Colloids and Surfaces
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Lecture - 29
Review and Summary of Helmholtz Model (or capacitor model) of Electrical Double Layer

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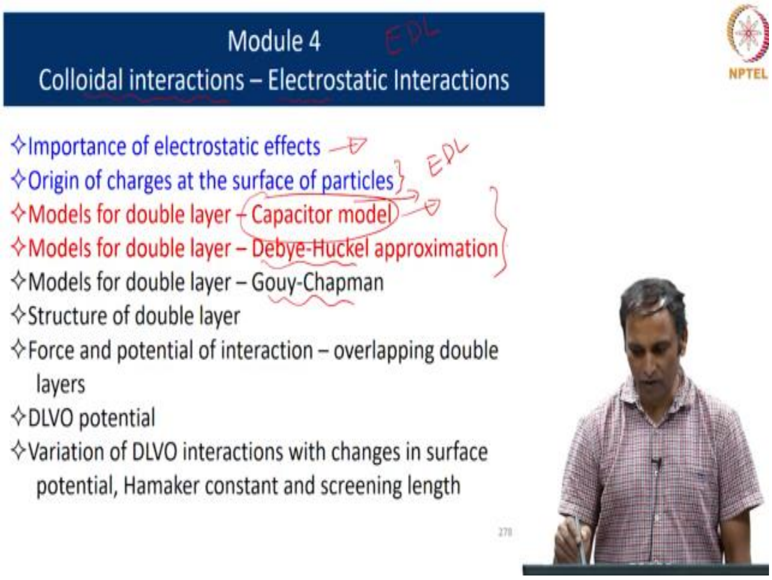

So, in the last class we started off with module 4, which is colloidal interactions, in terms of looking at what are called as electrostatic interactions or also called as electrical double layer interactions. So, we had briefly talked about what is the importance? Why are we trying to look at this particular module? And also about what are the different ways by which the particle surface gets charges? I had also mentioned what is an electrical double layer concept as well I just want to quickly recap that.

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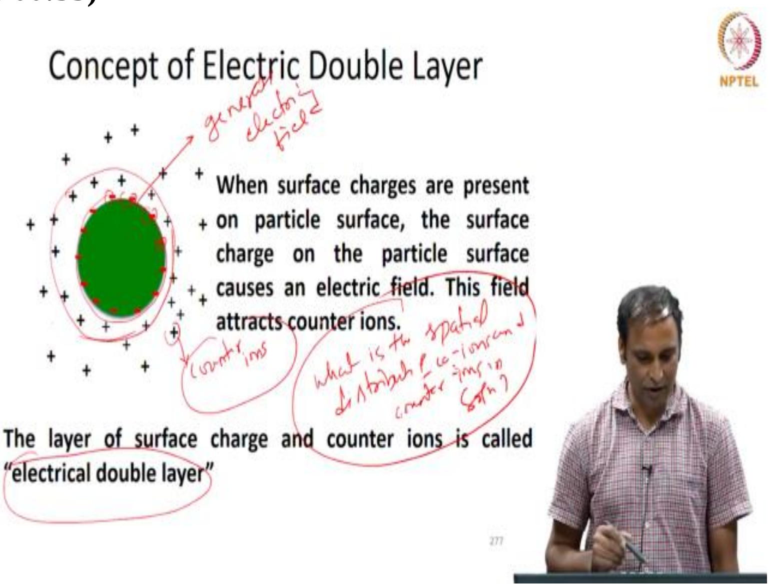

So, what you are looking at is a colloidal particle which has negative charges, which is represented by minus here. And the moment you have and of course, you are going to have these are the counter ions in solution. And whenever you have a charged species is going to generate this charged species is going to generate electric field and because of the electric field that is generated.

Because of the charges on the particle surface is going to attract oppositely charged ions or the counter ions are going to be attracted to the surface because of the electric field. Therefore, you are going to have a layer of charges on the particle surface and of course, you are also going to have the charges in solution which are kind of attracted to the surface because of the electric field generated.

Because of the charge on the surface and this particular arrangement where you have 2 layers of ions, which are opposite in polarity that is what is called as a electrical double layer what is really important when we are trying to look at electrical double layer interactions is that we are interested to ask a question such as what is the spatial distribution of co-ions and counter-ions in solution?

This is the question that we were trying to ask, and it turns out that answering this question is really important, if you want to understand the electrostatic interactions or the electrical double layer interactions. So, therefore, we are going to look at some models in which people have proposed different models, which kind of depict what is the distribution of counter ions and co ions in solution?

So, in that context there are, you know, some old models which are not valid anymore, I mean, but, you know, this kind of this capacitor model which I am going to discuss, they started off you know, the field of in a electrical double layer models. And then the more recent ones talk about what are called as a Debye-Huckel, you know model for electrical double layers or Gouy-Chapman model for electrical double layer. So, these are more of recent developments. So, we will try and look up each of them and then discuss a little bit about what these models say.

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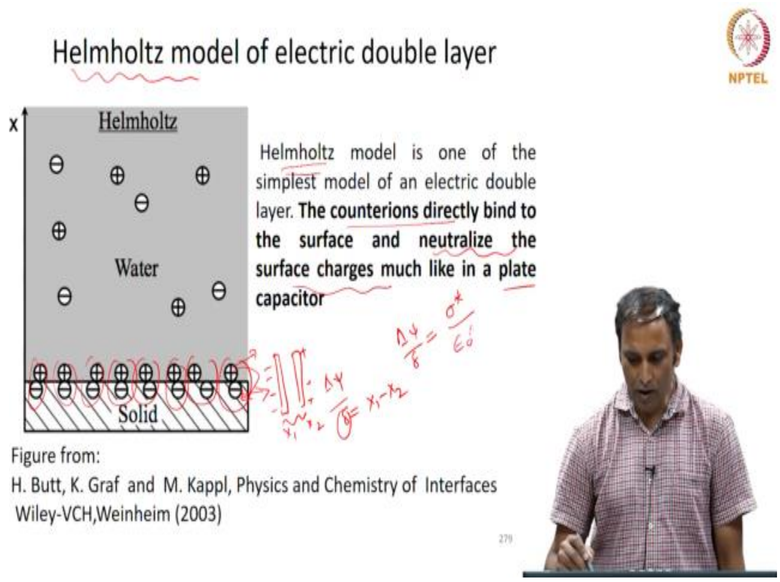

In that context the first model that we looked at was, so, there was a Helmholtz model for electrical double layer, in which it is assumed that the counter ions, these are the ions which have the charges that are opposite in polarity to the charges on the particle surface, in this case, the particle surface is negatively charged and these are the counter ions which are positively charged, the counter ions directly bind to the surface, they are kind of attached, you know, to the charge surface, and they kind of try and neutralize the surface charges.

We know very much like a capacitor. When I say neutralize, you can see the, for every, you know, there is an ion pair. For every charge on the solid surface, there is a charge in the solution which is kind of attracted to the surface and they are tightly bound and the charges in the solution, they essentially neutralize the charges on the particle surface that is one of the simplest model of electrical double layer.

And so to understand so, what we are trying to do is we are trying to develop an expression for a kind of a quantity which is if I have to so, this basically arrangement tells you something like capacitor. So, I have a, some charged some plate which is negatively charged, I have another plate which is positively charged. So, we would like to relate, what is the potential drop?

If I say that the potential drop is delta psi, del psi, and if the distance between the 2 plates if they are at a distance x 1 and x 2, your delta is going to be x 1 - x 2 or x 2 - x 1, that is the separation of these plates, we want to relate delta psi / delta 2 parameters such as the surface charge density and the dielectric constant of the medium between the 2 plates, that is what we would like to go about.

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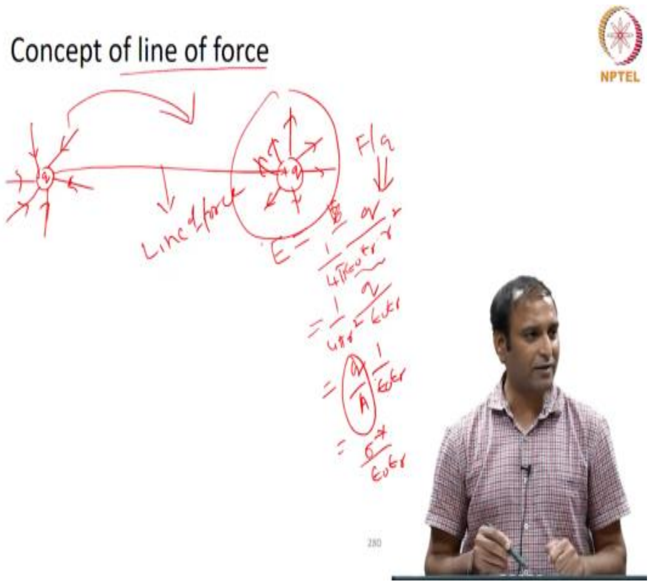

So in doing that, we would like to exploit a concept called a concept of line of force. You would have seen in electrostatics pictures like this, if I have a plus q charge or a minus q charge, we would have seen some lines like this. And if you remember, what are they? They are the electric field lines by convention, if it is a negative charge, then you know the field lines are going to be inward.

And if it is a positive charge, the field lines are going to be outward. So, this electric field it is actually you can calculate it as this electric field that is generated because of a point charge it essentially is given by force divided by the charge and the force is 1 / 4 pi epsilon 0 into epsilon r into r square into q that is F / q. Now, what I can do is, I can express this as q / epsilon 0 epsilon r and I have 1 / 4 pi r square.

Now, instead of assuming a point charge, if I assume that the charges are located on the surface of a sphere, this 1 / 4 pi r squared gives me the area therefore, I can write this as q / A into 1 / epsilon 0 epsilon r. Therefore, this q / A is essentially the surface charge density that is a number of charges divided by area that is going to be sigma star / epsilon 0 epsilon r. And we know that.

So, whenever we talk about this, so the understanding is if I have a test negative charge, and if I bring in a, you know, test positive charge and if I bring in a test negative or a positive charge near it, near to it, it is going to each of the charges are going to experience some force and you can imagine that this force acts along some line. And this is an imaginary line and that is what is called as a line of force.

Depending upon you know; the number of charges that you have, you know; there going to be so many number of lines of charges, in a way. So, you can think about line of force as a imaginary line, over which, you know, the a test charge, which is going to be brought into the vicinity of either positive or negative charge, the force that the test charge is going to experience. So and depending upon the polarity of the charge, this force can be either attractive or repulsive. So we are going to use concept like this.

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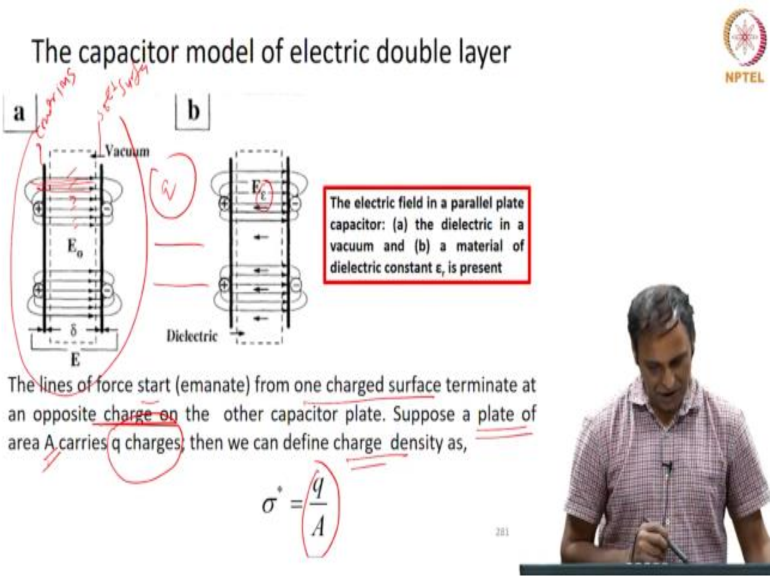

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So now, sir, yeah, is the same as field lines? Same as field line is this see, I mean, so see when I wrote this field line. So I mentioned that, so I can also imagine, instead of calling this as a lines that come up because of the field, I can also say that, you know, you can imagine that there is a there if I have 2 charges; there is going to be some force of attraction or repulsion now, and the force of attraction or repulsion is going to act along some line.

If I take a point charge is going to be acting along some line and this line is what are we are talking about. The lines of forces for some charge; and midline is for the unit charge, I mean. So if you see, when you talk about expressing the only difference would be that if you talk about forces, I would have to worry about, you know, resolving them if they are not acting in a particular line and stuff like that so you can.

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So now what you are looking at is 2 arrangements. One is, so you can imagine the minus to be the charges on the solid surface that is the charges on the solid surface. And these are the counter ions; that is a capacitor like arrangement. And in this case, they are in vacuum in this case there is a medium of some dielectric constant epsilon between the 2 plates. So we are going to we all these lines that you are seeing these are the lines of forces.

And depending upon the charge on the each plate then lines of forces are going to be different that means the spacing between these lines depends on the charge total charge. If I have very high q, you are going to have many more lines closely spaced and however if you know the, if the q is not very high, you are going to have sparsely populated lines. Now, so, what is so and by convention as we said that the lines of force they start from positive and they go towards negative that is the convention that is followed.

Now, if the plate carries a charge q. And if the area of the plate is A then I can define the surface charge density which is q / A. Now, the lines of forces that you see there, they start from one charge surface and they terminate at the opposite in the place which has the opposite charge.

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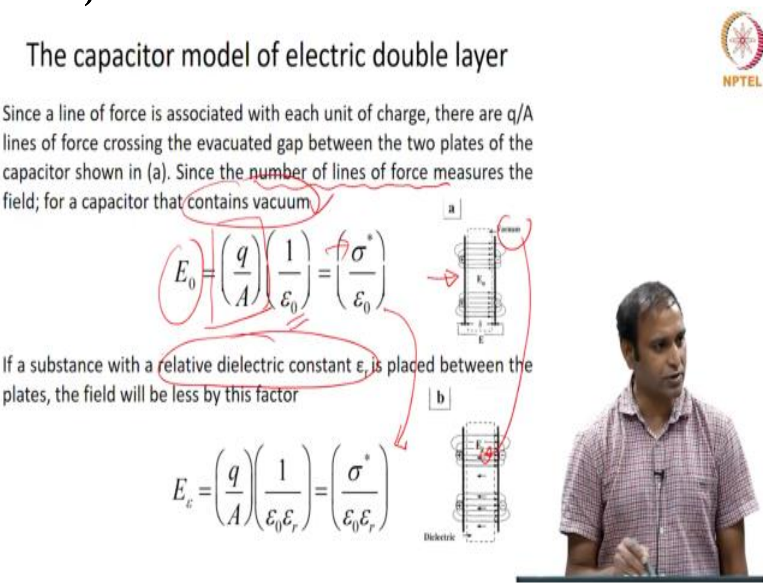

Now, we kind of derived this you know a while ago, so this electric field that is generated in the case where you have vacuum, I can write that as the surface charge density multiplied by 1 / epsilon and because q / A is defined as sigma star, therefore, E_0 essentially becomes sigma star / epsilon and similarly, if I replace the vacuum with a medium with a permittivity epsilon and I am going to write E epsilon as sigma star / epsilon 0 epsilon r.

And the understanding is that the number of lines of forces is a measure of the field strength. So, the more the number of lines of forces more is a field and of course, it is dictated by the whether the region between the 2 plates has vacuum or some medium with the dielectric constant epsilon r.

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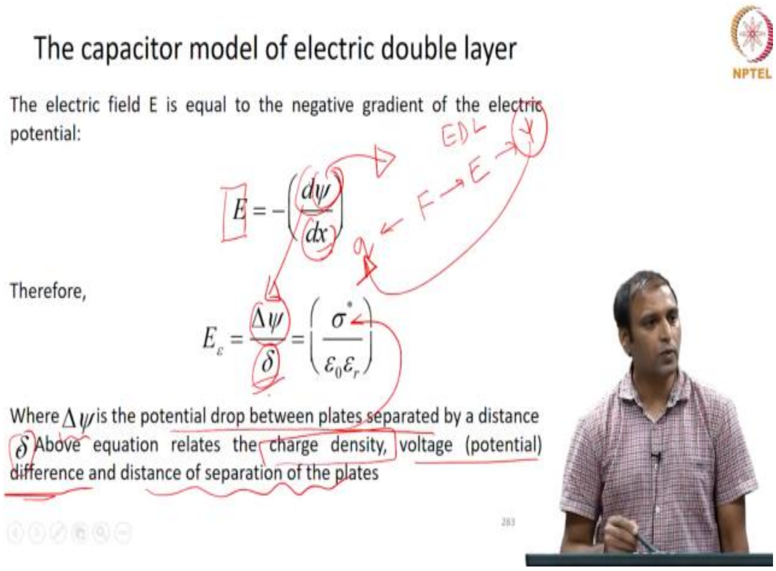

So, now, this electric field and the potential they are related this way electric field is a negative gradient of the potential we are going to use potential in the calculation that involves electrical double layer because of the fact that you know we know that the force depends on the charge if I know the force I can get electric field if I know electric field I can get psi therefore, if I have a way of finding out what is the surface potential?

Then I will have a way of telling something about what is this charge q on the particle surface so, there but the reason why everything that we are going to do will have psi because doing math is much, much easier if you work with science. So, now, so, this del psi / del x if I assume a small drop in the potential I can replace this d psi / delta psi and dx / delta and that is equal to sigma star / epsilon 0 epsilon r where delta psi is the potential drop between the 2 plates which are separated by a distance delta and this particular expression.

It actually relates the charge density which is sigma star and the potential difference that is delta psi, and the distance of separation between the 2 places which is delta.

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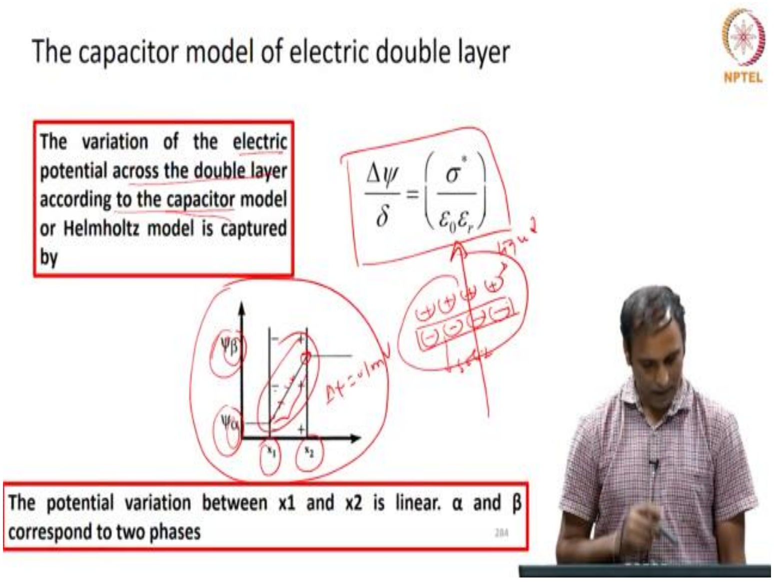

Now so, in the electrical double this essentially is the electric you know Helmholtz model for electrical double layer what you are seeing is a depiction where this alpha and beta they essentially refers to 2 phases in this case. So, we have we had a charged surface and they are going to be counter ions now, when I say 2 phases in this case one is a solid phase other one is a liquid phase.

Now, and this kind of arrangement that we are seeing it is actually seen at the interface at the interface of the as I go from one phase to another phase at the interface is what you are going to have arrangement like this. So, this is alpha psi beta and psi alpha refer to the potential at the 2 phases alpha and beta and they are separated by distance x1 and x2 and what this particular model predicts is that the variation of potential in the gap between the 2 plates the variation is linear.

So, the variation of the electric potential across the double layer according to the capacitor model is a linear variation of the charge. So, if I know what is the potential here? If I know what is the potential drop? That is delta psi is equal to say if I say point 1 you know millivolt or something like that, I should be able to calculate what is the how the potential varies across the entire gap. So, that is the, what is called as an electrical double layer model.

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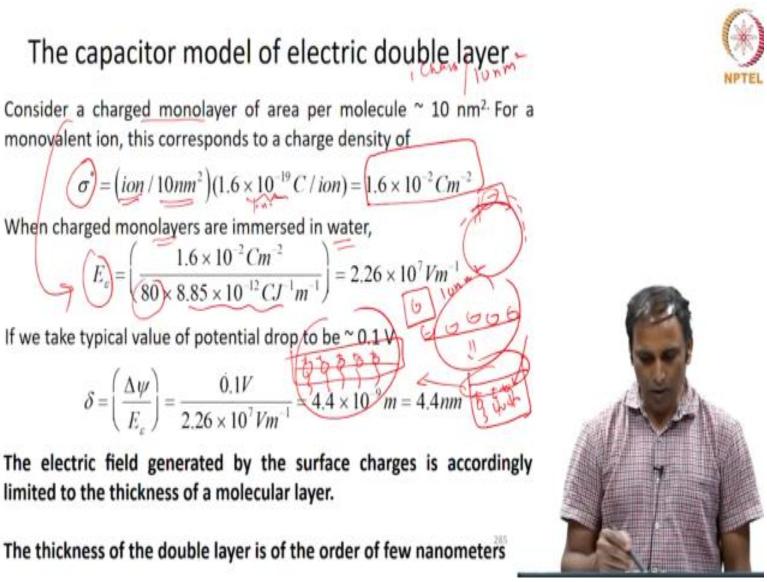

The capacitor model for electrical double layer so, we had again done this. So, if I take a case where I have a charged monolayer, charged monolayers are found in the several you can imagine that I have a spherical particle and say that I have charges on the surface. So, and if I look locally, I really have a flat region because you know, if I compare the size of the ions corresponding to the size of the particle, you know, you can imagine it is a flat line.

So, therefore, I am really going to have a charged monolayer in this case, other way to imagine charge monolayer could be I have a container I have water in it I add charged surfactant. And charged surfactant, are represented by something like that it could be positively charged or negatively charged, because the surfactants have a tendency of going to the interface.

If I look at interface, the arrangement looks something like this interface will have and because each of them will be charged under this dissociation, and we will have a monolayer of surfactant that is charge. So, if you take a case of a charge monolayer, where the monolayer has 1 charge it has 1 charge per 10 nanometer square area. So, I am basically looking at an arrangement either like this or arrangement like this.

I take an area, which correspond to 10 nanometer square if there is only 1 charge on the surface, then I can calculate sigma star the surface charge density that is 1 ion per 10 nanometers square it becomes 1.68 power - 9 coulombs per ion that is the charge on the 1 ion divided by 10 nanometer square. If I do that, I get sigma star to be 1.6 into 10 power - 2 coulomb per meter square. So, now to calculate now, if I assume that this is immersed this is in water, I have a charged monolayer and if that is in water, then I can calculate what is epsilon s?

We can go back to this expression. So, epsilon s is essentially sigma star / epsilon 0 epsilon r I know what a sigma star divided by this is epsilon r this is epsilon 0. So, I get epsilon you know E epsilon as 2.6 into 10 power 7 volt per meter inverse and typically you know if you know when we talk about the potential drop across such charged monolayers.

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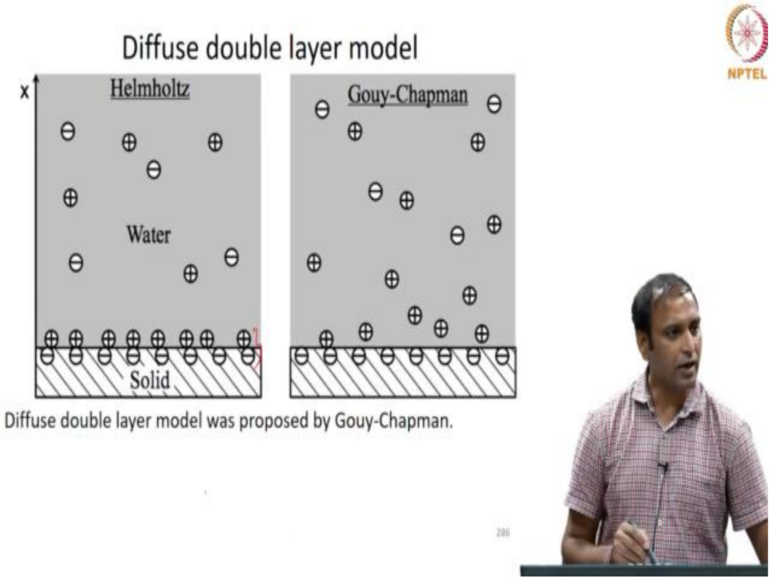

So, if I look at the potential drop in case like this. So, it typical value that people talk about is about point 1 volts if I substitute for point 1 volt I can actually get delta. So, this delta it is in a way it tells you something about the thickness of the electrical double layer the double layer in this case corresponds to this and this the thickness of the double layer is given by delta in a turn so, that I can calculate that and it turns out to be something like 4.4 nanometer.

So, therefore, you can say that the electric field that is generated by the surface charges it is in molecular dimension it because of the fact that the numbers are 4.4 nanometer, you know it is very close to the molecular dimensions. So, that is the kind of conclusion that you can draw if you work with what is called as a capacitor model or the Helmholtz model for electrical double layer and if you look at several different problems and if you calculate the double layer thickness, it will be few nanometers in dimensions.