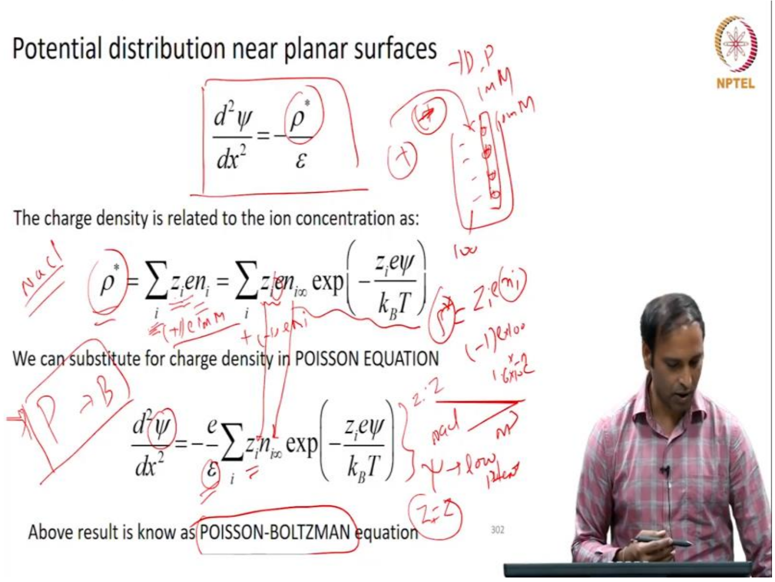
Colloids and Surfaces
Prof. Basavaraj Madivala Gurappa
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture – 32
Potential Distribution Near Planar Surfaces: Solution to the Linearised Poisson – Boltzmann Equation

(Refer Slide Time: 00:16)



Potential distribution near planar surfaces

$$\frac{d^2\psi}{dx^2} = -\frac{\rho^*}{\varepsilon}$$

The charge density is related to the ion concentration as:

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

We can substitute for charge density in POISSON EQUATION

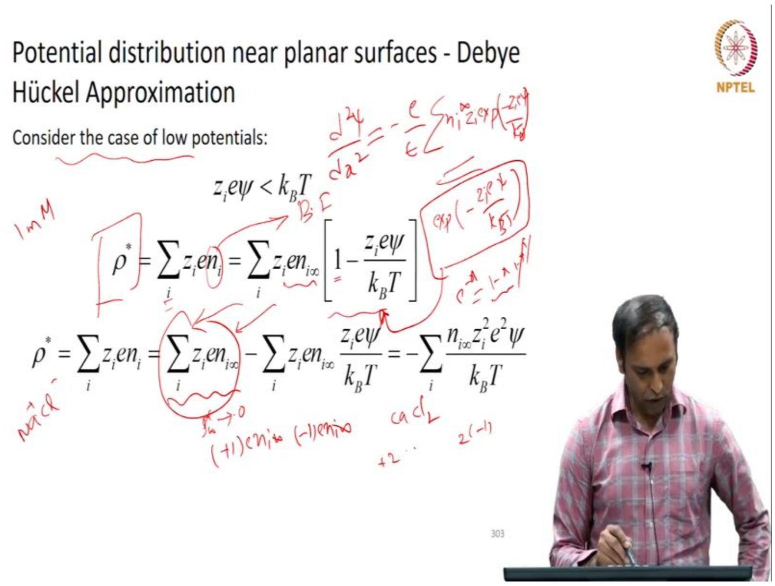
$$\frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon}\sum_i z_i n_{i\infty} \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

Above result is know as POISSON-BOLTZMAN equation

Now, I would like to solve this. So, what I have is this now I would like to solve this. So, we can either obtain a solution of this equation it depends on at what level you want to, you know, solve the problem, Either I can simplify and I can take some specific cases, or I can solve it for a very general case, you know, what I am trying to say is that, I can solve this I can simplify this equation and obtain a much simpler.

You know differential equation, which I can solve if I assume that I am working with low potentials or, I can take a case where I am working with z is to z electrolyte, that means I am working with symmetric electrolyte z is to z for example, NaCl is an example of a symmetric electrolyte, you know, that is z is to z, 1 is to 1 electrolyte. So, for cases like that, I think you can solve this, you know, expression fairly simply, but if you look at very complicated cases, where the potential is very high, you know, or when you are working with non-symmetric electrolyte this is know the solution is much more involved.

(Refer Slide Time: 01:38)



Potential distribution near planar surfaces - Debye Hückel Approximation

Consider the case of low potentials:

$$z_i e\psi < k_B T$$

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

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

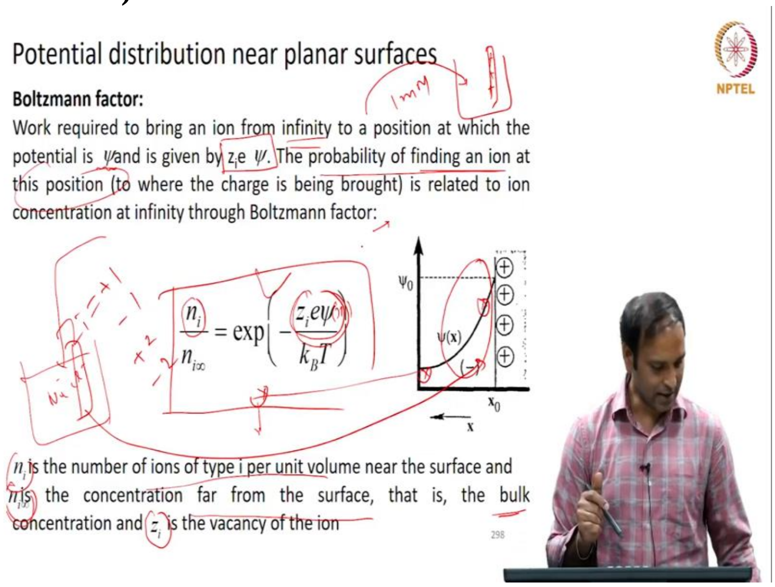
So, we will take a simple case of low potential. We will come back a little bit and then tell you what that low potential is. But for the sake of simple, you know, what we will do is. So, I have this expression, let me write that up. So, this is d square psi / dx square = – e by epsilon sigma n i infinity into z i exponent – z i, e psi divided by k B T. That is what we derived. So, now, so, when I say if you look at the right hand side, when I say it is a low potential, this rho star we were expressing it as sigma summation of I you know.

For all the species z i times e n i, and n i infinity I we used to represent it in the form of Boltzmann factor and Boltzmann factor had this exponent – z i e psi / k B T term. So, the moment I say low potential, I can take an exponential term. For a low potential I can write this as 1 – z i e psi / k B T. So, it means you have a e power – 6 for example, we know that I can write it as 1 – x + x square by you know, that is a series.

I can you know, kind of omit all the higher order terms, I can restrict only to the, the first term, therefore, I can actually write e power – x as 1 – x. Therefore, this exponent – of z i e psi / k B T. I am writing it as 1 – z i e psi / k B T. No. So if you look at this, so I am only talk about this term. I am only talking about that rho star. I have only rho star, rho star, we wrote it as sigma i z i, e, n i, n i infinity, I am supposed to write in terms of the Boltzmann factor. And there is an exponent – z i e psi by k_BT term.

I am going to write that as 1 – that I E, psi / k_BT. That is all we have done. So therefore, I can simplify this as sigma z i e n i infinity times 1, this term, multiply by – sigma z i e n i infinity at the next term, z i e, psi divided by k_BT. Now, if you look at this term, what can you say about this term? So anyway it is rho star infinity, Anyway rho star infinity, and rho star infinity is actually 0, because if I look at.

(Refer Slide Time: 05:25)



Potential distribution near planar surfaces

Boltzmann factor:

Work required to bring an ion from infinity to a position at which the potential is ψ and is given by $z_i e\ \psi$. The probability of finding an ion at this position (to where the charge is being brought) is related to ion concentration at infinity through Boltzmann factor:

$$\frac{n_i}{n_{i\infty}} = \exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

n_i is the number of ions of type i per unit volume near the surface and $n_{i\infty}$ is the concentration far from the surface, that is, the bulk concentration and z_i is the vacancy of the ion

So what you should imagine is this right? Whenever I talk about a distribution of ions in solution, so imagine that I have an electrolyte solution, Na + and Cl –. So we know that at equilibrium, there will be some distribution of ions in solution. And there is a, because it is a symmetric electrolyte, there is an equal probability of finding an Na + and Cl – everywhere in the solution. If you have a homogeneous solution, now, what I do is I bring in a charged species now.

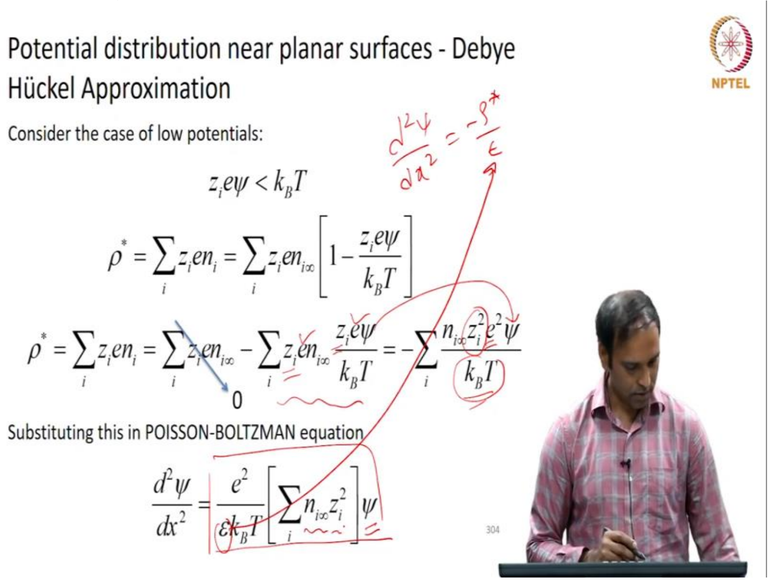
Whatever distribution that I had earlier, is going to be disturbed, there is going to be a lot of restructuring of ions and the leaps restructuring of ions will essentially lead to a electrical double layer formation. That means the concentration of counter ions close to the charge surface is going to be higher, but if I go to a sufficiently far away distance, then you will have again the distribution of ions it is going to be very similar. I am talking about one plate for example.

I am talking about when I say infinite distance that means it is sufficiently far away from the charged surface. And you will learn a little bit later, when I say sufficiently far away distance. We are talking about a distance called the thickness of the double layer. That means if you go to a distance which is farther than the double layer thickness, you know, there will be equal probability of finding the positive ions and negative ions in solution.

In such a case, this rho star infinity is going to be 0 because if I am working with like a simple case of, you know, Na + and Cl – this term is going to be + 1, e n i infinity – 1. Because of the Cl – E, n i, infinity, because if I add one milli molar NaCl solution, I am actually adding the same concentration of Na + and same concentration of Cl – ions. Therefore, it was even otherwise.

No, I am only talking about the only thing is if I take for example, CaCl 2, is going to be + 2 times whether there will be 2 times – . So, essentially, this is applicable irrespective of, you know on an average, the total charge there is 0. Therefore, the total potential will be 0.

(Refer Slide Time: 08:15)



Potential distribution near planar surfaces - Debye Hückel Approximation

Consider the case of low potentials:

$$z_i e\psi < k_B T$$

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

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

Substituting this in POISSON-BOLTZMAN equation

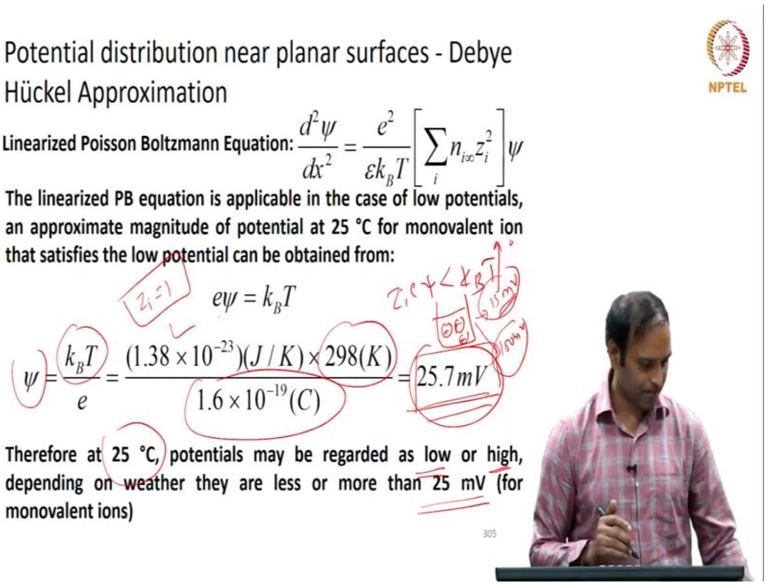
$$\frac{d^2\psi}{dx^2} = \frac{e^2}{\varepsilon k_B T}\left[\sum_i n_{i\infty} z_i^2\right]\psi$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho^*}{\varepsilon}$$

So therefore, the first term becomes 0, therefore, this term becomes 0, I am only left with the second term, therefore, I have z i here another z i there, therefore, there is a z i square that comes in. And you have e e therefore, you have e square and there is psi divided by k_BT. So, which I can express it as. So, there is a minus there. So because I had, so there is a rho star. So this is rho star and because I had d square psi / d x square = – rho star / epsilon, there is a minus, minus gets cancelled.

Therefore, I am left with and of course, another epsilon comes in because I had epsilon in the denominator. So therefore, d square psi / dx square = e square / k_BT and epsilon and summation of all the ions in the solution sigma i n i infinity into z i square, multiply by psi.

(Refer Slide Time: 09:43)



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:

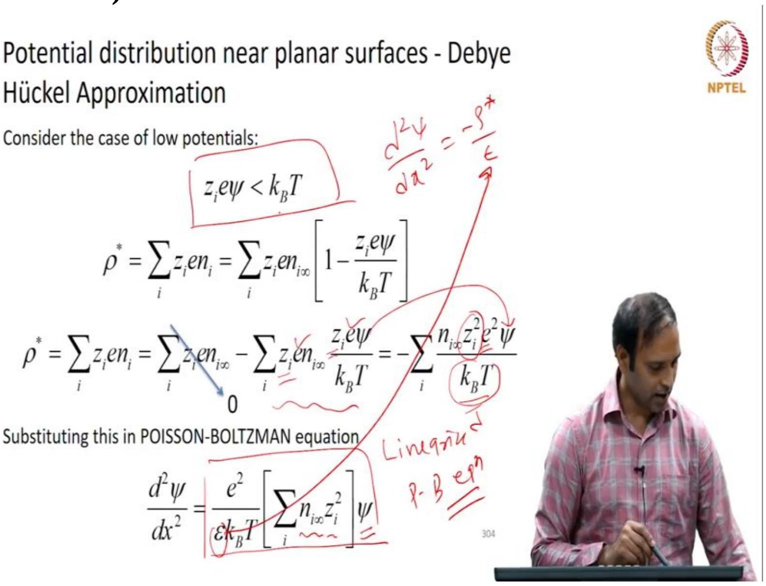
$$e\psi = k_B T$$

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

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)

305

(Refer Slide Time: 09:59)



Potential distribution near planar surfaces - Debye Hückel Approximation

Consider the case of low potentials:

$$z_i e\psi < k_B T$$

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

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

Substituting this in POISSON-BOLTZMAN equation

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

304

Now, let’s think a little bit about what is this you know, we said that, so this expression, I said this is a Poisson Boltzmann equation, now this expression is what is called a linearized Poisson Boltzmann equation, which is applicable only for the case of low potential, what do I mean by low potential is z i e, time psi must be much less than k_BT. So now you can put in some appropriate numbers.

So let us say that you know, so let us look at the limiting case. So z i e psi must be less than k_B T for me to assume for me to say that I am working with the low potential case, So, if I take e psi = k_B T, that means, you know, I am talking about again, you know, if z i = 1, therefore, e time psi = k_B T. I know what is k_B T the thermal energy so 1.3 10 power – 23 joules per Kelvin multiply we are working with you know 298 Kelvin and e is the charged electron the psi you know.

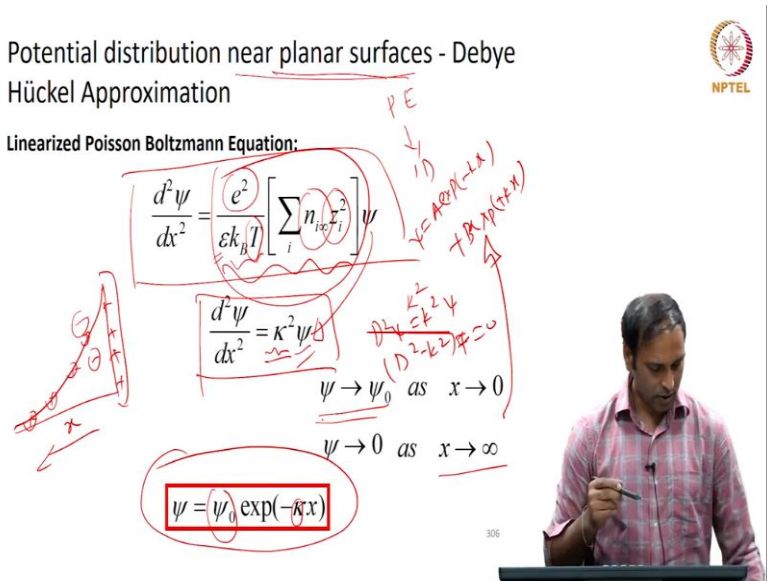
Comes out to be something like 25.7 milli volts, so you can say that if you are working with charged particles you know at 298 Kelvin at room temperature, if the potential if the zeta potential of the particle that you are measured. If that potential is 25.7 or lower, I can assume that the particle charges low. So, that is so, you can kind of get an estimate as to what do I mean by a low potential or high potential by this simple approximation.

So, this psi if you work with you know, if I work at 25 degrees centigrade, if you have potential can be regarded as either low or high depending upon, whether the charge surface that you are working with has a potential that is less than 25 millivolts are more than you know 25 millivolts. This number is important, because you know, sometimes you may be working with like say a charge stabilize dispersions say that it is charged positively charged particles.

You and somebody measures the charge on the particles and they say that it is 15 millivolts or you know, somebody works with the case where the charge is say – 100 millivolts. So, we know that definitely a higher charge means you know, it is more stable. But however, if you look at you know, this the case in even the case where the charges 15 milli volts or the surface potential is 15 milli volts there would still be electrostatic repulsion, however, it may not be sufficient right to know for the particles to be stable.

So, of course, the more closer to 0 it is that means you know, your charge interactions may not be very important at all. So, therefore, you can keep this 25 millivolts in mind that if the surface charge is such that the surface potential is 25 millivolts or lower you know, such systems exhibit very limited stability because of the electrostatic effects.

(Refer Slide Time: 13:53)



Potential distribution near planar surfaces - Debye Hückel Approximation

Linearized Poisson Boltzmann Equation:

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

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

$$\psi \to \psi_0 \quad as \quad x \to 0$$

$$\psi \to 0 \quad as \quad x \to \infty$$

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

PE → 1D

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

$D^2\psi = \kappa^2\psi$

$(D^2-\kappa^2)\psi = 0$

So, now you have this linearized Poisson Boltzmann equation and of course, if I so, this is a quantity of which you have control over that means, you know some of them are constants in the equation, so, is e square is constant epsilon you know is related to the medium in which the particles are dispersed. So, you will typically know those values and of course, k_B T is the thermal energy and if you work with finite temperature.

And of course, you have control over the concentration of the ions are in solution and also you will know their valence everything therefore, I can plug all these constant together into and say it is kappa square, it is kappa square times psi, therefore, d square psi / dx square becomes kappa square into psi. That is your linearized Poisson Boltzmann equation and of course I can solve this so you have if I use a boundary conditions that at for x tends to 0, psi becomes psi not.

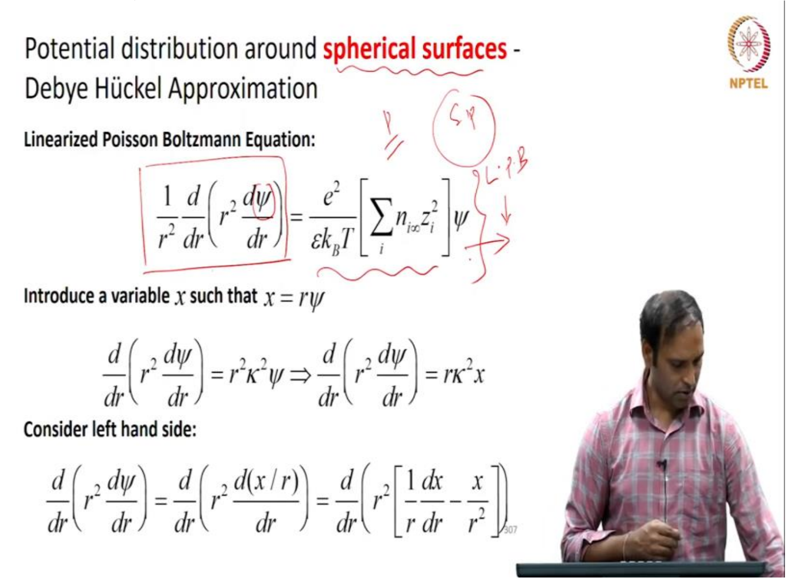
And as x tends to infinity, psi becomes 0, if I use these boundary conditions, so it turns out that psi becomes psi goes as psi not into exponent – k times x. you know how to do this. So, you will have psi, you can dial it as A times e exponent of – k x + B times exponent + k x. That is the solution and if I substitute the boundary conditions, you will essentially get this. So that is the solution for Poisson equation, in 1 dimension.

So, essentially, what this tells you is that if I have a charge surface with you know, some counter ions in solution. So, this potential essentially decays as an exponential function. So, now I with this given if I know what is kappa. I will be able to calculate what is the potential at every location, how does that vary as a function of separation distance and I should be able to calculate that given that I know what a sign not and what is kappa if I know that I can know what is the variation of potential with distance.

That is what we were after, no, it is kappa. So, psi = psi not exponent – k times X, you can work it out. So, you can write this as d square psi = kappa square psi d square – k square you know is equal to psi = 0. So, you can do that. So, what we have done is a case where we are trying to think about a potential distribution near a planar surface.

You can and this particular assumption that low potential it is what is called as a Debye Huckel approximation. So, what is called as a Debye Huckel approximation and Debye Huckel the 2 people who developed solution you know for the Poisson linearized Poisson Boltzmann equation which is applicable for low potential cases, that is why this particular solution that we are looking at is what is called Debye Huckel, you know, approximation.

(Refer Slide Time: 18:20)



Potential distribution around **spherical surfaces** - Debye Hückel Approximation

Linearized Poisson Boltzmann Equation:

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

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:

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

You can do a similar calculation for planar you know, other kind of geometries as well, instead of spherical, instead of planar surface, if I am working with spherical surfaces, I can, again do a similar kind of formulation and only thing at do is I am going to consider, again if you look at, you know, the spherical coordinate system, Again, going to assume that psi is a function of only r, it only varies as a function of r is only a function of r.

Therefore, I will take the only the first term that is 1 over r square d / d r of r square into d psi / r. That is the the first term in the general expression in the general poisson equation. Because I am only worried about how does psi vary with r that is the first term. And again, I can the right hand side again, I am going to linearize it. Therefore, I essentially end up with, again the linearized Poisson Boltzmann equation in the cylindrical in the spherical coordinate system. So that is going to be the starting point. And I can of course, solve this as well.

It is a fairly simple derivation, so you should be able to work it out. So what we will do is into in the next lecture, we will try and solve Poisson Boltzmann equation for the spherical surfaces case. And then we will talk a little bit about you know, what is the importance of this kappa square, You know, because this quantity is very, very important because in any calculations where you want to extract the electrical double layer interactions, you should know how to calculate that.

And we will talk a little bit about what is the importance of and how does it depend on the salt concentration how does it vary; we will discuss some of those things in the next lecture. Thanks.