Colloids and Surfaces
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Lecture – 33
Potential Distribution Near Spherical Surfaces: Solution to Linearised Poisson – Boltzmann Equation

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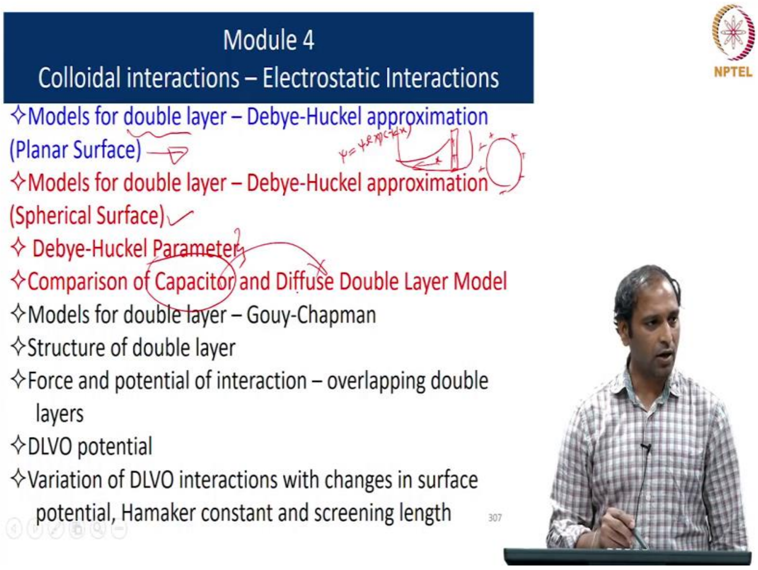

Module 4
Colloidal interactions – Electrostatic Interactions

✧Models for double layer – Debye-Huckel approximation (Planar Surface)
✧Models for double layer – Debye-Huckel approximation (Spherical Surface)
✧ Debye-Huckel Parameter
✧Comparison of Capacitor and Diffuse Double Layer Model
✧Models for double layer – Gouy-Chapman
✧Structure of double layer
✧Force and potential of interaction – overlapping double layers
✧DLVO potential
✧Variation of DLVO interactions with changes in surface potential, Hamaker constant and screening length

$\psi = \psi_0 \exp(-\kappa x)$

So we are, you are still looking at electrical double layer models. So, what we have done in the last class was to look at working out solution for a case where you have a planar surface that is charged, that is, you know, in a bath of electrolyte. We are trying to look at how does the potential varies function of separation distance x. And then we found that psi goes as psi 0 exponent - kappa x. That is what we derived.

That is we took a case of planar you know, surface. So what we are going to look at today is a case where, instead of a planar surface, I have a curved surface, if I have a spherical particle, for example, and if that is, you know, charged, we will think a little bit about how do we derive an expression for how does the potential fall with distance from the spherical surface. And then we will talk about a parameter that comes out of all the analysis that we have done, it is what is called as Debye Huckel parameter.

And finally, we will try and compare, we looked at capacitor model, which I said is one of the most simple model that people have developed, we try and compare that with diffuse double layer model. And by that comparison, you can actually draw some nice inferences. So we will discuss a little bit about that.

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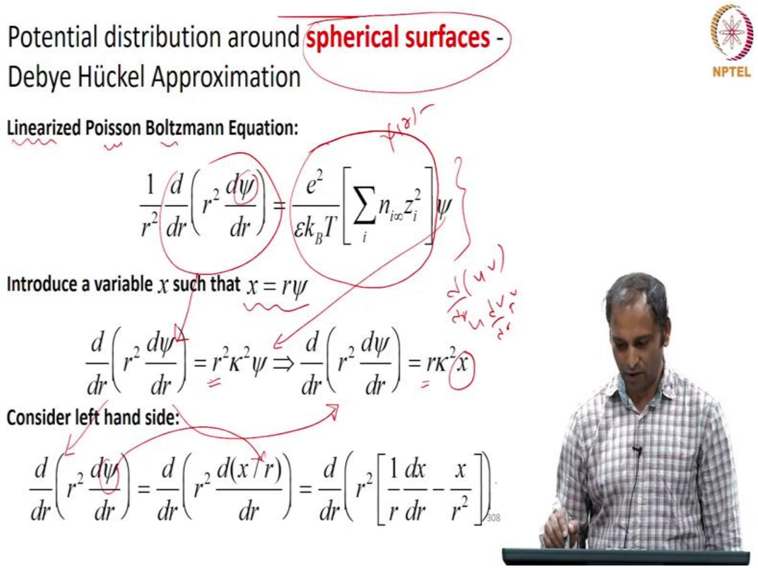

Potential distribution around spherical surfaces - Debye Hückel Approximation

Linearized Poisson Boltzmann Equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty}z_i^2\right]\psi$$

Introduce a variable x such that $x = r\psi$

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=r^2\kappa^2\psi \Rightarrow \frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=r\kappa^2 x$$

Consider left hand side:

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(r^2\frac{d(x/r)}{dr}\right)=\frac{d}{dr}\left(r^2\left[\frac{1}{r}\frac{dx}{dr}-\frac{x}{r^2}\right]\right)$$

So, briefly as mentioned this yesterday, this is now the linearized Poisson Boltzmann equation. But in the case, where I have a spherical surface that is charged, and I would like to look at the variation of psi with r and so to do so we start with the linearized PB equation. And we can do some simple modifications. I can, if I substitute for x as r time psi, there is just a simple steps because we would like to have an next have a differential equation.

Which I can eventually solve and then get an expression for how does psi vary as a function of r i that is what we are after. So we do a simple substitution, if you substitute x = r psi, that is this term here, I keep it the same, I will take r square to the right hand side. So therefore I have r square and this we know is kappa square. That is how we defined yesterday that has kappa square and you have psi. So therefore, I am going to keep the left hand side same the right hand side, instead of r time psi, I am going to replace it with x.

r time psi is going to be x, and I am going to retain 1 r and kappa square, that is what we done. This term d / dr of r square d psi / dr, I can actually write it as d / dr of r square instead of psi, I can replace it with x / r. Therefore, this become d / dr of r square into 1 - r, 1 / r into dx / dr. So, this is basically you know, if you have know d / dr of uv. It is u into dv / dr + v. So we are going to use a chain rule. That is how this is done therefore, this becomes d / dr of r square into 1 over r into dx / dr - x into 1 over r square - 1 over r square therefore, you get the right hand side.

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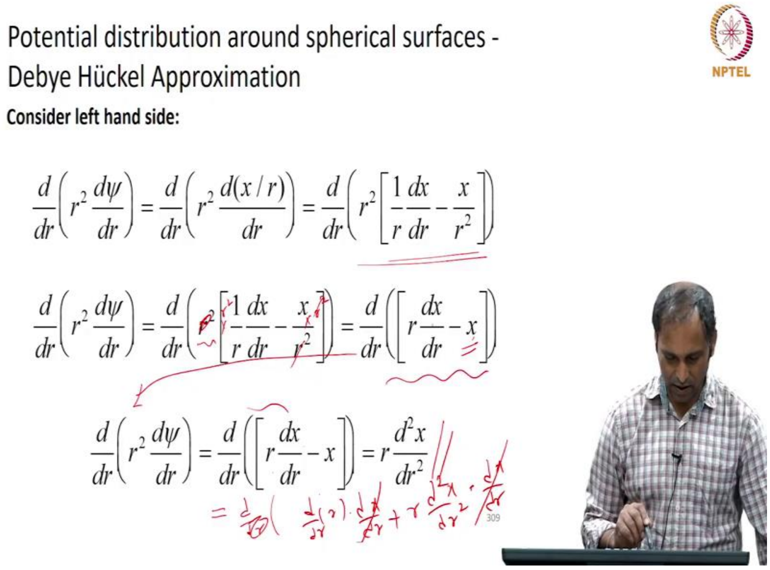

Potential distribution around spherical surfaces - Debye Hückel Approximation

Consider left hand side:

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(r^2\frac{d(x/r)}{dr}\right)=\frac{d}{dr}\left(r^2\left[\frac{1}{r}\frac{dx}{dr}-\frac{x}{r^2}\right]\right)$$

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(r^2\left[\frac{1}{r}\frac{dx}{dr}-\frac{x}{r^2}\right]\right)=\frac{d}{dr}\left(\left[r\frac{dx}{dr}-x\right]\right)$$

$$\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d}{dr}\left(\left[r\frac{dx}{dr}-x\right]\right)=r\frac{d^2x}{dr^2}$$

$$=\frac{d}{dr}\left(\frac{d}{dr}(r)\cdot\frac{dx}{dr}+r\frac{d^2x}{dr^2}-\frac{dx}{dr}\right)$$

So that is what is written here, this is what we essentially obtained. Now, because I have r square you know, I can multiply you know, I can take the r square inside therefore, this becomes multiplied by r square, multiply by r square and this r square is as we get cancelled. So, I have x here and this becomes r into dx / dr, just a simple manipulation. Therefore, d / dr of r square d psi / dx dr essentially is d / dr of r times dx / dr - x.

I can further expand this I can write this as d / dr of if I so, I can write this as dr. Again again I use the product rule. So d / dr of r into dx / dr + r into d square x / dr square - dx / dr. dx / dr and dx / dr gets cancelled essentially you are left with r into d square x / dr square.

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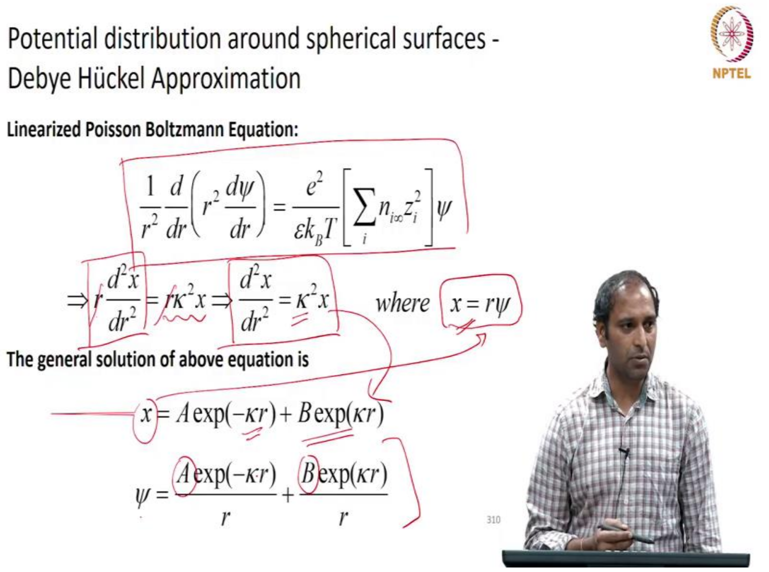

Potential distribution around spherical surfaces - Debye Hückel Approximation

Linearized Poisson Boltzmann Equation:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{e^2}{\varepsilon k_BT}\left[\sum_i n_{i\infty}z_i^2\right]\psi$$

$$\Rightarrow r\frac{d^2x}{dr^2}=r\kappa^2x\Rightarrow\frac{d^2x}{dr^2}=\kappa^2x \quad \text{where} \quad x=r\psi$$

The general solution of above equation is

$$x=A\exp(-\kappa r)+B\exp(\kappa r)$$

$$\psi=\frac{A\exp(-\kappa r)}{r}+\frac{B\exp(\kappa r)}{r}$$

So, therefore, essentially what we have done is, so, therefore, this is the equation that we started off with, it ultimately becomes with the simple manipulation becomes r into d square x / dr square is equal to the right hand side that we had right? r into k kappa square into x. Because, again we are defined x as r time psi. Therefore, I mean that is what we define. Therefore, d square x / dr square becomes kappa square into x because you know your x r and r gets cancelled here.

So essentially I have a simple differential equation now, which I can solve, I know that the solution for this particular differential equation is x is A exponent - kappa r + B exponent kappa r. That is the, this solution. And therefore, but because I know that x and psi are related, therefore, psi becomes A exponent - kappa r / r + B exponent kappa r / r. That is the solution of this differential equation. And of course, you would have to solve it. I mean, I have to get these constants A and B. For that I am going to use the boundary conditions.

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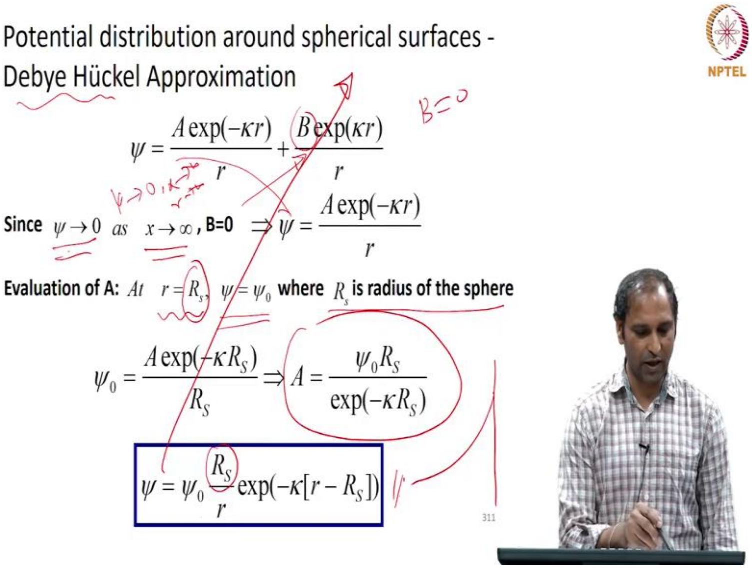

Potential distribution around spherical surfaces - Debye Hückel Approximation

$$\psi = \frac{A\exp(-\kappa r)}{r} + \frac{B\exp(\kappa r)}{r}$$

B=0

Since $\psi \to 0$ *as* $x \to \infty$, B=0 $\Rightarrow \psi = \frac{A\exp(-\kappa r)}{r}$

Evaluation of A: *At* $r = R_s$, $\psi = \psi_0$ where R_s is radius of the sphere

$$\psi_0 = \frac{A\exp(-\kappa R_S)}{R_S} \Rightarrow A = \frac{\psi_0 R_S}{\exp(-\kappa R_S)}$$

$$\boxed{\psi = \psi_0 \frac{R_S}{r}\exp(-\kappa[r - R_S])}$$

The boundary conditions, that we have is that psi tends to 0 as x tends to infinity. And if you look at this expression, this condition will only be satisfied if B = 0. The fact that psi you know tends to 0 if x tends to infinity, are r tends to infinity is only satisfied if B = 0 therefore, the solution becomes psi = A exponent of - kappa r / r. And if I use the other boundary condition, that is at the surface of the spherical particle, for example, if the size of the spherical particle that I am considering is Rs.

There is a radius of the spherical particle at r = R s, psi has to be psi 0. Where, R s is the radius of the spherical particle. If I substitute for that, then I can get the constant A out, therefore, psi goes as psi 0 r / capital Rs / r exponent of - kappa into r - capital R s. That is the solution we get. So again, like similar to the case of spherical linear, you know, for the case of flat surfaces, the potential in the case of spherical surfaces also, you know, falls exponentially with distance that is all this captures.

The functional form, whether it is a planar surface, or the spherical surface is very much similar. That is also because of the fact that we are considered a linearized version of the model. So that is the that is how you this is an expression that tells you something about the potential distribution around a spherical surface again, this is a Debye Huckel approximation because we are consider the case of low potential that is when we can have a linearized version of the Poisson Boltzmann equation.

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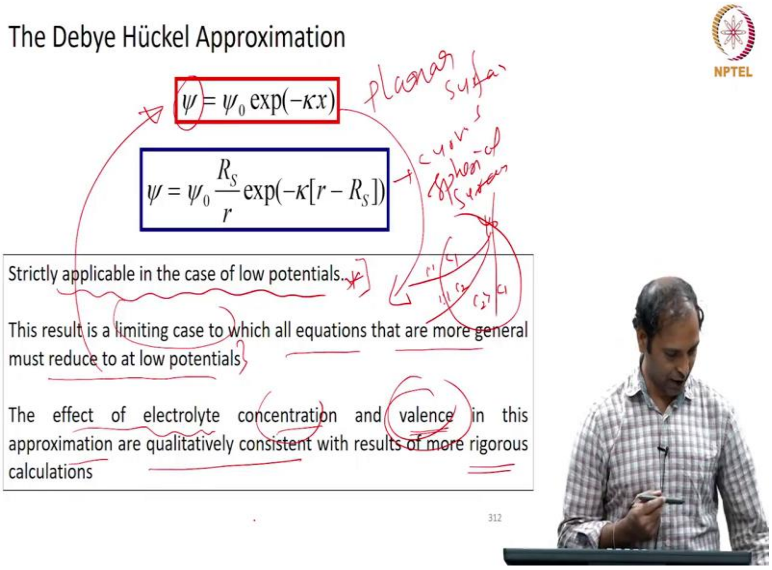

The Debye Hückel Approximation

$$\boxed{\psi = \psi_0 \exp(-\kappa x)}$$

planar surfaces

$$\boxed{\psi = \psi_0 \frac{R_S}{r} \exp(-\kappa[r - R_S])}$$

curved / spherical surfaces

Strictly applicable in the case of low potentials.

This result is a limiting case to which all equations that are more general must reduce to at low potentials

The effect of electrolyte concentration and valence in this approximation are qualitatively consistent with results of more rigorous calculations

So that is. That is just a comparison. That is for the planar surfaces. That is for curved or spherical surfaces. So, a couple of things to keep in mind when you are looking at these expressions are these are strictly applicable in low potential cases. That is what we have assumed throughout this derivation that is very important. And so, this result is a limiting case to which all equations that are more general must reduce to at low potential that means if I if I have a way of.

You know, deriving a similar expression for how psi varies with distance for more general case you know what I mean by more general case is you could have the potential need not be low if we have a very high potential case or if you have cases where I have variation both in x y and z direction. So, if you have a very general expression like that, and if I take that expression and then put in the condition that look.

I have an expression which is a general expression. Now I am going to apply the condition there is a low potential. So, if you use that all these equation that you develop should basically give rise to these limiting equations.

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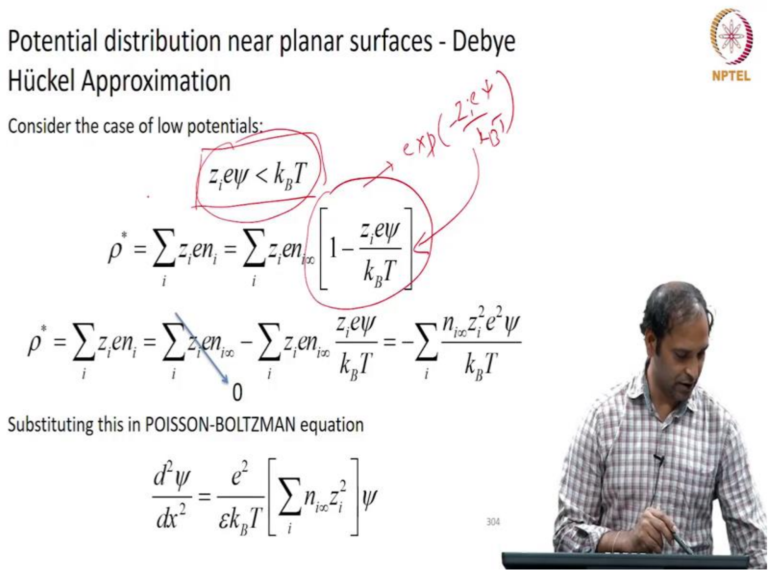

Potential distribution near planar surfaces - Debye Hückel Approximation

Consider the case of low potentials:

$$\boxed{z_i e\psi < k_B T}$$

$$\rho^* = \sum_i z_i e n_i = \sum_i z_i e n_{i\infty}\left[1 - \frac{z_i e\psi}{k_B T}\right] \quad \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

$$\rho^* = \sum_i z_i e n_i = \underbrace{\sum_i z_i e n_{i\infty}}_{0} - \sum_i z_i e n_{i\infty}\frac{z_i e\psi}{k_B T} = -\sum_i \frac{n_{i\infty} z_i^2 e^2 \psi}{k_B T}$$

Substituting this in POISSON-BOLTZMAN equation

$$\frac{d^2\psi}{dx^2} = \frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right]\psi$$

No, when I say see, this is, let me go back to that. So, what do I mean by low potential. So, when we wrote so, I said this was an exponential term. This was actually exponent - z i e psi / k$_B$ T, I can write this in this form only when z i e psi is < k$_B$ T.

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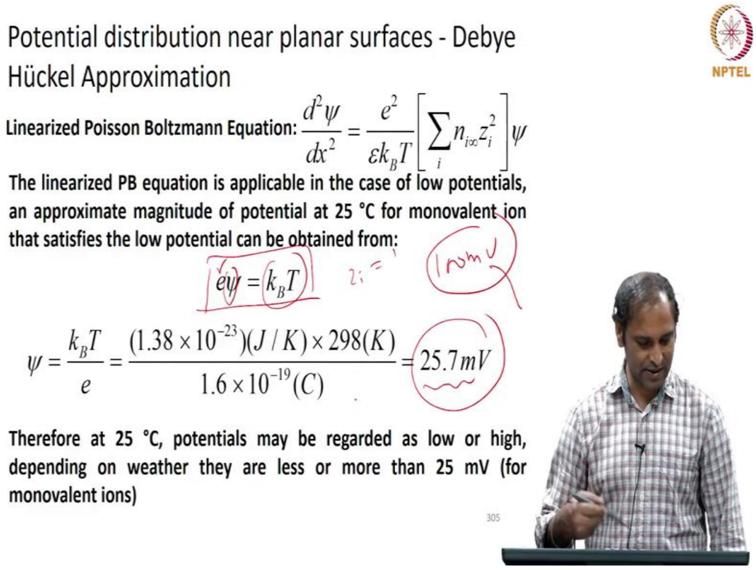

Potential distribution near planar surfaces - Debye Hückel Approximation

Linearized Poisson Boltzmann Equation: $\frac{d^2\psi}{dx^2} = \frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right]\psi$

The linearized PB equation is applicable in the case of low potentials, an approximate magnitude of potential at 25 °C for monovalent ion that satisfies the low potential can be obtained from:

$$\boxed{e\psi = k_B T} \quad z_i = 1 \quad 1\,mV$$

$$\psi = \frac{k_B T}{e} = \frac{(1.38\times10^{-23})(J/K)\times 298(K)}{1.6\times10^{-19}(C)} = 25.7\,mV$$

Therefore at 25 °C, potentials may be regarded as low or high, depending on weather they are less or more than 25 mV (for monovalent ions)

So that is how the low potential was derived that was thought of, and then we said that if I am working with the monovalent because you know this there was z i here, if I assume that I am working with a monovalent ions, z i is going to be 1. So, this limiting, you know, so, basically, I can estimate a potential, if I know what is the charge of the electron and the thermal energy, that potential turns out to be something like this.

And, and this is the limiting potential, below which I can say that the potentials are low potential. So, typically, a potential like this, I can say that the particles are reasonably less charged, you know, compared to cases, if I have like 100 millivolts, as a potential surface potential, for example, or zeta potential, that would be really highly charged, Whereas, if I have potentials, which are 20, 25 millivolts, or even lower than that, you know, you can take these cases to be low potential cases where I can.

You know, use this linearized solution of linearized Poisson Boltzmann equation to really understand the potential variation with separation distance. And, and as we are going to do, as we go to discuss later, how this potential varies with distance is really important. I do not have a solution here. So, let me just go back.

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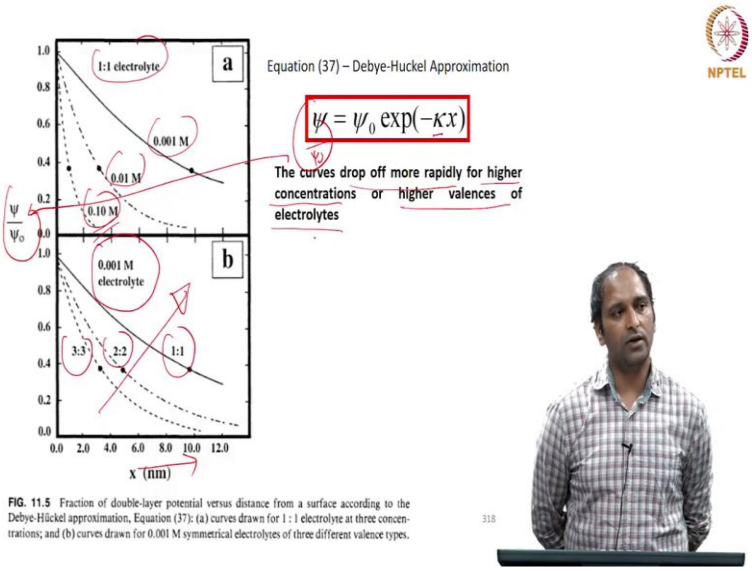

Equation (37) – Debye-Huckel Approximation

$$\boxed{\psi = \psi_0 \exp(-\kappa x)}$$

The curves drop off more rapidly for higher concentrations or higher valences of electrolytes

FIG. 11.5 Fraction of double-layer potential versus distance from a surface according to the Debye-Hückel approximation, Equation (37): (a) curves drawn for 1 : 1 electrolyte at three concentrations; and (b) curves drawn for 0.001 M symmetrical electrolytes of three different valence types.

So, how this potential varies with separation distance is really important, because that is what is going to determine the electrical double layer repulsion between the particles, we will discuss a little bit of that in the next you know, maybe a few lectures. So, again to recap, so, they are certainly applicable for low potential and this is a limiting case to which all the more general solutions should reduce to when we invoke the condition of low potential case and so, these expressions.

So, what these expressions also capture is the effect of electrolyte concentration and the valency. So, let me put it this way. So, these expressions, they capture the fact that psi varies in a particular way, when you have when the concentration of electrolyte in the solution changes or when the valency of ions in the solution changes. So, that means, if I have like say, let me put it this way.

So, if I have potential if this is psi 0 say that you know, the potential varies in this particular way with if I use say 1 is to1 electrolyte. Now, if I use the same electrolyte, but I go for a higher concentration. So, they say this is concentration 1. So, this is again 1 is to 1 the concentration to where concentration 2 is greater than concentration 1. So, there is a particular way, this potential will vary with distance as you change the concentration of the salt or as you change the valency of the ions that you have put in the solution.

So, these in the limiting cases, still capture the variation of psi 0 with separation distance, in a consistent way. We which is also captured by more rigorous calculation, the only thing is the magnitude may be slightly off, but the way psi varies with electrolyte concentration and valency is still qualitatively very similar, whether you use a rigorous model or these limiting cases, that is the point is that mean.

So the effect of electric concentration and valency in this approximation, or qualitatively consistent with the results of more rigorous calculation, there may be quantitative mismatch, because you have invoked the low potential case. However, in terms of the nature of variation, they are qualitatively they are similar to the more rigorous calculations.

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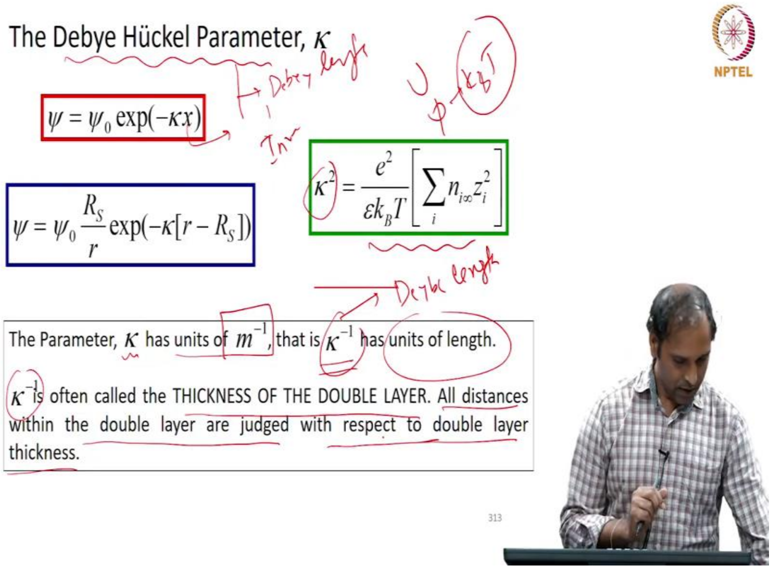

The Debye Hückel Parameter, κ

$$\psi = \psi_0 \exp(-\kappa x)$$

$$\psi = \psi_0 \frac{R_S}{r} \exp(-\kappa [r - R_S])$$

$$\kappa^2 = \frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right]$$

The Parameter, κ has units of m^{-1}, that is κ^{-1} has units of length.

κ^{-1} is often called the THICKNESS OF THE DOUBLE LAYER. All distances within the double layer are judged with respect to double layer thickness.

Now, in these expressions, this kappa square, we had taken it as it turns out, during the inner simplification kappa square comes out as epsilon square divided by e square divided by epsilon k_B T multiplied by summation of n i infinity z i square. Let us look at what is the unit of what is the unit of kappa? I will go by a simpler way of doing this. You look at this expression psi is equal to psi 0 exponent - kappa x x will have units of length therefore, kappa should have units of length inverse.

So, the parameter kappa should have a unit of meter inverse or k inverse should have a length unit of length. This kappa inverse is what is called as Debye Huckel parameter. That is because this comes out when you are looking at Debye Huckel approximation, the low potential case that is why it is called a Debye Huckel parameter and people often refer to k inverse as the thickness of the double layer.

Thickness of the double layer people also call this parameter as Debye Huckel. So, k inverse which has units of length is called as Debye length and k which has units of meter inverse is called inverse Debye length and stuff. So, but these are the names that people use interchangeably depending upon you know, different textbook and different. And so, like we mentioned that we always kind of compare the interaction potential U or phi, we always kind compare and they say something about what is the potential with respect to k_B T.

I mentioned that whenever you do any interaction potential calculation is always a good idea to scale your interactions with the thermal energy. Because that will give you a kind of a magnitude which you can easily connect to or similarly, all distances within the double layer are judge with respect to the double layer thickness. So, in many you are working with electrical double layer interactions in charge dispersions.

You will always ask a question is to what is the size of the particle compared to k inverse, what is the distance between the particles compared to k inverse. So therefore, so all the distances within the double layer, and, you know, all the interactions, the range of interaction that you talk about in electrical double layer interactions, you can people always try their judge with respect to the distance of the thickness of this double layer.

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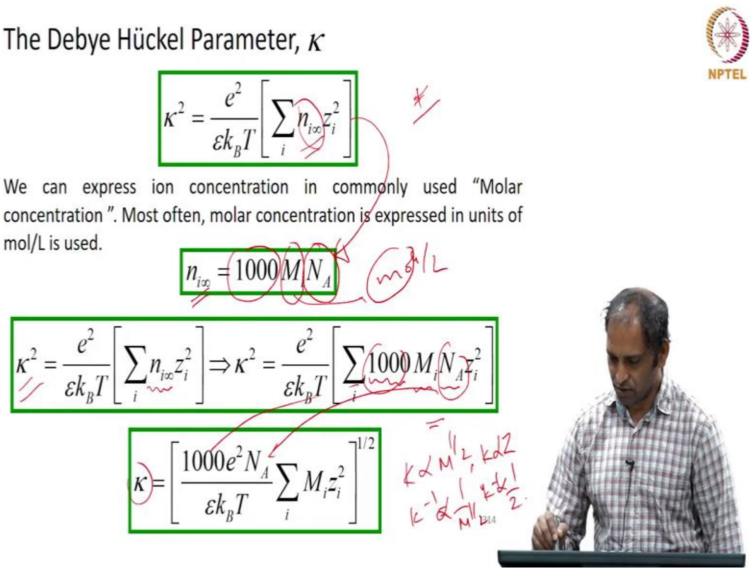

The Debye Hückel Parameter, κ

$$\kappa^2 = \frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right]$$

We can express ion concentration in commonly used "Molar concentration". Most often, molar concentration is expressed in units of mol/L is used.

$$n_{i\infty} = 1000 M N_A$$

mol/L

$$\kappa^2 = \frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right] \Rightarrow \kappa^2 = \frac{e^2}{\varepsilon k_B T}\left[\sum_i 1000 M_i N_A z_i^2\right]$$

$$\kappa = \left[\frac{1000 e^2 N_A}{\varepsilon k_B T}\sum_i M_i z_i^2\right]^{1/2}$$

$\kappa \propto M^{1/2}$, $\kappa \propto z$

$\kappa^{-1} \propto \frac{1}{M^{1/2}}$, $\kappa^{-1} \propto \frac{1}{z}$

Now, this n i infinity is the concentration of ions, that is, that is the number of ions per unit volume. That is what we had mentioned. You can express, you can actually kind of, just rearrange this expression and then express K square in terms of more measurable you know quantity. So, I can this n i infinity which is the concentration of ions in the solution, you know, you can express this in terms of the molarity of the salt that is added.

Because molarity will have units of moles per liter and because I want to convert that into moles per meter cube, i multiplied by 1000 and because I have moles, I would like to convert that into the number of, I would like to convert that into number of ions, therefore, I am multiplying by Avogadro number. Therefore, kappa square becomes e square divided by epsilon k B T, I can replace n i infinity with 1000 Mi N_A and z i square and N_A being a constant.

I can just take it out and 1000 also I can take it out therefore, kappa becomes thousand a square N_A divided by epsilon k_B T summation of I Mi z i square to the power half. So, I have list out so, that is kappa. This so far we are writing kappa square. So, the kappa essentially is the entire thing to power half.

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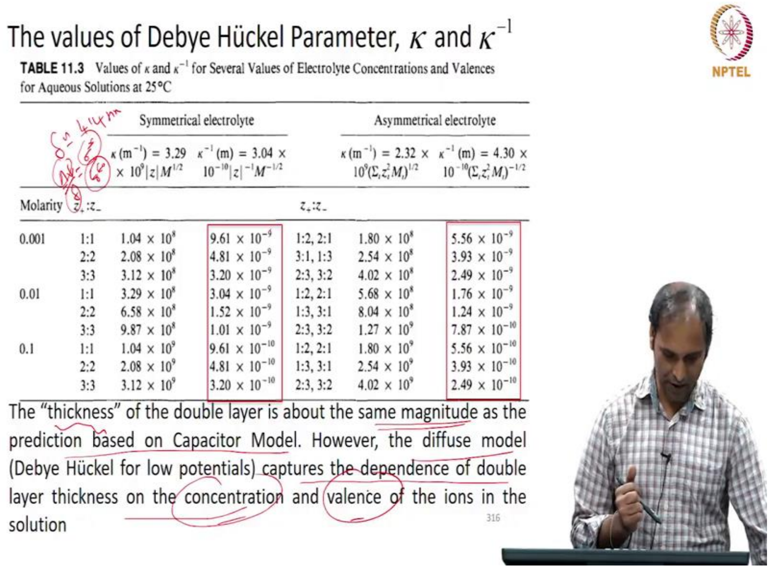

The values of Debye Hückel Parameter, κ and κ^{-1}

TABLE 11.3 Values of κ and κ^{-1} for Several Values of Electrolyte Concentrations and Valences for Aqueous Solutions at 25°C

$\delta = 4.4$ nm

		Symmetrical electrolyte			Asymmetrical electrolyte	
		$\kappa\,(\mathrm{m}^{-1}) = 3.29 \times 10^9 \lvert z\rvert M^{1/2}$	$\kappa^{-1}\,(\mathrm{m}) = 3.04 \times 10^{-10} \lvert z\rvert^{-1} M^{-1/2}$		$\kappa\,(\mathrm{m}^{-1}) = 2.32 \times 10^9 (\Sigma_i z_i^2 M_i)^{1/2}$	$\kappa^{-1}\,(\mathrm{m}) = 4.30 \times 10^{-10} (\Sigma_i z_i^2 M_i)^{-1/2}$
Molarity	$z_+ : z_-$			$z_+ : z_-$		
0.001	1:1	1.04×10^8	9.61×10^{-9}	1:2, 2:1	1.80×10^8	5.56×10^{-9}
	2:2	2.08×10^8	4.81×10^{-9}	3:1, 1:3	2.54×10^8	3.93×10^{-9}
	3:3	3.12×10^8	3.20×10^{-9}	2:3, 3:2	4.02×10^8	2.49×10^{-9}
0.01	1:1	3.29×10^8	3.04×10^{-9}	1:2, 2:1	5.68×10^8	1.76×10^{-9}
	2:2	6.58×10^8	1.52×10^{-9}	1:3, 3:1	8.04×10^8	1.24×10^{-9}
	3:3	9.87×10^8	1.01×10^{-9}	2:3, 3:2	1.27×10^9	7.87×10^{-10}
0.1	1:1	1.04×10^9	9.61×10^{-10}	1:2, 2:1	1.80×10^9	5.56×10^{-10}
	2:2	2.08×10^9	4.81×10^{-10}	1:3, 3:1	2.54×10^9	3.93×10^{-10}
	3:3	3.12×10^9	3.20×10^{-10}	2:3, 3:2	4.02×10^9	2.49×10^{-10}

The "thickness" of the double layer is about the same magnitude as the prediction based on Capacitor Model. However, the diffuse model (Debye Hückel for low potentials) captures the dependence of double layer thickness on the concentration and valence of the ions in the solution

So, this is some typical values. What is this is a table that I have taken from the book this is the molarity of the salt different salt concentration 0.001 molar 0.01 molar 0.1 molar and this is a z is to z electrolyte, This is for symmetric electrolyte 1 is to 1, 2 is to 2, 3 is to 3 these are all symmetric electrolytes. The next few columns are for asymmetric electrolyte, that is again z is to z but you could have 1 is to 2 or 2 is to 1 electrolyte or 3 is to 1 or 1 is to 3 these are asymmetric electrolyte.

And these are kappa values, that is a Debye Huckel parameter and this is kappa inverse that is the inverse you know or the double layer thickness, which has units of meter. And what is interesting to note is that all these numbers, if you look at all these numbers, they are again of the order of nanometers they are of the order of nanometer that is again important to keep in mind whenever you do any calculation, where you are being asked to calculate kappa inverse.

If you get values which are microns are really large that means there is something wrong with your calculation because kappa inverse values are supposed to be in the nanometer size range. And so, if I look at these numbers if I look at these numbers one comment that I can make is that the thickness of the double layer is about the same magnitude as the prediction based on the capacitor model if you remember the calculation that we made if we took a simple case and we showed that the thickness delta.

The delta there is a separation distance between the plates of the capacitor we said it was coming to be somewhere 4.4 nanometers or something like that. So, if you look up these numbers, the thickness of the double layer is of the same magnitude as that predicted with a capacitor model. However, the diffuse model captures the dependence of double layer thickness on the concentration and the valence of the ions, which is not there for the capacitor model.

For the capacitor model, delta was fixed by the potential drop, it was fixed with a potential drop. It was fixed by the dielectric constant the medium it was fixed by the sigma star, which is the surface charge density, because we had something like del psi / delta was going as sigma star divided by epsilon, epsilon 0. Epsilon r epsilon 0, I think that is what that was the expression that we had. So, this delta is fixed by the potential drop, the surface charge density and the permittivity.

You know, constant of the medium that you have between the plates. However, so the capacitor model did not capture the variation of delta with the concentration and the valency of ions is the solution. However, the diffused double layer model does you know capture that that is one of the differences.

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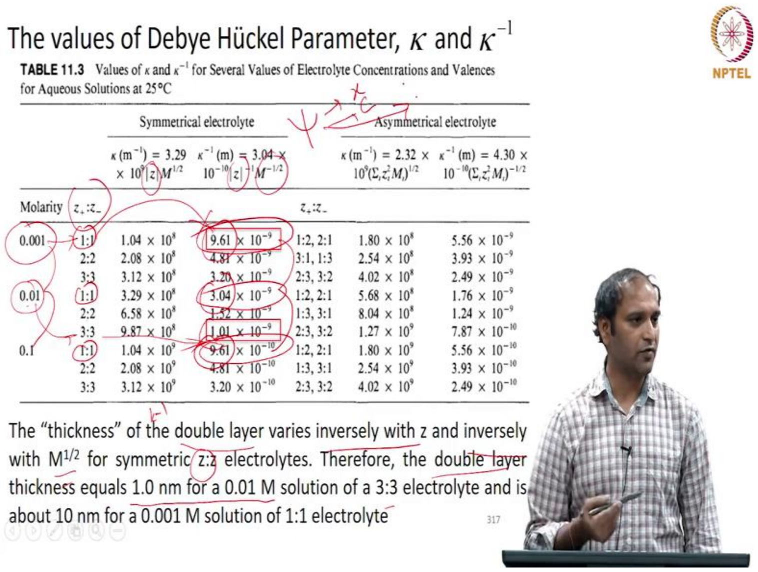

The values of Debye Hückel Parameter, κ and κ^{-1}

TABLE 11.3 Values of κ and κ^{-1} for Several Values of Electrolyte Concentrations and Valences for Aqueous Solutions at 25°C

		Symmetrical electrolyte			Asymmetrical electrolyte	
		$\kappa\,(\mathrm{m}^{-1}) = 3.29 \times 10^9 \lvert z\rvert M^{1/2}$	$\kappa^{-1}\,(\mathrm{m}) = 3.04 \times 10^{-10} \lvert z\rvert^{-1} M^{-1/2}$		$\kappa\,(\mathrm{m}^{-1}) = 2.32 \times 10^9 (\Sigma_i z_i^2 M_i)^{1/2}$	$\kappa^{-1}\,(\mathrm{m}) = 4.30 \times 10^{-10} (\Sigma_i z_i^2 M_i)^{-1/2}$
Molarity	$z_+:z_-$			$z_+:z_-$		
0.001	1:1	1.04×10^8	9.61×10^{-9}	1:2, 2:1	1.80×10^8	5.56×10^{-9}
	2:2	2.08×10^8	4.81×10^{-9}	3:1, 1:3	2.54×10^8	3.93×10^{-9}
	3:3	3.12×10^8	3.20×10^{-9}	2:3, 3:2	4.02×10^8	2.49×10^{-9}
0.01	1:1	3.29×10^8	3.04×10^{-9}	1:2, 2:1	5.68×10^8	1.76×10^{-9}
	2:2	6.58×10^8	1.52×10^{-9}	1:3, 3:1	8.04×10^8	1.24×10^{-9}
	3:3	9.87×10^8	1.01×10^{-9}	2:3, 3:2	1.27×10^9	7.87×10^{-10}
0.1	1:1	1.04×10^9	9.61×10^{-10}	1:2, 2:1	1.80×10^9	5.56×10^{-10}
	2:2	2.08×10^9	4.81×10^{-10}	1:3, 3:1	2.54×10^9	3.93×10^{-10}
	3:3	3.12×10^9	3.20×10^{-10}	2:3, 3:2	4.02×10^9	2.49×10^{-10}

The "thickness" of the double layer varies inversely with z and inversely with $M^{1/2}$ for symmetric z:z electrolytes. Therefore, the double layer thickness equals 1.0 nm for a 0.01 M solution of a 3:3 electrolyte and is about 10 nm for a 0.001 M solution of 1:1 electrolyte

So, the other influence that you can draw if you go back and look at you know, this expression is that k the kappa. It varies as M power half you know and it varies as proportional to z or kappa inverse is inversely proportional to M, the concentration of the electrolyte to the power half or kappa inverse is inversely proportional to z. So, that again is kind of. So, if you look at these values. So, this is a case where I have like if you look at some typical numbers are given.

So, this statement we already made the thickness of the double layer that is kappa inverse it varies inversely with Z that comes straight away from the expression that you had it varies inversely with M power half again I can make the statement only for z is to z electrolyte. So, that is again here it goes as inverse z kappa inverse goes as 1 over z and m power half minus half. But however, for the non-symmetric electrolyte is a little bit more complicated.

And the double layer thickness equals to about 1. If you look at this expression, so, I take 0.01 molar. And for 3 is to 3 electrolyte, the double layer thickness is about 1 nanometer. However, if I take 0.001 molar electrolyte and if it is 1 is to 1 electrolyte, the double layer thickness is about 10 nanometre, so you can get these numbers and think a little bit about how does so, essentially, what I am trying to tell is that if I compare for the so let us think about.

So, 3 cases 0.001, 0.01 and 0.1. Let us stick to 1 is to 1 electrolyte. I am keeping the same type of electrolyte 1 is to 1, but however, we are changing the concentration. Therefore, in one case, the double layer thickness is about 10 nanometer and I increase the salt concentration the double layer thickness becomes 3 nanometer, I increase the concentration further the double layer thickness becomes over 1 nanometer about this 9.61 10 power - 10 is 0.9.

So, therefore, if I keep the type of electrolyte same if I increase the concentration from 0.01 to 0.01 the double layer thickness goes from about 10 to about 3 to 1, it was 10 nanometer here is 3 nanometers there and it is about 1 nanometer here. So, basically this basically the formalism that we have done the Debye Huckel approximation essentially captures. How does both the potential vary with distance.

And how does it vary with the electrolyte concentration, how does it vary with the type of electrolyte that you have used these are the you know. So, this is a again a just a plot whatever I mentioned you know the previous last few seconds So, similar so what you are what is plotted is a scaled potential. So, I can divide this by psi 0, I can get this that is what is you know, on the y axis x axis is your separation distance, that is for 1 is to1 electrolyte.

And all that has been done is the salt concentration is systematically increased. That means you get a more steeper, more steeper drop in the, the potential with separation distance when you have a higher salt concentration and the fall becomes more gradual, if you have low salt concentration. So, in this case, the type of electrolyte is fixed and the concentration is change. However, if I fix the concentration of the electrolyte, and change the type of electrolyte 1 is to 1, 2 is to 2, 3 is to 3.

Again, symmetric light you will again see that the, the potential decrease becomes more and more gradual. If you change the electrolyte from 3 is to 3 to 2 is to 2 to 1 is to 1. So therefore, these potential, the plot of how the potential varies, they drop off more rapidly for higher concentration or higher values of higher willingness of the electrolyte. What do you think is implication of this?

What do you think is the implication of the fact that the potential drops off more gradually or more rapidly? What consequences do you think this has on the electrical double layer interactions? Take a little bit about this question. So, I will come back and we will come back and make a point.