**Colloids and Surfaces**
**Prof. Basavaraj Madivala Gurappa**
**Department of Chemical Engineering**
**Indian Institute of Technology - Madras**

**Lecture - 30**
**Models of Electrical Double Layer: Diffuse Double Layer Model / Gouy-Chapman Model**

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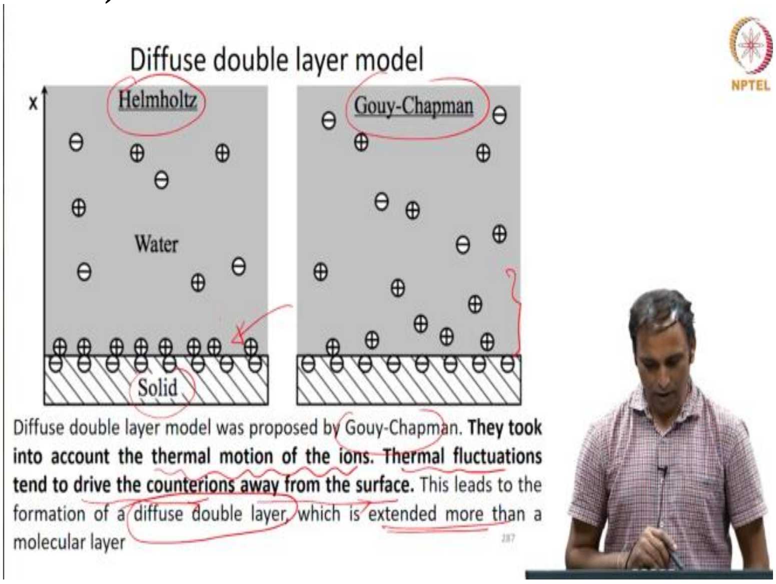


So, what you are looking at is a Helmholtz model and the second one is a model which is proposed by Gouy and Chapman, it is what is called as a diffuse double layer model can you look at and tell me what is the difference between the picture on the left and the right the name says it all diffuse. So, if you look at here the counter ions there if I look at a similar distance here I look at similar distance.

The number of counter ions that you have, for a particular distance say in this case x and a similar distance x, definitely the number of counter ions here are more compared to their right that you can get and the fact that there are also counter ions here you can say that the thickness of the double layer now it is kind of a little bit expanded. It is a little bit more. So, it turns out that this picture is more true than what was you know what comes out of Helmholtz model.

The reason for that is that the Gouy-Chapman model what is also taken into account is the thermal motion of the ions. So, we are saying that of course, you know, they could be bound to the charge surface. However, these ions can still exhibit thermal motion, you know, they can be disturbed because of the thermal motion these thermal fluctuations tend to drive the counter ions away from the charge surface, this leads to the formation of what is called as a diffuse double layer, which is extended more than a monolayer thickness.

So, that is a prime difference between Helmholtz model and the Gouy-Chapman model in which it is assumed that because of the fact that these ions exhibit thermal motion, these thermal fluctuations can drive the counter ions away from the particles surface away from the charge surface and the layer of counter ions is more diffused compared to what was the case for Helmholtz double layer model.

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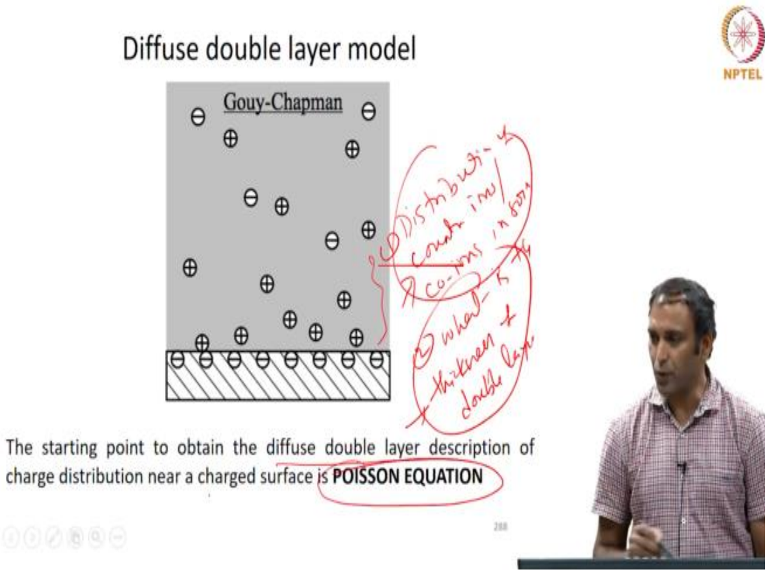


Now, again, similar to what we did for Helmholtz model, we are kind of interested to look at the distribution of counter ions in solution. So, we are interested in understanding distribution of counter ions as well as co ions in solution number 1, number 2, we also want to understand what is the thickness of double layer? If you would like to, you know, kind of get quantitative information of these quantities. So, for the diffuse double layer model, the starting point in obtaining the diffuse double layer model description is the, what is called the Poisson equation.

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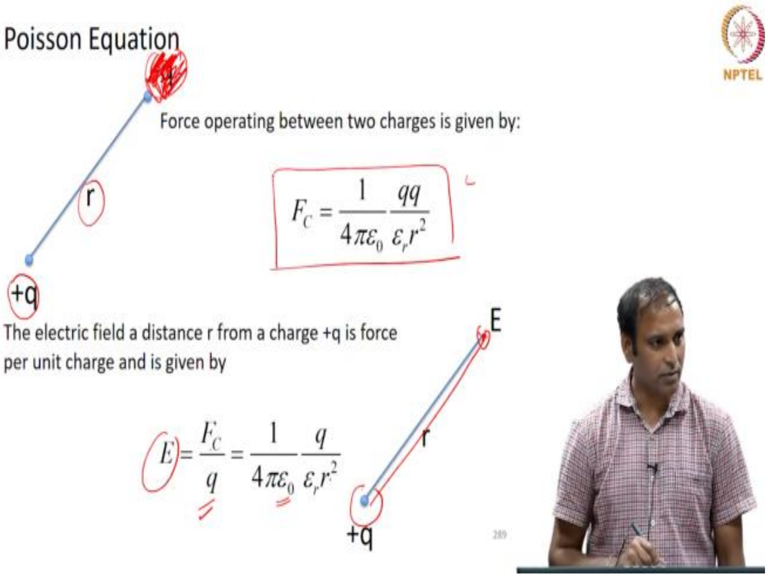


So we will think a little bit about deriving the Poisson equation to begin with. I am sure all of you know this. But we will try and give some very simple arguments. To show that you know, you can actually derive Poisson equation because this is a starting step for looking at electrical double layer model. I thought it would be nice to do it. Again this is in the textbook that I am following. So this is a point charge plus q minus q.

And the distance of separation is r. And the force is acting between the 2 charges is given by this, it is, the coulombs law, 1 / 4 pi epsilon 0 q 1 q 2 or q square / epsilon r you know r into r square that is the coulombs law. Now, if I you know somehow take this guy out if I take this out and ask a question as to if I have a positive charge q. And I ask a question as to what is the electric field that is generated at some you know distance r from this plus charge q. So, that electric field is given by $F_C$ / q which is 1 / 4 pi epsilon 0, q / epsilon r, r square we know that.

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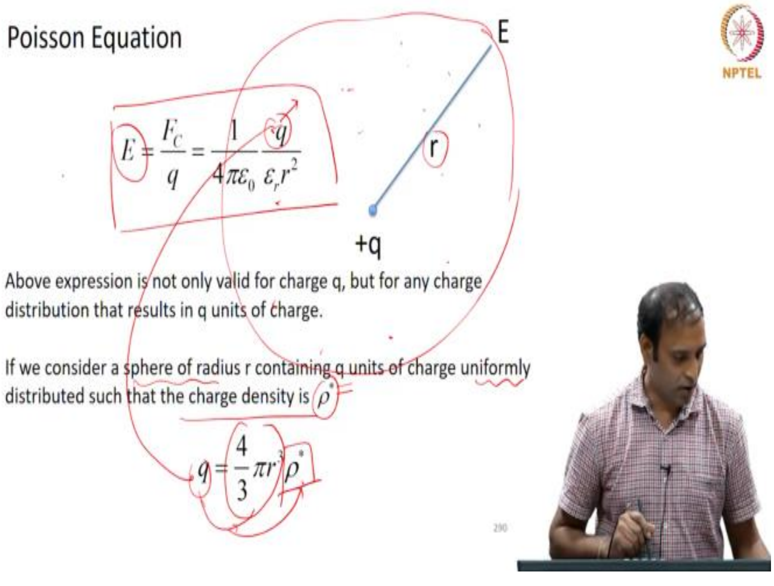

Now, it turns out that, so, the expression that we wrote earlier there are for point charges. Now, this expression holds good not only for point charges for however, for any distribution of charges such that the total charge is q. So, what I mean by that is if I imagine that you know I am going to enclose this in a sphere of radius r, I will consider some distribution of charges.

Now, if I have a distribution of charges, I can define again a charge density I can define a charge density q that is the number of charges or the charges per unit volume multiplied by the volume if rho star is the charge density. So, what we are doing is we are considering a sphere of radius r which contains q units of charge which are uniformly distributed such that the charge density is rho star therefore, this q I can relate that to the volume of the sphere and the surface charge density.

Instead of a point charge if I replace that with a sphere with certain distribution, but as long as the total charge is q in this case as well as this case, the same expression would hold good that is what I am trying to you know mention.

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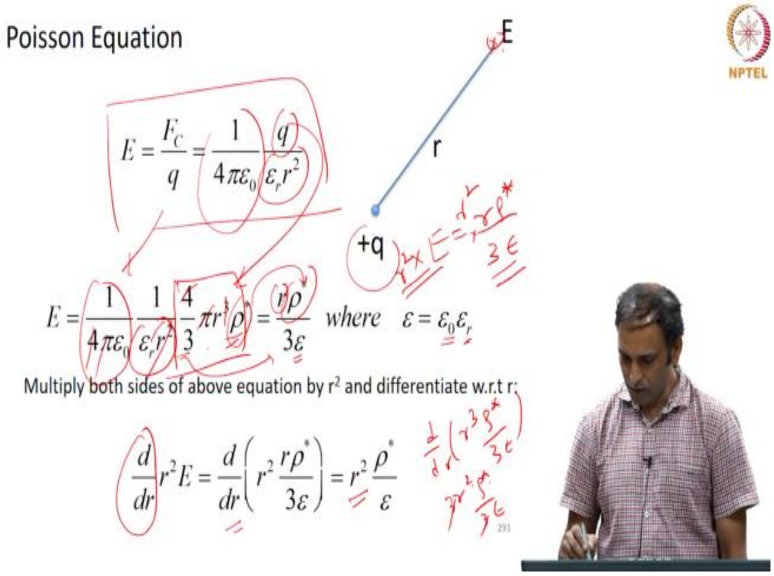


Now that we have this that is the electric field that is generated at some distance and at some distance r from a distribution of charges, which has a charge density rho star. So, what we can do is I can take this expression, so, I have E here 1 / 4 pi epsilon 0. So, I have epsilon r into r square here instead of q, I am going to replace q with this, instead of q I am writing this in terms of the surface charge density and the volume is that just comes from the definition itself.

So, we had done this here I mentioned that the electric field that is generated because of the point charge in this expression gives you the electric field that has generated because of the point charge which has a charge plus q or the same expression would also hold good if I replace the point charge by certain distribution of charge such that the overall charge is q that is given by the volume multiplied by the surface charge density or the charge entity itself instead of q I am replacing that with 4 / 3 pi r cube into rho star is it okay?

**"Professor-student conversation starts"**

Now, that is; yeah, go ahead. What is volume density rho? So, this is rho is what is called the charge density. This is the, if I say that there are 100 charges, which are uniformly distributed 100 ions for example. Is it uniformly distributed? Yeah uniformly distributed there is an assumption. And then you know the charge density is going to be 100 multiplied by 1.6 into 10 power - 19 coulombs divided by the volume otherwise the center of charge? We have to worry about. So if the distribution is not uniform then you know, we are assuming as uniform? It is a uniformly distributed charge.

**"Professor-student conversation ends"**

So, therefore, your I can cancel r square with here that leaves me r in the numerator and the rho star here and the 4 4 gets cancelled, the pi pi gets cancelled what you have here is a 3 that comes from here and epsilon, where epsilon is epsilon 0 into epsilon r therefore E, therefore this E becomes r rho star given by 3 times epsilon. Now, what I can do is I can write, I can take this expression I can multiply by r square on both sides and then I am going to differentiate that with respect to r, d / dr.

So, therefore, this d / dr of r cube into rho star / 3 epsilon, so, therefore, this becomes 3 r square into rho star / 3 epsilon, this this gets cancelled. So, essentially I am left with r square into rho star / epsilon.

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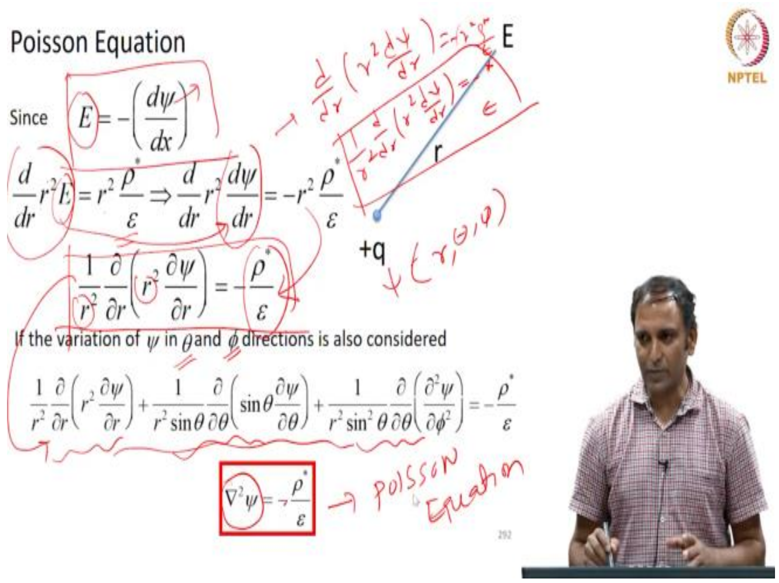


So, therefore, now that I know that there exists a relationship between the electric field and the surface potential left hand side is going to remain the same d / dr of r square into epsilon that comes from here, and the right hand side is going to be r square rho star into epsilon, that is what we just derived. Now, instead of epsilon E, I am going to replace that with d psi / dr. I am going to replace that with d psi / dr.

And because I have a negative sign here, so, I am going to get minus on the right hand side or left hand side depending on how you want to do it. So, therefore, essentially I end up with d / dr of r square d psi / dr = - r square into rho star / epsilon I can get this r square to the other side therefore, 1 / r square d / dr of r square d psi / dr = - rho star / epsilon that is what you so, that is essentially so, now in this case what was assumed is that the charge it the very so you if that is a so.

I want to go from if you look at this the same thing is written in a partial derivative form so because you know you could have a case where you know psi need not be varying only with respect to r, you could also have a case where the psi the surface potential can be a function of both theta, phi as well as r. So, what we derived is the first term in the equation similarly if you assume a variation only in theta or variation in only in psi.

And if I take a general case where psi is a function of both r, theta and phi so, you end up with this expression, the left hand side can be written as del square psi and the right hand side is essentially minus rho star / epsilon this is what is called a Poisson equation what this equation essentially tells you is that if I have a surface which is charged, how does the potential vary with distance, in different directions? That is what this expression essentially tells you about.

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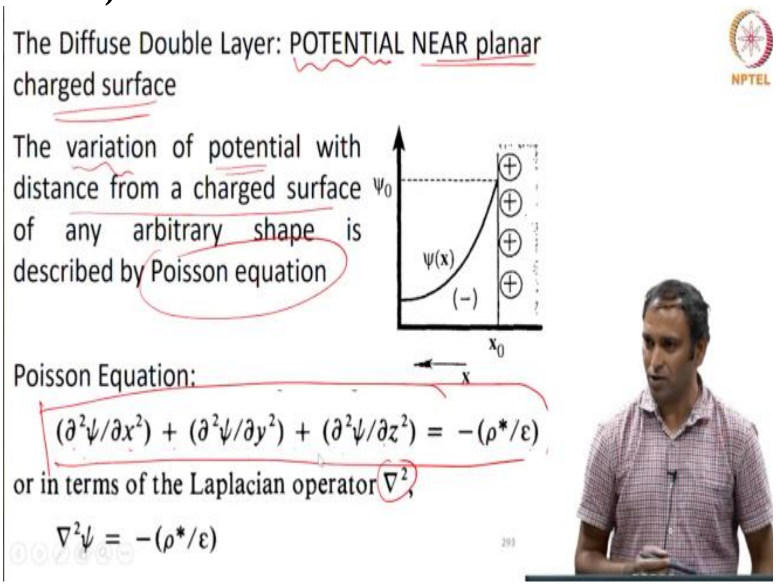


So, now, with this Poisson equation as a starting step, we would like to look at potential near a planar charge surface. So what we derived was a case where I have a spherical surface and what is the variation of surface potential with r, theta and psi is what we looked at but if I look at it, because the calculations are much more easier if you work with a planar charge surface.

We would like to look at derive you know start we would like to start with Poisson equation in the case of a planar surface the Poisson equation becomes del square psi / del x square + del square psi / del y square + del square psi / del z square = - rho star / epsilon. And so, basically the Poisson equation essentially tells you something about the variation of potential with distance from a charged surface it could be for any arbitrary you know surface that is what is described by the Poisson equation and this del square is what is called Laplace operators you know a little bit about it.

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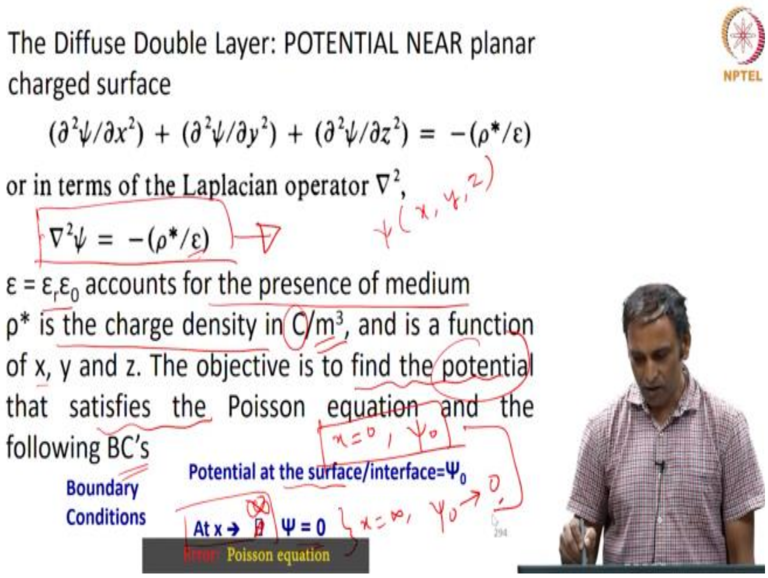


Now, what we would like to do is we would like to solve this because if I want to find out what is the variation? You know how does you know this, we know that you know this psi is a function of x, y, z I would like to look at the variation of size a function of x, y and z. So, for that we would have to solve Poisson equation. And what we are going to do is so epsilon is epsilon r multiplied by epsilon 0 which account for the presence of the medium and rho star is the charge density units are coulomb per meter cube.

And of course, psi is a function of x, y and z. So, the objective is to find a potential that satisfies the Poisson equation and with the boundary condition that at x = 0, sorry at x is equal to infinity, when x is tending to infinity, psi is going to be 0. If I have a charged surface, if I look at the distance very, very far away from the surface, the potential is going to be 0 that is one of the boundary condition. And the potential at the interface that is when x = 0.

The potential is going to psi 0, these are the 2 boundary conditions that we are going to use at x = 0 the potential is psi 0 at x is equal to infinity psi 0 is 0. So, we therefore, we would like to obtain an expression for the potential that satisfies the Laplace equation with these 2 boundary conditions. Is that okay?

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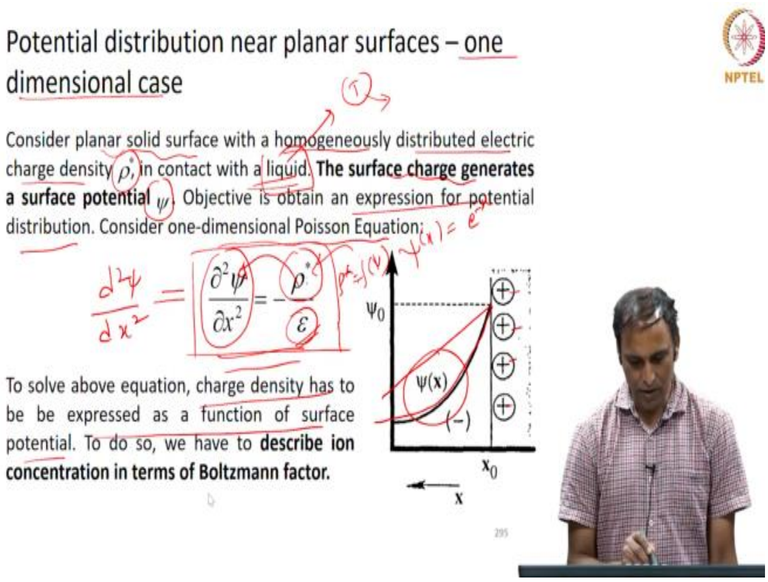


So, now, so, how do we do that? So I want to solve this so, we are going to. So, what you looked up here is an expression where we see that the potential varies with x as well as y as well as z, we are going to take even simpler case, we will only talk about the 1 dimensional case in which the potential varies only with x. So, therefore, I can write this as d square psi / dx square, that is equal to minus rho star / epsilon.

So, what we are looking at is a if we consider a planar solid surface with homogeneously distributed electric charges, such that density is rho star that is in contact with a liquid. And as a result of the charges on the surface, the surface generates a potential which is what is called which is represented as psi. And this psi would vary with distance in some particular way. We are after calculating what this function is?

We would like to find out whether psi of x is it, you know, an exponential function. Does it vary exponentially as a, you know as a as we move away from the surface, or does it vary linearly? Does it have any other functional form that is what we would like to look at the objective is to obtain an expression for the potential distribution. So for that, we are going to consider a 1 dimensional Poisson equation.

Now, in order to do this, so psi is a permittivity. So, that is going to be if I were to do an experiment in a liquid which is maintained at a particular temperature and if the medium I know everything about the medium your epsilon is going to be a constant, but however the sigma star. So, in order to actually solve this, I should somehow express rho star in terms of the potential itself that is when I can solve this expression to solve this expression, the charge density that is rho star has to be expressed as a function of potential only then you know.

If I have a way of writing like rho star you know, I would like to express rho star as a function of psi itself, then I can substitute for rho star I can go ahead with solving this. So, to do that, what we do is we use something called a Boltzmann factor.

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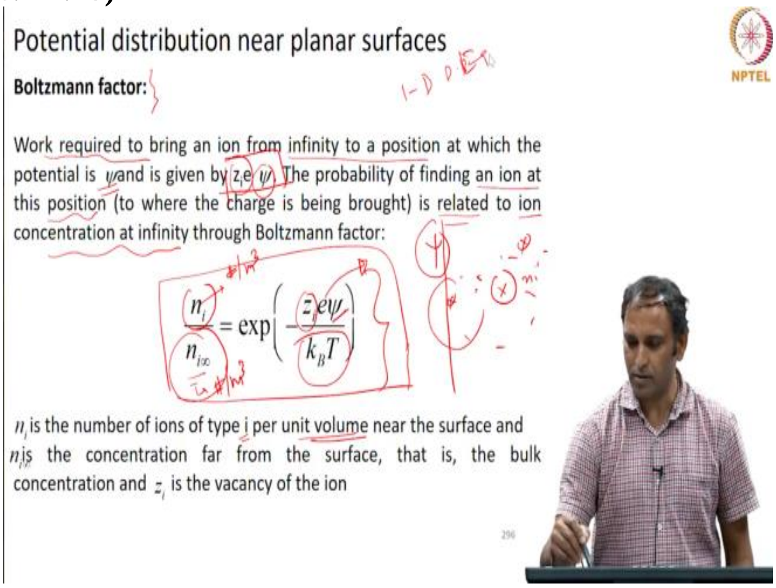


So, what is written here is n i is the number of ion types, i is the type of the ion that I am considering number of ion types per unit volume. So, units of this, is going to be number per volume near the surface. And n i infinity is the concentration of the ions at a distance very far away from the surface, again, this is going to have units of again number per unit volume and is that z i is the, the valency of the ions and i sorry, E is the charge of the electron psi is the potential and $k_B T$ is the a thermal energy, so that is the Boltzmann factor.

So, what this expression essentially tells you is that so, this tells you something about given that I have a surface potential whose potentially is psi, what is the probability of finding an ion? So, there will be several ions in the solution, there is going to be several ions in solution. Now, so, if you look up this so, let me just go through this. So, what this tells you is that you know, the work required to bring an ion from infinity to a position at which the potential is psi, so, say that I have ion say n i, at a distance very, very far away from the surface.

Now, for to move this ion from a very large distance away from the surface into a region very close to the surface and I have do some work. Is that is does it make sense? I would have to essentially do some work to move any ion from one location to the other how of work that I have to do depends on from where to where I want to move. If I want to move more to a distance very close to the surface, and am I have to spend more energy.

But if I am okay to move to a location, which is slightly away from the surface, I will have to spend less energy. So, this energy this work that has to be done in moving the surface in moving an ion is actually essentially given by $z_i$ times e times psi, this psi would be the, the potential at any location where you want to move it, the psi is the potential at a location where you want to move the charge.

And it will depend also on the, the valancy of the ions itself. If z i, that I have a monovalent ion or a divalent ion, it also depends on that. So the probability of finding an ion at this position is related to the ion concentration at infinity. This is the ion concentration at infinity through this Boltzmann factor. Think a little bit about this. So we will again discuss the Boltzmann factor in the next lecture. And then we will try and proceed with obtaining a solution for 1 dimensional Poisson Boltzmann equation Poisson equation, we will try into the next class, thanks.