

**Micro and Nanoscale Energy Transport**  
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**Lecture – 34**  
**Fundamentals of Electro Kinetics in Micro Channels Part 1**

Good Morning. We will look at a new topic for the next 2 or 3 class. So, this will be on electro kinetics. So, generally I mean when we talk about microscale phenomena although this is not part of know heat transfer. But, generally a very important aspect of microscale flow is how to manipulate some of the forces at that small scale and make use of those forces to drive the flow. So, this is very interesting topic and therefore, without mentioning this I do not think I will complete micro nanoscale part.

I think when you now deal with microscale phenomena as you have seen especially apart from the gas flows you know when you talk talking about the liquids there is really not. So far whatever we have seen with the single phase liquid flows through micro channels in terms of hydro dynamics or heat transfer is nothing much very new that you have. You know that you have to learn to understand know microscale Phenomena because, most of the correlations are equally valid for macro channels. And specifically we are highlighting certain important features such as you know the surface roughness and. So, on which becomes important, but they can also be considered for macro channel case.

So, in that sense you know if you have a course where only you know microscale Part is covered you may feel or you may underestimate the content and also the physics you might think that there is nothing really interesting or new to learn in the micro and nanoscale and it is all just you know re emphasis of the Macroscale phenomena with some alterations. So, that portray is a very simplistic kind of a picture and. In fact, in also to say hydro dynamically most of the microscale flows are in the laminar regime.

So, that makes it for a average you know fluid mechanics background person makes it far more easier to deal and understand then, with the macro channels with the with the macro channels you talk about separately laminar turbulent and you give a lot of emphasis to turbulent flows because most of the engineering problems are of you know

turbulent nature.

Therefore, you put so much of struggle to do experiments and modeling simulations of turbulence whereas, in the micro channel everything appears to be laminar and pretty straight forward. So, use the same continuum equations only that you call this as micro with the fancy name and you are still using the no slip boundary conditions. So, everything seems to be much easier only that it is the key words are you know far more captivating than in the macro case, but that is why I started with the nano scale transport.

So, if you want to really build a bottom sub approach you have to understand if there is a rigorous physics and theory at the nanoscale level yeah. So, you when you are building like this you know you understand the foundation is actually quite strong you know you talk about the atomistic scale energy carrier level approach. So, that is the foundation and that can be applied through all the regimes, but the microscale; however, is a little bit fuzzy patch.

So, there is no separate theory for microscale, either it as to be bottom sub approach or a top down approach. So, some microscale what happens is it is difficult to build a bottom sub approach because it is neither really nano nor macro. So, we resort to the top down approach we still use the continuum equations and everything and we only focus on certain flow physics which are more relevant when your channel dimensions becomes smaller, but in terms of the mathematics or rigor it is not very difficult whereas, the nano scale you cannot do a top down approach it will fail you are really talking about sub continuum.

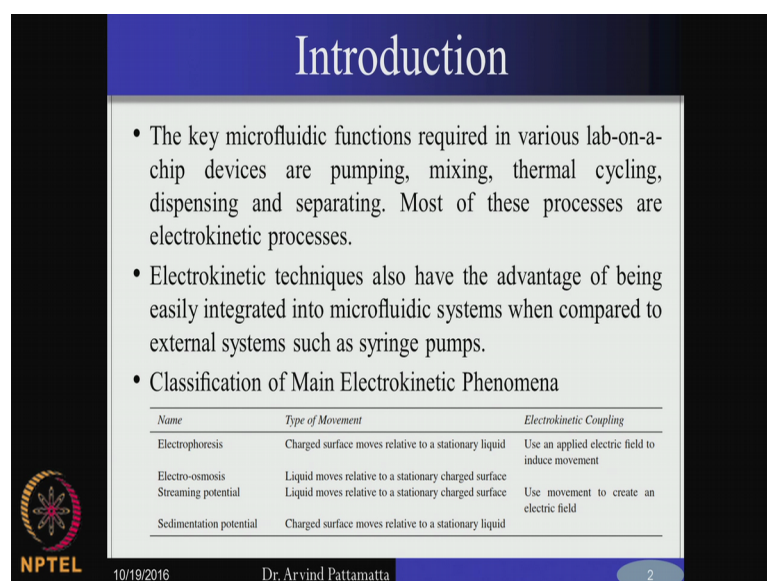
Therefore, we are building a completely new theory you know fundamental prospect from fundamental prospect we do not assume anything right no continuum nothing. So, we just start from the building blocks and we build it and the same approach can be extended to microscale. However, it is not worth doing such a very rigorous approach computationally it is very expensive to solve Boltzmann Equation for say liquid flow in micro channel when most of the flow physics can be explained by continuum equations. So, it is far easier to solve the Navier stokes equation than solving Boltzmann Transport. So, therefore, any subject on related to microscale unless you have a foundational

understanding of nanoscale will not look complete and also will make you feel that it is a very trivial course correct.

So, most of the correlations are equally valid macro and micro only for the gas flows you have the problem of Knudsen numbers exceeding 0.1 and therefore, you bringing all the slip boundary conditions, but for liquid flows there is absolutely no problem. So, now, therefore, people working in this field somehow have the privilege for sometime; to get away with using simpler equations, but trying to understand new phenomena at that small scale. So, electro kinetics is for example, one of them.

So, this is not a very topic only related to microscale this can be there even for any surface you know or any length scale, but this becomes more important these forces becomes more important when the channel dimensions becomes smaller. Therefore, you can significantly use this force to cause a motion and therefore. We talk about electro kinetics particularly in microscale transport the same physics or same theory holds equally well for any scale, but as we said that we still stick to the same equations, but we emphasize only the important physical phenomena occurring at the small scales. So, electro kinetics is one such phenomenon.

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**Introduction**

- The key microfluidic functions required in various lab-on-a-chip devices are pumping, mixing, thermal cycling, dispensing and separating. Most of these processes are electrokinetic processes.
- Electrokinetic techniques also have the advantage of being easily integrated into microfluidic systems when compared to external systems such as syringe pumps.
- Classification of Main Electrokinetic Phenomena

Name	Type of Movement	Electrokinetic Coupling
Electrophoresis	Charged surface moves relative to a stationary liquid	Use an applied electric field to induce movement
Electro-osmosis	Liquid moves relative to a stationary charged surface	
Streaming potential	Liquid moves relative to a stationary charged surface	Use movement to create an electric field
Sedimentation potential	Charged surface moves relative to a stationary liquid	

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Relevant about Electro Kinetics; the Electro Kinetics has become a very important branch of microscale flows because, the entire domain of Microfluidics. Microfluidics is nothing, but micro flows with electro kinetics. Other different kinds of kinetics which are brought in by external forces or forces which become very important at small scales surface based forces. So, this has brought about a completely new subject called Microfluidics and Microfluidics has become very important due to many applications in small scales electronic cooling could be one of them.

But more than that Microfluidics has spread into biological and medical applications and that is where it is gaining human popularity and. So, lot of people from biology and medical field since they do not have good knowledge of fluid mechanics. So, they want to; however, build devices which are of you know small scales where they can process synthesize you know separate, for example; DNA. So, that is one application separating platelets from plasma in the blood this is done very regularly sorting of blood you count the kind of platelets how do you count how many RBCs are there WBCs are there you know. So, there are some sorting and counting mechanisms which are conventional and which are expensive which takes time.

So, the idea is to build what is called as a lab on a chip device that is a portable hand held Microfluidic device where you put some sample of your say blood and this Microfluidic device uses these Electro kinetic or another you know kinetic principles and it will kind of say separate the plasma from the platelets and you would at the end of the small device you will be able to count how much is the platelets count in your blood. So, it is a hand held you does not even have to go to a laboratory and use the expensive equipment. So, such kind of you know very compact portable biomedical applications are all emerging now. So, even many companies including our Apollo pharmacy they are actively engaged in manufacturing such hand held lab on chip devices.

So, that is how Microfluidics has gained human popularity. So, it is essentially at that you apply these physical phenomena at these scales to put into use for you know medical applications where it is become necessary to make the devices diagnostic devices testing devices as small as possible. So, that you know everybody can buy it you know at a cheap price and they can just use it on their own right one example is how you test for

diabetes. So, some ten 15 years back all the time you have to go to a hospital where they prick your finger and then they tested. So now, you have portable glucose testing machines.

So, you just small strip you prick it you put it and immediately it will give you the digital value that is the very good example of a Microfluidic device. So, inside it is nothing, but a lab on chip device which will analyze the blood sugar level in your blood and immediately it senses what is the value, there could also be some chemical reactions that that you can induce within the small Microfluidic device some chemical has to mix with the blood some reaction should happen and you should find that. So, the chemical compound is converted into this much percentage of this. Therefore, this is correlated to your amount of blood sugar.

All these are usually built on such kind of principles. So therefore, most of the key Microfluidic functions require various labs on chip devices and what kind of principles they use what whatever we know pumping. But pumping cannot be now done like you are putting a conventional big pump it as to be done in such a way that you know you pump micro liters you know very small volumes of fluid and you have to also make sure that you do not have an external mechanical pumping device. So, it can be integrated within the same lab on chip device such a way that it uses the forces at the small scale to pump. So, we have to therefore, find ways to build a pump which is based on such kind of phenomena, therefore pumping mixing thermal cycling dispensing and separating.

So, mixing is another very important aspect in Microfluidic's because most of the times as I said the regimes laminar and therefore, the mixing is not. So, turbulence is always very good for mixing. So, in conventional case in heat exchanges, if you want to mix 2 fluids you make them turbulent you mix them, and you do not have any problems. So, the turbulent diffusion is quite high whereas, if you are talking about the micro channels where it is laminar. So, it is very difficult to achieve mixing and therefore, we have to find out alternate ways of promoting this mixing process separation.

So, you have to also find out ways to separate two different components of the fluid for example, if you take blood you want to separate the plasma out platelets out. So, how do

you device. So, you can have channel which is bifurcating. So, very simple phenomena, So, you have it appears very trivial to you, but people working in this area have to now use this and build devices which doctors think it is some completely novel because, they do not have any understanding of fluid mechanics and since all these have very good marketing potential, you go and built his device patent it you market it. So, that is how because the medical applications are the most you know demanding applications most common where you can generate lot of revenue compare to the other industries.

Therefore, a simple bifurcation where you have one small diameter channel the other is a large diameter channel the small diameter channel will definitely pose resistance to platelets. So, therefore, the fluids will take path of least resistance though platelets will run through the larger diameter one and then you have many of such bifurcations. So, that you increase the separation efficiency at the end of this device you can separate the plasma from platelets. So, this is the very device you know just path of least resistance and you alter the diameter of these channels.

But as such a very potential impact where you know the separation is a big problem you have to go to a equipment which is very expensive at large scale and you have to do it now if you have this Microfluidic device if you do it within your pump. So, that is how you know these get a lot of publicity in that sense. So, Microfluidics has become very important topic in microscale flows more important than for example, microscale heat transfer because the number of applications dealing with biomedical medical applications are, much more than with electronic cooling right and electronic cooling is kind of a saturating problem.

So, there is always you know you cannot increase the processors speed beyond a certain point because you are miniaturizing it already and you do not have too much of space to put very sophisticated cooling technology right. So, even if you build a micro channel within the chip. So, the processor can only be this much fast. Therefore, if you look at the average processor speeds in the last 4, 5 years they have not tremendously gone up. So, near about 3 Giga Hertz. Whereas, if you look at processors speeds in the last fifteen years you would see a big difference from mega hertz now we have gone to Giga hertz, but now once it has approach 0.5 then 2 3 Giga Hertz.

Now, you do not see a marked improvement worry very marginal improvement in the clocks speeds. So, that shows that you know thermal dissipation is a big problem and you cannot do much because already you are shrinking the size of these devices. So, at the same time you cannot increase the clock speed. So, there is a kind of saturation in the electronic cooling area. Whereas, if you look at biomedical applications there is always scope for everything a better diagnostic device better treatment device which is more comfortable which is more compact less intrusive.

So, all these keep on evolving there is a lot of challenge and most of the guys working in that area they do not have any understanding of how to build these devices let it be doctors or health professionals they do not have any understanding of the fluid mechanics. So, that is how the Microfluidics is gained lot of popularity because of the tremendous applications in biology. So, therefore, how do we achieve all these Microfluidic functions pumping mixing separating dispensing? So, these are a phenomenon which has been known for at least a hundred years, but we have never emphasized this for the large diameter channels because that small diameter channels all these forces surface forces now start appearing and we now can make use of these forces to cause all these functions.

I mean when you look at the different phenomena. So, what I am going to emphasize here you can you can talk about magneto kinetics also you can talk about using body forces or other surface forces capillary forces also to induce motions. So, you can have thermo capillary motion you can have capillary induced motion you can have magneto kinetics, but the most important fundamental and most commonly used feature is the electro kinetics. Therefore, if you look at the most important electro kinetic phenomena I would say there are two of them one is call the electro osmosis the other is called electrophoresis you can also have case where you have a movement and this can cause an change in the electric filed electric potential. So, those two come under what we called as streaming potential or sedimentation potential.

So, you have 2 types. So, one you make induce electric field you apply an electric field externally and then you move the flow you induce a flow. So, that is coming under electrophoresis or electro osmosis and when you say electro osmosis. So, this is where

you have fixed plates or fixed body walls. So, which are charged the charges are actually or accumulating at the walls enclose to the walls, but the walls are fixed and what is moving is the fluid bulk fluid in the case of electrophoresis you are talking about say particles or charged ions or metallic particles which have charged and these can actually move relative to the fluid. So, you can have therefore, two types of motion one the motion of the bulk fluid walls being fixed and the force the Coulomb force which is acting on this bulk fluid it is due to the electro static charge potential at the walls that is the electro osmosis process.

So, the other process is the electrophoresis where you can have charged bodies or charged particles in a stationary fluid and these can be accelerated by means of external electric field that is called electrophoresis and if you do the reverse. So, you can actually have a charged particle or charged metallic surface and you move them that will induce an external electric field that will induce the electric field. So, that is used in the case of streaming potential and sedimentation potential. So, those two will not look at in this lecture, but we will emphasize only on the electro osmosis and electrophoresis part.

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**Electric Double Layer (EDL) continued ....**

- Stern layer is fixed in place
- The diffuse layer has a net charge and can be moved with an electric field
- The boundary between the Stern layer and the diffuse layer is called the shear surface because of the relative motion across it.
- The potential at the wall is called the wall potential  $\phi_w$  and the potential at the shear plane is called the zeta potential  $\zeta$ .

The diagram illustrates the structure of the Electric Double Layer (EDL) near a charged surface. Part (a) shows a cross-section of the EDL with a solid surface at the bottom. The Stern layer is the region immediately adjacent to the surface, containing counterions. The Diffuse layer is the region further away, containing both counterions and coions. Part (b) is a graph of Potential  $\phi$  versus distance  $\delta$  from the wall. The wall potential  $\phi_w$  is the potential at the surface, and the zeta potential  $\zeta$  is the potential at the shear plane. The Debye length  $\lambda_D$  is also indicated.

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So, just to say how they what is the fundamental physics behind the electro kinetics in general. So, if you take any polar liquid. So, which as a net charge and you immerse an



object in this or boundary or a wall into this polar fluid what happens is this particular wall at this right at the surface will acquire some charge being in contact with the polar fluid.

For example, in this example it shows that the surface is now negatively charged. So, you have excess negative charge at the surface and this is common it need not be at small scales it can be at any scales, but at large scales you do not find this is causing any difference if you do not consider this into account, but at small scales this becomes quite important. So, therefore, you have a charge for example, it could be a negative charge and what happens now the base fluid that you have again has positive and negative ions for example, water you take  $H^+$  plus  $O^{2-}$ .

Therefore, the tendency will be for all the positive ions to come and settle down towards the wall right because the wall is now negatively charged. So, therefore, the first layer of positive charge which is accumulated on the wall this is called the stern layer. So, S T E R N, stern layer and as you see that this is almost stuck to the wall. So, it cannot move. So, these are positively charged ions which are stuck to the negatively charged body. So, the interaction potential is very large. So, you cannot simply separate them. So, it looks almost that that is stationary.

But what happens is there is a net negative charge at the wall this cannot be simply compensated by the stern layer positive ion. So, still some more positive ions from the bulk keep diffusing towards the wall. So, therefore, if you look at lengths which are much larger than the first layer which is the stern layer you see a diffusion of these positive ions closer and closer to the wall and far away from the wall there is no net charge accumulation far away from the wall the fluid becomes neutral electrical, but close to the wall the charge accumulation will diffuse. Therefore, there is another layer above this stern layer call the diffuse layer and outside the diffuse layer the fluid will become electro statically neutral.

If you therefore, draw the potential electro static potential right at the wall this is where the stern layer is the highest value of electro static potential that is the gradient this is related to gradient in the concentration of the ions or positively charged ions in this case

and this is that still stern layer and then, from this stern layer you have more gradual reduction in the potential and finally, this value becomes is equal to the bulk value.

So, asymptotically as you go to large distances from the wall this potential goes to 0. So, therefore, the combination of the stern layer and the diffuse layer together is called the electric double layer. So, when you really zoom you know with the microscope and you go to one ion distance from the wall you find this stern layer which is stationary for all practical purpose there is no motion of this stern layer, it is just there struck and above this you have the diffuse layer where you have a gradual reduction in the potential electrostatic potential. And finally, far away from the wall even this potential will  $d k$  and the fluid becomes neutral.

So, now what is? So, important about this; that means, there is a potential; that means, if you apply an electric field. So, these charges will now there therefore, move in the direction of the electric field. So, and this happens primarily at the diffuse layer because that is where the thickest layer is and that is where the maximum change in the potential happens. So, therefore, when you apply an external electric field you find all the ions in the diffuse layer actually moving and therefore, this motion will appear as though that the wall is now fixed, but there are diffuse layer is just moving it is like a quite flow.

So, the way to analyze this particular problem would be to therefore, solve for the region where you have the diffuse and stern layer get the solution at the edge of the diffuse layer you know what will be the velocity and now treat this problem like quite flow with the slip and apply the particular velocity as the slip boundary condition. So, the outer region will be a pure Navier stokes, without any external forces because the external forces cannot induce any motion in the out external flow because it is electro statically neutral. So, only the diffuse layer will actually move and to makes this problem simple we only solve the double layer separately with the Coulomb force calculate, the velocity at the edge of the double layer and give that as a slip boundary condition to the conventional Navier stokes equation.

So, in the end what you have is a net motion of the fluid and that will be if you take the simple case if you have 2 plates 1 on the top one on the bottom. So, you just have a

constant velocity between these 2 diffuse layers on the top and bottom because, that is the limiting case of the quite flow a quite flow with both walls top and bottom walls moving with the same velocity what will be the velocity profile. It will be the same as the wall velocities it will take the average velocity between the top and bottom wall if both the walls move at the same speed in the same direction.

Then, the net bulk motion will also be same as you if one wall moves in this direction the other wall moves then at the midpoint it will be 0 velocity top half will be moving in this bottom half will be moving. So, it is a linear profile. If one wall moves with  $u_1$  the other wall moves with  $u_2$  then the velocity profile will take average of. So therefore, in this case the simplest solution for quite flow will be whatever velocity you have at the edge of the EDL. So, that velocity will be uniform throughout the bulk.


Therefore, to just give you some definitions, we have the definition of  $\delta$  which is called the stern layer thickness right and we have the thickness of the diffuse layer which is given by  $\lambda_D$  and if you measure the potential difference between the bulk fluid and what is there at the edge of this stern layer. So, this is the edge of the stern layer correct. So, you have a certain value  $\phi$  at the edge of the stern layer for the bulk you have a certain potential  $\phi_{\text{bulk}}$ .

So that difference will give you what is called the zeta potential. So therefore, at the wall this potential difference is  $\phi_w$  the actual potential at the wall and minus the bulk value that is your  $\phi_w$  and at the edge of this stern layer this potential difference becomes what is called the zeta potential. So, these are some of the standard notations and definitions used for the electric double layer.

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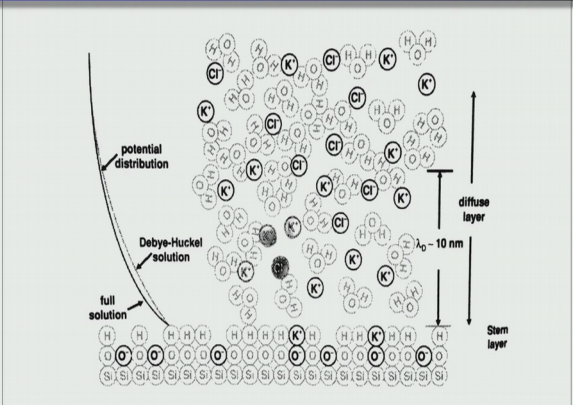
## Electric Double Layer (EDL)

- When polar liquid, such as water, and the solid are brought into contact, the surface of the solid acquires an electric charge.
- The surface charge then influences the migration of charges within the liquid near the wall.
- Ions in the liquid are strongly drawn toward the surface and form a very thin layer called the Stern layer in which the ions in the liquid are paired with the charges on the surface.
- The Stern layer then influences the charge distribution deeper in the fluid creating a thicker layer of excess charges of the same sign, as those in the Stern layer called the diffuse or Gouy-Chapman layer.
- Together these two layers are called the electric double layer (EDL).


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## Electric Double Layer (EDL) continued ....



The schematic of Electric Double Layer

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Now again this is another schematic very enlarge magnified view of the electric double layer. So, what it shows is you have silicon surface silicon materials which actually possess a negative charge that is what is given by this o minus. Now, when you put an aqua solution of potassium chloride, you can have some salts in your fluid in your water it need not be only pure water you know. So, you can have some salts it can be sodium

chloride or potassium chloride or some other ions.

Now what happens is all the positively charged ions are now pulled close to the wall. So, you can as you can see that there is a  $h^+$  ions and also  $k^+$  ions can also come and get stuck and slowly from this there is a buildup of the positively charged ions which makes the diffuse layer and far away above much above the diffuse layer again the net charge will be 0. So, you have more or less equal number of  $h^+$  and  $o^-$   $h^+$  minus  $k^+$  plus and  $Cl^-$  ions.

So, you do not have any induce any electrostatic potential, but close to the wall you have the stern layer right at the wall and you have the diffuse layer. So, what will be the, we are not really bothered about calculating the stern layer thickness because that is really not go in to effect anything it is almost motionless. So, it is not going to appear anywhere. So, the most important layer will be the diffuse layer and generally the diffuse layer can extend of the order of few tens of nanometers it is again nanometer scale phenomena. So, if you are drawing the potential distribution the same potential distribution that we draw here you have the wall potential at the wall and slowly gradually it drops to the bulk, therefore if you take the potential difference between the bulk and the particular point. So, that will be your potential difference and that will be 0 at the bulk and at the wall you have the maximum.

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**Ions distribution and potential in EDL**

- Consider aqueous solutions containing dissolved ionic species, which is denoted by 'i'.
- Each ion has a bulk concentration ' $c_i$ ' and a valence or charge number ' $z_i$ '.
- For example, if we have a 1mM solution of NaCl,  
 $c_{Na^+} = 1\text{mM}$  and  $c_{Cl^-} = 1\text{mM}$  and  
 $z_{Na^+} = 1$  and  $z_{Cl^-} = -1$
- We use subscript 'bulk' or ' $\infty$ ' to define properties in the bulk, far from the wall.


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Yeah. So, therefore, if you consider this particular case, we have an aqua solution containing dissolved ionic species each of this is denoted by I it could be h plus or k plus Cl minus o h minus. So, each of this species is denoted by the index I and each ion as a bulk concentration  $c_I$  and a valence charge number  $z_i$ . So, just to tell you what these values are if you for example, have a 1 milli mole solution of sodium chloride the bulk concentration of n a plus and Cl minus will be both same, but the valence number will be different this is n a plus and this is Cl minus. So, the valence number for the n a will be one plus one and Cl will be minus 1. So, therefore, we use the subscript bulk or infinity to define properties in the bulk far away from the wall.

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**Ions distribution and potential in EDL**  
continued ....

- Double layer potential is given by:  $\varphi = \phi - \phi_{\text{bulk}}$ .
- The value of ' $\varphi$ ' specifies how the electrical potential at point differs from that in the bulk far from walls.
- From the Boltzmann statistics, we can write in general that:  
 $c_i = c_{i,\infty} \left( -\frac{z_i F \varphi}{RT} \right)$  : where ' $z$ ' is ion valence, ' $F$ ' is Faraday constant and its value is 96485 C/mol.
- The local net charge density ' $\rho_E$ ' as the function of the local potential is given by:  
$$\rho_E = \sum_i c_i z_i F$$
- Therefore, the Boltzmann solution is given by:  
$$\rho_E = \sum_i c_{i,\infty} z_i F \exp \left( -\frac{z_i F \varphi}{RT} \right)$$



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Now, why are we bother about these bulk concentration and valence number, now, we know the double layer potential is given at any point in that from right from the wall to any region in the diffuse layer it is the potential difference is nothing, but the actual electrostatic potential at that particular location minus the bulk value. Therefore, if you want to understand how to calculate the net charge density based on this particular potential right. So, this net charged density is what is going to cause the motion if you place an electric field external electric filed.

So, how do we calculate the net charge density? So, this net charge density is calculated for each species of the ion. So, you know what is the particular bulk concentration time what is the valence number time's f, f is call the faradays constant. So, if you multiply them and sum them over all the species, you get the net charge density and the question is how do we calculate c I because c I is actually a local concentration. So, it as to be related to the bulk values c I infinity. So and how it is related through the Boltzmann statistics. So, we are using Boltzmann statistics again after we talk about nanoscale, now again in terms of concentration distribution.

So, in the actual Boltzmann statistics for energy we had in the numerator energy e divided by k b t. So, that is rewritten. So, that energy now is replaced by z I f into phi

corresponding to the charge electrostatic potential. So, this gives you the distribution of your concentration from the wall to the bulk value at  $c$  I infinity therefore, if you say your  $\phi$  equal to 0. So,  $\phi$  equal to 0 means this is at the bulk  $\phi$  is equal to  $\phi$  minus  $\phi$  bulk. So, when can  $\phi$  be 0 only if you have electrostatic potential is same as your bulk value? So, in that case the value of  $c$ , I will be equal to. So, there should be an exponential here there is a mistake please correct it that should be  $c$  I infinity into exponential of that. So, when  $\phi$  equal to 0.

So, your concentration equals the bulk concentration and that bulk concentration is given by this correct and from there what happens to this concentration as your  $\phi$  keeps increasing as your  $\phi$  becomes larger and larger reduces. So, therefore, using this Boltzmann statistics we can now plug in into the expression to calculate the net charged density  $\rho$  correct because the net charged density will give you at particular level what is the concentration based on that concentration of ions you can calculate the charge density.


So, in order to know the concentration distribution we use the Boltzmann statistic substitute into this and therefore, the net charge density can now be written as the function of the potential difference  $\phi$ . So, express through the Boltzmann solution, and now what do we do with this  $\rho e$ ? Now, this  $\rho e$  is at a particular location right this is the net charge density at a particular location.



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**Ions distribution and potential in EDL**  
continued ....

- The Poisson distribution which links potential to the local net charge density is given by:  
$$\nabla^2 \phi = -\frac{\rho_e}{\epsilon}$$
- So, the Poisson-Boltzmann equation is given by is given by:  
$$\nabla^2 \phi = -\frac{F}{\epsilon} \sum_i c_{i,\infty} z_i F \exp\left(-\frac{z_i F \phi}{RT}\right)$$
- Normalizing the above equation we get:  
$$\nabla^{*2} \phi^* = -\frac{1}{2} \sum_i c_{i,\infty}^* z_i F \exp(-z_i \phi^*)$$



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So, we have expressed this in terms of the local electrostatic potential difference and as a function of the bulk concentration of this species. So, now, based on this at a particular location you calculate what is the value of the net charged density and once you know that you can write your Poisson's equation which states that you are Laplacian of your electrostatic field electrostatic potential is related to is nothing but minus your rho e by epsilon. So, here epsilon should be the permittivity. So, therefore, you solve the Poisson distribution. So, this Poisson distribution function will.

So, this particular equation links your potential to the local charge density and therefore, we now plug in from the previous equation the expression for rho e into the Poisson equation and this equation is now called Poisson Boltzmann equation because the original Poisson's equation has the local charge density and through the Boltzmann distribution we are bringing in the relation with respect to the free stream concentration of a particular species. So, therefore, this particular equation is called the Poisson Boltzmann equation.

So, you can also non-dimensionalize this equation. So, we can call this as phi star where phi star can be f phi by r t this some kind of non dimensional electrostatic potential in terms of faradays constant r and t and similarly you can non-dimensionalize the length

scales using the length  $d$  by length  $\lambda_D$ . So, so this  $d$  by length is also referred to as the length of the diffuse layer right. So, we have mentioned that the diffuse layer given by the height  $\lambda_D$ . So, that is also sometimes called the  $d$  by length.

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**Ions distribution and potential in EDL**  
continued ....

- Where,  $\phi^* = \frac{F\phi}{RT}$  and length is normalized by Debye length  $\lambda_D$ .

$$\lambda_D = \left( \frac{\epsilon RT}{2F^2 I_c} \right)^{0.5}$$

- The Debye length gives a measure of the characteristic length over which the over potential at a wall decays to the bulk.
- 1D form of non-linear Poisson-Boltzmann equation is:

$$\frac{\partial^2 \phi^*}{\partial y^{*2}} = -\frac{1}{2} \sum_i c_{i,\infty}^* z_i F \exp(-z_i \phi^*)$$

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So, we have already talked about mean free path. So, this is something similar to that. So,  $d$  by length gives a measure of the characteristic length over which the over potential at the wall decays to the bulk very simple definition.

So, the over potential is basically your  $\phi$  minus  $\phi$  bulk, from the wall. So, it takes a distance of  $\lambda_D$  or the  $d$  by length to decay to the bulk value. So, the over potential should become's 0 from the wall potential. So, this distance is given approximately by an empirical correlation from scaling arguments. So, you can use this particular expression to approximately calculate the order of magnitude of  $d$  by length and most often it turns out to be of the order of a ten nanometer or so. So, therefore, the Poisson Boltzmann equation if you non-dimensionalize using a non dimensional electrostatic potential and  $d$  by length you write it in terms of non dimensional numbers.

So, we will stop here tomorrow we will see how we can solve the equation because this equation write here is it a linear or non-linear. So, this is going to be a non-linear

equation because you have function of phi in both the side's left hand side and write hand side. So, in order to solve this you have to guess the solution for phi and substitute it and see if it satisfied and do this iterative process. So, therefore, to get a simple analytical solution we try to Linearize this equation and solve directly for phi.

So, we will therefore convert the non-linear Poisson Boltzmann equation into a linear Poisson Boltzmann and find the solution for phi, that we will continue tomorrow.