Microfluidics
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Lecture - 14
Electrokinetics

Okay. So, let us talk about electro osmosis. Before we talk about electro osmosis, let us talk about the electrical double layer, the debye layer which is an important concept in electro osmosis.

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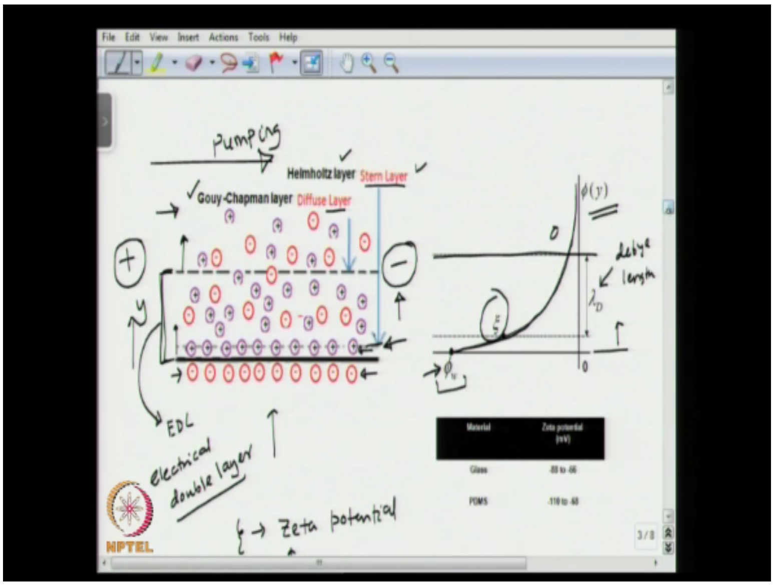

Material	Zeta potential (mV)
Glass	-88 to -66
PDMS	-110 to -68

So, if you look at here we have a surface which has negative charge okay and over the surface we have a liquid present an ionic liquid, because of the negative charge on the surface, the positive charges are attracted towards the wall and at the very interface on the wall, these positive charges are strictly bound on to the negative charges and these positive charges are immobile okay. So, they form an immobile layer which is known as stern layer.

They are very strongly bound to the negative charge wall and because of the negative charge on the wall more positive charges are also attracted towards the wall so, there is a region close to the wall where we would find net positive charge okay. And that region is known as electrical double layer okay. And beyond this electrical double layer we would have the neutral liquid where you will have equal number of positive and negative charges. So, this immobile static layer is known as stern layer or Helmholtz layer.

And the region of the liquid close to the wall where we have net positive charge provided the surface is negative is known as diffuse layer or it is also known as Gouy-Chapman layer okay. Now, when we apply a voltage difference between the 2 terminals, these positive charges as this region is rich in positive charges, they tend to move towards the negative electrode which is the cathode. So, in doing so, they carry the bulk of the liquid along with it so we have a pumping action taking place from positive to negative terminal okay. So we have a pumping action taking place.

If we look at the potential variation from the wall into the bulk of the liquid, let us call this z direction or in this case, let us call it y direction. Then this is how, it is going to vary. This is how the potential phi is going to vary from the wall into the bulk of the liquid. The potential right on the wall is the wall potential which is denoted by phi wall and the potential odd the strong layer or the immobile layer is known as zeta potential okay.

So, xi is called zeta potential which depends on the surface as well as the liquid that is present on the surface. So, this zeta potential is the potential at the Stern layer okay. So, the electric potential from the wall is reduced into the bulk and about to the land scale of lambda D, it reduces to 0 into the bulk okay. And this land scale is known as lambda D is known as debye length okay. So, lambda D is called debye length, which is the land scale at which the potential reduces to 0 in the bulk liquid okay.

So, this is a very important parameter in the definition of electrical double layer okay which is called debye length. Now, if you look at the zeta potential for different materials, as I told it also depends on the liquid that we are talking about. For glass, the zeta potential is varying from -88 to -66 depending on the liquid and for pdms, it is found to vary between -110 to -68 okay. And this zeta potential as you would see in subsequent lectures, you would see that this zeta potential is a very important parameter that governs the electro osmotic flow okay.

Now let us talk about the continuum model for the electrical double layer.

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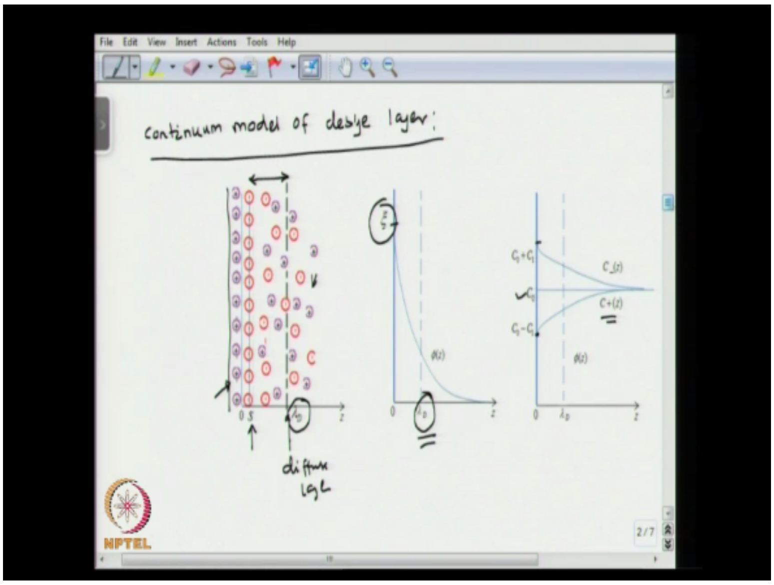
continuum model of debye layer:

So here if you look at this case, we will be considering this case okay. So, here we talk about continuum model of debye layer okay. So here, we consider a positively charge surface, so the surface is positively charged okay as you can see here. It has got positive charge. So we would have a charges from the liquid, the negative charges will come and bind to the surface because the surface is positively charged and inside the diffuse layer we would have net negative charge okay.

Because the surface is positive, we would have negative charge close to the surface in the diffuse layer and the bulk will be neutral okay. So this is the stern layer and this is the diffuse layer okay. And lambda D is representing a land scale where the potential vanishes to 0 from xi potential at the stern layer. So you can see a potential at the wall or at the stern layer is given by xi and it vanishes to almost 0 at the debye layer land scale.

And if you look at the concentration of the charges, what do you see here, the coence are suppressed near the walls, since the wall is positively charge, the positive charges in the liquid is less at the wall and it increases to a value C0 in the bulk. Similarly, the counter ions are higher at the wall and they reduce to C0 into the bulk okay. So, if you want to talk about the continuum model for debye layer, we can assume the charges follow the Gauss law okay.

As ideal gas we can assume the charges as ideal gas. If you do that so you have to consider for thermo dynamic considerations and in that case, we will have to consider what is called the potential of the liquid okay. So, the chemical potential of the liquid is what we have to consider.

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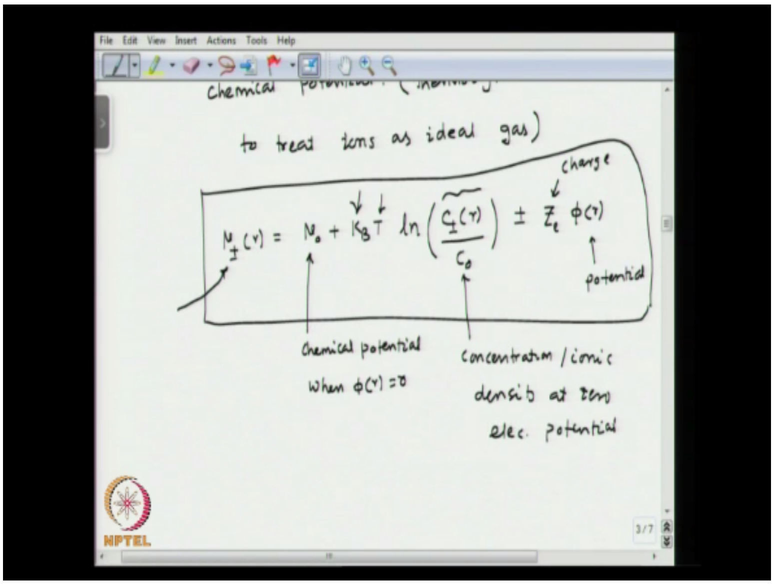

Chemical potential (

to treat ions as ideal gas)

$$\mu_{\pm}(r) = \mu_0 + \overset{\downarrow}{k_B}\,\overset{\downarrow}{T} \ln\left(\frac{\widetilde{C_{\pm}(r)}}{C_0}\right) \pm \overset{\text{charge}}{\overset{\downarrow}{z_e}}\, \underset{\underset{\text{potential}}{\uparrow}}{\phi(r)}$$

Chemical potential when $\phi(r) = 0$

concentration / ionic densit at zero elec. potential

So, we can define the chemical potential okay for thermo dynamic consideration to treat charges or ions as ideal gas. So you can write the expression for the chemical potential as this. So you can write mu +- r = mu 0+ Boltzmann's constant * temperature * lan of C+-r divided by C0 +-ze * pi r. so this is the charge and this is the potential okay. This is the chemical potential in the absence of electric potential.

So chemical potential when pi r = 0 and so this is for a given pi r, this is the chemical potential and this is the Boltzmann's constant and this is temperature okay. And this are the ionic concentration. And C0 is the concentration or the ionic density at 0 electric potential okay. Now, if we talk about thermo dynamic equilibrium, the chemical potential inside the ionic liquid has to be uniform okay. If it is not uniform, the charges or ions can reorganize themselves to generate energy okay.

So, the thermo dynamic equilibrium consideration, the chemical potential must be uniform okay. So the gradient of the chemical potential must vanish okay.

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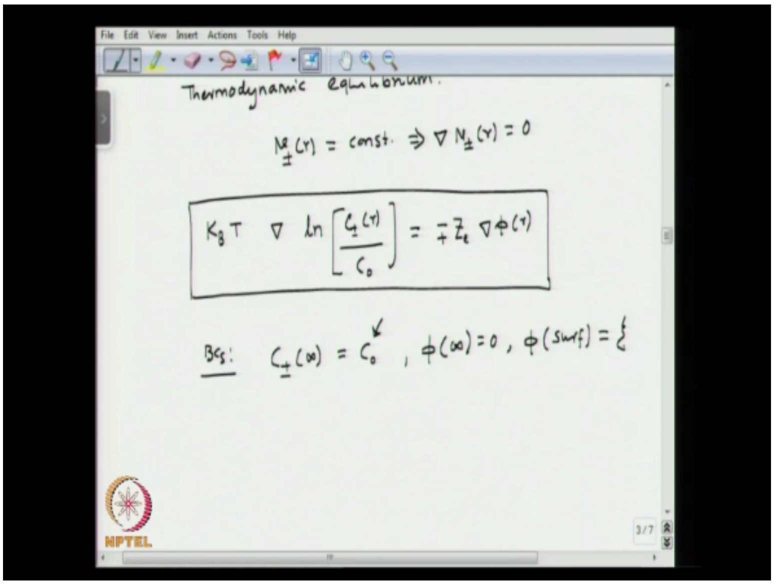

Thermodynamic equilibrium.

$$\mu_{\pm}(r) = \text{const.} \Rightarrow \nabla \mu_{\pm}(r) = 0$$

$$\boxed{K_B T \ \nabla \ln\left[\frac{C_{\pm}(r)}{C_0}\right] = \mp Z_e \nabla \phi(r)}$$

BCs: $C_{\pm}(\infty) = C_0$, $\phi(\infty) = 0$, $\phi(\text{surf}) = \zeta$

So, for thermo dynamic equilibrium, the chemical potential mu r will be constant so the gradient of chemical potential will be 0. So, if you take gradient of the chemical potential here, what you will get is this, you will get K B * T Boltzmann's constant * temperature gradient of lan C+-r divided by C0 will be = -+Ze * variant of phi r okay. So that is what we would get.

Now, we have the boundary conditions that C+-infinity at Z = r = infinity, the concentration is going to be C0, that is in the bulk of the liquid and the phi at infinity will be 0 okay. No potential in the bulk and phi on the surface will be zeta potential okay.

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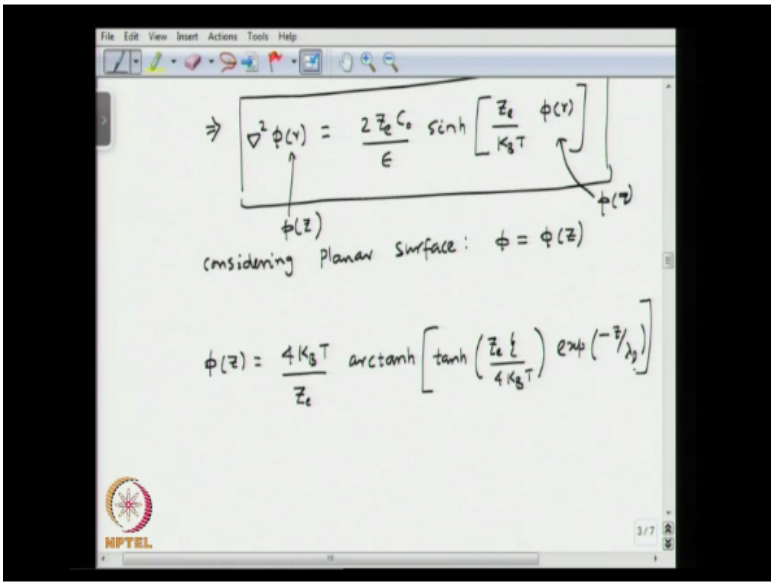

$$\Rightarrow \boxed{\nabla^2 \phi(r) = \frac{2 Z_e C_0}{\epsilon} \sinh\left[\frac{Z_e}{K_B T} \phi(r)\right]}$$

$\phi(z)$ $\phi(z)$

considering Planar surface: $\phi = \phi(z)$

$$\phi(z) = \frac{4 K_B T}{Z_e} \operatorname{arctanh}\left[\tanh\left(\frac{Z_e \zeta}{4 K_B T}\right) \exp\left(-z/\lambda_D\right)\right]$$

So, if you apply these boundary conditions, on this equation what you would get is this, you will get the distribution of the ions C+-r is C0 * exponential -+Ze over K B * T * phi r okay.

So, this is the distribution of the ionic density. So if you know distribution of the negative and positive ions, you can calculate the electrical charge density can be calculated as Z e * so this is across r could be C+r-C-r, so this is the charge density which you can be calculated as -2Z e C0 *Sin of h sin hyperbolic * Z e over Boltzmann's constant temperature * potential okay.

Now, if you apply this Maxwell equation that we had studied del square phi r will be -1 over epsilon * electrical charge density okay. So if you use this equation, so we have an expression for electrical charge density which is this. So, we can find del square phi r will be 2 Z e * C0 over epsilon * sin hyperbolic Z e over K B T * phi r okay. So, this is what we would get. Now, if we consider that the surface is flat okay, then we are considering that the variation is going to happen only along the direction normal to the surface okay.

So, in that case, phi can vary in a one dimension okay. So, if you are considering a flat surface, planar surface, you can say that phi, let us say it is function of phi Z okay, where Z is this direction here okay, this direction is Z okay. So, you can write del square so here you can say this is phi Z and that is here is phi Z, so you can substitute solve for the potential and write that phi Z is going to be 4 K B * T divided by Z e * tan inverse hyperbolic arc tan h tan h of Z e * zeta potential divided by 4 k B T exponential -Z/lambda D.

So, this is how the potential is going to vary away from the wall in a direction normal to the wall into the liquid okay. Now, we have introduced one parameter here lambda D which we call as debye length okay.

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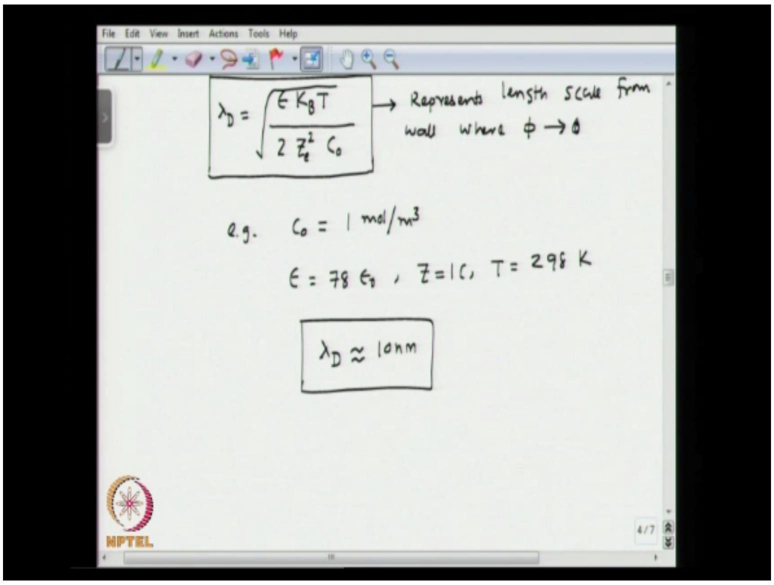

$$\boxed{\lambda_D = \sqrt{\frac{\epsilon K_B T}{2 Z_e^2 C_0}}} \rightarrow \text{Represents length scale from wall where } \phi \rightarrow 0$$

e.g. $C_0 = 1\ \mathrm{mol/m^3}$

$\epsilon = 78\,\epsilon_0$, $Z = 1$, $T = 298\ K$

$$\boxed{\lambda_D \approx 10\,nm}$$

And here lambda D is defined as epsilon * Boltzmann's constant * temperature divided by 2*charge square * C0. That is the concentration or ionic density in the bulk. So that is how the debye length is determined there is a square root of that. So, this is this represents, the land scale from wall where the potential is reduced to 0 okay.

So, this is reduced to 0 and if you take an order of miniature you can take an example, so the concentration of the charge ionic density let us say about 1 mol per meter cube okay and let us say we consider water so epsilon is 78 times epsilon 0, the permittivity and let us say charge is 1 unit, and the room temperature which is 298 kelvin okay. Consider 1 column then we can find the lambda D is about 10 nano meter okay. So, that is an estimation of how thick the debye layer is.

So debye layer is up the order of 10 nano meter okay. So, next we move on and talk about the debye Huckel approximation.

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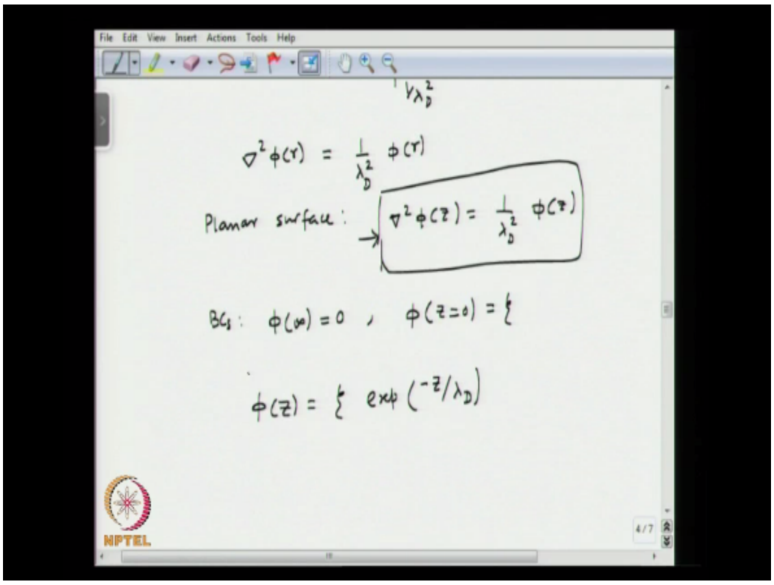

$$1/\lambda_D^2$$

$$\nabla^2\phi(r) = \frac{1}{\lambda_D^2}\phi(r)$$

Planar surface: $\rightarrow \boxed{\nabla^2\phi(z) = \frac{1}{\lambda_D^2}\phi(z)}$

BCs: $\phi(\infty) = 0$, $\phi(z=0) = \zeta$

$$\phi(z) = \zeta\, \exp(-z/\lambda_D)$$

So, we talk about Debye Huckel approximation. So the approximation is best on the fact that the electrical energy is < as compared to the thermal energy okay. So, that is the approximation on which the Debye Huckel approximation is best on. So, we can say that Z e * xi is << so this is energy right charge * voltage is << the thermal enrgy is Boltzmann's constant * temperature.

Now, if you impose this condition on this equation here okay, on this equation there then what we see here a sin h of some term right and we know that sin h u will be = u when u is small okay. So, if you impose this condition coming from the Debye Huckel approximation on this equation here, then we can simplify the equation for the potential we can write that del square phi r will be = 2 Z e square C0 divided by epsilon * phi r divided by K B T okay.

So, this is what we get okay Z e over K b T * phi r becomes u and the sin hyperbolic goes out. So, 2 Z e C0 over epsilon right so, we have this Z e here so that makes it Z e square * C0 over epsilon * phi r over K B T. So, we can write this as here if you look at the expression for lambda D okay, so you can lambda D square 1 over lambda D square will be this right. So, this is nothing but 1 over lambda D square. So, you can write this as 1 over lambda d square * phi r right.

So, we have the equation del square phi r is 1 over lambda D square * phi r. now, if you have a planer surface, we can write del square phi Z will be = 1 over lambda D square * phi Z. Now, to solve this equation, we can apply the boundary conditions. The boundary conditions are the potential when Z = infinity will be 0, so that is in the bulk liquid. And the potential at Z = 0 will be the zeta potential. So if you apply that to this equation, what we would see is we get an expression for the potential, which is zeta * exponential - Z over lambda D.

So, this shows how the potential varies from the wall into the bulk. So, we see that the potential decreases exponentially from the surface into the bulk. And that is what we see it here okay, if you look at what we have represented pictorially here we see that the phi is reducing exponentially into the bulk liquid okay right. So, see that phi Z decreases exponentially into the bulk liquid okay.

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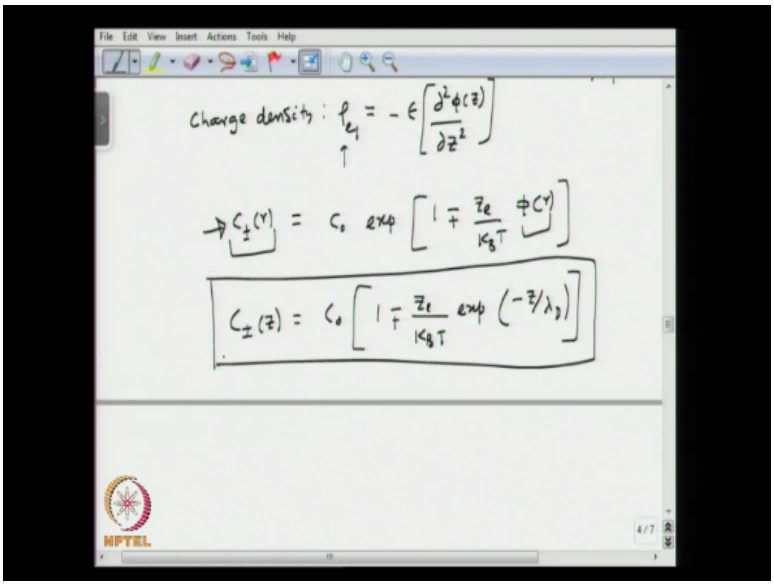

Charge density : $\rho_e = -\epsilon \left[\frac{\partial^2 \phi(z)}{\partial z^2}\right]$

$$\uparrow$$

$$\rightarrow \underbrace{c_\pm(r)} = c_0 \exp\left[1 \mp \frac{ze}{K_B T} \underbrace{\phi(r)}\right]$$

$$\boxed{c_\pm(z) = c_0 \left[1 \mp \frac{ze}{K_B T} \exp\left(-z/\lambda_D\right)\right]}$$

Now, we can find the charge density. Charge density can be found so electrical charge density will be = -epsilon del square phi Z over del Z square right. So, this is nothing but this equation that we just talked about this equation okay. So, we can find the charge density moving the charge density, we can find what is the concentration of the ion. The ionic density is C0 * exponential 1-+Ze over K B T * phi r okay.

So, this is the general expression how we can know what is the ionic density knowing the potential distribution okay. So, we can write in this one dimensional case, C +- Z will be = C0 * 1-+Ze+K B T and we have an expression for phi Z okay. We have one expression for phi Z here. So, say exponential -Z over lambda D okay.

So, what we see here is if you look at the ionic density distribution, it says that the co-ions okay if the wall is negatively charged, the negative charge in the liquid are suppressed close to the wall and it can increase into the bulk whereas the counter ions are more close to the wall and they reduce into the bulk of the liquid. And so this is what we observed here okay. So, the co-ions are suppressed near the wall and the counter ions are more near the wall.

The co-ions increase into the bulk and the counter ions are maximum at the wall and decrease into the bulk and they reach a value which is the value when the potential is 0, which is into the bulk of the liquid okay. So, this is what we observed from this equation.

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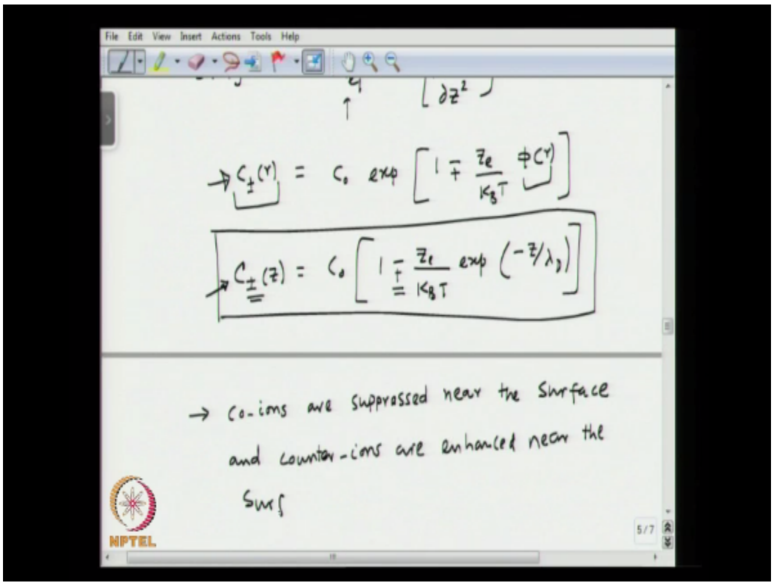

$$\rightarrow C_{\pm}(r) = C_0 \exp\left[1 \mp \frac{ze}{K_BT}\phi(r)\right]$$

$$\boxed{C_{\pm}(z) = C_0\left[1 \mp \frac{ze}{K_BT}\exp\left(-z/\lambda_D\right)\right]}$$

→ co-ions are suppressed near the surface and counter-ions are enhanced near the surf

What we see here, is co-ions are suppressed near surface okay. You can say that if you look at the sign here and there, we can predict this, co-ions are suppressed near the surface and the counter ions are enhanced near the surface okay. So, if you have the wall which is negatively charged then, if you look at the charge distribution inside the liquid, there will be more positive charges close to the wall and it is going to reduce into the bulk and there will be less negative charge close to the wall and it is going to increase into the bulk of the liquid okay.

So, with that next let us talk about the debye layer capacitance. So, as we understand the debye layer stores some charges and because of waste there is capacitance that develops across the debye layer and we try to see what is the value of this capacitance okay. So, let us talk about debye layer capacitance let us first.

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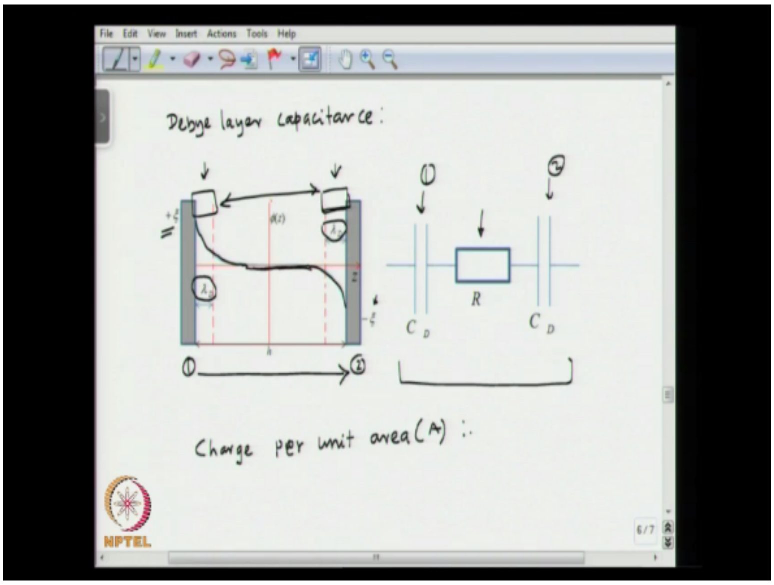

Debye layer capacitance:

Charge per unit area (A) :

So, this is shown pictorially here so we will talk about debye layer capacitance okay. So, you can see here there are 2 plates, 1 plate is as positive zeta potential and the second plate has the negative zeta potential and this is how the potential is going to vary from plate 1 to plate 2, this line okay. So, this is how the potential is going to vary between the 2 walls okay. Now, you have debye layer close to both these walls, this is specified by lambda D okay.

So, what is happening is you have a capacitor configuration here okay, because it is storing charge and you have another capacitor here and then inside the bulk, you have some kind of a register. So, if you look at the electrical equivalent if what is happening between the plate 1 to plate 2, this is how you can represent. So, you have you know capacitor here okay and then you have another capacitor close to wall 2 here and then the bulk of the liquid can be considered as a resistor element okay.

So, you can calculate the charge per unit area at each of these walls.

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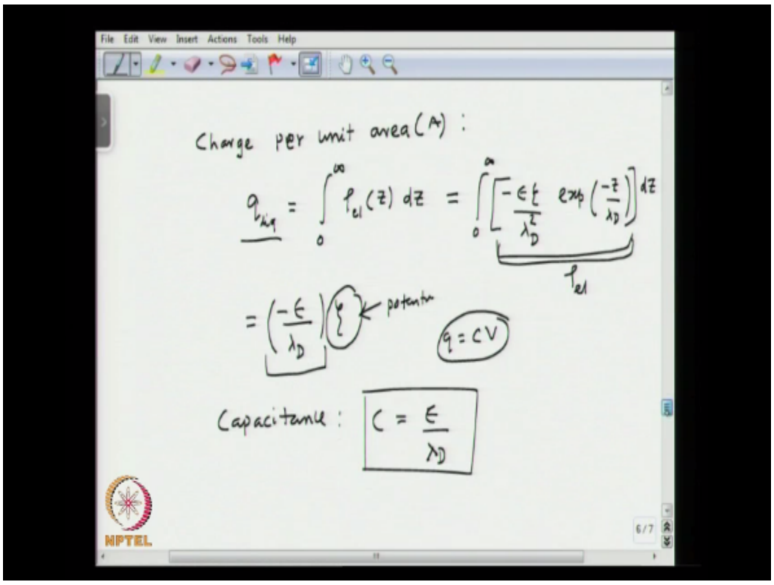

Charge per unit area (A):

$$\underline{q_{liq}} = \int_0^\infty \rho_{el}(z)\,dz = \int_0^\infty \underbrace{\left[-\frac{\epsilon\zeta}{\lambda_D^2}\exp\left(\frac{-z}{\lambda_D}\right)\right]}_{\rho_{el}} dz$$

$$= \underbrace{\left(\frac{-\epsilon}{\lambda_D}\right)}\zeta \leftarrow \text{potential}$$

$$q = CV$$

Capacitance: $\boxed{C = \frac{\epsilon}{\lambda_D}}$

So, you can calculate charge per unit area A and so this is how you would calculate the charge q liquid will be integration 0 to infinity, the variation of the charge density along Z * dZ okay. So, we can 0 to infinity we have an expression for the charge density which is given by - epsilon xi over lambda D square * exponential - Z over lambda D okay * dZ okay. So, this charge density expression we have already derived it here right. So, this is you know the positive and negative ions.

So, you can find out what is going to be the charge density from this what we have written here from here okay. So, you can find the electrical charge density, which will come out to be this okay. So this is the electrical charge density. Now, if we integrate, what you get is - epsilon divided by lambda D * xi okay. So, you are saying charge is given by this ratio here * the zeta potential oaky. So, this acts as a potential, is a zeta potential.

So, you can write capacitance okay. You know q = the charge = capacitance * potential. So, capacitance we can write C is epsilon over lambda D okay.

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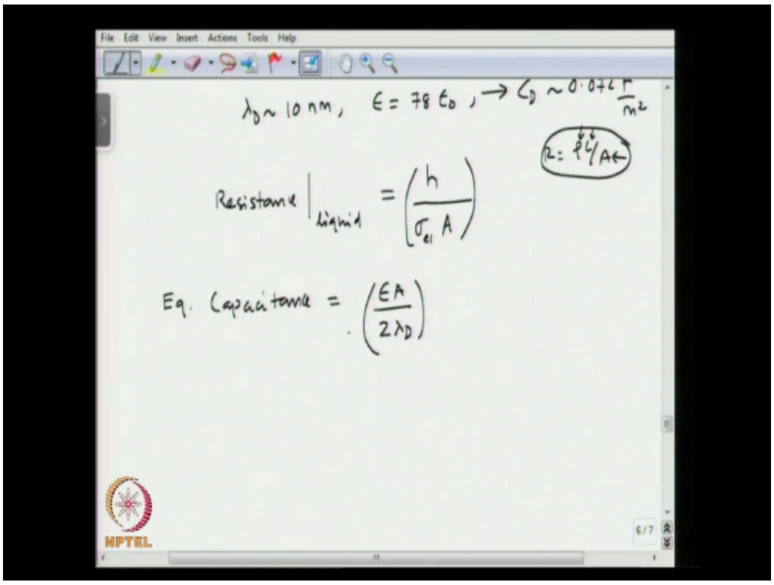

$\lambda_D \sim 10\ nm, \quad \epsilon = 78\ \epsilon_0, \rightarrow C_D \sim 0.072\ \frac{F}{m^2}$

$\boxed{R = \rho L / A}$

$$\text{Resistance}\Big|_{\text{liquid}} = \left(\frac{h}{\sigma_{el} A}\right)$$

$$\text{Eq. Capacitance} = \left(\frac{\epsilon A}{2 \lambda_D}\right)$$

Now, if you use lambda D as about 10 nano meter and it is liquid, so epsilon is about 78 times epsilon not, which is for the free space. Then you can get an expression for, get a value for the capacitance across the debye layer, which is of the order of .072 Faraday per meter square. So, this is the charge we are calculating per unit area of one of this plates okay. Now, we have a liquid which is having finite electrical conductivity okay.

So, the liquid that is present between these 2 plates as got finite electrical conductivity. So, we know it is resistivity also, which is inverse of the electrical conductivity. So, from there we can say the resistance of the liquid will be the thickness divided by electrical. So, resistance is sl over A right. This is resistivity * length divided by the area of cross section. So, 1 over rho is the resistivity * h divided by area. So, this is the resistance okay.

So, this is the resistance of the liquid okay. And the capacitance, so, we have 2 capacitors here okay, they are connected in series okay. So, we can find the equivalent capacitance. So, equivalent capacitance will be epsilon A over 2 lambda D okay.

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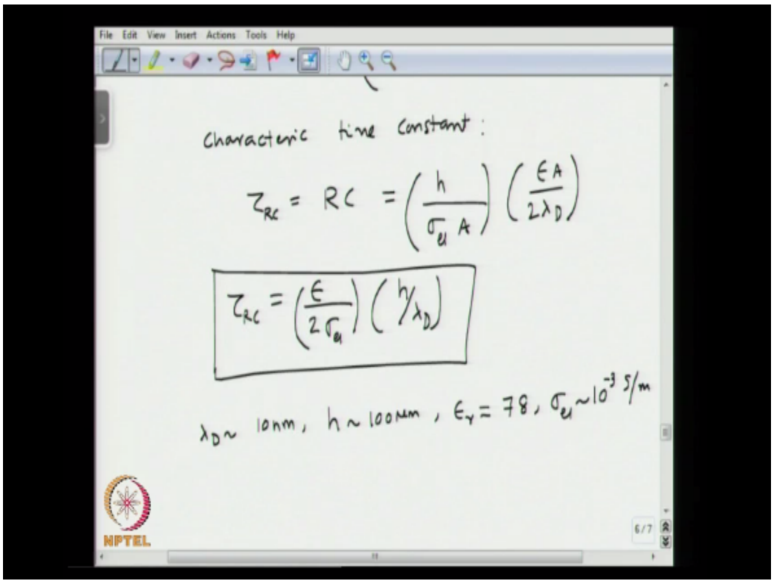

Characteristic time constant:

$$\tau_{RC} = RC = \left(\frac{h}{\sigma_{el} A}\right)\left(\frac{\epsilon A}{2\lambda_D}\right)$$

$$\boxed{\tau_{RC} = \left(\frac{\epsilon}{2\sigma_{el}}\right)\left(h/\lambda_D\right)}$$

$\lambda_D \sim 10\,nm$, $h \sim 100\,\mu m$, $\epsilon_r = 78$, $\sigma_{el} \sim 10^{-3}\,S/m$

So, we can define a characteristic time constant, which is tau RC = resistance * capacitance okay. So, which = h over electrical conductivity * area, that is RC is epsilon A over 2 lambda D right. So, you can write this as epsilon / 2 * electrical conductivity * h over lambda D. So, this is the expression for the time constant. So, this is the time constant for this system, where we have 2 capacitors and 1 resistors in series.

So, if we say lambda D is up the order of 10 nano meter and the height h is up the order of 100 micron, sorry the h, that we define for the resistance is the resistance of the channel, this is lambda D okay, h is here. So, this is h, this is basically the gap between the channel, because lambda D is very small. So, this is shown here, this is h. so, that is the resistance of the liquid. So, h is about 100 micron and the relative permittivity, assuming it is water, so it is about 78 and electrical conductivity is about 10 to the power -3 siemens per meter.

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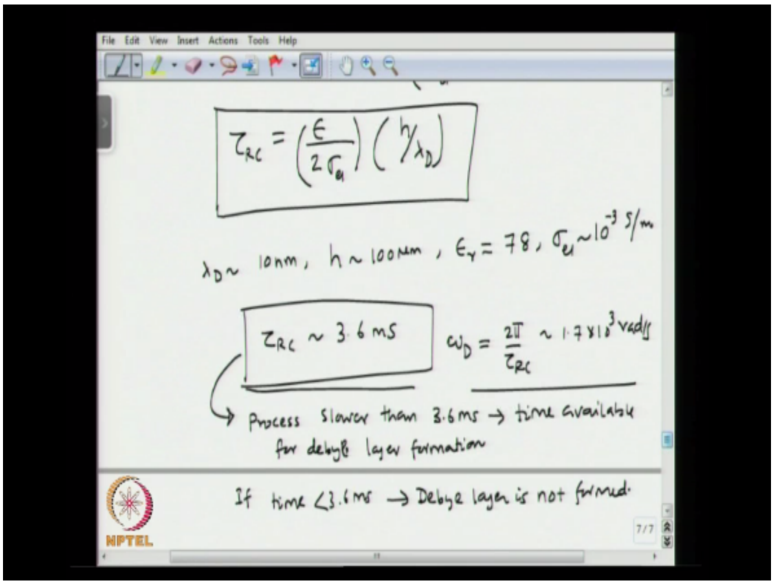

$$\boxed{\tau_{RC} = \left(\frac{\epsilon}{2\sigma_{el}}\right)\left(h/\lambda_D\right)}$$

$\lambda_D \sim 10\,nm$, $h \sim 100\,\mu m$, $\epsilon_r = 78$, $\sigma_{el} \sim 10^{-3}\,S/m$

$$\boxed{\tau_{RC} \sim 3.6\,ms} \qquad \omega_D = \frac{2\pi}{\tau_{RC}} \sim 1.7 \times 10^{3}\,rad/s$$

→ Process slower than 3.6 ms → time available for debye layer formation

If time < 3.6 ms → Debye layer is not formed.

So, from there we can find tau RC is up the order of 3.6 millisecond and we can find the angular frequency also 2 pi divided by tau RC, which is about 1.7 * 10 power 3 radian per second okay. So, from this characteristic time constant what we understand that, if we have a process okay, let us say you are trying to use AC electro osmosis, if the frequency of the applied voltage is such that the time available for the debye layer to form is < 3.6 millisecond, then the debye layer will not be able to form okay.

So, you need at least 3.6 millisecond for the debye layer to form to make the electro osmotic action to happen okay. If you use AC electro osmosis and the frequency is sufficiently high that the time available is < 3.6 millisecond, then it will not work. The electro osmotic pumping will not work okay. Considering this example for the height and lambda D and the liquid that we consider okay. So, here what we understood is that, process slower than 3.6 millisecond you have time available for debye layer okay.

And if the time is < 3.6 millisecond debye layer is not found okay. So, that is an important conclusion we learn from by talking about the debye layer capacitance okay. So, let us stop here.