Colloids and Surfaces
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Lecture - 36
Models of Electrical Double Layer: Gouy Chapman Theory - II

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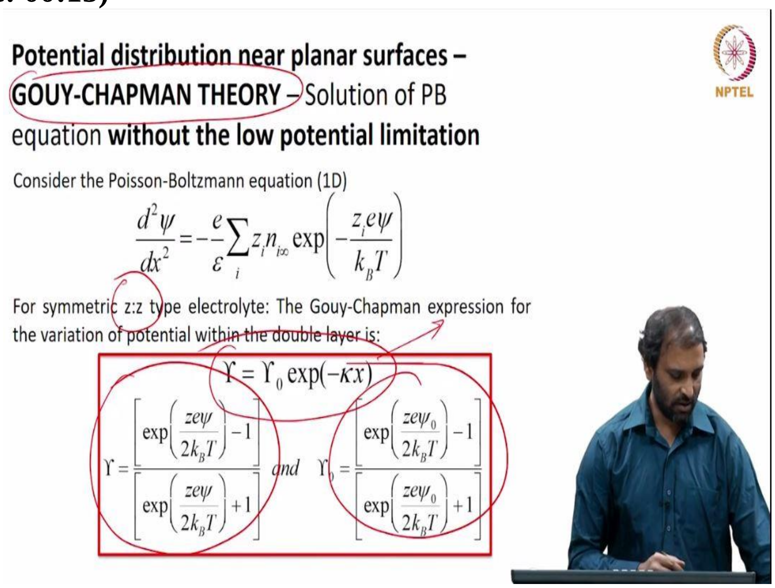

So now what we will do is we will try and look at simplifying this general expression to some specific cases.

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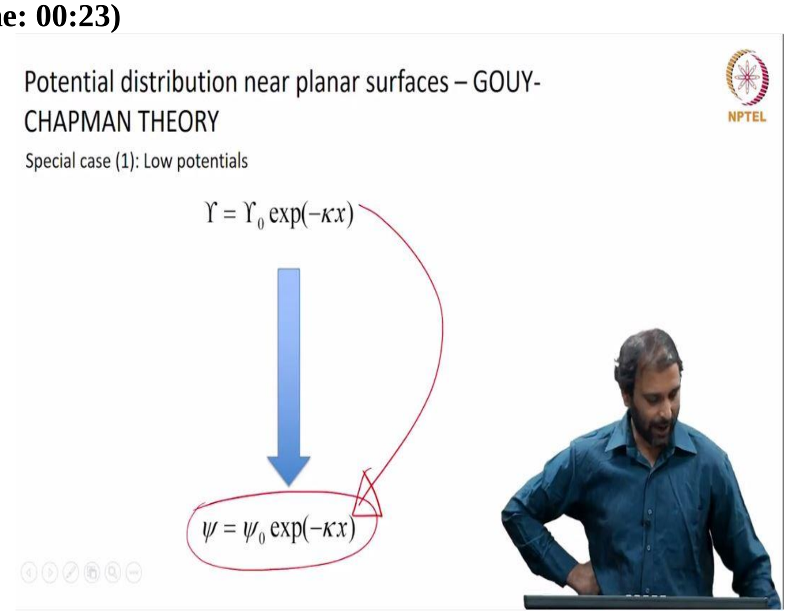

What we know is that z gamma is gamma nought exponent - kappa x is valid for any potential as long as the electrolyte is z is to z. Now so we know that this expression should can be simplified to psi = psi naught exponent - kappa x.

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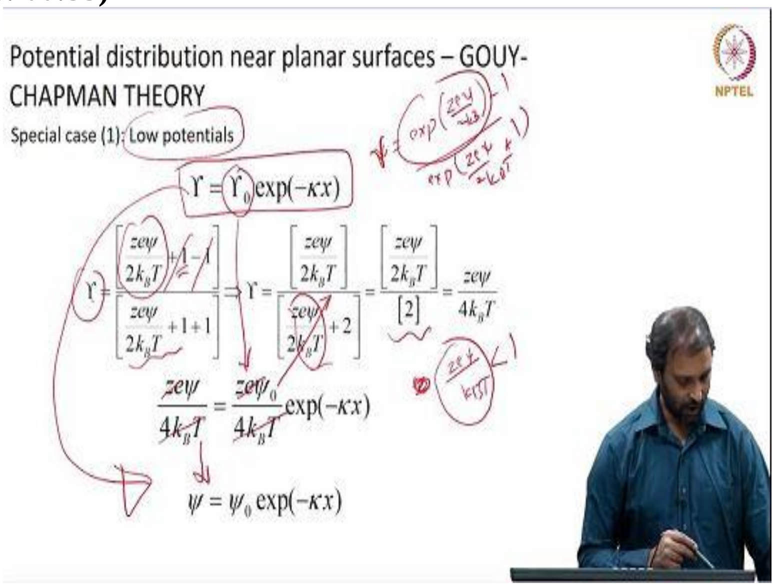

Of course, for the case of low potential, so, let us look at how we do that. So, that is the Gouy Chapman solution. And we know that gamma is exponent of z psi divided by 2 k_B T - 1 divided by exponent of z e psi divided by 2 k_B T + 1, that is what, that is a gamma naught. That is a gamma That is what was here So that is, what is here Now, if we assume the low potential case, so what I can, what one could do is this exponent term, I can write as a, I can neglect the higher order term.

And I can write exponent of z e psi divided by 2 k_B T as z e psi, divided to k_B T + 1, and I am going to neglect all the higher order terms. Similarly, denominator also the same thing I am going to only retain the first 2 terms in the series expansion of exponent of z e psi divided by 2 k_B T. So, therefore, gamma becomes so I can cancel these 2 in the numerator, I have z e psi divided by 2 k_B T divided by in the denominator I have z e psi divided by 2 k_B T + 2 because we are taking low potential case, we had.

So, the low potential case is when z e psi divided by k_B T is less than 1. And because at e psi divided by k_B T is less than 1 and that divided by 2 is going to be even further less than 1 therefore, I can neglect this term. So, denominator essentially will be just 2 therefore, gamma becomes z e psi divided by 4 k_B T. I can do a similar simplification also for gamma nought as well, which again turns out to be z e psi nought divided by 4 k_B T and this this gets cancelled this this gets cancelled and you end up with the expression for the low potential limit.

Therefore, the general Gouy Chapman solution you know simplifies it is to the Debye Huckel approximation for the case of low potential.

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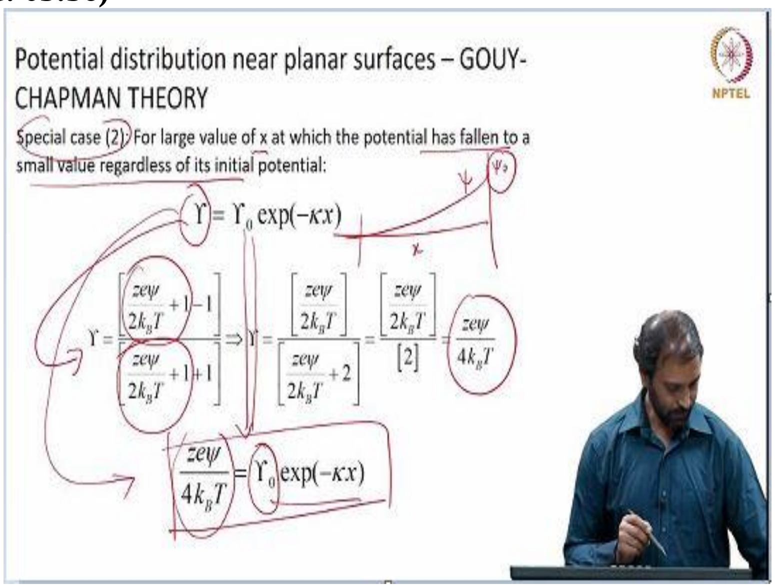

So, the other simplification one can do is that is a special case 2 this is for large value of x at which the potential has fallen to small values regardless of its initial potential. Now, we know that potential varies with distance if you go away from if this is psi nought is initial potential and as we go away from the charge surface, we know that the potential is going to decrease. Now, if we take some distance, that is x such that it is very large that the potential has fallen to a very low value regardless of this initial potential.

So, in such a case, what I can do is I can simplify gamma as z e psi divided by 4 k_B T because again I can invoke the condition that at a very large separation distance the potential is low I can again only consider the first 2 terms neglect the higher order terms. So, therefore, gamma becomes z e psi divided by 4 k_B T. However, because psi could be larger psi could be any potential. Therefore, I will have to continue to retain gamma nought as it is because I cannot invoke the low potential case like we did for the earlier case.

Because now, gamma could be gamma nought could be significant or gamma nought psi being could be any value. Therefore, I am going to retain gamma as gamma nought therefore, for the case where for a very large value of x such that the potential has fallen to a very small value regardless of the initial potential, I can simplify the Gouy Chapman theory to be to take the form z e psi divided by 4 k_B T that is on the left hand side the right hand side remains the same.

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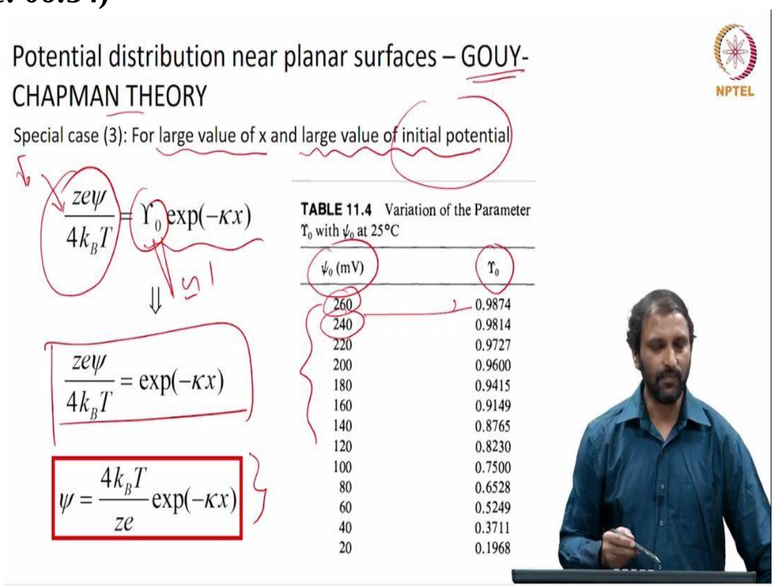

If you take the third special case again this is for a very large value of x such that the potential has fallen to a low value. Therefore, the simplification that we have done in terms of writing gamma nought as z e psi divided by 4 k_B T will still hold and on the right hand side you had gamma nought exponent - kappa x. What do you see here is a table where gamma nought is tabulated as a function of psi nought that is psi nought in millivolts.

This is gamma nought if you look up this table it turns out that if you look at very large values of psi nought gamma nought essentially is very close to 1 therefore if the surface potential if the initial potential is very large gamma nought will you can it is approximately equal to 1 that is from this table therefore, z e psi divided by 4 k_B T becomes exponent of - kappa x itself because gamma nought = 1. Therefore, from this I can write psi as 4 k_B T divided by z e into exponent of - kappa x. So, these are the 3 simple you know special cases one could derive from starting with the Gouy Chapman theory.

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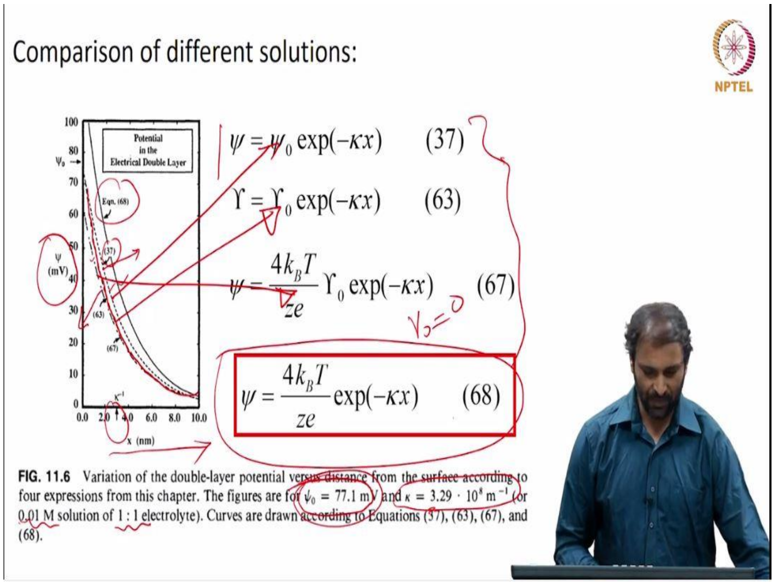

What is plotted here is a potential in millivolts and that is the separation distance and if you look at this plot, there are 4 expressions there are 4 lines a continuous line, a dashed line and dashed and dotted line, there are essentially 4 there are essentially different solutions that is the Debye Huckel approximation. That is the Gouy Chapman theory and this is for the case where the potential has fallen to a very low value regardless of the initial potential and this is the case where the potential is fallen to a low value regardless of the initial potential.

And the initial potential being very high so, if you look at the solution that is plotted for specific case, psi nought is 77.1 millivolts. This is a significant potential, this is not the low potential because we said that the potential has to be of the order of 25 millivolts for one to consider the potential to be the low potential case. So therefore, psi nought = 77.1 is a not a low potential case. And kappa is given by this. So kappa inverse is marked here. That is a kappa inverse corresponding to this kappa value.

And this is the kappa value that you have is for 0.1 molar solution of electrolyte and so, the best expression that one could use to predict the variation of potential with separation distance in this particular case is going to be this expression because this is the Gouy Chapman theory, which is valid for the symmetric electrolyte 1 is to 1 in this case and we know that it is applicable for you know any potential because we are not invoking the low potential limit case.

Therefore, this particular line that is this line that I am tracing now, that is the solution that corresponds to the Gouy Chapman theory, but however, if you look at the other 2 lines, that is this line, as well as this line, these are one is for the low potential limit and the other one is for the case, where the potential is fallen to a low value regardless of what is the initial potential, we know that these 2 also do a reasonably good job that means, both that means though the potential is best described by the Gouy Chapman theory that is this expression.

This as well as this still do a very good job of predicting what is the variation of potential with the separation distance. However, because of the fact that the potential that we are considered is 77.1 millivolts, that means, it is not significantly large to take gamma nought = 1 as it is evident 63 the expression is equation 68 that is the case corresponding to the special case for large value of x and large value of initial potential, it is does not do a good job of predicting how the potential varies with separation distance. Therefore, depending upon the situation, you should be able to use one of these expressions to find out how the potential varies with separation distance.

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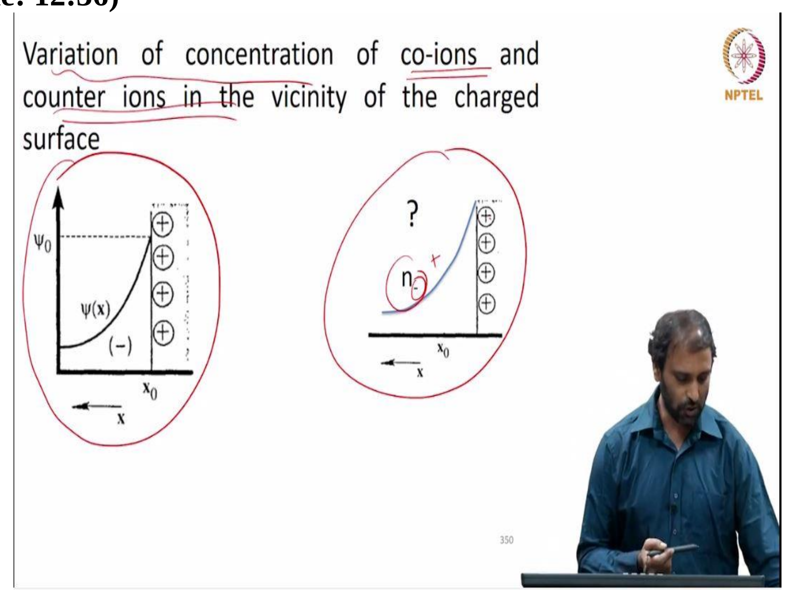

Now, that we know how the potential varies with separation distance, we can also look at the variation of the concentration of co-ions and the counter ions as well you know, in the vicinity of the charge surface. So, we know how the potential varies with separation distance, but however, if you want to know how does the concentration of in this case you have positively charged surface therefore, the negatively charged ions are going to be the counter ions. Of course, I could also have positively charged ions as well in the solution, which are going to be coins and how does their concentration vary with separation distances is also of interest?

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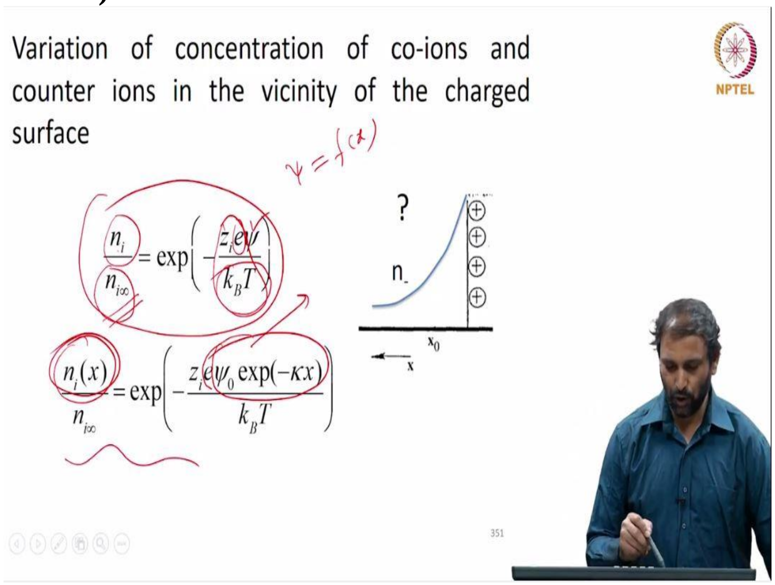

So, for that what we are going to do is to again start with the Boltzmann factor. So, we know that n i divided by n i infinity is exponent of minus z e z i e psi divided by k_B T and this n_i is not a constant and n i infinity is fixed by the concentration of the electrolyte in the solution that is a fixed quantity for a given concentration and this is a constant this as well and z_i is the valence of the ions. So, once that is fixed, so, everything is a constant here except for psi and n_i varies with separation distance, we know that psi also varies with separation distance.

Now, because we have derived how does psi you know depend on various with separation distance? We can substitute relevant expression for psi. So, if I assume the low potential case, I can replace psi to be psi nought exponent of - kappa x. Therefore, now, that I know how psi varies with separation distance I should be able to also calculate what is how does the concentration of the ion varies with separation distance.

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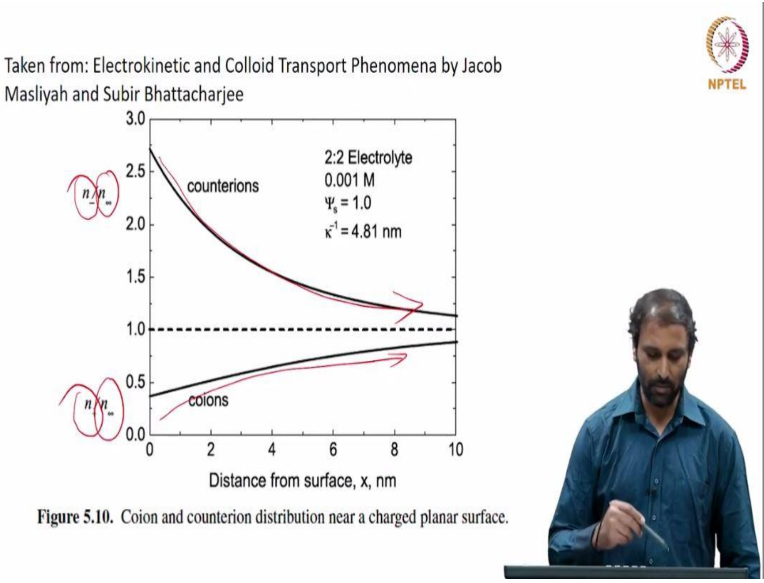

So, therefore, from this approach, I can actually calculate what is the concentration of the counter ions? And what is the concentration of the co-ions? In this case both of them are scaled with n infinity which is the concentration of the electrolyte that I have in the solution. How does the concentration of the counter ion decreases as you go away from the separation distance and how does the concentration of the co-ions again varies with separation distance one could calculate from this approach.

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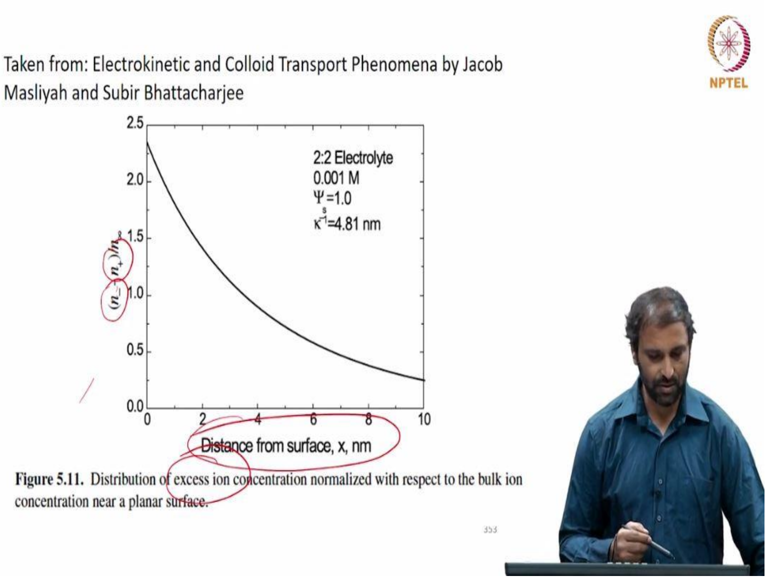

What would also be interest would be what is called as the distribution of excess ion concentration that will be given by n minus minus n plus that is the difference in the concentration of the co-ions and the counter ions and how does that vary with seperation distance one we should be able to calculate all of this from this simple formulations.