Colloids and Surfaces
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Lecture – 28
Introduction to Models of Electrical Double Layer: Helmholtz Model / Capacitor Model

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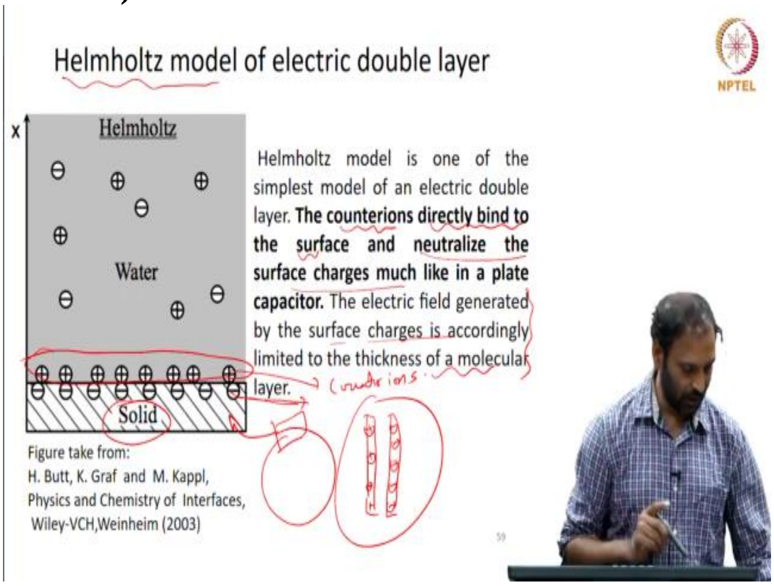

So we are going to look at models of electrical double layer. So I am going to start with a simplest model, it is what is called as Helmholtz model. This is one of the first models that was put forward and so, in this case what is you know thought of is the counter ions, they are directly bound to the surface of the so, if what you are looking at is a picture where you have a solid surface.

It could be you can think about it as a part of a spherical particle. So I could, you know, look at a spherical particle, I am only looking at a small portion that is a solid surface that is a particle of interest it could be. And these are the charges on the particle surface, but these are the counter ions. So, in this Helmholtz model, what is assumed is that the counter ions are directly bound.

They are directly bound or attached, you know, to the particles surface and they neutralize the charges on the surface, they neutralize the charges on the surface giving an arrangement which looks more like a capacitor. So capacitor we know you have you can think about 2 plates which are you know oppositely charged. So that is a capacitor like arrangement so, in this particular double layer model.

It is assumed that the counter ions directly bound to the surface, and then they neutralize the surface charge and give you some kind of arrangement which look like a capacitor, this point, we will come back to it later. So, what is mentioned here is the electric field generated by the surface charges in such a system is limited to the thickness of a molecular layer that I will come to this particular point a little later.

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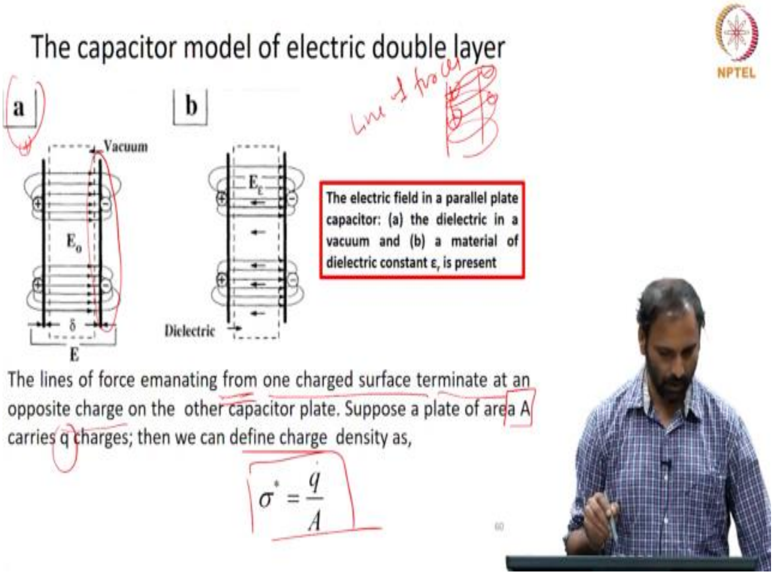

So, what is shown here is a 2 arrangement like a capacitor like arrangement so have a charged plate. So, this could be the charge you know the plate that is because of the counter ions in the solution and that is the charges you can think about this as the charges that arise because of the particle surface. And in case a, you have vacuum between the 2 particles, in case b you have some medium, which will be the case if you look at, you know, colloidal particles in solution, you will always have some medium between the 2 layers.

And in so, what we are going to do is we are going to use a concept called line of forces, which you will you would have seen in electrostatics. So you say that, you know, if I have a charge plate, say that, you know, some, you know, there is a positive or negative charge on the surface. You talk about you know, the lines of force that start from a negative charge and they go to the positive charge and you know, they can continue so, we are going to use a concept like that.

So, the lines of force that start from one charge surface, they start from one charge surface and they terminate at the other charge surface. And if you assume that the particles I mean the surfaces have a area A suppose that the plates are of area A and the total charges that each of these plates carry is q, then we can define a quantity called the surface charge density which essentially is the charge per unit area I can define that, this is the, surface charge density sigma star, which is the total charge divided by the area of the plates.

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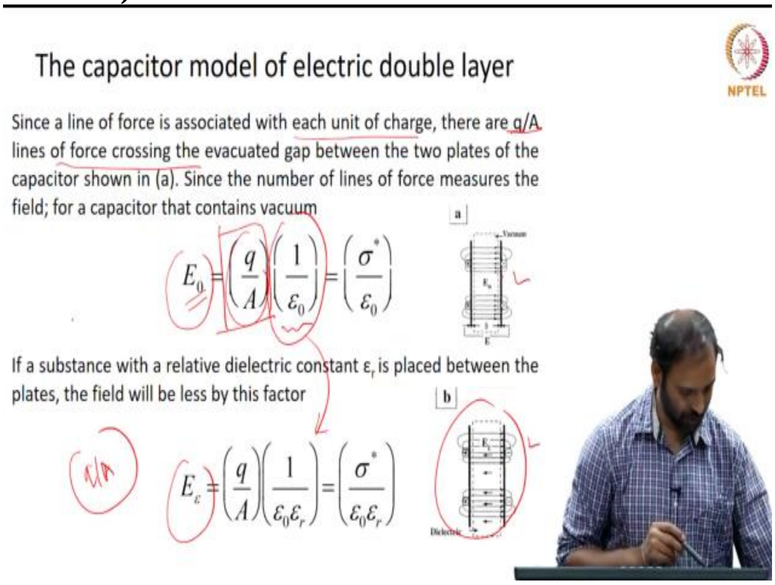

Now, what you can do is that, so, since a line of force, is associated with each unit charge, for every charge that you have there is going to be a line of force. So, because you have a charge density q / A I can say that there are q / A lines of forces that cross from one you know the charge plate to the other charge plate. And therefore, you can say that this E_0 that is the electric field that is arising because of you know q / A lines of forces is (q /A) / 1 over epsilon.

So, that is in a way this tells you what is the force see, this is q /A is the number of lines of forces and the electric field generated is proportional to the number of lines of forces and of course, you know you have you know to take care of the effect of the medium between the 2 plates in one case the medium between the 2 plates is a vacuum therefore, you have 1 over epsilon 0 in the second case, when you have a medium dielectric medium present, you know this factor you want to replace that with 1 over epsilon 0 into epsilon r.

So, in essence this epsilon r and epsilon 0 tell you something about what is the electric field that is generated because of the 2 arrangements which are shown here. So, if you look at this expression this very similar to what we what I was mentioning about so, we had mentioned that so, in a way, we will come back to that point.

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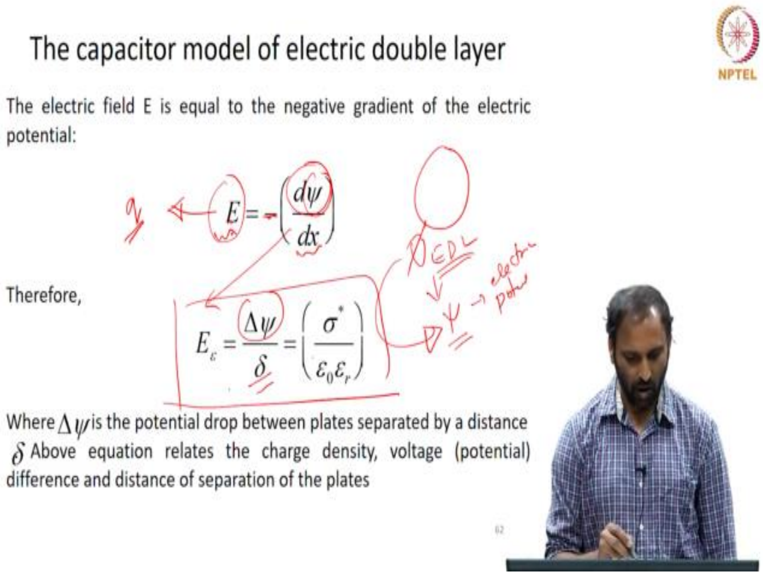

Now, so, now I would have to relate this is the electric field. You will see that in Colloids literature when people work with charged particles. You will always see that say turns out that you know for getting working equations for like say the interaction potential for example phi you know electrical double layer interaction you will see that you know the such the expressions that deal you know that concern electrical double layer interactions.

They are always represented you know in terms of the surface potential you know, you do not see the charges directly in the expression, but you will see that you know, all the equations have the psi which is what is called as electric potential. And that electric potential is related to the electric field that is that is generated because of the charges and which in turn is related to the charges that are associated with the particles.

And this electric field E is given as negative gradient of the electric potential. Therefore, what I can do is if I assume that the drop in the potential is very, very small I can replace d psi / delta psi and this dx is the distance over which the potential is you know the distance over which the potential is changing and this delta there is a distance between the capacitor plates. And that will be equal to sigma star / epsilon 0 into epsilon r.

That is for the case where you have a medium of you know epsilon is a dielectric constant of the medium between the 2 plates. Now, to show that so now I will come back to this point we had mentioned that the electric field generated by the surface charges is accordingly limited to the thickness of a molecular layer.

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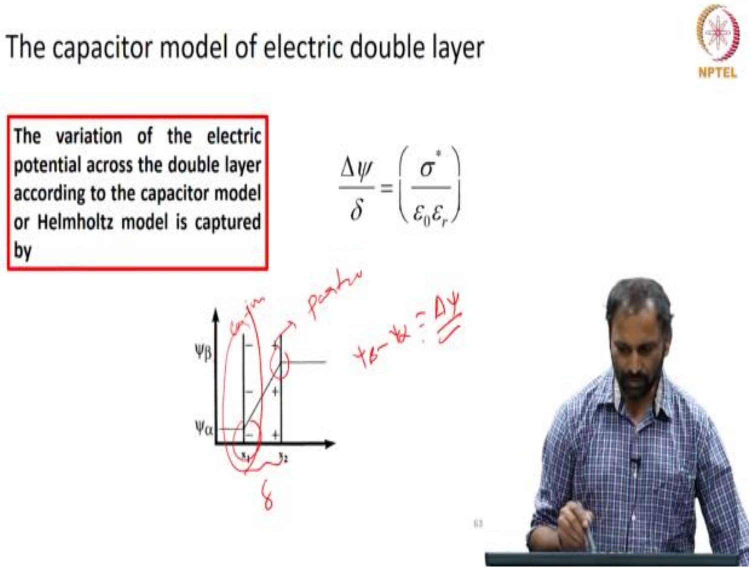

I just to make the point, what I am going to do is to calculate few, so this is in essence, what is the capacitor model? So, if you have, you know, you could have a positively charged plate for example, and negatively this is the charges on the particle surface and this could be the charges in the counter ions, that is that these are the ions which are tightly bound to the charges surface and that is the distance delta and this psi B - psi alpha is the potential drop and you can do some simple calculation.

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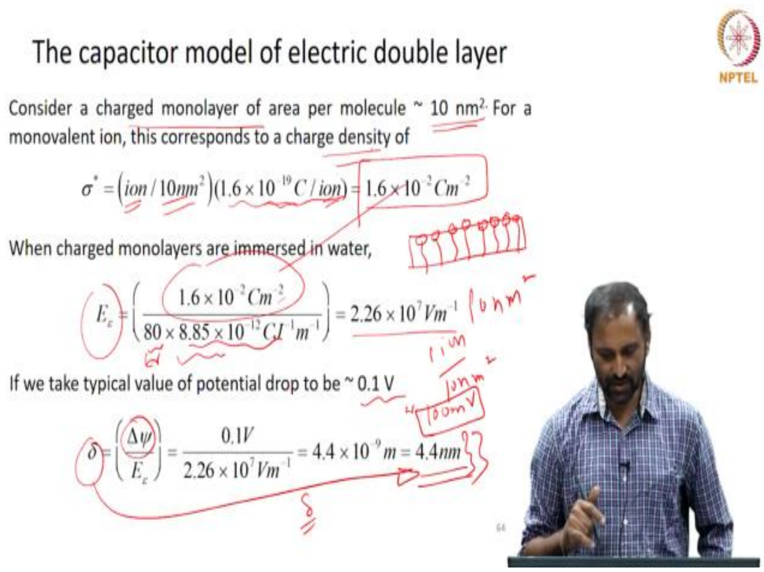

I have taken a case where you have a so let us think about a simple case where I have a charge surface and imagine that you know this is a charge surface which is because of a surfactant molecules which are attached to the particle surface. Now, if the charged monolayer so I am talking about monolayer because I have a single layer of surfactant attached to the particle surface if the charge monolayer has an area which is 10 nanometers square, a charged monolayer of area 10 nanometers square is what I am considering.

Now, if you for a monovalent ion, this corresponds to charge density. So, what you can do is say that you know, I have a 10 nanometer square area and I have 1 ion per 10 nanometer square if I have 1 ion, the charges on the ion is going to be 1.6 into 10 power - 19 coulombs per ion therefore, I can get a charge density. So, you should imagine that you know I have a monolayer surfactant.

And if I say that there is 1 ion for every 10 nanometer square area, for every 10 nanometer square, there is 1 ion present then the charge density is going to be 1 ion per 10 nanometer square therefore, this number becomes 1.6 into 10 power - 19 coulomb divided by you know per ion that is a charge per ion therefore, you get a sigma star which is 1.6 into 10 power - 2 coulomb meter square coulomb per meter square.

And you calculate epsilon electric field that is sigma star we go back here sigma star I plugged in sigma star here 1.6 into 10 power - 2 coulomb meter square and epsilon 0 that is epsilon 0 and that is epsilon r therefore your epsilon you know E epsilon becomes 2.26 into 10 power 7 volts per meter and typically when people talk about you know, charged surfaces, typical potential drop you know are of the order of 0.1 volts or 100 millivolts, that is a typical potential drop people talk about.

If I substitute for a delta del epsilon or the change in the drop in the potential I can get delta and the delta comes out to be 4.4 nanometer. So, therefore, you can say that you know, because we are assuming that the counter ions are directly bound to the particle surface and typical the thickness of the double layer one can think about is of the order of 4.4 nanometers in this particular example.

Therefore, in the capacitor model we should assume that the electrostatic interactions. So, in a way this tells you something about the range of distance over which the electrostatic interactions are operative. Can I make the statement this is what we are saying is that if you look at this particular picture, that's a charged that is the charge surface. And we are saying that you know the surface charges are bound to the counter ions are bound to the particles surface they are strongly bound in essentially neutralizing the entire surface.

And because of the fact that they are strongly bound, you know, we can imagine that the, the electric field that is generated by the surface charges, is would be of the order of molecular layer thick. That is what we kind of proved by looking at some typical numbers of the delta that we get for a particular case. So maybe just go back and take a look at this again, maybe we will discuss this example again in the next class.

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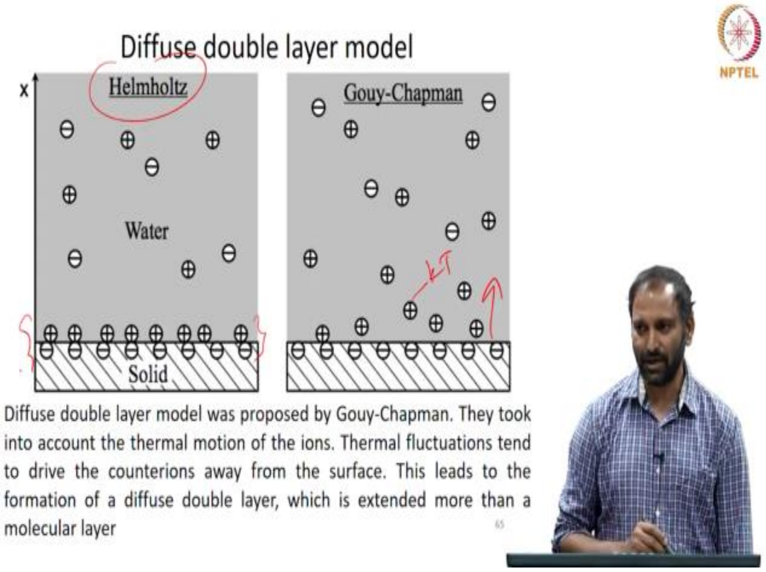

So, the first simple picture that we looked at is Helmholtz model but the more realistic picture is that the such a strong binding that is, you know, kind of assumed in the electrical in the Helmholtz model is actually not completely true. That is because the counter ions there that are there in solution, they are also free to move around. They know they also have you know, thermal energy KT and because of the thermal energy they can also, you know, go away from the surface.

And then, you know, you get a kind of a distribution, which is not exactly, you know, like a capacitor arrangement. Of course, there is going to be a larger concentration of counter ions close to the surface, but the arrangement is not exactly like a capacitor kind of a concept. We will try and talk about it in the next class.