

**Micro and Nanoscale Energy Transport**  
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**Lecture - 35**  
**Fundamentals of Electro Kinetics in Micro Channels Part-2**

So, we have looked into the concept of electric double layer yesterday. So, when you immerse a solid object or solid wall in a fluid, which is a polar liquid for example, you can have an aqueous solution of sodium chloride or potassium chloride. So, the wall will actually acquire a net charge, which could be negative or positive. So, suppose if you consider the wall acquires a net negative charge.

So, the positive ions in the fluid tend to migrate and attach as a first layer to the walls. So, this layer is called the stern layer, and even if you apply an external electric field this stern layer appears static, and it does not really move along with the fluid. So, for therefore, practical calculations you do not have to really consider the thickness or what is the effect of the stern layer, but from the stern layer onwards there is a buildup of positive ions which is a gradual diffusion-like process and therefore, you have a secondary layer called the diffuse layer, which builds on top of this stern layer and extends all the way into the bulk of the fluid. And far away from the wall the net electrostatic potential difference from the bulk value will be 0.

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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 consists of two parts, (a) and (b). Part (a) is a schematic showing a solid wall at the bottom with a negative charge. Above the wall, there is a Stern layer containing positive ions (represented by circles with '+' signs) and a Diffuse layer containing both positive and negative ions. Part (b) is a graph of Potential  $\phi$  versus distance  $\delta$  from the wall. The potential starts at a high value  $\phi_w$  at the wall and decays towards zero. The zeta potential  $\zeta$  is indicated as the potential at the shear plane, which is the boundary between the Stern and Diffuse layers. The Debye length  $\lambda_D$  is also shown as the characteristic length scale of the diffuse layer.

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So, therefore, if you plot the actual potential value right at the wall you may have a very high value of potential and then slowly gradually decrease and asymptotically it reaches the value of the bulk potential, for large values of  $y$ . So, if you define over potential which is  $\phi - \phi_{\text{bulk}}$ . So, that gives you the excess potential on top of the bulk and that value becomes 0 for large values of  $y$ . So, therefore, from this we define what is called the Debye height Debye thickness or you know diffuse layer thickness  $\lambda_D$ , which gives you the distance approximate distance over which you know this excess potential decrease to 0, right and the corresponding value of the potential difference, excess potential from the stern layer value to the bulk value. So, this is called zeta potential right.

So, the higher the zeta potential more is the electro kinetic capability of this particular fluid and solid object combination correct. So, generally one measure is before you check whether you can actually use the phenomena of electro kinetics you first generally people measure the value of the zeta potential with the electrostatic part of the fluid with before applying the electric field, and then they decide whether this fluid and solid combination is good enough to drive all the electro kinetics by an external field.

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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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So, I think this part is pretty much clear to you. So, we have taken the example of an aqueous solution of say sodium chloride and then we said that suppose you assume the bulk which is an electrostatically neutral, you have equal number of  $n$  a plus ions and  $c$  l

minus ions and also the valence number which denotes the charge will be equal and opposite in this case.

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

- Double layer potential is given by:  $\phi = \phi - \phi_{\text{bulk}}$ .
- The value of ' $\phi$ ' 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:  

$$c_i = c_{i,\infty} \exp\left(-\frac{z_i F \phi}{RT}\right)$$
 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:  

$$\rho_E = \sum_i c_{i,\infty} z_i F \exp\left(-\frac{z_i F \phi}{RT}\right)$$

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So, therefore, the next part will be calculated, what is the net local net charge density rho e.

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

The diagram illustrates the structure of the Electric Double Layer (EDL) near a solid surface. On the left, a curved line represents the potential distribution, which is labeled as the Debye-Huckel solution. Below this, a horizontal line represents the full solution. The diffuse layer is shown as a region containing various ions (K<sup>+</sup>, Cl<sup>-</sup>, H<sub>2</sub>O) and is labeled with a thickness of  $\lambda_D \approx 10 \text{ nm}$ . The Stern layer is shown as a thin layer adjacent to the solid surface, containing a layer of water molecules and ions. The solid surface is represented by a grid of atoms (S, Si, O, H).

The schematic of Electric Double Layer

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So, this is required because we do not know how the potential actually varies.

We are only showing this as you know upfront, but this is a solution we have to solve this equation with appropriate boundary condition then only we will know that distribution varies like, this all we know the only the value at the wall and the value at large values of y right. So, in intermediate variation is not clear. So, for that we have to solve the Poisson's equations.

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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:  

$$\nabla^2 \phi = -\frac{F}{\epsilon} \sum_i c_{i,\infty} z_i \text{Exp}\left(-\frac{z_i F \phi}{RT}\right)$$
- Normalizing the above equation we get:  

$$\nabla^2 \phi^* = -\frac{1}{2} \sum_i c_{i,\infty}^* z_i \text{Exp}(-z_i \phi^*)$$

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So, the Poisson's equation, where you have an electrostatic which solves for the electrostatic potential phi, so, is just the Laplacian operator on the left hand side that is equal to the net charge density, the local charge density on the right hand side.

So, to get the local charge density, so, we have to look at all the ions locally. So, the concentration of each individual ion multiplied by the corresponding charge whether it is positive or negative charge correct. So, if it is positive. So, this will be rho if positive and negative and so, on. So, I multiplied by what is called the Faraday constant. So, the value is given there. So, the question is how do, I exactly determine the local concentration. So, for this we make an assumption of Boltzmann distribution. So, that, we can relate the local concentration of these ions to the bulk value  $c_{i,\infty}$ , so, through this exponential function distribution function. So, this exponential distribution function is a function of the over potential that is  $\phi - \phi_{\text{bulk}}$ . If your  $\phi$  equal to  $\phi_{\text{bulk}}$  at large values of y, so, this exponential term will become one and therefore,  $c_{i,\infty}$  will be equal to  $c_{i,\infty}$ .

So, therefore, this is the implicit function of  $y$ , because here over potential is actually a function of  $y$ . So, you can say that  $c_i$  is the function of  $y$ . So, therefore, once you express this in terms Boltzmann statistics, the substitute for the expression into the expression for the local charge density. And which looks like this is the pretty straight forward arrangement now we therefore, substitute this  $\rho_e$  into the expression for poisson equation. So, then the resulting equation is called as the poisson Boltzmann equation, because we have the classical poisson equation into which we put in the Boltzmann approximation, distribution approximation. So, this is called the poisson Boltzmann approximation and as you can see this is the summation term and this is also a non-linear equation, you have  $\phi$  on both sides. Which cannot be directly solved for, but if you want to solve this the boundary conditions, you have to solve this iteratively, you have to guess these solution and then put this make sure that you balance the equation. So, if it does not balance then you re guess. So, so like this is an iterative travel and error process. So, if you normalize this you can non-dimensionalize the potential  $\phi$  as well as the coordinates.

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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, if you use the following non-dimensional notation. So, you can non-dimensionalize a  $\phi$  with multiplying by faraday constant divided by universal constant times temperature, and that is you are  $\phi^*$  similarly all the coordinates are non-dimensionalized with Debye length. The Debye length whatever expression is showed here, it is a coming from simple scaling arguments, where you combine all these parameters. So, those units are in

terms of meters, and these are a non-dimensional group of you know different parameters. So, this will be unit of exactly meters. So, if you non-dimensionalize with this Debye length. So, you get everything in terms of x star and y star and so on.

So, therefore, if you right it in one dimensional notations, suppose if I want to solve the poisson Boltzmann equation, for just the vertical profile right the variation of excess potential as a function of only y or a simple case a single plate. So, in this case therefore, I have to right this laplacian operator, del square, phi star, as only function of y. So, this becomes d square phi star by d y star square on the right hand side, I have the Boltzmann distribution function now this is a non-linear equation. So, if you want to solve this analytically. So, we make an assumption to make this a linear equation. So, how do we linearize this equation? So, we make an assumption that if you look at this exponential term exponential minus z i phi star.

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**1D Linear Poisson-Boltzmann Equation**

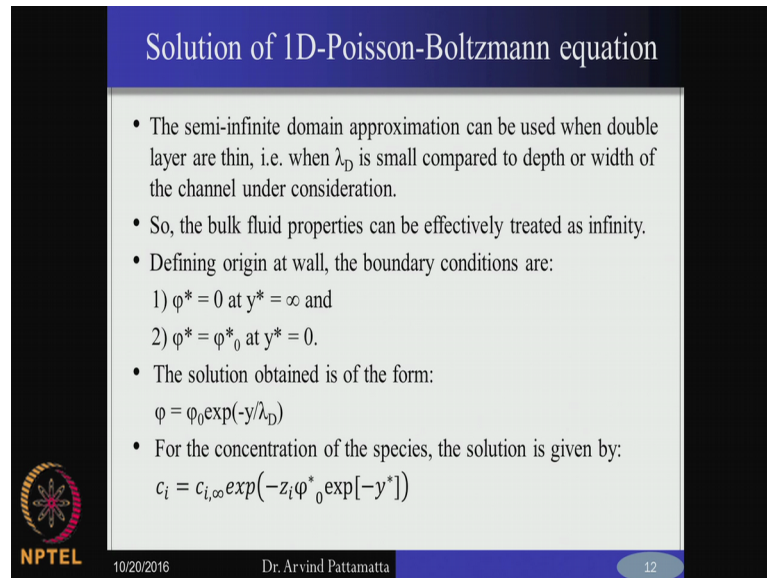
- If ' $z_i \phi^*$ ' is small relative to unity, the exponential term can be replaced with a first order Taylor series expansion by setting  $\exp(x) = 1 + x$ .
- Thus, the equation is of the form:
 
$$\frac{\partial^2 \phi^*}{\partial y^{*2}} = -\frac{1}{2} \sum_i c_i^* z_i^2 \phi^*$$
- By, using Debye-Hückel approximation we get the linearized Poisson-Boltzmann equation as:
 
$$\frac{\partial^2 \phi^*}{\partial y^{*2}} = \phi^*$$

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We can use a Taylor series approximation, we can express exponential of x is equal to 1 plus x, and if your x is much smaller than 1. So, then this becomes you know linear. So, therefore, this is what we are going to now do it. So, what we are planning saying that this fact the z i phi star, is actually a very small quantity compare to 1. So, z i is the valence number it could be plus or minus 1. So, multiplied by phi star the actual value of phi star the non dimensional phi, will is actually a very small value compare to 1 is much smaller than unity if you calculate. So, therefore, if you relay compare the relative order

of magnitude of these two terms you can therefore, replace 1 plus x which simply them. So, this becomes  $c_i$  into  $z_i$  square. So, we just right this as you know there is some problem here.

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**Solution of 1D-Poisson-Boltzmann equation**

- The semi-infinite domain approximation can be used when double layer are thin, i.e. when  $\lambda_D$  is small compared to depth or width of the channel under consideration.
- So, the bulk fluid properties can be effectively treated as infinity.
- Defining origin at wall, the boundary conditions are:
  - 1)  $\phi^* = 0$  at  $y^* = \infty$  and
  - 2)  $\phi^* = \phi_0^*$  at  $y^* = 0$ .
- The solution obtained is of the form:
 
$$\phi = \phi_0 \exp(-y/\lambda_D)$$
- For the concentration of the species, the solution is given by:
 
$$c_i = c_{i,\infty} \exp(-z_i \phi_0^* \exp[-y^*])$$

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So, we just so, we ignore all the higher order terms, so, what we are saying is that you have 1 plus x plus x square plus x cube and so, on. So, therefore, if this is small value all the higher order terms will be negligible. So, were x square x cube x power 4 terms will all be negligible. So, therefore, we needed only the term with x power 1. So, 1 plus x is the term that we used and then if you substitute that this should come out to this particular form you have  $z_i$  square  $\phi^*$ . So, we have  $c_i$  c star, we have  $z_i$  square, where is f. I think some problem with this formulation here. So, I think there is an f missing, and also there should be 1 plus x. I think there is some mistake so.

So, now, from this point for the case n a plus c l minus. So, we know that  $c_i$  infinity for n a plus c l minus, they are similar, if you consider 1 milli mole solution. So, they are each equal to unity, and similarly if you look at the value z they are equal and opposite. So, therefore, if you substitute into this expression, I think then it should be coming out correctly you have 1 times on plus you have 1 times minus, 1 square. Which is 2, so, 2 and 2 cancel and therefore, you only have  $\phi^*$  is that. So, you have basically if you look at aqua solution of n a plus and c l minus you can you look at only n a plus and c l minus species concentrations.

So, for that case if this reduces to  $\phi^*$ , but think there is still some issue with the sign and also it's not I will get back to you tomorrow on this. So, how this  $f$  is observed is not very clear, but from this part you reach the following form and this is called the Debye Huckel approximation. So, the Debye Huckel approximation is actually used for cases, where you have equimolar aqua solutions for example,  $n a + c l -$  or  $k + c l -$ . So, for equimolar for same values of molarity and also the valence numbers or equal and opposite, so, for a such a limiting case this summation now drops out and you have an explicitly equation in terms of  $\phi^*$ , and this is called Debye Huckel approximation. So, we can now therefore, solve this Debye Huckel approximation which is nothing, but the reduced form of the linear, linearized poisson Boltzmann equation. So, we linearize it with this step where we ignore the higher powers of  $x$ . And we convert it into this form, but still you have a summation which we reduce it for the case equimolar aqua solutions and then you get the Debye Huckel approximation.

So, now we can go ahead and solve this particular equation this is a simple ordinary differential equation of second, order you need two bound a conditions. So, therefore, we can apply the condition that at  $y$ ,  $y$  equals to 0. So, since this is a non-dimensional coordinates, we can give define everything in terms of non dimensional values. So, you have  $y^*$  equals to 0 the corresponding value at the wall the over potential will be value of  $\phi^*$  not, or you can use  $w$  if you want to represent this at the value at wall. So, what it means is that is the value of potential at the wall minus bulk. So, this excess potential or over potential is therefore,  $\phi^*$  not and at large values of  $y$ .  $y^*$  going to infinity your excess potential goes to 0 right.

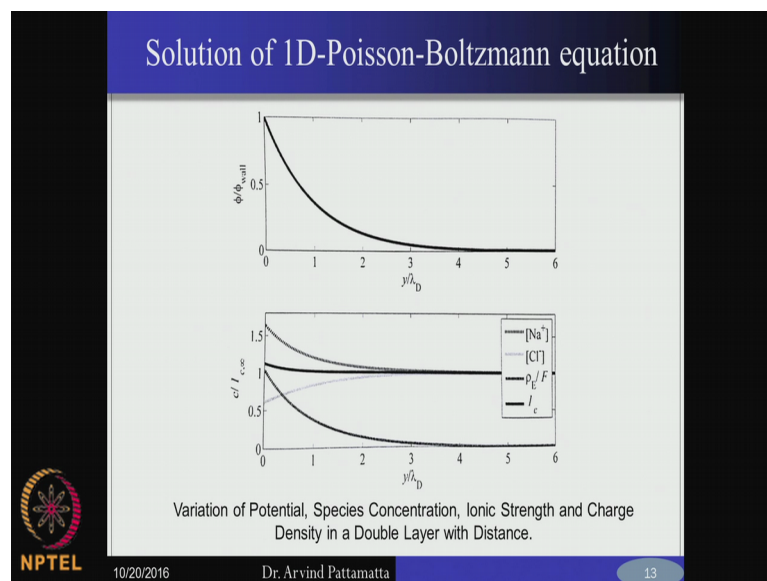
So, with these two boundary conditions if you solve this equation you have an exponential we will get an exponential solution so; that means, you  $\phi$  will turn out to be  $\phi^*$  not exponential minus  $y$  by  $d$ . So, I will give you a few minutes for you to actually workout. So, you know the solution to this equation. So, you can apply these boundary conditions and check whether you get this particular solution. So, once you get this you substitute into the expression for  $c$  from the Boltzmann statics. So,  $c$  in terms of exponential minus  $z i f \phi$ . So, you substitute for  $\phi$  into this, and we can write in an expression for the concentration of the species in terms of in non-dimensional  $y$  coordinate.



So, please do these two things, please check the solution and also get the expression for concentration. So, you have solution as  $c_1 \exp(-\kappa y)$  or  $c_2 \exp(\kappa y)$  right. So, at  $y$  going to infinity the exponential  $\exp(\kappa y)$  will also go to infinity, but solution should be 0. So, therefore, the constant  $c_1$  should be 0. So, therefore, the solution should be  $c_2 \exp(-\kappa y)$ . So, use the second boundary condition and you will be able to find out  $c_2$ , the constant should be  $c_0$  and you can write this as  $\psi^*$  is nothing, but  $\psi$  by  $\lambda_D$ .

So, therefore, if you substitute this into the Boltzmann distributions for concentration you can elaborate get an elaborate expression for  $c_i$ , is it clear till here. So, this is the solution to the one dimensional Poisson Boltzmann equation. So, now, you know exactly the nature of the electrostatic potential, how varies with it  $y$ . So, it is an exponential decay. So, therefore, if you plot this function  $\psi$  by  $\psi^*$  you can normalize.

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This with the value of  $\psi$  at wall, so, that it fits between 0 and 1, and you plot this is as a function of  $y$  over  $\lambda_D$ . So, you see the exponential variation very clearly. So, for large values of  $y$  by  $\lambda_D$  this value of  $\psi$  goes to 0. So, this is basically your excess potential variation, the other is your concentration variation. So, from this for particular species for  $n$  a plus for  $c_1$  minus for each of this you can plot the variation of concentration with respective  $y$  for example, if you have a negatively charged wall. So, the concentration of positive charged ions will be in excess close to the wall right. So,

therefore, you see the concentration  $n_+$  is very high at the wall and then it progressively decays, and then reaches the bulk concentration which is equal to 1. Whereas for the  $n_-$ , it is deficient lower than 1 at wall and then increases progressively and becomes equal to one in the bulk. And once you know the value of  $\phi$  you can also express the local net charge density, because this is expressed in terms of  $\phi$  from the Boltzmann solution. So, that also can be plotted as a function of  $y$ .

So, the thick line  $\rho_e$  vs  $y$  variation is also plotted here. So, therefore, from this 1-dimensional solution you get a lot of information. So, how the electrostatic potential varies, how the local net charge density varies, you know how the concentration of these ions can actually vary. So, now, this is the starting point of looking at electrokinetics. There is still now, there is still now, kinetics, it is just statics.

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## Electroosmosis

- When electric field is applied to the microchannels, bulk fluid motion is observed.
- The velocity of the motion is proportional to the applied electric field and depends on the material of the microchannel and solution in contact with wall.
- This motion is called as electroosmosis and is due to electrical forces on ions in the EDL.

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So, when we put an external electric field, now what immediately what we can observe is the phenomena of electro osmosis. So, you apply an electric field along the positive  $x$  direction and these results in the Coulomb force. So, this is denoted by this notation  $f_{\text{coulomb}}$ , this is a coulomb force. Which is equal to the local charge density  $\rho_e$  times the electric field so. So, therefore, you have the electrostatic potential like this. So, have a variation up to the Debye length beyond which the value becomes 0 excess potential values and it is symmetric. So, this is the case of flow between two parallel plates. So, you will have a symmetric distribution.

About the center line for the electric static potential and now if you therefore, apply and electric field what happens. So, you have the electric force the acting in the momentum equation will be  $\rho_e$  times; that means, wherever you have the local net charge density value positive the finite values. So, there you will experience acceleration ok. According to this expression if you look at  $\rho_e$ , this is the very strong function of  $\phi$ , so, wherever you have large values of  $\phi$ .

So, that is where the local charge density also will be quite significant therefore, close to the wall is where all the force is exerted and if you move away from the wall were potential becomes 0 there is no force . So, therefore, you can actually divide this problem into two regions, one problem which is an inner problem which is close to the wall. Where you consider only the diffuse layer, solve for the separately try to get velocity layer in the diffuse layer and then you go to the second region which is the outer region, which is not influence directly by electric field, but by apply the velocity as the boundary condition ok.

So, therefore, so, the electro osmosis problem can be divided into two sub problems.

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### Electroosmosis continued ....

- For the analysis of the electroosmosis flow, we find two asymptotic solutions:
  - 1) Inner solution: It is corresponding to EDL, in which we keep track of Coulomb forces and the resulting velocity gradient and vorticity but we assume external electric field uniform.
  - 2) Outer solution: The fluid is assumed to be electroneutral and irrotational, but external electric field is varied spatially.

inner solution      location of the Debye condition      outer solution      here,  $\delta$  varies because  $E_{ext}$  is varying. Coulomb forces are ignored  
 effective slip boundary condition      inner solution      here,  $\delta$  varies because of viscous drag at the wall and Coulomb forces on the ions in the electrical double layer  
 $E_{ext}$  is assumed constant here       $\lambda_D$

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One we have an inner solution the inner solution is only for the EDL, then we have the outer solution where we have the bulk fluid which is electro mute.

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### Inner Solution

- Navier-Stokes equation for thin region near wall is given by:
 
$$\rho \frac{\partial \bar{u}}{\partial t} + \rho \bar{u} \nabla \bar{u} = -\nabla p + \eta \nabla^2 \bar{u} + \rho_E \bar{E}_{ext}$$
- $\bar{E}_{ext,wall}$  is caused by the external power supply and is uniform within EDL.

$\phi = 0$  if  $y \gg \lambda_D$   
 domain of integration       $\lambda_D$   
 $u(y)$        $\phi(y)$        $E_{ext}$

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So, if you want to write down the Navier Stokes equation for the inner solution, now you might ask a question whether we are talking about you know Debye length of the order of tens of nanometers. Whether we can use continue of the equations, but again you should remember that the mean free path is also very small for a liquids. So, therefore, you might be still in Knudsen number range which is less then much less than 0.1. So, you do not have to really worry about breaking the continue assumption, were as for the same length skills if this was gas flow defiantly no correct. So, the same continue Navier Stokes equation is written. So, you have the time durative you have the convert the acceleration pressure gradient viscous the diffusion plus you have the colon force which is the driving force in this region.

So, here the electric field is applied externally, it is not what is coming internal this is an external electric field. So, therefore, this is denoted has  $e$  external and this acting only on the EDL. So, this we solve this EDL now when you solve this we make some more assumptions to get analytical solution that is we want to look out fully developed velocity profile when a reason. So, that the convective acceleration becomes 0 and we are also looking at study state solution. So, the entire left hand side the entire acceleration term on the left hand side goes to 0 therefore, also when you are applying this for plate where there is no pressure gradient right therefore,  $d p$  by so, this solution now not for a channel we are doing this only for 1 plate. So, thing like flows pass the plate, so, in this case there is no pressure gradients. So, your  $\Delta p$  also becomes 0. So, only 2 forces are there, one is the viscous force the other is Coulomb force.

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## Inner Solution continued ....

- Considering steady isobaric flow along x-direction N-S equation reduces to:

$$0 = \eta \frac{\partial^2 u}{\partial y^2} + p_E E_{ext,wall}$$

- The uniform permittivity Poisson equation:

$$-\epsilon \nabla^2 \phi = p_E$$

- Substituting for  $p_E$ , we get:

$$0 = \eta \frac{\partial^2 u}{\partial y^2} - \epsilon \frac{\partial^2 \phi}{\partial y^2} E_{ext,wall}$$

- Integrating from wall to a point outside the EDL, we get:

$$\eta u = \epsilon E_{ext,wall} \phi + C_1 y + C_2$$



So, this two will perfectly balance. And you get the velocity profile out of this moment term balance. So, therefore, the other terms are 0 assuming, you have fully developed fully developed steady state and solution for flat plate with 0 pressure gradients.

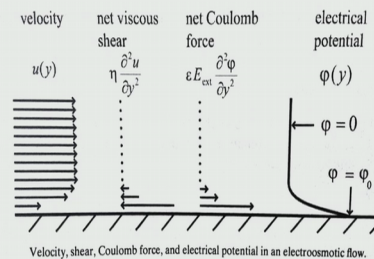
So, now we substitute for the poissons you know the poissons equation. So, we can actually write here rho. So, please correct this, this is not look like P E, but is actually rho e. So, this is this is rho e right. So, this rho is actually we written form the poisson equation has epsilon into del square phi. So, you just substitute for that into the term rho e on the right hand side and therefore, if you express this, this becomes this is your kinematic velocity times d square by d y square minus epsilon permittivity into d square 5 by d y square this is coming from the poisson equation into the external electric field. So, now if you integrate this as a function y, so, you get the following solution for velocity, velocity profile has a function of phi and y.

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## Inner Solution continued ....

- Applying the no-slip boundary condition and forcing the velocity to be bounded at  $y = 0$ , we obtain:

$$u_{inner} = \frac{\epsilon E_{ext,wall}}{\eta} (\phi - \phi_0)$$



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So, therefore, if you apply the no slip boundary condition, at the wall  $y$  is equal to 0 the velocity 0 when you finally, end up with the solution inner region for the velocity profile this turns out to simply at epsilon  $e$  times phi by eta, and we also apply the condition that  $y$  equal to 0 phi becomes phi not right that is your values of phi at the wall. So, therefore, we get this particular solution for the velocity profile. So, if you plot this velocity profile. So, this is how it varies. So, it is kind of a linear variation with respect to phi right and how does phi vary exponential.

So, therefore, has a function  $y$   $u$  will also the exponential variation. So, having known the inner solution, now we do not have to again come back to this. So, we can assume that the out solution is driven by solid wall with velocity of these particular values. So, basically the EDL is a very thin layer close to the wall right. So, few nanometers, so, since we have the velocity profile for the EDL. So, at the edge of the EDL we can apply this as a boundary condition, and we can see that the entire bulk flow is driven by the motion of the EDL. So, edge of the EDL can be assumed to be a wall which is moving with particular velocity given by these values. So, this will be like a quite flow. So, you have the bottom wall on the edge of the EDL, which is moving top side outside the edge of the EDL there is another wall is moving with the velocity and therefore, the bulk value will be nothing, but the average value between the top and bottom.

So, if both of these values are same. So, you have the values of the bulk velocity also same the boundary values.

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## Outer Solution

- In a flow where the distance from the wall is much greater than  $\lambda_D$ ,  $\phi=0$ . Substituting this in solution of inner flow we get Helmholtz-Smoluchowshi solution:  

$$u = -\frac{\varepsilon\phi_0 E_{ext,wall}}{\eta}$$
- The governing equation for the outer flow is given by:  

$$\rho \frac{\partial \bar{u}_{outer}}{\partial t} + \rho \bar{u}_{outer} \cdot \nabla \bar{u}_{outer} = -\nabla p + \eta \nabla^2 \bar{u}_{outer}$$
- The N-S equation for outer flow is solved with interior boundary condition as which is electroosmotic slip velocity:  

$$u_{outer}(y=0) = -\frac{\varepsilon\phi_0 E_{ext,wall}}{\eta}$$

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So, this basically what you now translate this solution into a slip boundary condition, for the outer solution. We solve the routine Navier Stokes equation that is not Coulomb force on that because, net charge densities 0 that; however, we apply slip boundary condition with the same velocity what we got from the inner solution right therefore, the value of velocity that we apply will be equal to this.

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## Electrokinetic Pumps

- Electrokinetic Pump are ones in which an electric field is applied along a capillary to generate flow and pressure.
- Consider a system in which an electric field  $E=\Delta V/L$  applied across an open rectangular microchannel with depth  $2d$ , width  $w$ , length  $L$ , and cross-sectional area  $A=wd$ .
- Assume no pressure gradient and  $\lambda_p \ll d \ll w \ll L$ .
- For a 2D system, the electroosmotic and pressure driven flow is given by:

$$Q_{EOF} = w \int_{-d}^d u_{wall} dy$$

$$Q_{PDF} = w \int_{-d}^d \frac{1}{2\eta} \left( \frac{\partial p}{\partial x} \right) (d^2 - y^2) dy$$

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Because, if you write down the solution for  $u$  inner at  $y$  equal to  $\lambda d$  right. So, that is the edge of the EDL. So, at that point you can assume your  $\phi$  to be approximately 0, axis potential almost reaching the bulk values at 0 therefore, this turns out to be  $-\epsilon \phi_{naught} / \eta$ . So, this will be slip boundary condition that you give for the outer solution. So, this boundary condition is called Smoluchowski slip, but we since we apply it for a case of the elector.

Electro kinetics this is called Helmholtz Smoluchowski, Smoluchowski slip boundary conditions. We have the same Smoluchowski in the gas flows for temperature also; temperature slip is also called Smoluchowski. So, for the case of electro kinetics we called this is Helmholtz Smoluchowski slip boundary condition. So, therefore, for the outer flow if you assume you have acceleration you have pressure gradient you can include all of these and you can solve this right with the slip boundary conditions alright. So, so you do not have to basically ignore  $\Delta p$ , because still this is a channel flow. So,  $\Delta p$  will be there. So, you may have  $\Delta p$  you have the viscous diffusion you may also have the developing region where initial terms cannot be neglected.

So, if you want to get the full solution you can go ahead and still solve it in a conventional, but with the following Smoluchowski slip boundary condition at  $y$  equal to 0 for the limiting case where your  $\Delta p$  equal to 0, you have a fully developed profile you have a steady state profile then what will be the value of bulk velocity same as that of the boundary condition. So, there you will have all these terms going to 0 you have  $d^2 u / dy^2$  equal to 0

So, this will give you linear profile. So, since you have a same value of velocity at  $y$  equal to 0 and the top wall. So, this will that therefore, becomes equal to the value or the boundary itself alright. So, that will become your quite flow solution. So, this is all about the electro osmosis. So, you have any questions or doubts on this. So, the entire electro osmosis is now broken into two sub problem. So, one where we find solution for the inner region use that as a boundary condition for finding solution for the outer region.

So, what is the application of such kind of electro osmotic flows? So, one is when you design what are call electro kinetic pumps. These are not conventional mechanical pumps where you drive flow by purely pressure gradient. So, these are flows where you can have simultaneously, both electro osmotic driven flow plus also a pressure gradient

driven flow right. So, where as if you take pure channel case you have only pressure gradient which drives the flow there. So, it is pure mechanical pump pumping process where as in the electro kinetic you also use the electro osmotic motion for creating flow.

So, therefore, if you want to develop one such application of this electro osmosis it is designing electro kinetic pump. So, we therefore, apply in an electric filed along a capillary is capillary means it should be of the order of few millimeters. So, that you get a strong electro osmotic motion and you also generate flow, and there is also a pressure gradient which is driving the flow right this is the channel case. So, if you suppose apply an external field is equal to  $\Delta v$  by  $l$  potential difference, over a length  $l$  and you assume the rectangle micro channel to be of depth  $2d$  in a width length and cross sectional area and so, on. And therefore, in this case, so, you do not have directly assume a pressure gradient right away, but you can also have this and you also make sure that you are  $d$  by length is much smaller than you are depth or the height of the channel and this height should be lesser than the width. So, that it can be made a 2 dimensional assumption and this width should be lesser than  $l$ .

So, therefore, for a  $2d$  system the electro osmotic and pressure driven flow. So, if you want to calculate the flow rates. So, how do you get it? So, for the electro osmotic flow you integrate. So, you have the velocity at the wall which is you are boundary condition, and if you solve the bulk value also without any pressure gradient. So, what happens as I said you get the same bulk value as the wall? So, therefore, it is nothing, but you are wall velocity which is your uniform throughout. So, if you integrate this from minus  $d$  to  $d$  across the entire channel height. So, you get your net volume, volumetric flow right. So, this is the component coming from the electro osmotic process you can also have a pressure driven component as well suppose you assume that there is only a pressure gradient which is driving the flow, and there is no electro osmosis in that case you put your  $\epsilon_s = 0$ , your external electric filed you compute your conventional solution for flow in a channel with a pressure gradient. So, in that case you get your classical solution.

So, this pressure driven flow is I think all of you know this is for a channel case. So, now, if you therefore, look at a generic capillary you can have both of these combinations a portion of this coming from the first term the portion of this coming from the second term, because the first term we got by neglecting the pressure gradient

completely second by we got by neglecting the 1 complete electric field, but the actual case will have both of these governing the flow.


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### Electrokinetic Pumps continued ....

- Integrating and setting the net flow rate equal to zero, we get:  

$$\frac{\Delta p}{\Delta V} = -\frac{3\mu_{EO}\eta}{d^2}$$
- This are the limiting cases: an open capillary with maximum flow rate and closed microchannel for which flow rate is zero.
- Therefore,  $Q = 2wu_{wall}d + \frac{2w}{3\eta} \left(-\frac{dp}{dx}\right) d^3$
- Rearranging this terms we get:  

$$Q = Q_{max} \left(\frac{\Delta p_{max} - \Delta p}{\Delta p_{max}}\right)$$

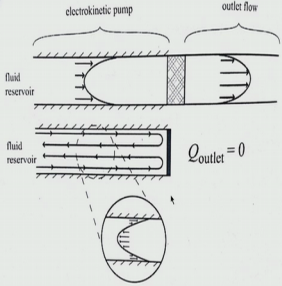

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So, therefore, the total flow rate Q if you integrate this you will be able to get an expression of this particular form right. So, it is driven by both the slip velocity at the wall which is nothing, but the electro osmotic solution for the EDL and the pressure gradient. So, this is the mechanism of the electro kinetic pump. So, you have both these contributions coming to pump the flow.


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### Electrokinetic Pumps continued ....

- Where,  $Q_{max} = 2wd\mu_{EO} \frac{\Delta V}{L}$  and  $\Delta p_{max} = -\frac{3\mu_{EO}\eta\Delta V}{d^2}$
- Thermodynamic efficiency can be defined as:  $\xi = \frac{\Delta p Q}{\Delta VI}$



Flow field inside an electrokinetic pump


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So, you can have two limiting cases as I said. So, you can have two limiting cases, one in which the pump works where you have a full flow without any pressure gradient that is only by the electro osmosis. And the second case where there is no flow, but only pure  $\Delta p$ ; that means, you close the exit you cross the maximum pressure rise to happen so; that means, there is no outlet for the flow to go, but you have the maximum pressure rise. So, there are. So, these are the 2 extreme cases. So, therefore, we can find out the solution for the 2 extreme cases for example, the second case where your  $Q$  outlet equal to 0. So, we have to put the conditions  $Q$  equal to 0 from this expression second expression we should be able to find a relation for  $\Delta p$ , because we know the solution  $u$  wall. So,  $u$  wall I am right, to putting substituting into this expression and getting solution for  $\Delta p$ .

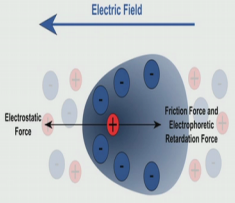
So, you can. So, this is one solution the other solution is where you have the maximum pressure rise. So, the maximum pressure rise can also be obtained. So, what it says you can therefore, calculate what is the thermodynamic efficiency for a particular pump which has both these contributions, you can have an electro osmotic and also the pressure driven contribution. So, how do you define the thermodynamic efficiency whatever pumping power that it generates divided by what is the total input power, to the system the total input power is the external electric field. So, that is here  $\Delta \eta$  and  $\phi$  and whatever pumping power it generates it is your  $\Delta p$  times  $q$ ,  $Q$  is the volume matrix flooded  $\Delta p$  is a pressure draw. So, so with this you can actually check different modification to this electro kinetic pump, and see whether you can improve your thermodynamic efficiency usually the efficiency is for these kind of pumps are very low less than 10 percent, but never the less these are an alternative way of pumping apart from using a mechanical pump externally right. So, you just supply an electric field and then you drive the flow.

So, this is not bad idea, if you want to drive very small flow rates, but the efficiency is are also very less of the order of less than ten percent. So, we will stop here, so, tomorrow or in the next class on Tuesday.

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## Electrophoresis

- Chemical species are transported through fluids due to both diffusion and convection.
- Species diffusion refers to the migration of species owing to Brownian motion in the system.
- Species convection is due to the fluid flow and motion of the chemical species due to electric field.
- In the presence of electric fields, charged ions move in response to the Coulomb force they feel in that electric field, this process is termed as electrophoresis.
- The force exerted by electric field is given by:  
$$\vec{F} = ze\vec{E}$$



The diagram illustrates a central particle with a positive charge (red circle) and a negative charge (blue circle). An arrow labeled 'Electric Field' points to the left. Three force vectors are shown: 'Electrostatic Force' pointing left, 'Friction Force and Electrophoretic Retardation Force' pointing right, and another 'Electrostatic Force' pointing right.

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We will look at the second of the electro kinetic which is called the electrophoresis. So, the electrophoresis this kind of an extension to the electro osmosis, because in electro osmosis case your walls are stationary, and the fluid is moving in the case of electrophoresis, we assume this particles we apply this primarily to particles. So, you can call this as particle electrophoresis. So, these particles are actually moving due to charge accumulation around these particles. So, when you put an external field. So, these particles actually move. So, you can assume that the bulk fluid is actually not moving, but the charges are all concentrated around these particles in these particles actually move relative to the bulk fluid.

So, this is what we are going to study and this is quite important, when you consider particle dispersions in fluids. So, most of the times these particles dispersion also have a electro statistic potential, the electric double layer formation is there. We may not be able to see it, but definitely you put an electric field you will find all of these particles and start migrating. So, this is also a very important phenomena when you consider say nano fluids right. So, just quickly same theory whatever we apply for calculating the velocity, we will apply that here also we make an assumption that the particle and d by layer everything moves together. So, that there is no slip between the particle and d by layer. So, whatever solution we got for the d by layer velocity will also be directly apply to the particle here. So, we will quickly rap up this case.

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### Nernst-Planck equations continued...

- Thus, the transport of the species 'i' in the absence of chemical reactions can be described by Nernst-Planck equation:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot [-D_i \nabla c_i + \bar{u}_i c_i]$$

Species fluxes for Cartesian control volume

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And then, I will briefly introduce the equation for solving for the concentration the advection diffusion equation for concentration of this species. Because the earlier case the Boltzmann distribution function can be used, but the actual distribution will be more complicated if you have a flow right. If you have a flow it is not a simple the Boltzmann distribution is there for these static fluids, but the actual concentration will also change you have a motion.

So, in that case we cannot use only that. So, we have to solve for the advection diffusion for the concentration and get the actual value of concentration. So, this is given by what is called the Nernst Planck equation of course, So, they are detailed topics, I do not want to spend a lot of time because our emphasis is to look at heat transfer I am just giving you some overview of this.

So, if you take a course on micro fluidics for example, so, these are usually covered in a greater detail, there are also other phenomena like dielectrophoresis, dielectro track phoresis. So, they are all phenomena which are emerging areas of research so, but I also do not want to talk about them in this basic course, because the most commonly used electro kinetics mechanisms are these 2, osmosis and electro phoresis, in heat transfer you have equal into this, this is called thermophoresis. So, you have a temperature gradient which is driving the motion. So, you have thermophoretic pumps similar to

electro osmotic pumps so, but; however, those kinds of phenomena with thermophoresis can appear at even a large scale it depends on the temperature gradient.

Thank you.