Colloids and Surfaces
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Lecture – 35
Models of Electrical Double Layer: Gouy Chapman Theory - 1

So we will continue with module 4. In today's lecture we will try and look at 2 aspects, one is models for double layers looking at Gouy Chapman theory and hopefully if we have some time we will also look at structure of electrical double layers.

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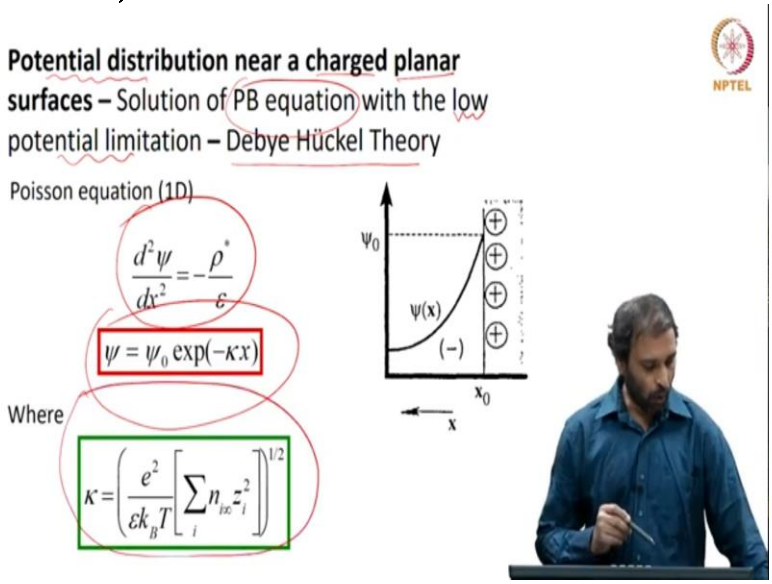

So what we have done so far is to look at potential distribution near a planner charge surface. In that context, we have looked at solution of Poisson Boltzmann equation. However, with the limitation that we are only considering the low potential case which is what is called as a Debye Huckel theory. In which we started off with one dimensional Poisson Boltzmann equation. And then we showed that psi essentially goes as psi naught exponent minus Kappa x, where Kappa is given by this particular expression.

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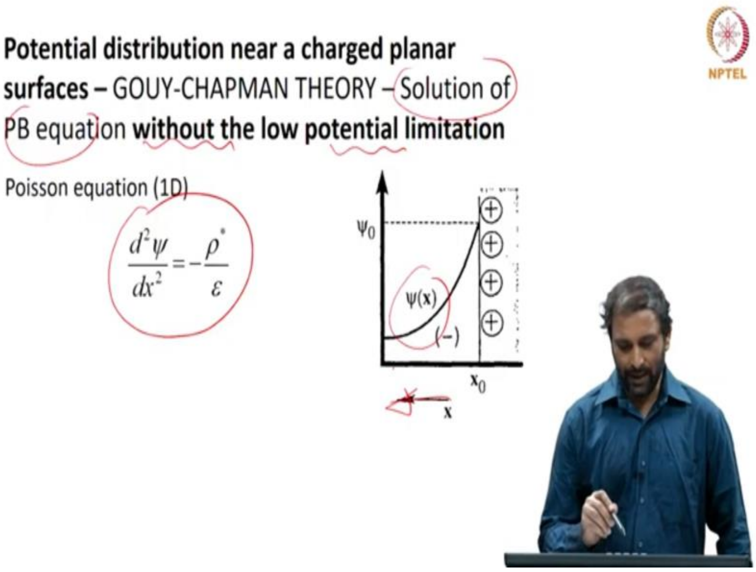

So now what we want to do today is to essentially take out this limitation of low potential that means, we would like to obtain a solution of the Poisson Boltzmann equation without the low potential limitation that is what we would like to do. Again the starting expression is going to be one dimensional Poisson Boltzmann equation, because we are assuming that psi varies only in the x direction. That is we are only considering that psi is a function of x alone.

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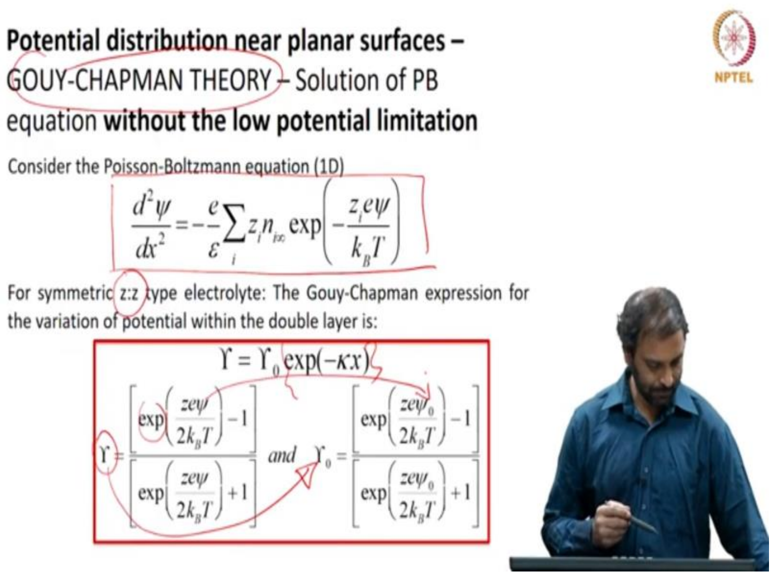

And the solution for this particular case is given by what is called as a Gouy Chapman Theory. So for that we will again solve one dimensional Poisson Boltzmann equation and it turns out that for z is to z electrolyte again the dependence of potential with separation distance is still going to be exponential and is given by gamma = gamma naught exponent minus Kappa x, where gamma is exponent z e psi / 2 k_B T - 1 divided by exponent z e psi 2 k_B T + 1.

And similarly, gamma naught is same as it takes the same similar functional form as gamma with psi replaced by a psi naught. So that is what we are going to derive in today's lecture.

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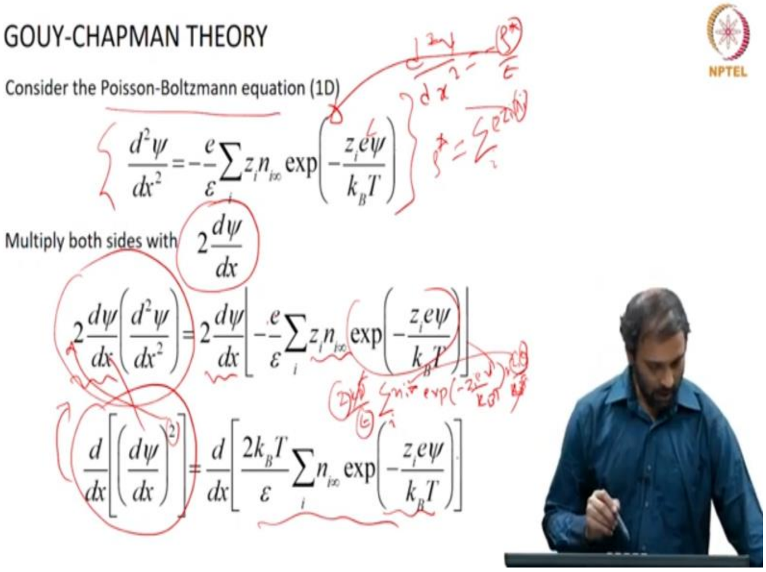

So again we will start with Poisson Boltzmann equation one dimensional case. And if you remember this, so we had d square psi / dx square = - rho star divided by epsilon, instead of rho star, we have used the Boltzmann factor and then we have written an expression for rho star, which essentially is a summation for all the species that I have in the solution, I would have to sum up the contribution from all the ions that I have in the solution.

Which is essentially is e times z_i times n_i and with n_i being given by the Boltzmann factor. So what we will do is we will start with this expression. And we will do some simple manipulations so we are going to multiply both the sides of this equation by 2 times d psi / dx, so that is what we have on the left hand side. And that is what we have on the right hand side as well.

Now if you look at the left hand side, I can write this as d / dx dx of d psi / dx whole square. So if I differentiate this function, so what I will get is, I get 2 times that is 2 here, times d psi / dx, multiplied by d square psi / dx square. So that is the left hand side term, and the right hand side term, I can write this as d / dx of 2 times k B T divided by epsilon into sigma i n_i exponent of minus z_i e psi / k B T.

So if I differentiate this term, so the first term remains the same k_B T divided by epsilon, and what you have here, so I am going to have sigma i n_i infinity, and if I am going to replace, differentiate this term is still going to be exponent minus z_i e psi / k_B T multiplied by, so it is going to be multiplied by z_i e divided by k_B T. And this k_B T, k_B T gets cancelled, and so therefore and you have e here that is the e there and I have psi sorry epsilon. So I have e / epsilon and z_i is here z_i n_i infinity that is this term.

And of course, this term is as it is. And of course I have 2. So essentially, this by this simple manipulation, I can write the one dimensional Poisson Boltzmann equation as d / dx of d psi / dx whole square is equal to d / dx of 2 k_B T divided by epsilon summation i n_i infinity exponent of minus z_i psi divided by k_B T.

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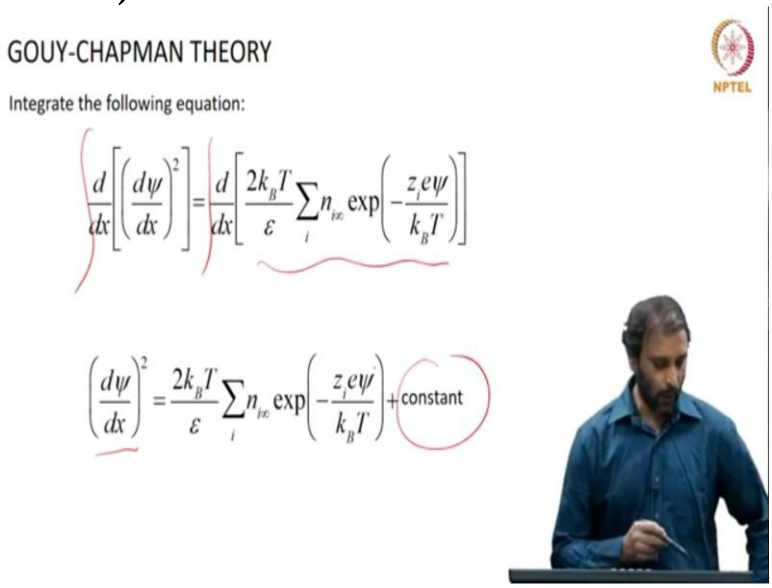

So now if I can integrate this expression, so I can integrate this on both the sides. So what I will be ending up with this d psi / dx whole square is equal to this plus a constant term. So we can evaluate the constant fairly easily.

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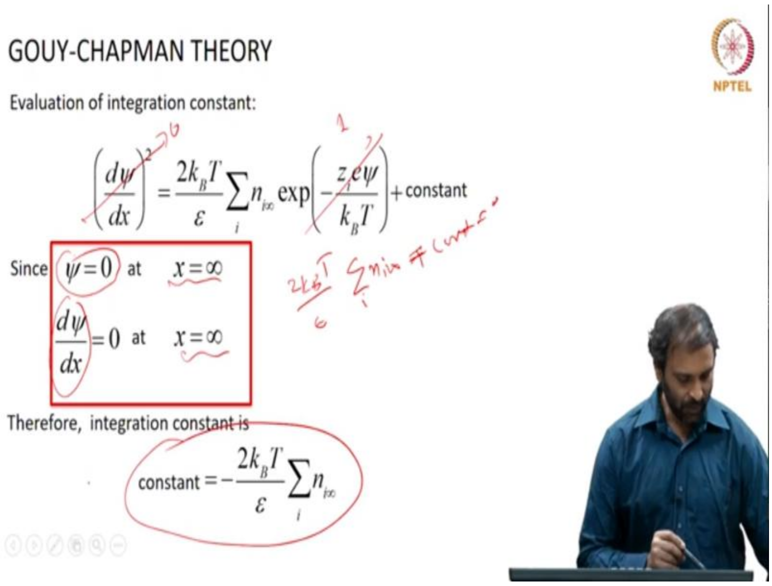

We know that psi = 0 at x = infinity and d psi / d x. Therefore, because psi = 0, you can also say that d psi / dx = 0 at x = infinity. So, if I substitute for these conditions, so this is you know 0 and if I substitute psi = 0, this term becomes 1. Therefore, essentially I have 2 k_B T divided by epsilon summation i n_i infinity and plus constant is equal to 0. Therefore the constant essentially becomes minus 2 k_B T divided by epsilon summation i n_i infinity. So therefore, we have been able to evaluate the constant. I can substitute for the constant.

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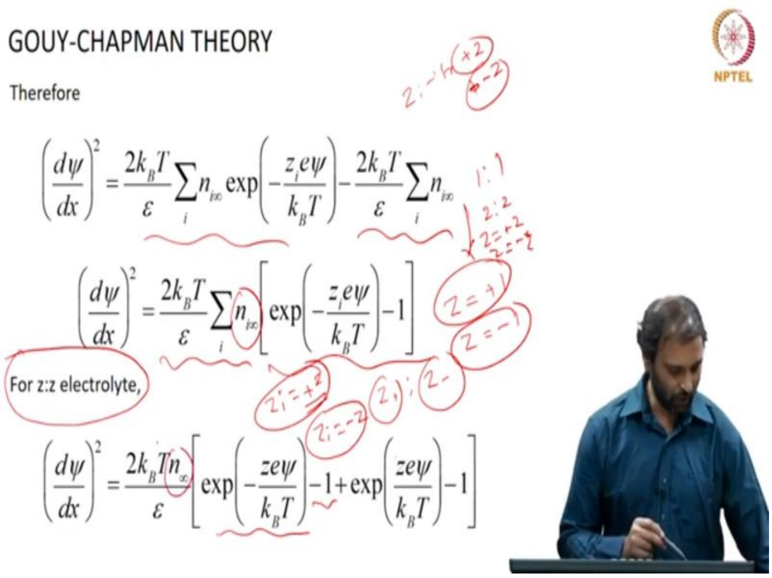

So therefore, I could write d psi / dx whole square as the first term minus the constant term and because I have 2 k_BT by epsilon summation i n i infinity as a common I can take it out. Therefore, in the parenthesis I will have exponent minus z_i e psi divided by k_B T - 1. Now I can simplify now because we are considering a specific case of z is to z electrolyte, what I can do is I can take this term and then whenever I have z is to z electrolyte there is going be z plus and z minus type of ions.

Therefore, there so because it is taking a symmetric electrolyte case, what I can do is I can wherever I have z in, I can substitute for plus 1 as well as z = -1. So that I count for both the co ions and the counter ions in the solution. Therefore, the first term remains the same and exponent of if I substitute z_i as plus z therefore, the first term is going to be exponent of minus z e psi divided by k_B T - 1.

And the next term if I substitute for z_i to be minus z, so therefore, the next term essentially become the exponent of z e psi divided by k_B T. So, the substitution of z = +1, z = -1 is specifically for 1 is to 1 electrolyte. If you have a 2 is to 2 electrolyte, I would have to substitute z = +2 and z = -2, but because we are considering the case of a general z is to z electrolyte.

Therefore, it makes sense to replace z_i with minus z_i and z_i with plus z_i. Therefore, d psi / dx whole square essentially becomes 2 k_B T and infinity divided by epsilon into exponent minus z e psi divided by k_B T - 1 + exponent Z e psi divided by k_B T - 1. The reason why we have taken n_i infinity out of the summation sign is because for a given concentration n_i for both plus z and for minus z ions is essentially the same. Therefore, I can actually take it out of the summation term and it will become n infinity.

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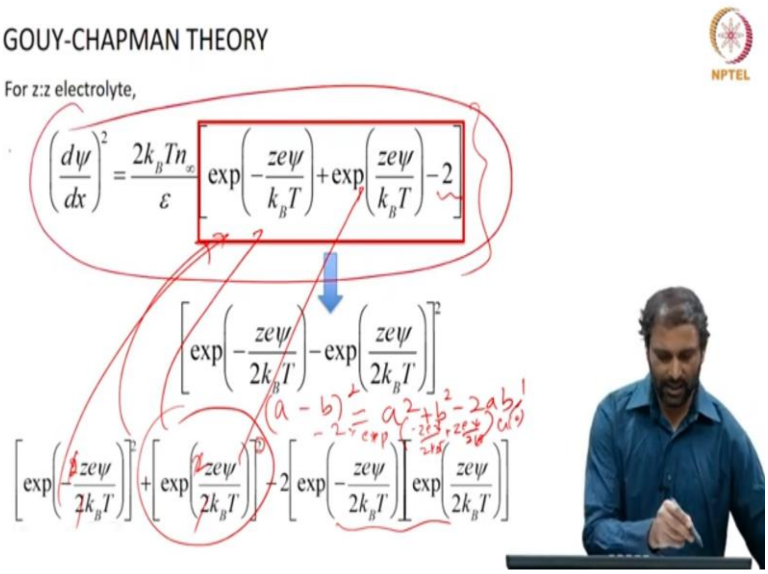

So, now that we have this. So, what I can do is so this is what we had earlier. So, there is minus 1 here and minus 1 that becomes minus 2 and in the parenthesis you have exponent of minus z e psi divided by k_B T + exponent of z e psi / k_B T. If you look this up, you can write this as exponent minus z e psi divided by 2 K_B T - exponent z e psi divided by 2 K_B T whole square.

These are the form a - b whole square, which is same as a square + b square - 2ab, therefore I can recover this expression. So that I have the first term whole square that is this. So, if you look at this expression, so I have exponent z e psi divided by 2 k_B T whole square. Now, I can simplify this. I can take the 2 in the numerator, this, this gets cancelled essentially I have the first term.

Similarly, that is this term similarly, so I have again I can take the 2 in the numerator, so I can this, this gets cancelled. So, I essentially have the first term here and the second term there. And if you look at this, this essentially is minus 2 times exponent - z e psi divided by 2 k_B T + z e psi / 2 k_B T essentially it is exponent of 0 which is 1. Therefore, I recover the minus 2.

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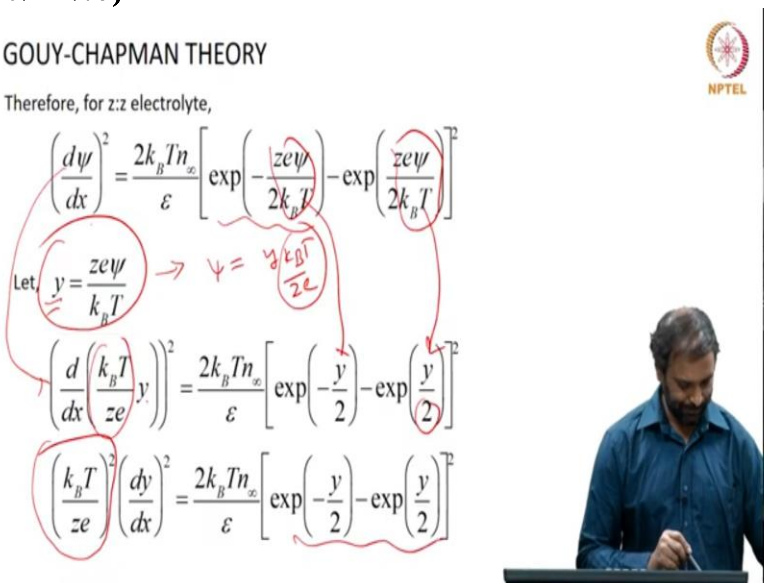

So therefore, so I can express this particular expression as d psi / dx whole square is 2 k_B T n infinity divided by epsilon into exponent - z e psi by 2 k_B T - exponent z e psi divided by 2 k_B T the whole square. Now again, we are going to do some more manipulation. So we are going to assume or we are going to put z as z e psi divided by k_B T, this is a simple substitution. So therefore, from this what I get is I get psi to be y k_B T divided by z e.

So therefore, I can replace for psi in terms of y, so I have d / d x, instead of psi, I am going to replace it with y k_B T divided by z e, that is this term multiplied by y, and the right hand side becomes 2 k_B T an infinity / epsilon into exponent - y / 2 - exponent of y / 2, because we are substituted this to be y, therefore I have y here and I have 2 in the denominator, the same thing is also true for this case.

So therefore, and because for a given electrolyte and given temperature k_B T divided by z e is constant. I am going to take k_B T square divided by k_B T divided by z e whole square outside. So I have dy / dx whole square = 2 k_B T n infinity / epsilon multiplied by this term.

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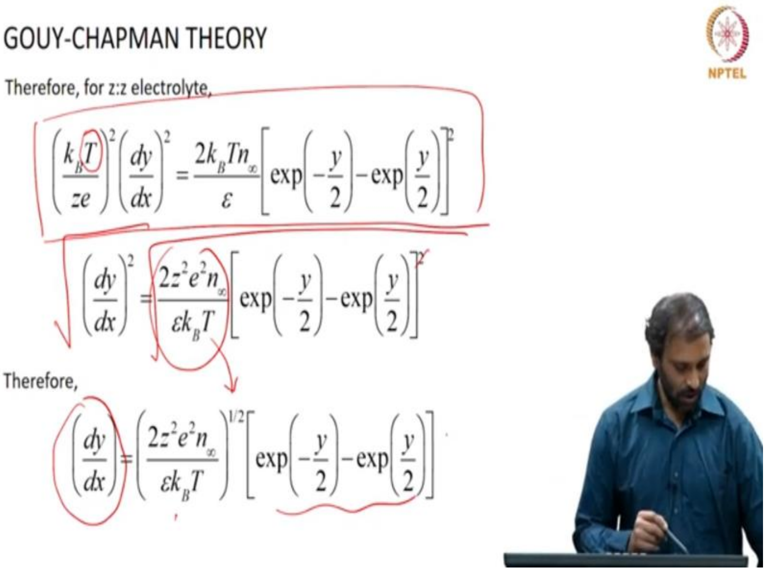

That is of course which is valid only for a z is to z electrolyte and at a given temperature. So and what I can do is I can take the square root on both the sides of this expression, so I will end up with dy / dx on the left hand side and this term raised to the power one and a half and this and the square gets cancelled, I have exponent of minus y divided by 2 - exponent of y divided by 2.

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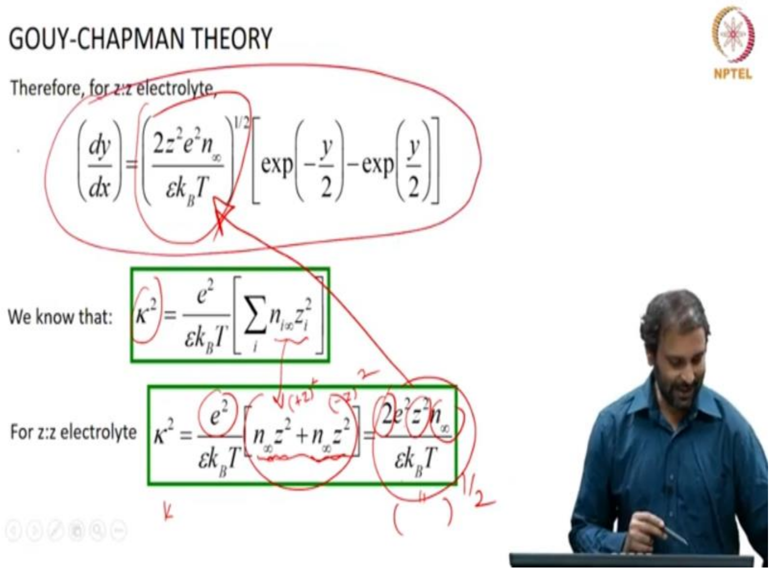

Now, if you look at, if you take a closer look at this expression, it turns out that you can relate that to the Kappa. So what we know from the definition of Kappa is that Kappa square = e square divided by epsilon k_B T multiplied by summation of i n_i infinite into z_i square. Now because we are considering z is to z electrolyte, I can write this as n infinity times plus z whole square plus n infinity into minus z whole square.

Therefore, I will have 2 times z square into n i infinity that comes from the term in the parenthesis and I have of course, e square divided by epsilon k_B T. So, now if you look at this expression and compare it to this, so what you essentially have is, if I take the square on both sides, I have what I have is Kappa is same as this term to the ratio of one and a half. So therefore, so this particular expression which is valid for z is to z electrolyte.

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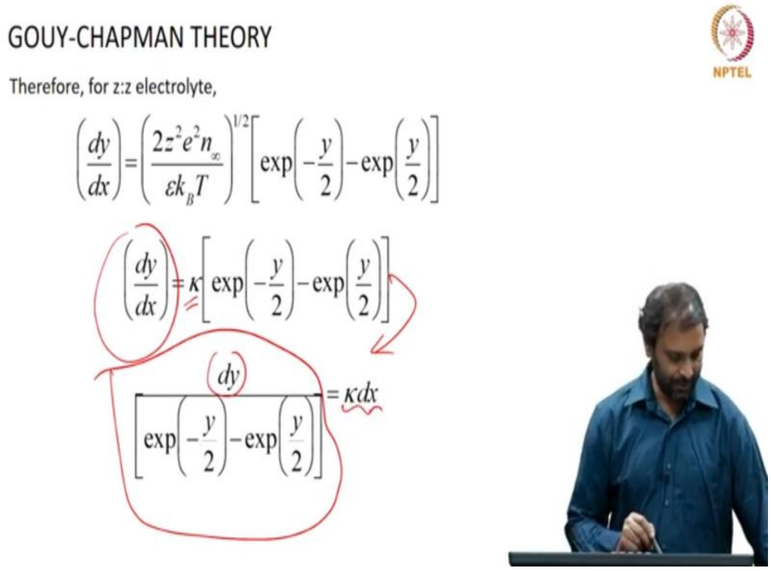

I can write it as dy / dx is equal to Kappa times exponent of minus y / 2 - exponent of y / 2. Now I can separate the variables. So I have dy the terms with y on the one on one side I can just rearrange this you know a bit. So therefore, I end up with dy divided by exponent of minus y / 2 - exponent minus y / 2 = Kappa times d x.

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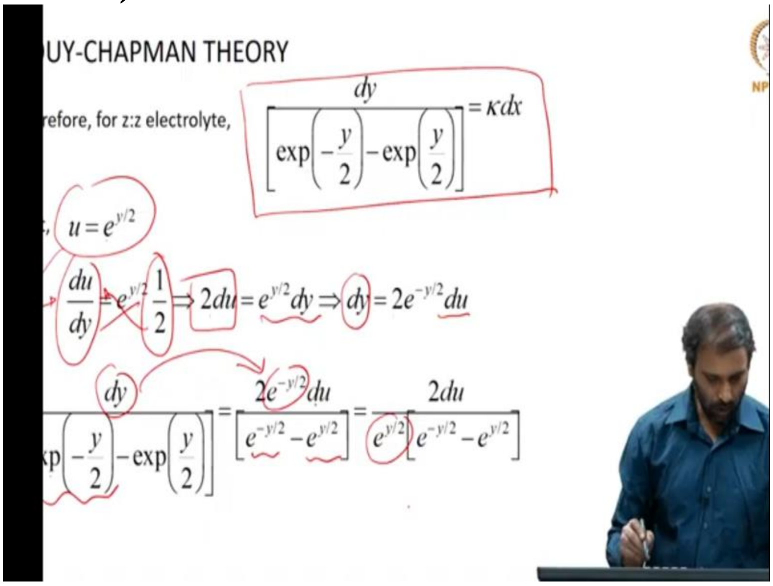

And which if you want to evaluate this further, again we are going to substitute for u as e power y / 2 therefore, du / dy is e power y / 2 divide multiply by one and a half. So therefore, 2 times du, I can cross multiply them, 2 times du is e power y / 2 times dy, therefore dy essentially becomes 2 e power -y / 2 into du. So therefore for dy, we are going to substitute it as 2 times e power -y / 2 into du.

And this because we are substituted, so therefore exponent of minus y / 2 - exponent of y / 2 they remain the same, so therefore now what I can do is we could take this term to the denominator. Therefore I have 2 dy multiplied by e power y / 2 multiplied by e power -y / 2 - e power y / 2. So, if I take e power y / 2.

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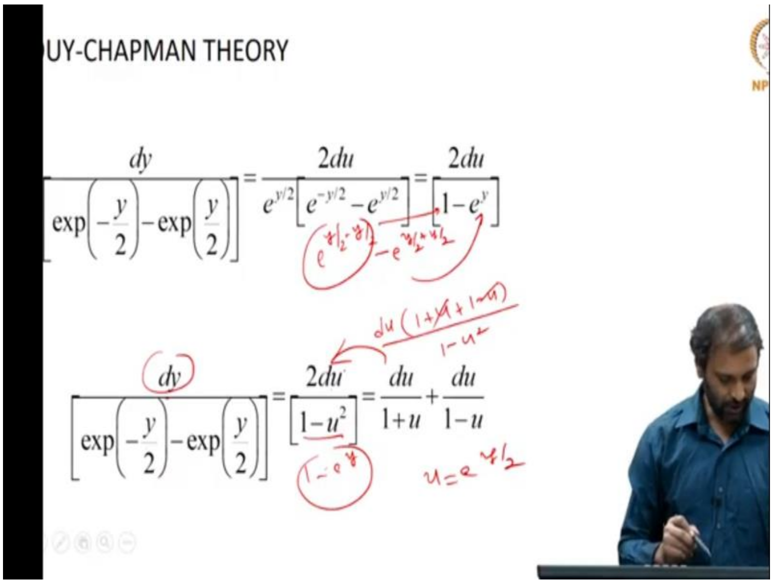

Again inside the parenthesis so I essentially have e power y / 2 - y / 2 - e power y / 2 + y / 2. So, this becomes 1 and e power y / 2 + y / 2 essentially is e power y itself. So therefore, dy divided by exponent of minus y / 2 - exponent y / 2 becomes 2 times du divided by it was actually 1 - e power y and because u is e power y / 2 essentially this becomes 1 - u square which I can write it as du divided by 1 plus u + du divided by 1 - u. So therefore, if I sum, if I simplify this it becomes du times 1 + u + 1 - u divided by 1 - u square this gets cancelled, essentially you end up with what you had earlier.

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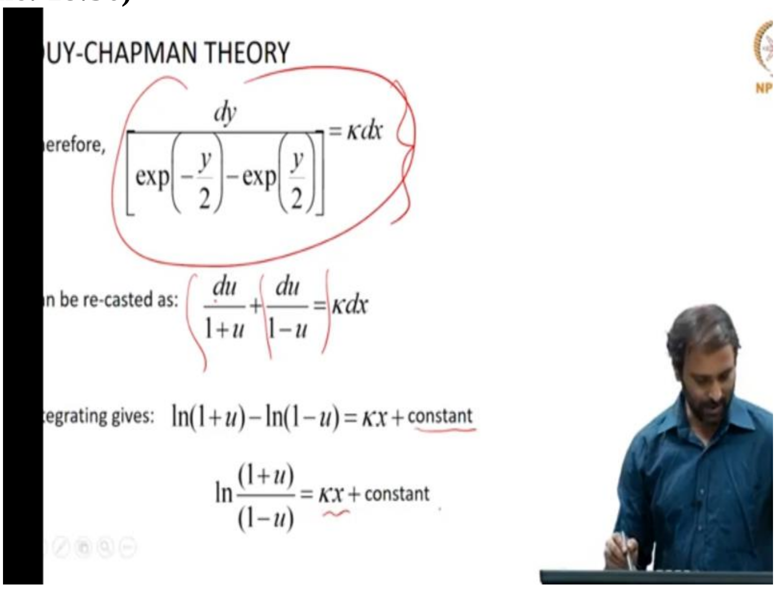

So therefore, if you have been able to simplify this, we have been able to recast this expression as du / 1 + u + du divided by 1 - u is Kappa times dx. So, I can integrate this easily. So, if I integrate this what I essentially end up with is ln of 1 + u - ln of 1 - u = Kappa x + constant. Therefore, ln of 1 + u divided by 1 - u = Kappa times x + constant.

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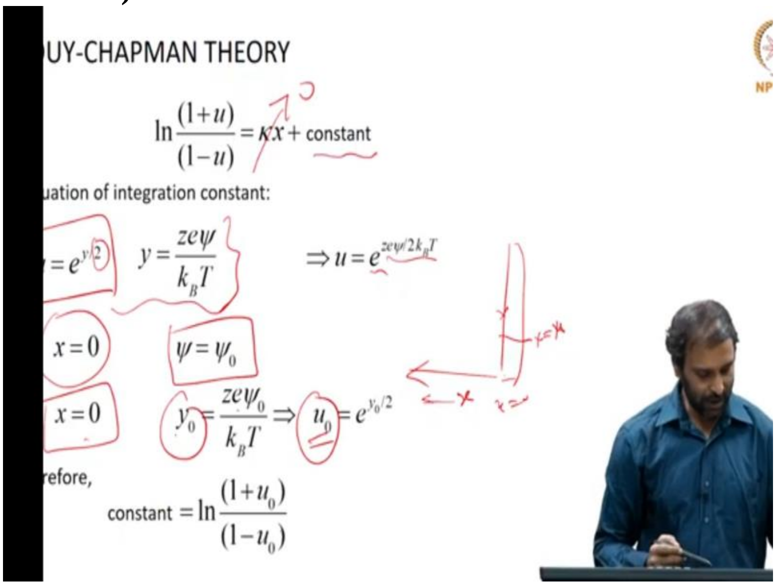

So, I can integrate again, evaluate the constants we have substituted u as e power y / 2 and therefore, y becomes z e psi divided by k_B T that is what we have done. So, if you go back so it is u = e power y / 2 and so therefore, we substituted y to be z e psi divided by k_B T. So therefore, so this is comes from the substitution that we have done. Therefore, u essentially becomes e power instead of y I am going to have z e psi divided by k_B T and of course, I have the one over 2 term there.

Therefore, u becomes e power z e psi divided by 2 k_B T. We know that at x = 0 that means; if I have a charged substrate and if this is how the x varies from the surface at x = 0, the potential is psi naught. So, if we have that, so now and therefore at x = 0 y naught becomes z e psi naught divided by k_B T and u naught becomes e power y naught divided by 2. So, we are essentially re evaluating all the initial conditions and the boundary conditions in terms of y naught and u naught. So therefore, if I substitute for x = 0, so this term goes away and what I end up with this the constant = ln of 1 + u naught divided by 1 - u naught.

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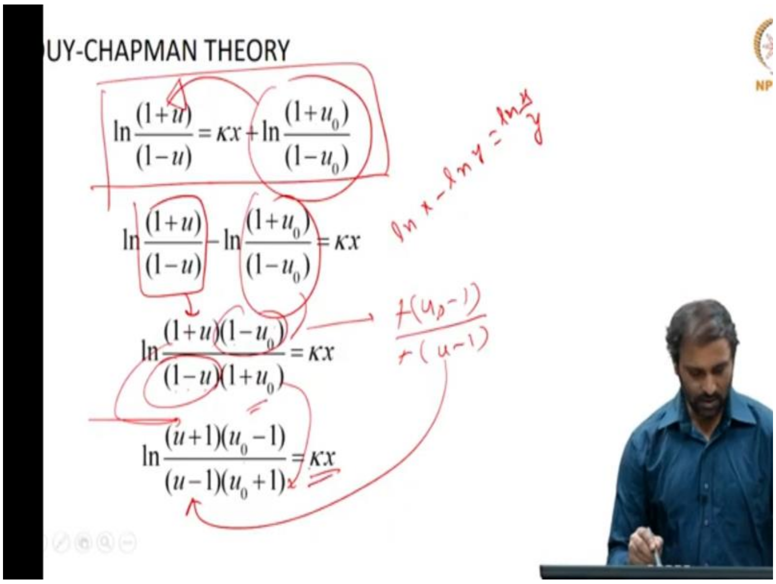

So therefore, we end up with ln of 1 + u divided by 1 - u = Kappa x + ln of 1 + u divided by 1 - u. I can take this on to the other side and if I again use the condition that ln of x - ln of y = ln of x / y. So therefore, I have this term here and because it is y divided by y, so this you know is, you can notice 1 - u is in the numerator and 1 + u is in the denominator. So, what we can do here is that I can if you look at these terms, I can write this as minus of u naught - 1. I can write this as minus of u - 1 this gets cancelled.

Therefore, what I end up with this 1 + u or u + 1 that remains as it is and 1 - u I can write it as u naught - 1 and 1 - u I can write it as u - 1. So therefore, ln of u + 1 divided by u naught - 1 whole divided by u - 1 multiplied by u naught + 1 is Kappa x.

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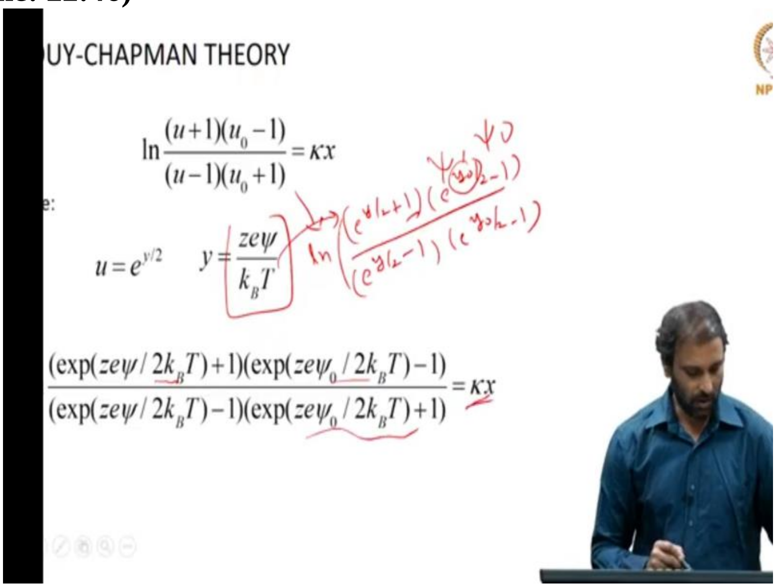

And, and so of course, we would have to obtain an expression in terms of psi and psi naught. Therefore, we could do again substitute back. So, because u is e power y / 2 and y is z e psi divided by k_B T, I can write this u as e power y / 2 + 1 times e power y naught / 2 - 1 whole divided by, so maybe let me just do a better job. So, I can substitute, I can write this as ln of e power y / 2 + 1 multiplied by e power y naught / 2 - 1 divided by e power y / 2 - 1 times e power y naught / 2 - 1.

And because y is z e psi divided by k_B T, I can substitute again for y here. So, essentially I end up with ln of exponent of z e psi divided by 2 k_B T + 1 times z e psi naught because you have y naught here, I have z e psi naught divided by 2 k_B T - 1 whole divided by exponent of z e psi / 2 k_B T - 1 and that will be equal to Kappa x.

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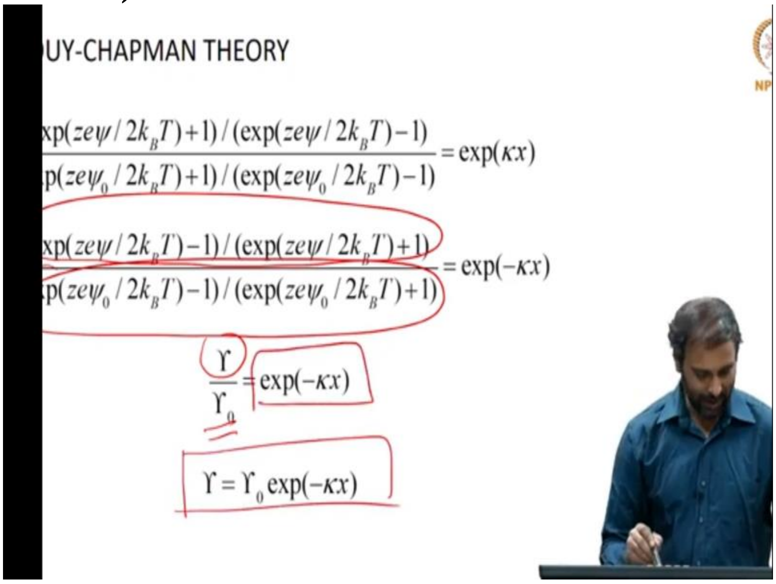

So, again some simple rearrangements I can put together all the psi terms together and all the psi naught terms together. Therefore, gamma divided by gamma naught is exponent of minus Kappa x. Therefore, gamma = gamma naught exponent - Kappa x.

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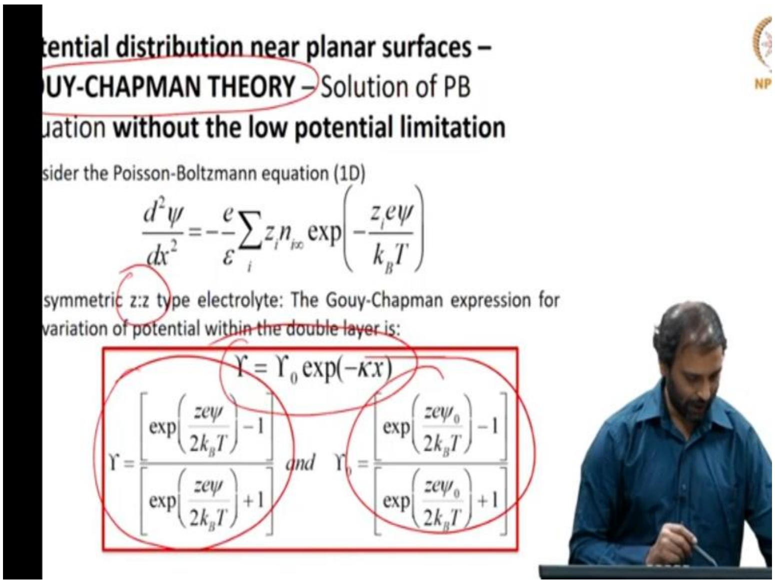

Where gamma and gamma naught are given by these expressions, so therefore, we have been able to show, we have been able to obtain what is called as a Gouy Chapman theory or Gouy Chapman expression that was derived by Gouy and Chapman for how the potential varies with separation distance without limiting to the case of low potential that means this expression is valid for any situation except for the fact that we will still have to consider the symmetric z is to z type of electrolytes.