# Bio-Physical Chemistry

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## Lecture - 07
## Forces in Protein Folding (Contd.)

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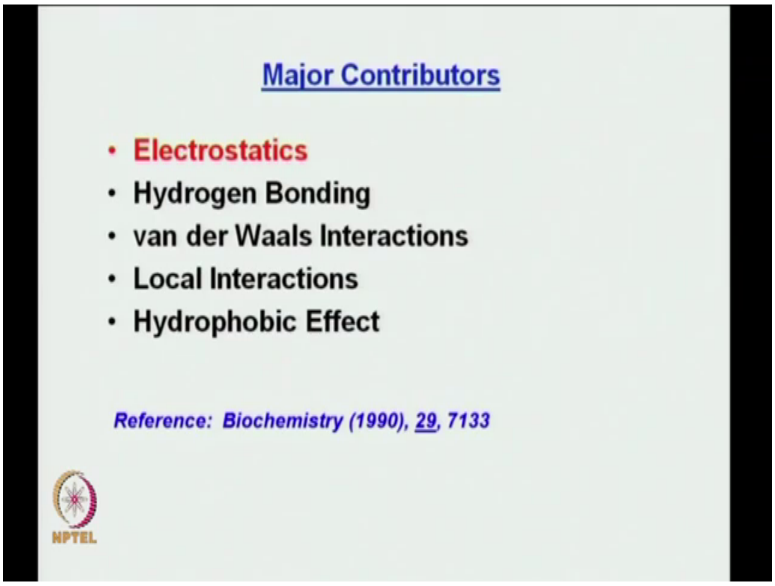

**Major Contributors**

- Electrostatics
- Hydrogen Bonding
- van der Waals Interactions
- Local Interactions
- Hydrophobic Effect

*Reference: Biochemistry (1990), 29, 7133*

So, continuing with the discussion on forces in Protein Folding. We looked at these being the major contributors right electrostatics hydrogen bonding van der Waals local hydrophobic.

We went through a couple of issues before we actually started looking at electrostatics. One was the range of forces right and the other one was local non local interactions right these have to be defined when you talk about proteins essentially or any polymers. Then we started with electrostatics that is what we are going to continue our discussion on.

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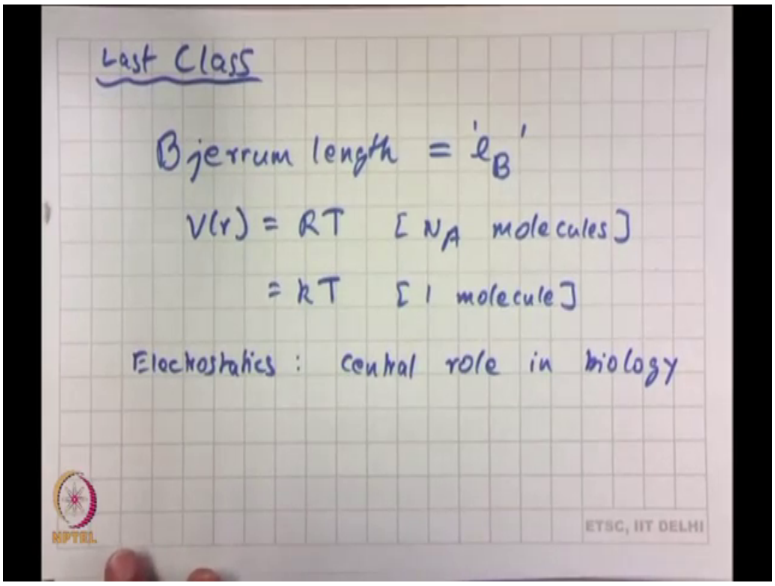

Last Class

Bjerrum length = '$l_B$'

$V(r) = RT$ [$N_A$ molecules]

$= kT$ [1 molecule]

Electrostatics : central role in biology

So, last class what we looked at just a quick recap. So, we looked at this length known as the Bjerrum length right and this is equal to as we said or represented by l of B right. And, what did we say the significance was? The significance was if we have a potential energy of interaction V of r then Bjerrum length is defined as that length where V of r is equal to?

Student: Thermal energy .

RT, if I am talking about an Avogadro number of molecules right.

Student: Hm.

Or is equal to kT if I am talking about?

Student: One molecule.

One molecule, right. And, then we said we actually showed an example or looked at an example of you know what this RT essentially means right. And, we discussed that if you know salts would you know how would sodium chloride ionize in water as I would see that at that distance or whatever distance you have this inter lattice or inter ionic spacings in the crystal lattice then it would be just equal to 2 RT right from last class.

And, hence because it is almost equal to your thermal energy that is why they cannot remain as an ionic bond like you know your crystal lattice energy that gets disrupted and they you know dissociate and dissolving solutions as independent species right. You knew this in terms of your lattice energy right like this Born-Haber cycle you have done in inorganic chemistry and all these things we can do those, but now you are in the solvent form that is in water where you put in the dielectric constants as d.

Now, electrostatics let me tell you one more thing. So, electrostatics why do people really care about it? Now, we will see as we go through the course. It plays a central role in biology; it plays a central role in biology and that is why we have to care about electrostatics.

Now, what do you mean by central role? What you mean is this; that means, it is present every time we talk about a biological molecule. You talk about a protein a protein has different charges a protein has salt bridges right.

Now, depending upon the charge of the protein say at a certain pH, a protein has say positive charge. Then around the positive charged positively charged protein what would you find mostly? Mostly, negative ions coming from your salt or whatever you have in solution right. Now, the question is given a system like this, how can we describe the charge distribution? How can we look at the charge distribution as a function of distance from the protein molecule? What does it mean?

What it means is, if I do have a protein molecule right if I do have a protein molecule say I have globule or a spherical protein molecule the charge agglomeration accumulation would be maximum near the protein surface. But, as you slowly move away from the protein surface what happens that would slowly die down right because the effect of the protein slowly diminishes that is something we are we are going to look at today, right.

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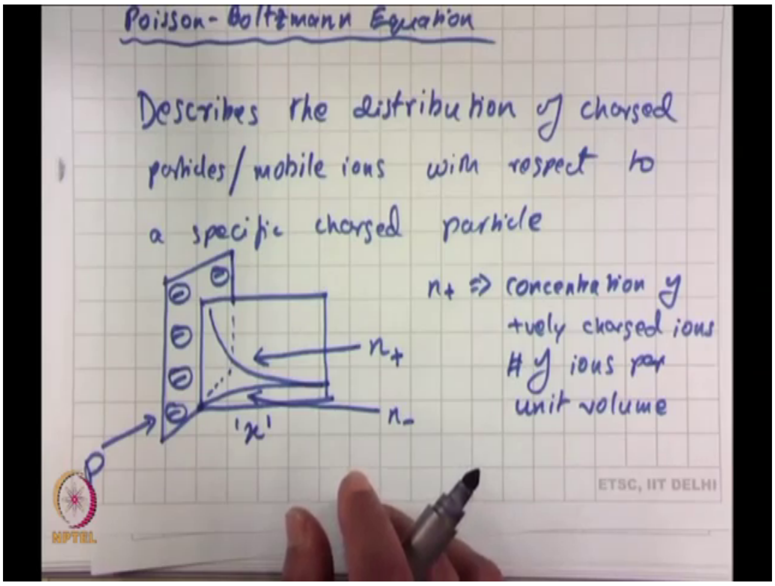

Poisson-Boltzmann Equation

Describes the distribution of charged particles / mobile ions with respect to a specific charged particle

$n_+ \Rightarrow$ concentration of +vely charged ions
# of ions per unit volume

So, the topic we are going to start today is the Poisson Boltzmann equation which describes which describes the distribution which describes the distribution of charged particles slash mobile ions; slash mobile ions coming from your salts with respect to a specific charge particle; with respect to a specific charged particle.

Now, this charged particle in our discussion actually would be a protein that is where we are trying to go finally, ok. So, let us look at a picture. You know always a picture is always worth a thousand words. So, let us look at a plane right it is a plane I have I am given a plane like this. So, let me draw it. Say suppose this one is a plane; that means, a planar surface essentially a 2-dimensional surface does not matter what it is.

Now, what I am saying is or what we are saying is this plane is essentially negatively charged right ok. Let me extend this coordinate x coordinate is your distance x from the plane. So, this you understand right? So, if you have a plane this is my x coordinate I am slowly moving away from the plane right. If I am moving away from the plane, how will my charge distribution vary?

Now, if I have a salt solution I would be having both what? Negative and positively charged ions because the plane is negatively charged, what should I be having mostly near the negative charged plane?

Student: Positive ions.

Positive ions right. So, what I can do is I can draw a potential like this or a distribution like this which goes this and this one corresponds to n plus. What is n plus? n plus is the concentration of.

Student: Positively charged.

Positively charged ions; positively charged ions that is number of ions positively charged per what? Unit volume, is it not? That is how you define a concentration.

Now, you can see what happens do not worry about how this function looks or how the distribution of n plus looks, but you can at least rationalize, right. That means, the closer you are to the negatively charged plane p the concentration of positively charged ions that is n plus would be high right because there is attractive potential as you slowly start moving away what happens? The concentration on negatively charged ions would.

Student: Fall, decrease.

Fall decrease. Now, how quickly or how slowly will fall, it will fall will depend upon something else, what is that?

Student: (Refer Time: 08:31).

It will depend upon the intervening salt ions we have right because these salt ions would potentially screen certain charges from each other. For example, if we have a spherical if we have a planar particle is negatively charged, if we have another planar particle say which is a negatively or positively charged does not matter what it is.

If we have intervening salts then depending upon what the concentration of my salt is the distance through which these two planes would experience their attractive or repulsive force would be determined by the number of charges we have in between, right. And, that is essentially what we are going to look at that is how a charge distribution varies with respect to a static or fixed plane and then take it over to a protein molecule. But, before saying too many words let us look at this again. So, this was n plus, but you know our solution is electrically, what?

Student: Neutral.

Neutral. So, I should be having n minus 2, but n minus should be staying away from this right. So, if this is the decaying potential, I can say or decaying graph I can say this would be so looking something like this which here this one is for n minus. Why because n minus near the plane would be the least, because the plane is negatively charged.

So, it will repel the negatively charged ions and as we move far away what will happen? Their concentration would grow that is essentially what you are seeing right. Now, how to put it in a mathematical format?

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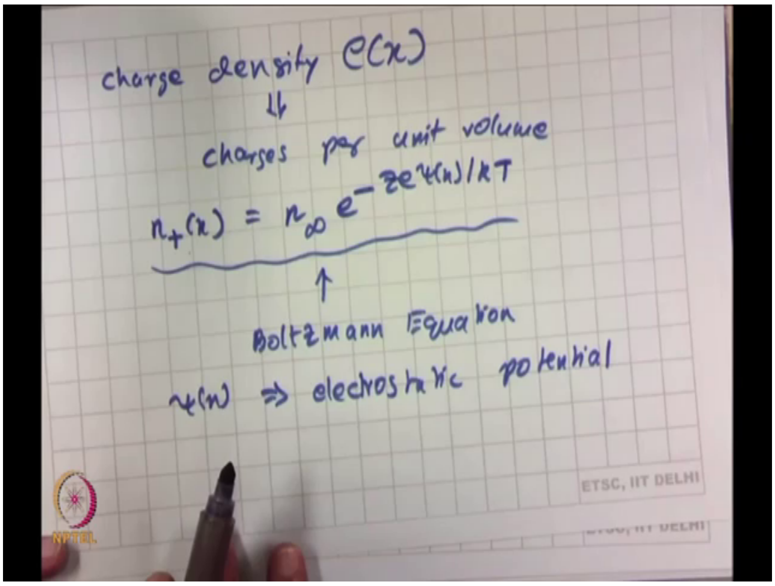

charge density $\rho(x)$

$\Downarrow$

charges per unit volume

$$\underbrace{n_+(x) = n_\infty e^{-ze\psi(x)/kT}}$$

$\uparrow$

Boltzmann Equation

$\psi(x) \Rightarrow$ electrostatic potential

So, what we do is you know keep this figure in mind we will refer to this all the time. What we will do is we will look at something known as charge density; we will look at something known as charge density given by rho of x and what do you mean by charge density? What is density? A charge density would be

Student: (Refer Time: 10:33).

Charges.

Student: (Refer Time: 10:35) minus 1 by n.

Per.

Student: Radius (Refer Time: 10:37).

Unit volume right essentially, but in this case remember when we are taking rho of x it is like your one-dimensional Schrodinger equation, it is a one-dimensional problem. I am just taking it along one-dimension that is why we are saying rho of x, I am not saying rho of xyz ok. We are just starting with a very simple picture like you did in quantum mechanics for a particle in a 1D box like a 1-dimensional box right.

Now, if I look at rho of x I am going to look at rho of x now. Now, this probably you guys know I can say n plus as a function of x is equal to n infinity; I will tell you what infinity is, e to the power minus z e psi of x over kT. I will tell you what this means, but just for the time being we consider this coming from your Boltzmann equation.

Now, what are we looking at? What do you mean by n infinity? So, if you go back to the slide again or the slide means the previous figure see infinity means that in finite distance. That means, this is forming n infinity; that means, I have moved at infinite distance from the plane. Now, come back to your Boltzmann equation. What do we have here we have n plus x that is a concentration of positive ions.

So, number of positive ions per unit volume is equal to n infinity; that means, whatever you have at in finite times e to the power minus z e psi x by kT. What is z? You guys know

Student: Charge (Refer Time: 12:35).

Is the charge of that respective ion, right. What is e?

Student: (Refer Time: 12:40).

Is electronic charge, right. What is psi of x? Psi of x is the corresponding electrostatic potential psi of x is a corresponding electrostatic potential, right and we will see what it means very soon. But, just for the time being try to understand the relevance of this equation; try to understand the relevance of this equation.

If you remember Boltzmann equation, do you remember Boltzmann's equation? What does it say? You have n say number of molecules at a given state energy state I is equal to what?

Student: e to the power.

n 0 e to the power minus e over.

Student: kT.

kT; is it not this one very similar? That is essentially what you are looking at right and this one if you take it just like that psi is a potential e is a charge I mean electronic charge and z is obviously, the corresponding valance of the actual charge on the ion these also have an energy contribution. So, what you are looking at is essentially something which is very similar to energy that is what you are looking at.

So, now, at least do you have do you understand where this expression comes from right it just nothing these three together represents form of energy that is why you write Boltzmann equation.

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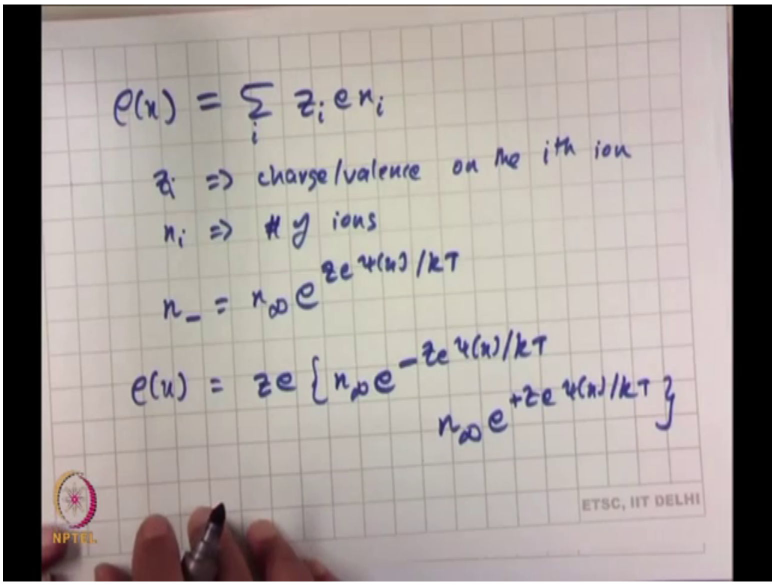

$$\rho(x) = \sum_i z_i e n_i$$

$z_i \Rightarrow$ charge/valence on the ith ion

$n_i \Rightarrow$ # of ions

$$n_- = n_\infty e^{ze\psi(x)/kT}$$

$$\rho(x) = ze\left\{n_\infty e^{-ze\psi(x)/kT} \quad n_\infty e^{+ze\psi(x)/kT}\right\}$$

Now, if you look at the total charge density if you look at the total charge density rho of x I can write it as a summation of all charges present all charges; that means, I can write sigma i where i is the ith charge or summation of i z i e n i I can write like this. What is z i? Again, let me write it. It is the charge or valence on the ith ion right and obviously, n i you know is the number of ions.

But, guys when we talk about the total number of ions we also have negative and positively charged ions right. We have already seen we have already seen before that n plus of x is equal to n infinity to the minus z of e psi x over kT. Now, this is for n plus this was for n plus, I can write a similar equation for?

Student: n minus.

n minus. See, if I have to write a similar equation for n minus then what I can write is tell me what I should write now? n minus is equal to again I say n infinity, then e to the power what should I write now?

Student: Plus.

It should be plus right why? Because now?

Student: (Refer Time: 15:43).

The z itself is negative.

Student: Negative.

And we have negative sign out there. So, it becomes positive right. So, we have z e psi of x over.

Student: k of T

k of T. So, then I can express my rho of x as now look at this I can express my rho of x as z e z e then what I can write? I can write n plus plus n minus.

Student: Yes.

There is a total n plus plus n minus. So, I will skip that that step and I will write this is n infinity e to the power minus z e psi of x times kT right. Then, what should I write?

Student: Plus , plus, n, plus n infinity..

Correct good.

Student: Plus.

I should write n infinity then?

Student: e to the power.

e power plus.

Student: (Refer Time: 16:50).

z e

Student: Psi x.

Sub x.

Student: kT .

kT ok.

Now, remember your n plus and n minus they have what? Opposite charges, do not they? n plus and n minus they have opposite charges right. So, what I can this I can just put a negative sign out here, just to take the charge effect into consideration. Now, this is your total rho of x this is your total rho of x; that means, the total charge density, but how do I relate it to something more fundamental?

So, remember when we started with this we said it was a Poisson – Boltzmann equation is it not? We said it was a Poisson – Boltzmann equation. We have looked at the Boltzmann equation, but where does the Poisson come from? Right.

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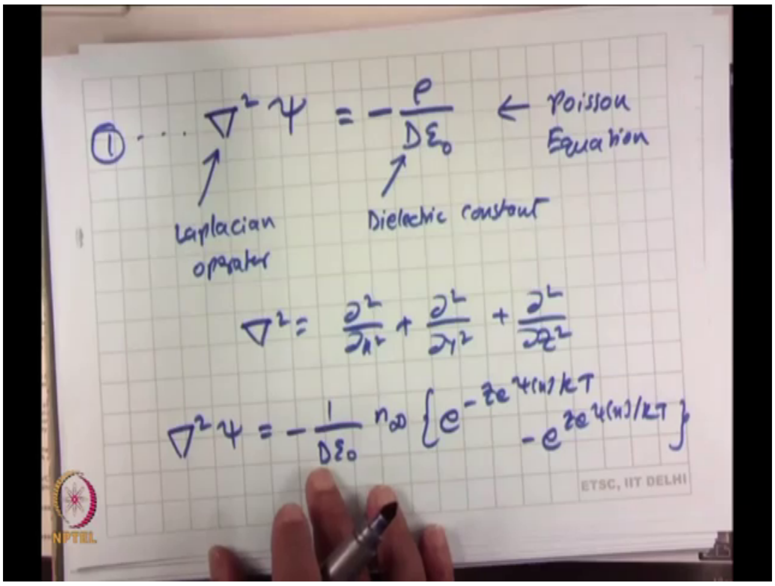

$$① \cdots \nabla^2 \psi = -\frac{\rho}{D\varepsilon_0} \leftarrow \text{Poisson Equation}$$

Laplacian operator

Dielectric constant

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\nabla^2 \psi = -\frac{1}{D\varepsilon_0} n_\infty \left\{ e^{-ze\psi(x)/kT} - e^{ze\psi(x)/kT} \right\}$$

So, the Poisson equation I will not show the derivation, just take it from me. The Poisson equation is known by this del square psi, where psi is a electrostatic potential or contribution is equal to minus rho times d over say epsilon 0. So, this equation is known as the Poisson equation this equation is known as the Poisson equation. And, you know what rho is already? Rho is the?

Student: Charge density.

Charge density, what is d?

Student:Dielectric.

D is a dielectric constant. We know what epsilon 0 is from previous class. It is permittivity in vacuum right. So, that is your right hand side of the equation; come to the left hand side the psi you know is a electrostatic potential, right. What is del square?

Student: Laplacian.

Laplacian. So, del square is a Laplacian operator and del squared in the general terms del square in the general terms is given by what del 2 over del x squared in Cartesian coordinates then del 2 over del y squared plus del 2 over.

Student: Del z square.

Del z squared that is what you know by your Laplacian. So, now can you realize why it is referred to as a Poisson – Boltzmann equation? This is your Poisson equation. You have the charge density expressed in terms of what equation?

Student: Boltzmann.

The Boltzmann equation where, n plus (Refer Time: 19:33) equal to n infinity to the minus that stuff. So, essentially what do we have here? We have combined two stuff right, we have combined the Poisson equation with the charge density which is already there in the Poisson equation, where we have an expression of charge density coming from the

Student: Boltzmann.

Boltzmann equation. These two in combination give you the?

Student: Poisson. Poisson-Boltzmann equation. Are you guys with this?

Student: Yes.

Actually, fine, right. So, now, let us focus on this Poisson equation let us focus on this Poisson equation. Let us name it equation 1, right should have done on the right side but I have already written it there. Then I can write del square of psi is equal to see look at the Poisson equation and think about your Schrodinger equation. Your h psi is equal to e psi right here also you have an operator del square psi. So, you also need a psi out there right and where does your psi come from?

Student: (Refer Time: 20:28).

Your psi comes from rho because you have a psi out there, you check. So, then del square psi is equal to now there is a minus sign well we will take the minus into consideration. So, I can write it as 1 by D epsilon 0 right and then what can I express this one as? This rho? This rho I can express as I can take n infinity outside. Then what am I left with? I am left with e to the power minus z e psi x over k of T, then minus e to the power z e psi x over k of T with a negative sign in front.

See, now you have psi on both sides of the equation. So, you understand what you are going to do right; that means, if you are going to solve this equation like when you solve Schrodinger equation what do you get? You get psi; that is a wave function; obviously, along with the eigenvalue of the energy. Similarly, here if I am going to solve this equation what am I going to get?

Student: Psi. (Refer Time: 21:33).

I am going to get psi provided I know what? Provided I know D, provided I know the number of ions and all these things. So, this is the or one of the major equations or most important equations in electrostatics where on solution of this problem you will get the electrostatic potential that your charge particle is giving out. That means, the salt or ions round your charge plane is experiencing this potential of psi of x.

Student: Yes.

Is everybody clear with that ok?

So, I will do a you know small algebraic thing. So, what I will name this as equation 2

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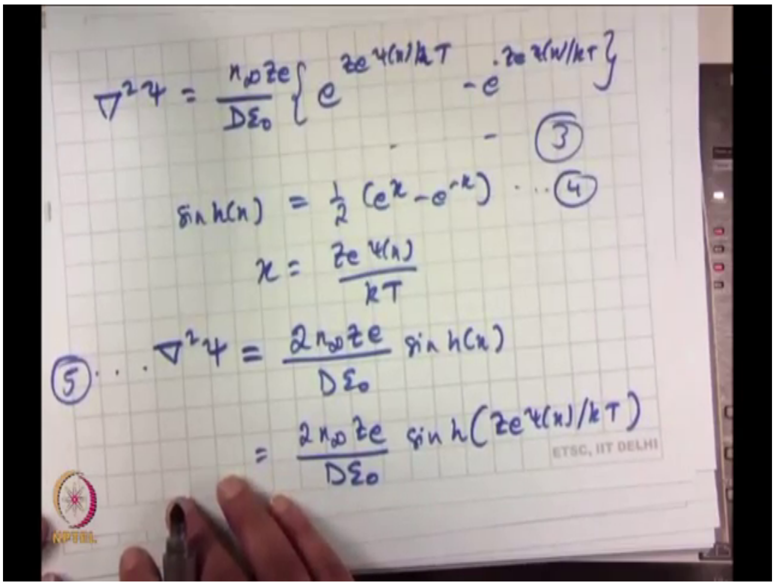

$$\nabla^2\psi = \frac{n_\infty ze}{D\varepsilon_0}\left\{e^{ze\psi(x)/kT} - e^{-ze\psi(x)/kT}\right\} \quad ③$$

$$\sinh(x) = \frac{1}{2}(e^x - e^{-x}) \cdots ④$$

$$x = \frac{ze\psi(x)}{kT}$$

$$⑤ \cdots \nabla^2\psi = \frac{2n_\infty ze}{D\varepsilon_0}\sinh(x)$$

$$= \frac{2n_\infty ze}{D\varepsilon_0}\sinh(ze\psi(x)/kT)$$

Now, what I will do is I will write this one as del squared psi is equal to n infinity by D right epsilon 0 and I can write e to the power z e psi x over kT minus e to the power minus z e psi x over kT. So, this is equation 3 ok, but I am missing one thing. Can you tell me what I am missing?

Student: (Refer Time: 22:59).

So, I missed the. So, what I missed was if you look at this equation I should be putting what?

Student: z (Refer Time: 23:06).

I should be putting z e out here and then automatically it would also come here right z e. Now, we will do a simplification. If you guys know your sin of hyperbolic x is given by half of e to the power x minus e to the power minus x. This is an expression for sine hyperbolic in terms of your exponential function ok. Let this be 4. See, if I have this I express so, here you know what x is? Your x is your z e psi x over kT that is your x.

So, where x is equal to z e psi of x over k of T. Then my Poisson equation or Poisson – Boltzmann equation becomes del square psi is equal to I should be having a factor of 2 infinity z times e by D epsilon 0, then I can write sin hyperbolic x is equal to 2 n infinity z e by D epsilon 0 sin h. Let me put in x z e psi of x over k of T. And, this is this should be my equation 5.

So, this equation guys; you are ok with the derivation up till this for?

Student: Yes.

Right. You have followed the steps.

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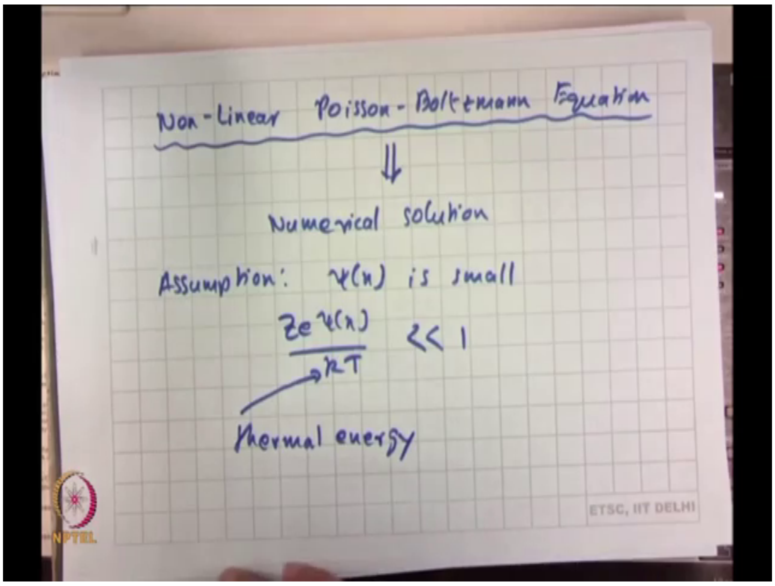

Non-Linear Poisson-Boltzmann Equation

$\Downarrow$

Numerical solution

Assumption: $\psi(x)$ is small

$$\frac{ze\psi(x)}{kT} \ll 1$$

Thermal energy

Now, this equation this you have to this derivation you have to remember that this equation is known as the non-linear Poisson-Boltzmann equation. Now, this is known as the non-linear Poisson-Boltzmann equation.

See, if it is a non-linear Poisson Boltzmann equation, the problem is you cannot solve it in a straightforward manner. The only way of solving it is to do a numerical solution; is to do a numerical solution, but we will simplify matters for us. What we will do is we will make an assumption.

The assumption we are going to make is; the assumption we are going to make is now that psi of x is small; that means, psi of x is small that is the electrostatic effect is small and if that is the case then can I write this z e psi of x over k of T is much less than 1.

Student: Yes.

So, what am I saying again? What I am saying is my electrostatic potential is much smaller with respect to the thermal energy kT because this kT represents my thermal energy ok. Now, based on this assumption based on this assumption what I can do? Remember that sin h of x that hyperbolic h is equal to what? Half e to the power x minus e to the power minus x, right that is what it was ok.

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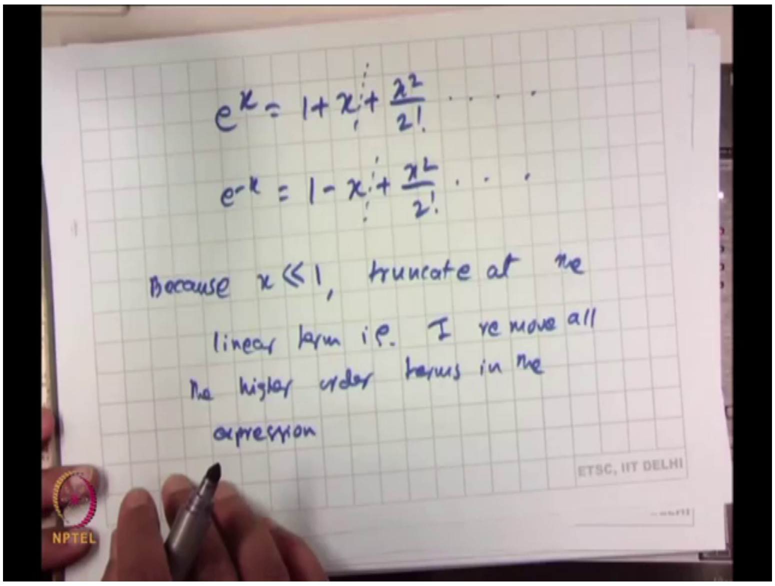

$$e^{x} = 1 + x + \frac{x^2}{2!} \ldots$$

$$e^{-x} = 1 - x + \frac{x^2}{2!} \ldots$$

Because $x \ll 1$, truncate at the linear term i.e. I remove all the higher order terms in the expression

Now, what is e to the power x if x is small 1 plus x plus x squared by factorial 2 and so on. Then what is e to the power minus x equal to?

Student: 1 minus (Refer Time: 27:11).

1 minus?

Student: Minus x.

x plus x squared by factorial 2 and so on, but because x is much less than 1 or x is very small what I can do is, I truncate at the linear term; that means, that is I remove all the higher order terms in the expression. Is that clear? So, what am I left with then? e to the power x I will left with only

Student: (Refer Time: 28:08).

This one; e to the power minus x left with only what?

Student: 1 minus

This one ok.

Now, go back to your original expression what we started with. This was your non-linear Poisson-Boltzmann equation. What did you have? This is this was sin of h which was half e to the power x minus e to the power?

Student: Minus x.

Minus x. Now, you have made the assumption that x is very small right. So, what will this boil down to? This guy what will this boil down to?

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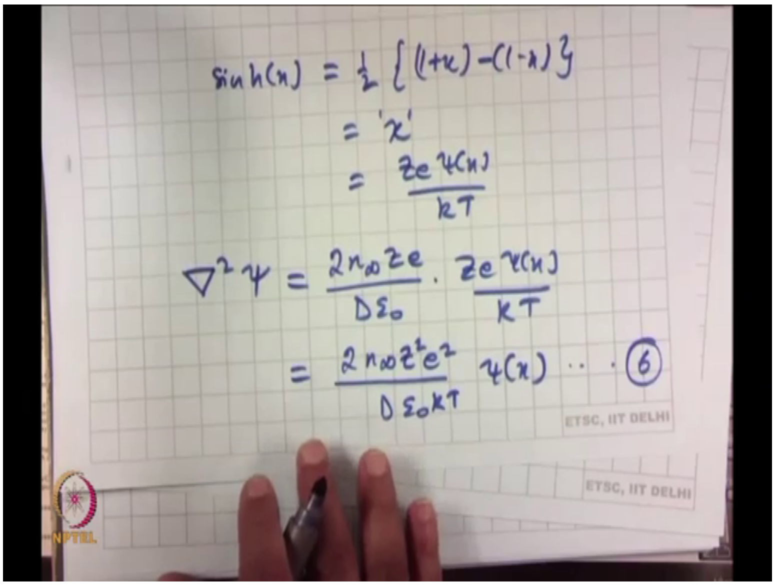

$$\sinh(x) = \frac{1}{2}\{(1+x) - (1-x)\}$$

$$= 'x'$$

$$= \frac{Ze\,\psi(x)}{kT}$$

$$\nabla^2 \psi = \frac{2 n_\infty Z e}{D \varepsilon_0} \cdot \frac{Z e\,\psi(x)}{kT}$$

$$= \frac{2 n_\infty Z^2 e^2}{D \varepsilon_0 k T}\,\psi(x) \quad \cdots \; ⑥$$

So, I can write that sin h of x is equal to based on our assumptions half the first one is what e to the power x which is?

Student: 1 plus x

1 plus x. The next one is?

Student: 1 minus x.

1 minus x, excellent. So, what do we get?

Student: (Refer Time: 29:10).

Where x and this x as we had defined was z e psi of x over?

Student : kT (Refer Time: 29:20).

k of T right. So, my non-linear Poisson-Boltzmann equation now looks like this. So, what does it look like? It looks like del squared psi is equal to what are the factors I had? The factors I had were 2

Student: n.

n infinity right then z and e over D epsilon 0. Now, this whole sin of hyperbolic x gets replaced by what? Only x.

That means times z of e psi of x over

Student: (Refer Time: 30:04) kT.

k of T. To, simplify it I get 2 n infinity z squared e squared over D epsilon 0 kT times psi of x right. So, this was this should be what equation number 6, we get. So, what do you think is the major difference between equation 6 and equation 5? Equation 5, as we discussed just now was a non-linear equation and we had to solve it numerically, but now we made this assumption right that x is small and if x is small what I have done is we have transformed a non-linear problem to what problem?

Student: Linear problem.

A linear problem by doing this assumption.

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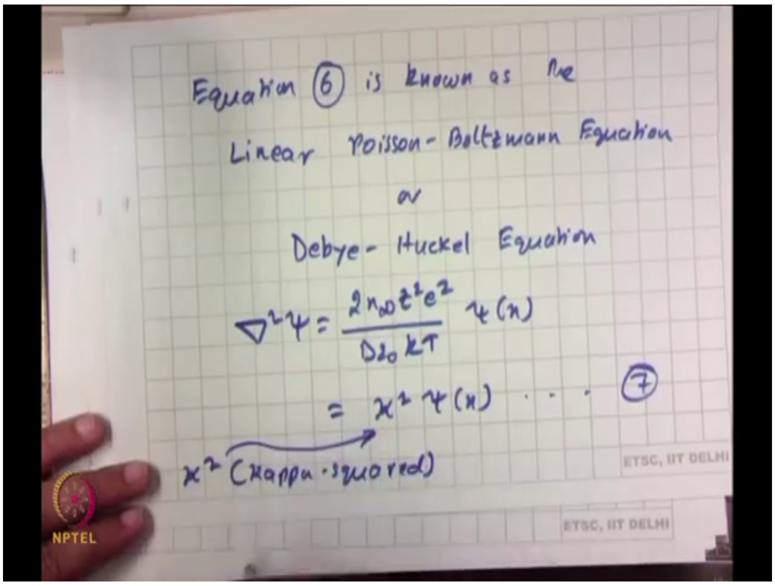

Equation ⑥ is known as the

Linear Poisson-Boltzmann Equation

or

Debye-Huckel Equation

$$\nabla^2\psi = \frac{2 n_\infty z^2 e^2}{D\varepsilon_0 kT}\psi(x)$$

$$= \kappa^2 \psi(x) \quad \cdots \quad ⑦$$

$\kappa^2$ (kappa-squared)

And, hence what we say is that this equation or equation 6 is known as the linear Poisson-Boltzmann equation or do you know what is the other name of it? This is something very familiar to you.

Student: Debye phenomena..

Yes, it is known as a Debye-Huckel equation because it was first formulated by Debye and Huckel. You guys must have studied at some point of time the Debye-Huckel limiting law, right. It actually comes from this. So, what we just saw was your formal derivation of your Debye-Huckel limiting law you have are not yet gone there, but this is where everything starts.

So, from first he took a charged plane, he took some mobile salt ions, he looked at the charge density which and then he expressed a charge density in terms of the Boltzmann equation after that he related the charge density to something known as the electrostatic potential through the Poisson equation. He combined Poisson and Boltzmann that is why it is called the Poisson-Boltzmann equation.

Then we saw that in it is fundamental form it is a non-linear type we make the assumption of low psi of x, a low electrostatic potential and then we simplify to the linear regime or linear Poisson-Boltzmann equation which is also known as the Debye-Huckel equation right. This is a fundamental equation for you which you guys have to keep in mind and realize the important of this.

So, writing down the equation again just bear with me. See, if I write down del square psi is equal to 2n infinity z squared e squared over D epsilon 0 k of T, then psi of x. This I can write to be equal to kappa squared psi of x this is say equation 7. So, this is kappa squared kappa squared.

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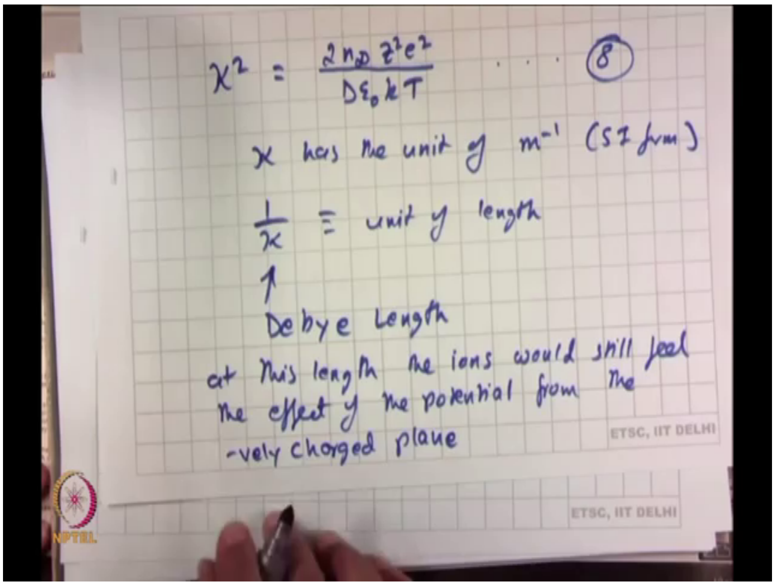

$$\kappa^2 = \frac{2 n_\infty z^2 e^2}{D \epsilon_0 k T} \quad \ldots \quad ⑧$$

$\kappa$ has the unit of $m^{-1}$ (SI form)

$\frac{1}{\kappa}$ ≡ unit of length

↑

Debye Length

at this length the ions would still feel the effect of the potential from the -vely charged plane

So, I can write kappa squared which is this guy. So, what is my kappa squared equal to? My kappa squared based on our definition is equal to 2n infinity z squared e squared by D epsilon 0 k of T right. So, let this be 8.

Now, what is the relevance of kappa squared? Let me tell you the relevance of kappa square. If you do if you put in all the respective values out here; that means, the units I should say, you would see that kappa has the unit of meter inverse. This is in the SI form is in the SI unit, meter inverse right; that means, it is the inverse of what? Length; that means, 1 by kappa would be having unit of length right 1 by kappa would be having the unit of length.

So, what do you think is the significance of this unit of length or this 1 by kappa?

Student: (Refer Time: 34:50)

This 1 by kappa is referred to as?

Student: (Refer Time: 34:54).

The Debye length; this 1 by kappa is referred to as the Debye length. What do you think is significance of this Debye length? What do you think it should be? It is very simple actually. Remember that Bjerrum length? Where V of r was equal to?

Student: R of T.

R of T or k of T; that means, if your length is beyond Bjerrum length you are definitely going to have full dissociation. Why because your thermal energy totally overwrites whatever intermolecular force of attractions you have in terms of your attractive potential.

Now, translate the same idea to this one what does 1 by kappa mean which is the Debye length? Debye length means this Debye length means at that length 1 by kappa the particle or the ion would still feel the effect of the charge of the plane P; remember the plane we started with. ok. So, that means, at this length at this length the ions would still feel the effect of the potential from the negatively charged plane that we started with right, a plane was negatively charged.

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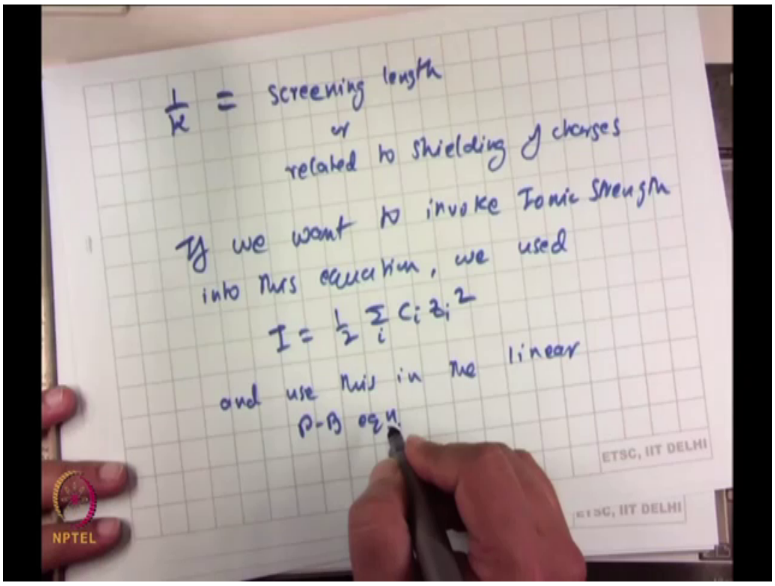


$\frac{1}{\kappa}$ = screening length
or
related to shielding of charges

If we want to invoke Ionic Strength into this equation, we used
$I = \frac{1}{2} \sum_i c_i z_i^2$
and use this in the linear P-B eqn.

In other words, what we can refer to it as is 1 by kappa is something known as the screening length or related to shielding of charges. What do I mean by screening or shielding? By screening or shielding this is what I mean; that means, if we have a plane P out here and if we are at the Debye length 1 by kappa, it is still feeling some effect of?

Student: (Refer Time: 37:25).

The plane P. You move beyond that length the effect is no longer there right the effect is absolutely no longer there.

This is why it is one of the most important things; that means, under a given for a given system given number of ions that n the concentration the given dielectric constant you can estimate from a given plane or a surface up till what distance are your ions going to fill some effect of this particular or charge particular plane. Are you guys with the discussion on this, right the inherent meaning?

Now, second look what kappa depends upon. Kappa or kappa square, anyway you have to put a square root over it to get kappa. What does it depend upon? It depends upon n infinity which is the concentration essentially, z which is the valence of the charge of the ion; e obviously, is electronic charge that is what it is directly proportional to. What do we have in the denominator?

Student: (Refer Time: 38:39).

We have temperature.

Student: (Refer Time: 38:41).

We have the dielectric constant. So, see how many how many different physical parameters can affect this kappa. It is not only your concentration of ions it is a unique feature out there.

It is not only a charge, but it is also your interfering dielectric constant and it is also the temperature in which you are measuring this because temperature finally or after all is a measure of what your thermal energy. See, you always will have to take the temperature into consideration because you started with Boltzmann's equation right where temperature is a playing a significant role right.

Now, guys translate this and think about something you know from chemical or from chemistry point of view. There is a parameter I, what is I?

Student: Ionic strength.

Ionic strength. What is ionic strength equal to?

Student : Half.

Half summation of?

Student: C i Z i squared.

C i Z i squared right, do you see that coming in here?

Student: Yeah..

You do right? Because n infinity is essentially what?

Student: (Refer Time: 40:01).

Your concentration.

Student: Concentration .

Is number of ions per unit volume right. You have the z which is the charge, right and then you can actually put in your ionic strength in this equation ok. So, what that is out next point. So, what I can now say is then that if we want to invoke ionic strength into this equation into this equation we use I is equal to half sigma i C i Z i squared right and use this in the linear Poisson-Boltzmann equation to get a relation between kappa and ionic strength.

Apart from the assumption or the fact that the electrostatic effect was really small there was one more assumption we took before, can you tell me what? When we did the derivation there was one more assumption we took. Just look at the derivation. Let me see if I can go back to that page where I did the main thing.

Student: (Refer Time: 41:48).

Look at this one. Look at this expression rho of x is equal to z e right. Why could I take z e out, on what premise? See e is electronic charge that is not a problem.

Student: Neutralization (Refer Time: 42:04).

Not only neutralization, well neutralization will be there, but why can I take z common?

Student: It charges are (Refer Time: 42:10).

Charges are same.

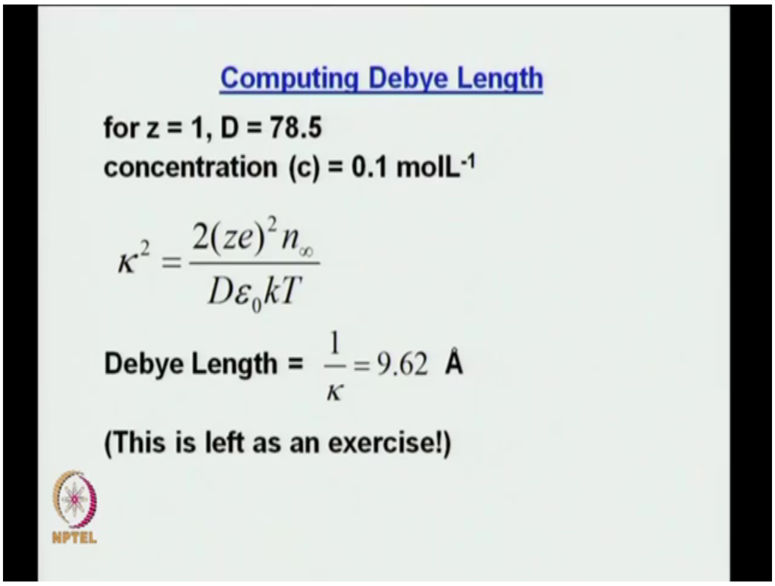
Student: (Refer Time: 42:12).

Right, it is like sodium chloride z plus is equal to or z plus is equal to 1; z minus is equal to 1 minus 1 right. So, that means, that z the magnitude of the charges is the same that is why I could take z e out. If it had not been the case then I would have to maintain that asymmetry condition and actually do the problem.

So, this was the other assumption; that means, it is like a one is to one electrolyte. Sodium chloride that is why I could do it ok, but this is also valid for anything where you do not have this symmetric (Refer Time: 42:45) that is why that is an asymmetric situation.

So, do you have any questions with respect to the derivation of this Poisson-Boltzmann's equation? So, my request to you guys is for the exam you have to know how this derivation was done and the significance of the different parameters; specially the Debye length, kappa – you have to understand the significance of that and to understand the significance of that let me actually go to the slide and show you a quick example.

(Refer Slide Time: 43:22)



## Computing Debye Length

**for z = 1, D = 78.5**
**concentration (c) = 0.1 molL$^{-1}$**

$$\kappa^2 = \frac{2(ze)^2 n_\infty}{D\varepsilon_0 kT}$$

**Debye Length =** $\frac{1}{\kappa} = 9.62$ **Å**

**(This is left as an exercise!)**

So, this is an example of computing Debye length right. So, if I can get this slide going for z equal to 1 what I am doing? I am computing the Debye length for z equal to 1; D is equal to 78.5 that is a dielectric constant; concentration I have taken c to be 0.1 moles per litre, right.

See if I do a Debye length calculation based on whatever we have you know derived the Debye length comes to be which is 1 by kappa 9.62 angstroms ok. The Debye length comes to be 9.62 angstroms. Now, this is left as an exercise for you to do ok. It will come as 9.62 angstroms, given the fact z is equal to 1; D is equal to 78.5; the concentration c is equal to 0.1 moles over litre. I am giving you the concentration right away right.

So, please do it, you will understand you know how people do these calculations because Debye length obviously, has a very important place in electrostatics in chemistry.

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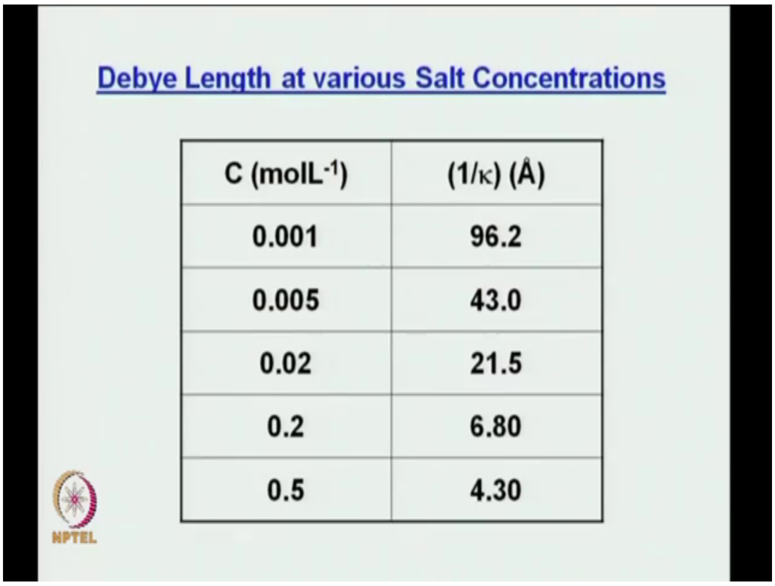

## Debye Length at various Salt Concentrations

| C ($molL^{-1}$) | ($1/\kappa$) (Å) |
|---|---|
| 0.001 | 96.2 |
| 0.005 | 43.0 |
| 0.02 | 21.5 |
| 0.2 | 6.80 |
| 0.5 | 4.30 |

Now, look at what happens to the Debye length at various salt concentrations. See whether this makes sense or not? If you have the concentration moles per litre and then you have the Debye length on the right hand side, what happens to the Debye length as we increase the salt concentration?

Student: Decreases. It decreases.

It decreases does it make sense to you?

Student: Decrease.

Why should it decrease?

Student: (Refer Time: 45:03) Sir because concentration is mostly (Refer Time: 45:04) decrease.

Exactly; that means, your concentration is now increasing. If your concentration is increasing; that means, between this ion and this P, your more and more ions coming in.

Hence obviously, the length is going to come closer because you have too much of shielding, too much of screening depending upon the concentration. So, this is at you know direct fallout of what you just derived.

Now, in the rest of the class you know whatever time I have well I do not have much time, but I will just do a quick derivation and you will see what I mean.

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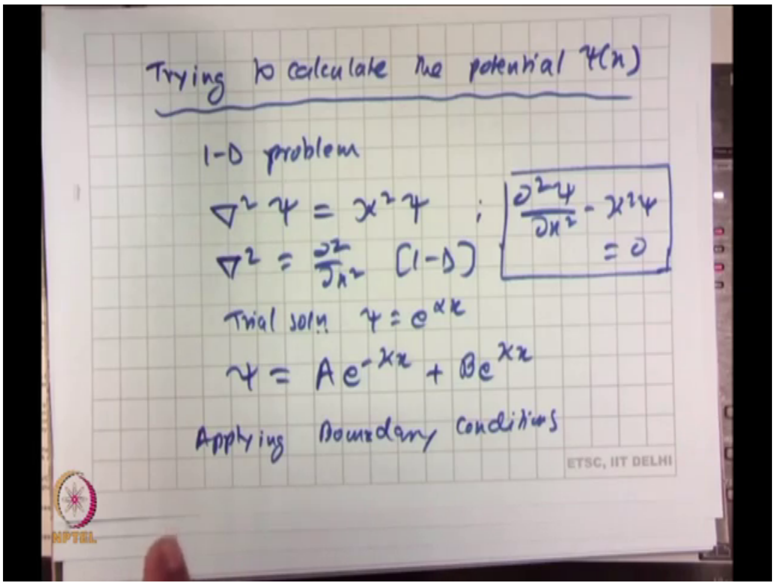

Trying to calculate the potential $\psi(x)$

1-D problem

$\nabla^2 \psi = \chi^2 \psi$ ; $\boxed{\frac{\partial^2 \psi}{\partial x^2} - \chi^2 \psi = 0}$

$\nabla^2 = \frac{\partial^2}{\partial x^2}$ [1-D]

Trial soln $\psi = e^{\alpha x}$

$\psi = A e^{-\chi x} + B e^{\chi x}$

Applying boundary conditions

So, here what I am doing is I am actually trying to calculate I am actually trying to calculate the potential psi of x I am actually trying to calculate the potential psi of x right. When I am trying to calculate the potential psi of x, I am sticking to a 1-dimensional problem; that means, I am only taking the x axis or the x direction and I am solving this equation your Poisson equation that you just derived.

Del square psi is equal to what kappa squared psi that is what we just derived right del square psi is equal to kappa squared psi where kappa squared is a usual thing. Now, if this is the equation we are going to start with, I am trying to solve for psi remember I am trying to solve for psi because it is a 1-dimensional my del squared becomes what?

Student: Del square.

Student: d by dx square.

Not d by dx.

Student: Del square over (Refer Time: 46:53).

Del square over?

Student: Del x square

Del x squared, right; then it becomes a differential equation you have to solve. If you solve the differential equation if you solve the differential equation by taking that del squared is equal to del 2 over del x squared 1D right and you take us take a trial solution take a trial solution of say psi to be e to the power alpha x. You have to go back to your differential equation solutions

Student: (Refer Time: 47:27).

Right. Then what are you going to get psi to be? Psi to be A.

Student: (Refer Time: 47:34) kx.

e to the power minus kappa x right?

Student: Yes.

Plus B e to the power plus kappa x.

Student: Yes.

Why? Because when you put e to the power alpha x in this equation when you put e to the power alpha x in this equation what do you get? You get e to the power alpha x times alpha squared minus kappa squared is equal to 0. Do you understand?

Student: Hm.

Because you are differentiating it 2 times. So, d of dx of e to the alpha x is what? Alpha e to power alpha x squared then d 2 over dx squared is alpha squared e to the power alpha x.

You also have a psi out here you can bring kappa square on this side the equation we are going to solve is therefore, del 2 psi over del x squared minus kappa square psi is equal to 0. This is the one you are solving right. So, you can see you already have a solution; that means, you already know here what your wave function is, not wave function in this case it is what the electrostatic?

Student: Potential.

Potential.

After this you start applying boundary conditions and this is where we will start off in the next class based on the solution, but I will tell you what the boundary conditions are to just end the class. You can understand one thing, x can be infinity and the other one is x can be 0; x 0 means you are close to the plane just write down the plane, x is equal infinity means you are at infinite distance from the plane. At x equal to infinity what will happen to psi of x? Remember psi of x is from the plane, it should be 0

Student: 0.

Because you are much you know farther away than your Debye length.

So, if it is 0; that means, psi would be 0. So, you can understand if you put x equal to infinity here this guy goes to 0 anyway because it dies out right, but this one does not go to 0. This one can go to 0, but your psi has to go to 0, at x equal to infinity then which one will go to 0? B will go to 0, did you get it or not?

Student: Yes.

Look at this if you put an x equal to infinity here in this we will do it next class, but just think about it. If we put an x equal to infinity here this is e to the power minus infinity it goes to 0 anyway. What about this? This is B e to the power?

Student: (Refer Time: 50:01).

Infinity, but I know that psi at x equal to infinity is what? 0.

Student: 0.

This one cannot be 0 then what will be 0?

Student: B.

B will be 0; this is how you did it for a particle in a 1D box if you remember or not right applying a boundary conditions. What is the other boundary condition? The other boundary condition is; that means, your B is equal to 0 so, your psi essentially is A e to the power minus kappa x now. Your other boundary condition is x is equal to x 0. When you have x equal to x 0, then psi equal to psi 0 which is the surface charge on the plane P and then we get A in terms of psi 0 that is what we are going to look at in the next class.

So, that day what we will do is this we did for a plane, but now remember proteins are not planar molecules right; proteins are what?

Student: (Refer Time: 50:41).

Spheres. So, we will actually look at del square in terms of a spherical symmetry or spherical potential and try to think what do you solved for your del square or when you used your hydrogen atom what did you do? You used a spherical symmetric potential, we will go to spherical polar coordinates and only take the radial distribution of the radial part of the Laplacian operator, ok.

Student: Yes.

Ok.

Thank you.