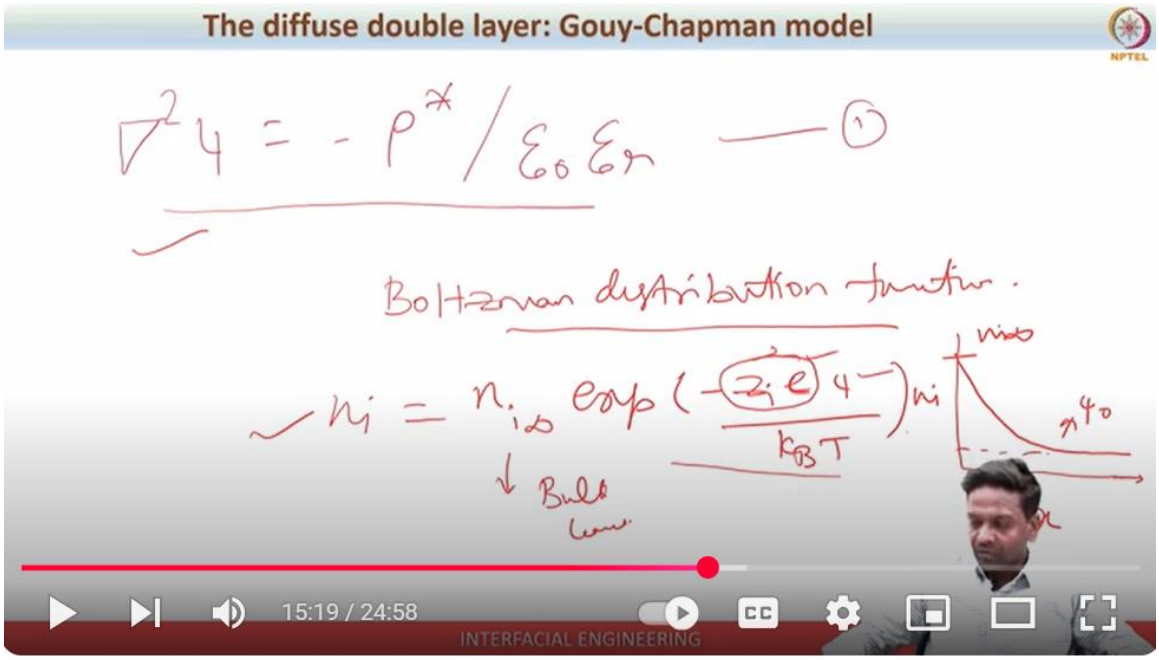

So, this is how the function, you know, will reflect, okay? When you incorporate the Boltzmann distribution function right so what is ρ* here,

$$\rho * = (n_i z_i e)$$

Now you have to substitute this ρ* here back into this equation and you substitute you will have

$$\nabla^2\psi = -\frac{\rho^*}{\varepsilon_0\varepsilon_r} = -\frac{n_i z_i e}{\varepsilon_0\varepsilon_r} = -\sum_i n_{i\infty} \cdot \left[\exp\left(-\frac{z_i e\psi}{k_B T}\right)\right] \times \frac{z_i e}{\varepsilon_0\varepsilon_r}$$

So, this is what we have, So, we can actually use this equation as it is. So $\nabla^2 \Psi$. So, you can express this. So, we can actually use the power series, right? So, let's say we have what is known as the Debye-Hückel approximation. Okay. Debye-Hückel approximation. Okay, what it says is that at a very low potential, especially

$$z_i e \Psi << k_B T$$

Then you can use this power series. So, you can expand like

$$\exp(-x) = 1 - x + x^2$$

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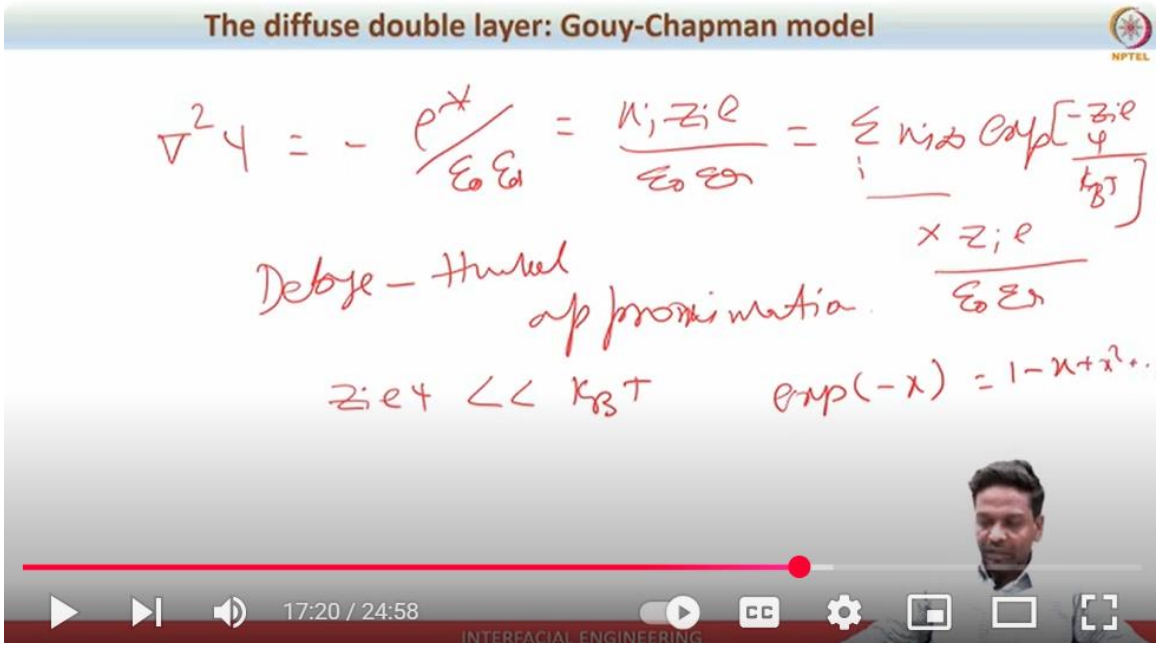

So, this is what we are going to use in this case as well. So, in such cases, if I have to expand this,

$$\exp\left(-\frac{z_i e\psi}{k_B T}\right) \approx 1 - \frac{z_i e\psi}{k_B T}$$

$$\nabla^2\psi = -\left[\sum_i n_{i\infty}\left(1 - \frac{z_i e\psi}{k_B T}\right)\right] \times z_i e \Big/ \varepsilon_0 \varepsilon_r$$

$$= -\left(\sum_i n_{i\infty} z_i e - \sum_i \frac{n_{i\infty} z_i^2 e^2}{k_B T}\psi\right) \Big/ \varepsilon_0 \varepsilon_r$$

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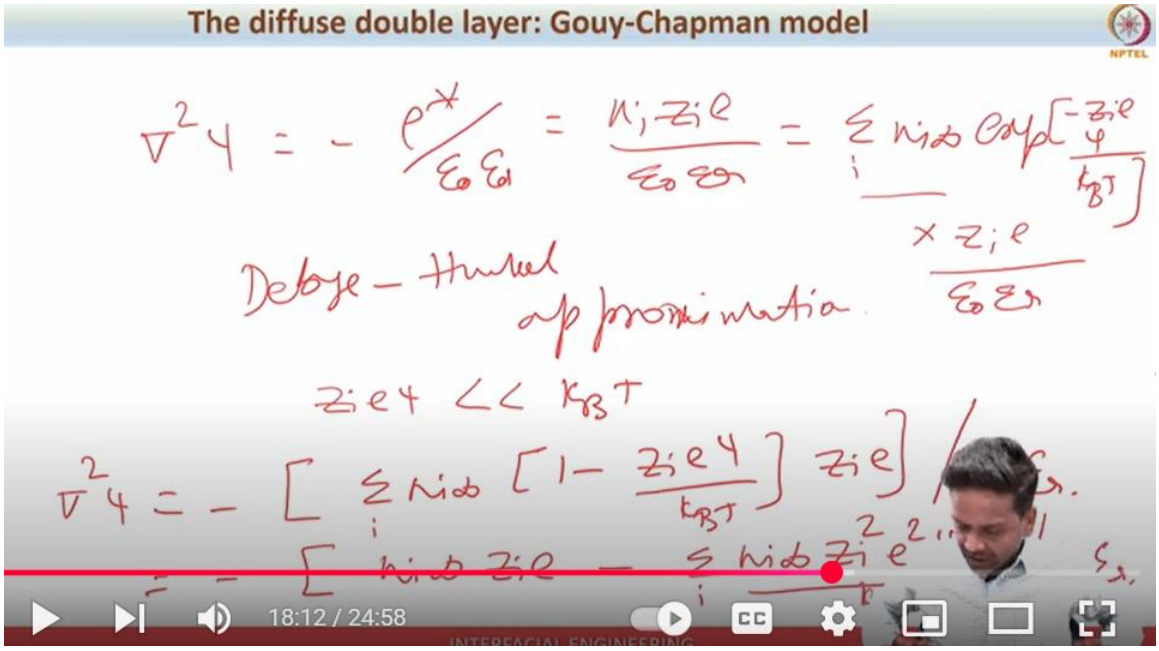

So, this is what exactly we will have so remembered when I expand this $n_{i\infty}$ z_i e will be zero because When you expand, you will have for a symmetric electrolyte, we are talking about symmetrical electrolytes. Our assumption is for a symmetrical electrolyte like NaCl, okay, like NaCl, you can say that there will be equal number of distributions, right? For example,

$Z_{Na} = +1$

$Z_{Cl} = -1$

In such cases you will have equal magnitude but opposite in sign right so all will get cancelled with each other this will be almost this will be like equal I mean this will be equal to zero okay, which also satisfies the electroneutrality condition, right

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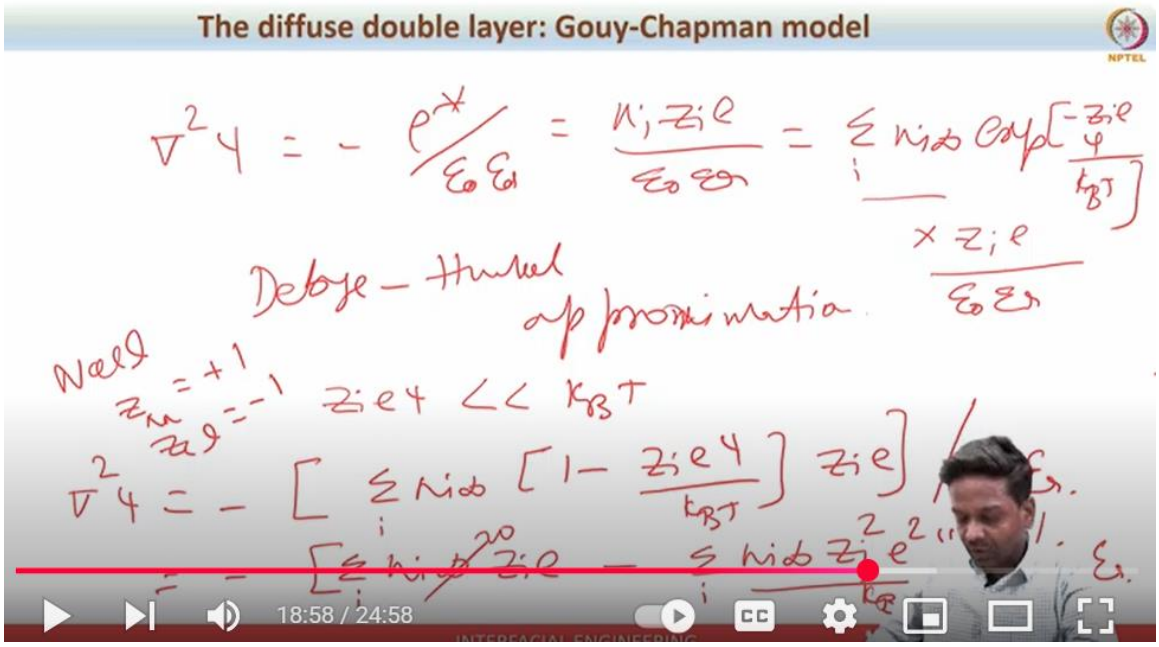

So, this term will no longer exist now we will only have this term which means that we will have

$$\nabla^2\psi = \left(\sum_i \frac{n_{i\infty} z_i^2 e^2}{k_B T \varepsilon_0 \varepsilon_r}\right)\psi$$

Now you can call all this constant term as

$K^2 \rightarrow$ Debye-Hückel parameter

So, if you just incorporate this as

$$\nabla^2\psi = \kappa^2\psi$$

Now you have to just expand this equation. So, if you solve this equation, OK, you will be getting

$$\Psi = Ae^{kx} + B\,e^{-kx}$$

So, if you use this boundary condition, that is

- $x \rightarrow 0$
- $\Psi \rightarrow \Psi_0$
- $x \rightarrow \infty$
- $\Psi \rightarrow 0$

Which means that in first instance, you will get

$$A + B = \Psi_0$$

In second, when you apply second boundary condition, you will get

- $A = 0$
- $B = \Psi_0$

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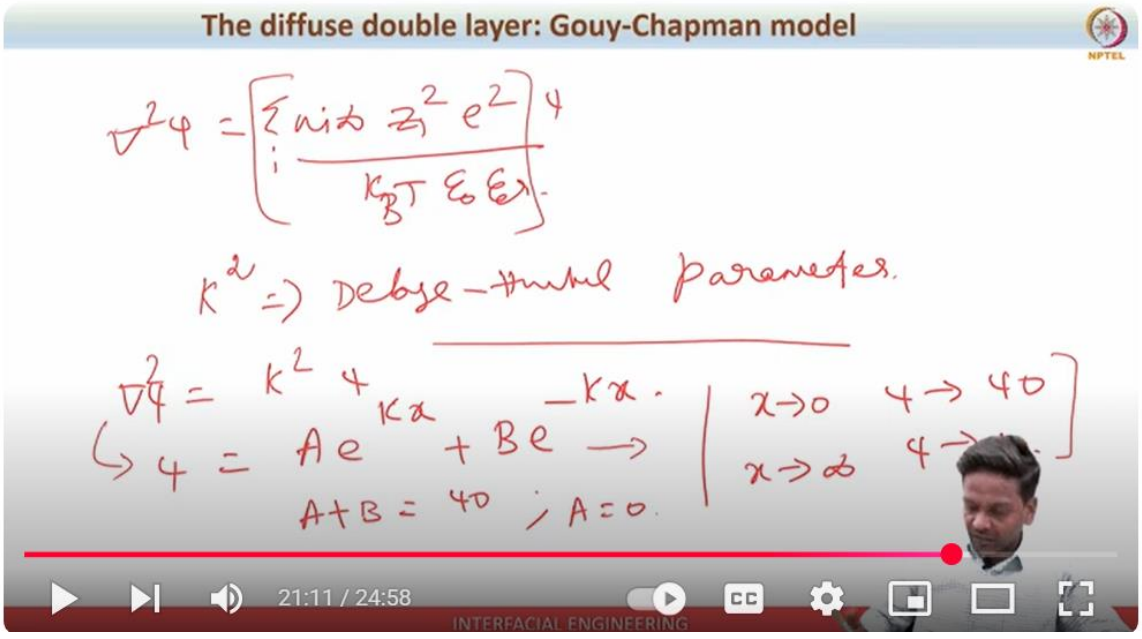

So if you use this two-boundary condition okay you will get

$$\Psi = \Psi_0 e^{-kx}$$

This is our equation if you refer to this equation you will see that Ψ is expressed okay Ψ is expressed as a function of x and the, remember K is the Debye-Hückel parameter, which is a function of concentration, $n_{i\infty}$, okay? So, if the concentration of salt or electrolyte goes up, this will change. So, this equation is dependent on distance as well as concentration, electrolyte concentration. And that's how the Gouy-Chapman model has been proposed. By assuming that, by following certain assumptions like Debye-Hückel approximation is valid, Symmetrical electrolyte. By making these two assumptions, you can express this model, Gouy-Chapman model, as a function of x, that is distance, as well as the electrolyte concentration. This is represented, electrolyte concentration is explicitly mentioned in the equation that is Debye-Hückel parameter itself. Yeah,

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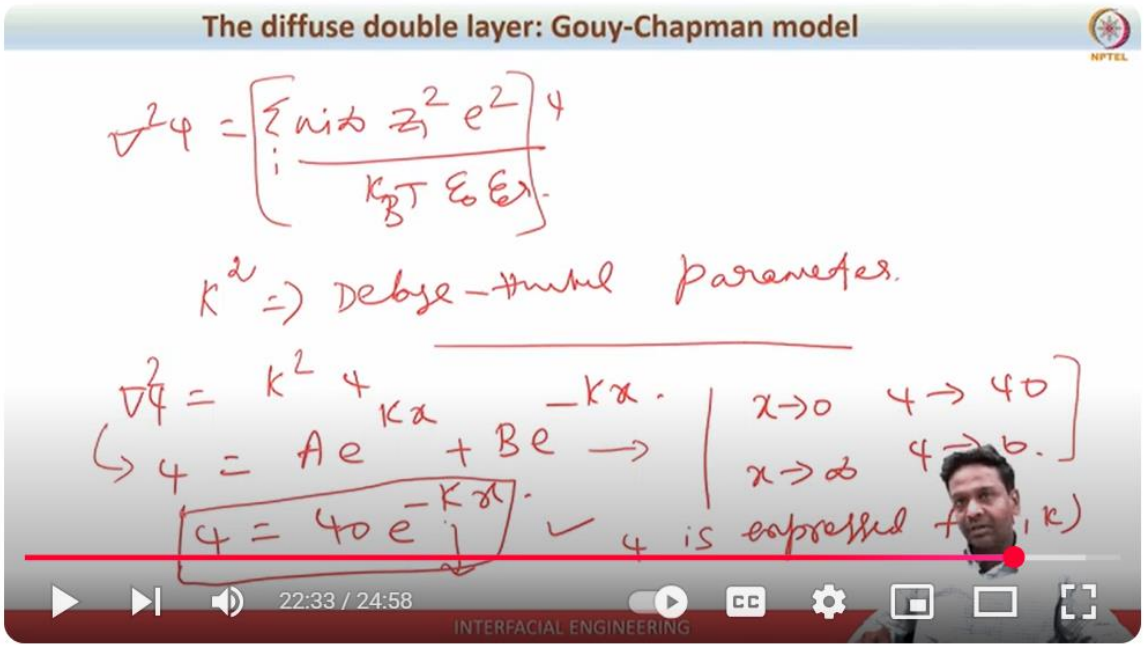

So there is some correction over here.So here we have... obtained the equation as a function of you know distance and electrolyte concentration, for this problem we have chosen one dimensional equation right so we have only considered that only you know this variation of Ψ in the x direction is considered okay and rest of the coordinates were ignored so that's how this equation has been derived okay just keeping this note I mean just keep it noted that, we have obtained this equation by ,you know, assuming that the problem is applicable in one dimension only, okay .

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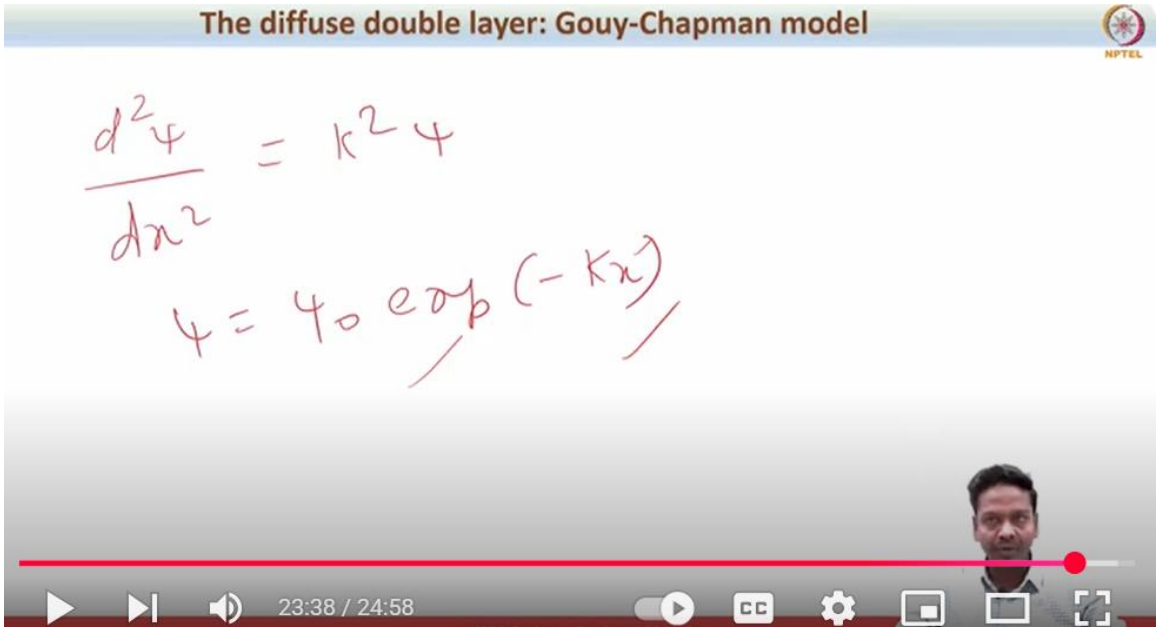

So similarly for spherical geometry as well as cylindrical geometry, one can obtain the function, right, equation of Ψ as a function of, you know, the radial distance, right, as well as the electrolyte concentration, okay, as given here, right? So, one can use the Poisson-Boltzmann distribution equation and then try to solve various geometry using the approach shown here. for like for example for spherical geometry how you can get the Ψ as a function of the distance as well as the electrolyte concentration

$$\psi(r) = \psi_0(R_s/r)\exp[-\kappa(r - R_s)]$$

Similar way for cylindrical surface how one can gets the electrical I mean, the surface potential as a function of distance as well as electrolyte concentration can be obtained using this approach shown here.

$$\psi(r) = \frac{\sigma K_0(\kappa r)}{[\varepsilon\kappa K_1(\kappa R_c)]}$$

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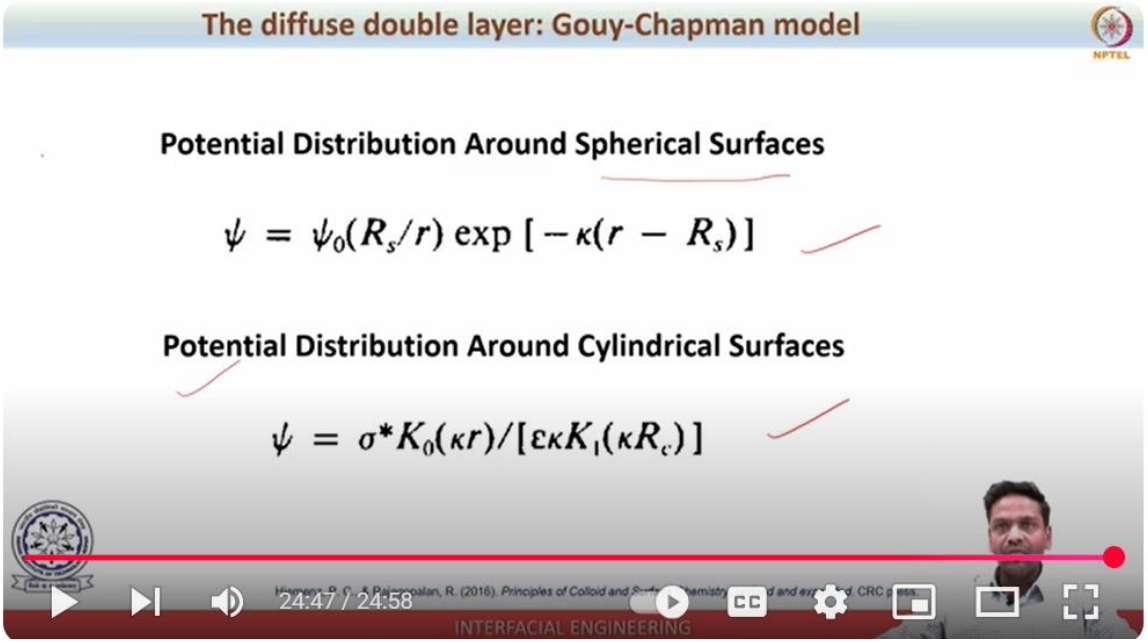

We will stop here. We will continue from the next lecture. Thank you.