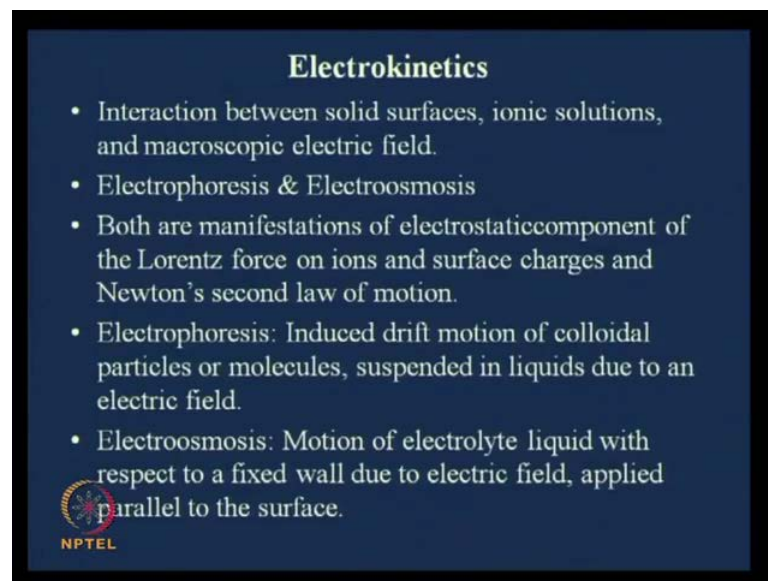


Microscale Transport Processes
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Lecture No. # 20
Electro Osmosis


Well, transport process what we have been discussing in the last class was electro kinetics; I mean near the end of the last class, we started this topic of electro kinetics.

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Electrokinetics

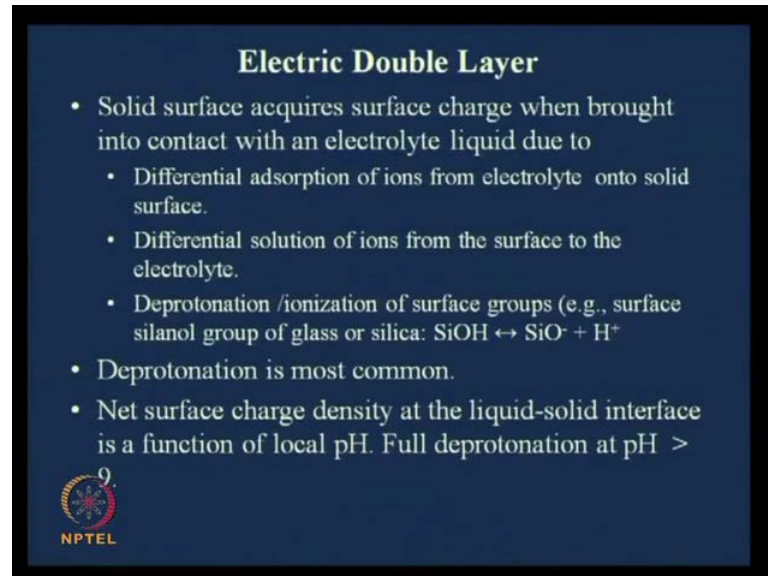
- Interaction between solid surfaces, ionic solutions, and macroscopic electric field.
- Electrophoresis & Electroosmosis
- Both are manifestations of electrostatic component of the Lorentz force on ions and surface charges and Newton's second law of motion.
- Electrophoresis: Induced drift motion of colloidal particles or molecules, suspended in liquids due to an electric field.
- Electroosmosis: Motion of electrolyte liquid with respect to a fixed wall due to electric field, applied parallel to the surface.

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What we had on this power point slide here is by electro kinetics, what we mean is interaction between solid surfaces, ionic solutions and macroscopic electric field. And there are two types we **have we** were having investigated in the or we **we** have discussed in the last class, one is electrophoresis and other is electro osmosis. We started with this electro osmosis, and we later we **we** will get back to this electrophoresis, both are manifestation of electrostatic component of the Lorentz forces; Lorentz force on ions and surface charges and Newton's second law of motion that we have already discussed. Electrophoresis we will come back to this later, electro osmosis is basically motion of


electrolyte liquid with respect to fixed wall due to electric field applied parallel to the surface.

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Electric Double Layer

- Solid surface acquires surface charge when brought into contact with an electrolyte liquid due to
 - Differential adsorption of ions from electrolyte onto solid surface.
 - Differential solution of ions from the surface to the electrolyte.
 - Deprotonation /ionization of surface groups (e.g., surface silanol group of glass or silica: $\text{SiOH} \leftrightarrow \text{SiO}^- + \text{H}^+$)
- Deprotonation is most common.
- Net surface charge density at the liquid-solid interface is a function of local pH. Full deprotonation at $\text{pH} > 9$.

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So, what we **what we** mentioned in the last class is that when there is a solid surface, and an electrolyte next to it. Electrolyte dissociates the that there is **there is** a dissociation of positive and negative ions, and there would be some sort there would be acquiring of surface charges on the solid surface. So, solid surface acquires surface charge when brought into contact with an electrolyte liquid due to various reasons. One was differential adsorption of ions from electrolyte onto solid surface, the second is differential solution of ions from the surface to the electrolyte, and the third is deprotonation of or ionization of surface groups such as surface silanol group of glass or silica.

So, what we have is SiOH on the surface that breaks down into SiO minus and H plus and H plus goes to the solution. So, there is a there is a charge developing on the surface deprotonation is most common and depending on the pH of that solution that you have on the surface there would be a net surface charge density at the liquid solid interface which is a function of local pH and full you can expect full deprotonation to occur at pH greater than nine this we discussed in the last class.

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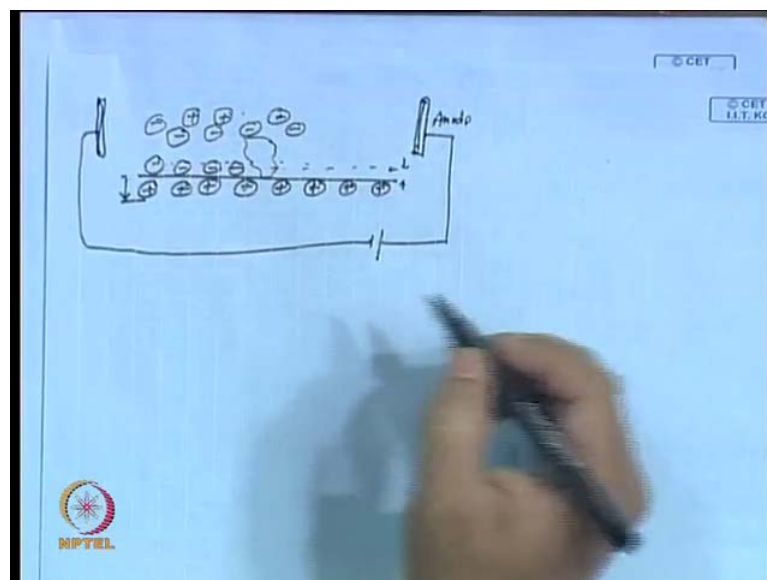
Electric Double Layercontd.

- Ions of opposite charge in the electrolyte are attracted and the like charges are repelled.
- The net excess of mobile ions near the interface with charge, opposite to that of the wall is referred as EDL.
- These excess charges can be used to impart a force on bulk fluid through ion-drag.
- Counter-ions reside in compact layer next to the wall (Stern layer) in adsorbed state.
- Counter ions also reside in more diffused layer next to the wall, where the ions are free to move.



What we had as a so the immediate effect of this is ions of opposite charge in the electrolyte are attracted, and the like charges are repelled; that means, what we had discussed in the last class is if there is a surface.

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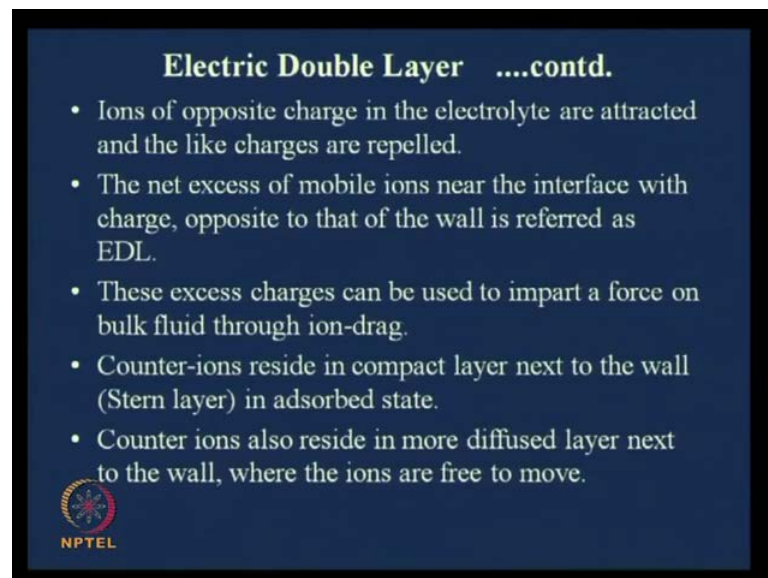


Then there would be some charge developing on the surface. And I said that these charges would be existing up to a distance maximum is point two nanometer to the depth of this solid **solid** material. And these charges will be attracting the opposite the counter ions. So, the counter ions would be attracted now these counter ions there would be a

very thin layer of these counter ions which would be adsorbed on the surface. Apart from various neutral molecules which are also at the same time being adsorbed on the surface. So, there would be the counter ions there would be a compact layer of counter ions next to the surface immediately next to the surface.


This thickness is pretty small and there would be a diffused layer of counter ions. So, there would be some co ions also present, but it is predominantly the counter ions. So, this is basically a diffused layer of counter ions that would be existing at the same time and these counter ions can be pulled by putting an electrode here and here and applying a positive charge. So, so this **this** if **if** this acts as an anode; that means, if you put a voltage across these two electrodes, then automatically these negative charges will be pulled to one electrode, and by that way there would be ion drag possible on the fluid that is existing on the channel, and by that method the fluid will start moving, because as I said in the earlier class also that in the Navier-Stokes equation there would be a body force term arising from the arising from this ion drag. So, this **this** is something which we referred as electro osmosis.

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Electric Double Layercontd.

- Ions of opposite charge in the electrolyte are attracted and the like charges are repelled.
- The net excess of mobile ions near the interface with charge, opposite to that of the wall is referred as EDL.
- These excess charges can be used to impart a force on bulk fluid through ion-drag.
- Counter-ions reside in compact layer next to the wall (Stern layer) in adsorbed state.
- Counter ions also reside in more diffused layer next to the wall, where the ions are free to move.

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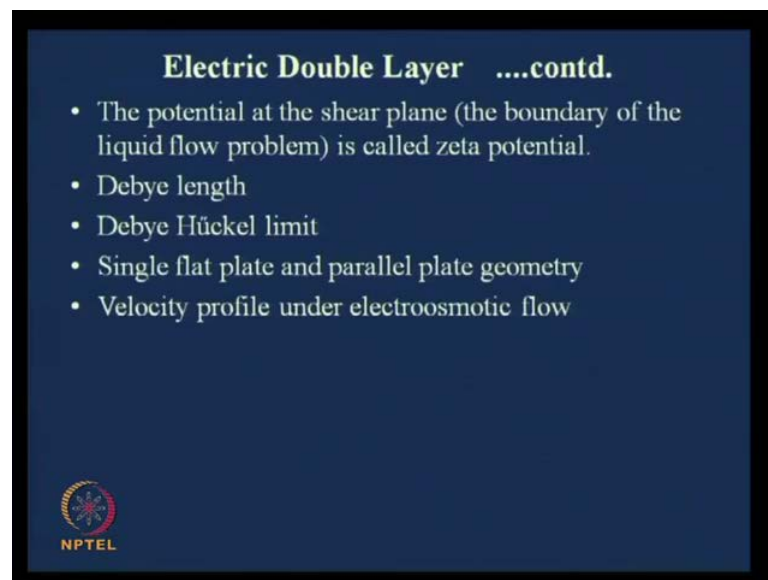
So, what **what** we discussed in the last class quickly through this power point slide ions of opposite charge in the electrolyte are attracted and the like charges are repelled the net excess of mobile ions near the interface with charge opposite with **with** the charge with that is opposite to that of the wall is referred as electric double layer. These excess

charges can be used to impart a force on bulk fluid through ion drag, which is exactly what I mentioned here.

Now, counter ions reside in compact layer next to the wall which is referred as stern layer, and this **this** layer these counter ions reside in adsorbed state adsorbed state means, these **these** counter ions are not available for mobility not available for flow. On the other hand there would be a diffused layer of counter ions counter ions that reside in more diffused layer next to the wall, that is up to a distance away from the wall that is that is referred as the counter ions that counter ions that reside in more diffused layer and next to the wall these ions are free to move.


So, we **we** had we had talked about something called a stern layer we had we had talked about something called a stern layer. Where there is this adsorption and these are pretty much mobile ions, and there is a diffused layer. There is a scientist by the name Chatham and there is there is some contribution from him. So, this this layer also is referred as this diffused layer also there there is some name attached to it.

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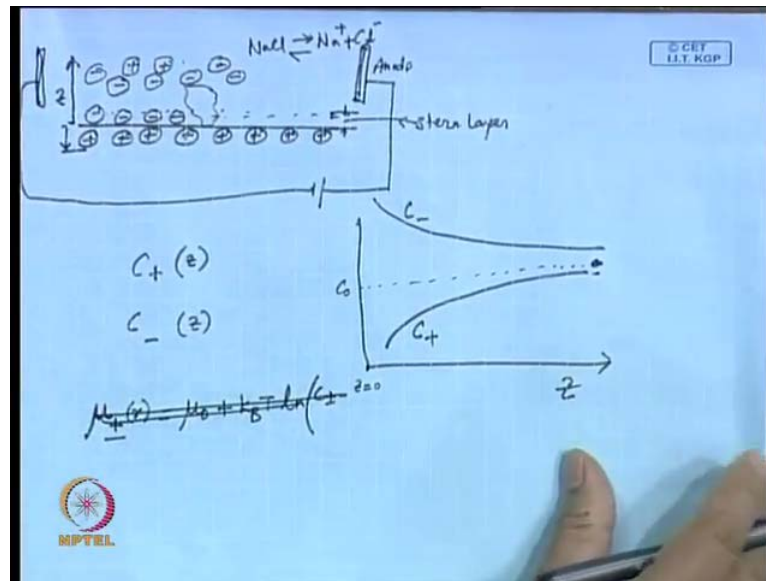
Electric Double Layercontd.

- The potential at the shear plane (the boundary of the liquid flow problem) is called zeta potential.
- Debye length
- Debye Hückel limit
- Single flat plate and parallel plate geometry
- Velocity profile under electroosmotic flow

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Now, if we try to find out **if we try to find out** what **what** would be in the last class we **we** mentioned that our our aim is to find out.

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What would be the concentration profile we if **if we if we we** call it C plus and C minus if we call it C plus and C minus as a function of z. What would be the concentration profile as a function of z? So, that **that** is what is important to us at this point. So that means, how the concentration will change with z, as you go z is, z is what? z is the distance from the wall in this direction. So, in this direction the distance from the wall is given as z. So, what would be the positive ion concentration and the negative ion concentration as a function of z that is **that is** what is of primary importance to us, because once we find that, then we can think of the body force these ions can apply.

So, before we **before we** get to that. So, first we have to establish what is the functionality for C plus z and C minus z? Now if somebody plots if I **if I** try to plot if this is z and this is say concentration. So, let me let me put it this way say this is the C 0 that we have, what is C 0 c 0 was the concentration to start with there was; that means, C plus is equal to C minus is equal to C 0 to start with. So, at infinity or at further. So, at wall is here z is equal to 0. So, this is the wall. So, at away from this far away from this at infinity what would be the C plus and what would be the C minus they will fall on C 0 you think of this. So, you have NaCl, now NaC C I has been dissociated into Na plus and Cl minus. So, Na plus and Cl minus.

Now, C I this C I minus has been attracted to the wall and n a plus has been repelled, but the this find the concentration of n a plus and C I minus they will be uniform at bulk they

they will be same at bulk so; that means, these C_+ and C_- they will approach this value c_0 at z is equal to infinity we or or not infinity z is equal to some substantial value which you consider as bulk which is not next to the surface. So, that is a value now what would be the C_+ ion concentration or C_- ions concentration near the wall if we follow this particular picture if we follow this particular picture. We expect the C_- to be more and C_+ to be less than C_0 near the wall am I right. So, that means, you can expect a plot something like this and a plot something like this both are merging to c_0 .

Now, one is for C_+ and other is for C_- . As per this picture which one is what the bottom one is c_+ bottom one is C_+ bottom one is C_+ and the top one is C_- . So, this is the function this is **this is this is** what I expect what we expect here and what we need to know is how do we how do we give a functional form to this. See how do you theorize this **this** I mean I can understand intuitively the concentration will change like this, but how will we put together a functional form for this c_+ is C_+ is equal to something e to the power minus z etcetera. So, we have to come up with some kind of functional form and for that I need to understand what the governing equations are. So, we have to get in to this governing equation boundary conditions. So, that we can give a functional form to this concentration profile.

Now, here I must mention that we have to resort to this term called chemical potential, which we will be defining as μ . So, In fact, I mean since we we will be talking about this navier stokes equation as well to find out what would be the ion drag at the later stage. So, that time viscosity we will define as η for this for this analysis. So, because chemical potential it is it is defined as μ I mean, those you must be having sufficient background of thermodynamics, you know that how chemical potential it is defined by μ .

Now I put **put** here one expression I mean I do not have I mean, I cannot give the derivation of it here, but you have to you have to accept what I say, but I can tell you what is a origin of this expression. Now I started a wrong place it is I mean, I use another page.

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$$\mu_{\pm}(r) = \mu_0 + k_B T \ln\left(\frac{c_{\pm}(r)}{c_0}\right) \pm \sum z e \phi(r)$$

chemical potential in absence of electric field
 Boltzmann Constant.
 ionic density in absence of electric field.
 elementary charge (charge of an electron) 1.602×10^{-19} coulomb.
 $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$

Chemical Potential is constant throughout its system.
 $\nabla \mu_{\pm}(r) \equiv 0$
 $k_B T \nabla \ln\left(\frac{c_{\pm}(r)}{c_0}\right) = \mp \sum z e \nabla \phi(r)$
 $c_{\pm}(r) = c_0 \exp\left[\mp \frac{z e}{k_B T} \phi(r)\right]$

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Do not worry This is an expression for chemical potential, where we have this plus and minus charges; that means, these ions are available and here this μ_0 term which is basically the chemical potential in absence of an electric field. This μ_0 is chemical potential in absence of electric field, and this c_0 is the concentration or I would say this c_0 is the ionic density. Let us call it ionic density. And what is this electric field? This is the electric field that we are talking about. r is just a position vector. This z is do not confuse this z with the small z that we have. So, to differentiate this I mean, I put a mark here this is the capital z , upper case z is basically the valency, this z would be one for NaCl , this z would be two for CaCl_2 it is that way. So, that is that is the value of this z . So, z would be the valency number and this e is the elementary charge e is called the element or elementary charge. Elementary charge basically what this means, is a charge of an electron charge of an electron it is value is 1.602×10^{-19} coulomb.

So, this is this e is elementary charge this now what we have we have this T which is absolute temperature I am not writing it, you you know what T is and k_B is Boltzmann constant. So, k_B is Boltzmann constant I have already given you the value of Boltzmann constant before. So, I do not write it here. Now what you have here is what what what we have here is this chemical potential, this is constant throughout a system that is that is

that is something which is which we have to honor chemical potential is constant throughout the system **constant throughout a system throughout the system.**

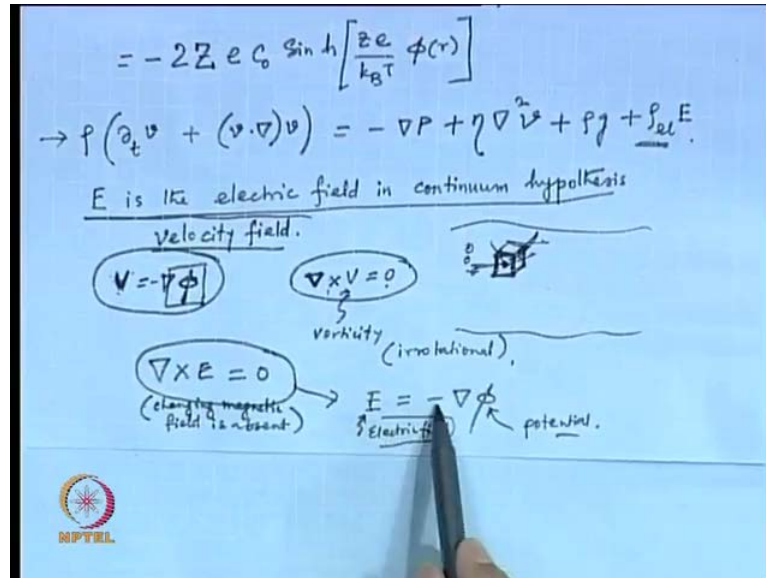
This equation that I have written here for plus and minus this if **if** you write it as plus then this should be plus, if you write it as minus then this should be minus that is the idea of this expression. And this function r I mean, do not confuse this r later on we will write it in terms of z . z is the direction say z is the distance away from the wall. So, that that is what is z now this r is a general position the the general coordinate system. So, that is why it is written as r .

Now, this expression comes from the fact that chemical potential can be written as the derivative of free energy. Basically $\Delta g / \Delta n$ at constant pressure and temperature. You **you you** must have seen this expression in connection with chemical potential when you study thermodynamics. So, this is the origin I mean, this this is the place from which this expression can be drawn. I am not getting into this I am not getting into this, but you you can you can refer thermodynamics book to find out how **how** we can arrive at this expression. So, this is basically the guiding expression for this **this** chemical for this for this ion ion ionic or or charge profile above the surface.

Now, what you have is since I said that chemical potential is constant throughout the system this you have to honor. So, what you have to write is $\Delta \mu$ plus minus r this has to be equal to 0, which means; the derivative of this μ that has to be equal to 0. What the means, is if you if you utilize this expression what you get here, is this is the expression that you get if you **if you** have the grad of μ is equal to 0 then you get this as the expression next what you do is you have a boundary condition,. Let us write down the boundary condition here the boundary condition for this C plus minus at z is equal to infinity that is equal to c_0 . That we already we have accepted that at the bulk, the co-ion and counter-ion concentration they are equal and that is equal to the c_0 .

So, you can use this boundary condition and you can come up with an expression for the which will appear like this. You will come up with an expression for concentration profile which will appear like this.

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Now if we if we write the if we define a charge density. Charge density which is I mean, for a general case this charge density is given defined as rho e l. rho e l which is equal to summation of I is equal to one to infinity N I Z I into e. That is that is that is all the types of charges that are possible here, but here in this case since it is a symmetric electrolyte, symmetric for a symmetric electrolyte **for a symmetric electrolyte** the charge density is given written as Z e C plus minus C minus. So, that is the charge density that you can write ideally for all charges you need to sum them up, but since these are equal and since is a symmetric electrolyte; that means, n a n a C l breaking dissociating in to n a plus and C l minus.

So, this the it is a symmetric electrolyte. So, C plus and. So, it would be C plus r minus C minus r. So, in that case if you bring in this expression that you already have for the concentration profile, if you bring in this expression what you get is that rho e l r this is equal to minus 2 Z e C 0 sin hyperbolic z e divided by k B T into phi I r why how are we getting sine hyperbolic, because it is E to the power minus something plus, E to the power plus something what is what is this E to the power here we have this expression. here we have this expression and here we have E to the power something. So, for minus sign it is e to the power minus and then E to the power plus. So, you end up with this expression for charge density which is equal to this quantity.

Now, this charge density is which is something **something** which is important to us in nervier stokes equation, because if we try to **if we try to** write the nervier stokes equation like this derivative with respect to t, plus those convective terms that is equal to the grad

of p , plus I said that viscosity has to be written in terms of η and not μ , plus if you have a hydrostatic head, plus this is the body force term arising from this ion drag and this is given by $\rho_e l$ into e . So, this is the Navier-Stokes equation that you need to solve if you have to find out what would be the velocity profile where. What would be the velocity profile in this case? In **in in** this if you have an anode and a cathode and if you have these ions being dragged. So, then in that case you need to solve this Navier-Stokes equation where this $\rho_e l$ term this is primarily operational.

So, if you do not give a pressure **if** you do not if your inlet pressure and outlet pressure if they are same if Δp does not exist there. So, in that case it would be just for a steady state case it would be just an interplay of this term and this term. So, this would be interplay between these two terms, because; obviously, if the viscosity is more, then it would be difficult for the fluid to be dragged by ions. So, it would be an interplay between these two terms, and that will define what velocity you get for electro osmosis.

So, this **this this** is how this $\rho_e l$ is coming into picture and that is what we are **we are** trying to find out. Now we **we** will get to this Navier-Stokes equation little later; however, let me **let me** let give let me get some more feel of this what what are these individual terms. Let us first see what is e e is the electric field in continuum hypothesis in fluid mechanics you have already studied something called a velocity field. Do you understand what a velocity field is this is velocity field is defined based on a continuum hypothesis. I mean, people who are I mean, as a matter of fact if this also comes under micro scale fluid flow discussion is that this I mean, there **there there** there are there are two two different concepts you already know one is Eulerian formulation another is a Lagrangian formulation right. Lagrangian formulation is when you track the particle I mean, the **you you** consider the fluid to be composed of several particles and you are tracking the individual particles as it proceeds. And in Eulerian formulation what you do is in the space, you set up suppose in this in the **in the** space you set up a box and you try to find out how what the velocity of the fluid particles what **what** is that velocity of the fluid particles that are passing through this through this block.

So, that is **that is** what that is what is important to you that is the velocity that you are trying to find out. Now it is it then then it is called a velocity field, because you are assuming that the velocity changes in a continuous manner. So, it is not that some

particle basically why this velocity is if **if** you think of this fluid come fluid is comprising of several particles.

So, some particles are entering, some particles are colliding, some particles are leaving, may be the number of particles entering, a number of particles leaving, there is a mismatch of little bit with time it changes. So, this all these things are not considered in an **eulerian**- eulerian formulation in eulerian formulation you consider that there exists a field, there exists a velocity field; that means, that means it is **it is it is** like you have you must have you must in the **in the** first class itself we discussed about this this functionality I mean, when you **when you** plot this density or when you **when you** plot any function with the with the probe volume and we said that as you increase the probe volume if it I think **I think** that that was discussed in the first class itself.

If you **if you** go if you get the probe volume too small, then you get atomic fluctuations that is affecting the measurements; and if you get the probe volume which is too big then the **the** mechanism itself the **the** macroscopic mechanism itself that leads to a fluctuation. So, your probe volume has to be within certain limits. So, when you **when you** make this continuum hypothesis you are assuming that you have a probe volume you **you** have a velocity here, you have another similar volume and the change in velocity from this to this is continuous. So, similarly you have a e which is the electric field in continuum hypothesis.

Now, you I am sure you remember there is a term called velocity potential which is referred as ϕ . And you must have already you you already know that this velocity this potential it **it is it is** like a it is **it is** complimentary to something called a stream function, which you must have studied in fluid mechanics there exists a potential function which is called ϕ , which is complimentary to stream function which is referred as ψ . Now this ϕ this ϕ exists only when $\nabla \times \mathbf{v}$ is equal to 0, where \mathbf{v} is the velocity field. This is **this this** exists only if $\nabla \times \mathbf{v}$ is equal to 0 and then this then \mathbf{v} is defined as minus of $\nabla \phi$ \mathbf{v} is defined as minus $\nabla \phi$ that that is how it is defined, \mathbf{v} is what is \mathbf{v} \mathbf{v} is the velocity field, And what does this $\nabla \times \mathbf{v}$ means this is basically curl of a $\nabla \times \mathbf{v}$ means, curl of velocity vector. And this refers to the vorticity of this velocity field the vorticity of the velocity field and if this is equal to 0 then you consider this flow to be irrotational.

So, then this the then in that case $\nabla \times \mathbf{v}$ is equal to 0 and one of the primary primary criteria that you have a velocity potential defined. Velocity potential will only exist will exist only if this $\nabla \times \mathbf{v}$ is equal to 0, curl of this velocity field is equal to 0 then only, because potential flow exist only if the flow is irrotational. So, this is **this is the this** is the. So, that is how the velocity is then defined velocity is equal to minus of $\nabla \phi$.

So, similarly in this context of this electric field, we have a very similar concept in electric field what you have is you write that $\nabla \times \mathbf{e}$ that is equal to 0. And if $\nabla \times \mathbf{e}$ is equal to 0, then you have electric field \mathbf{e} defined as minus of $\nabla \phi$. Where this \mathbf{e} is referred as **this e is referred** as electric field which is synonymous to the velocity in our understanding and this ϕ is referred as potential. So, just like we had for velocity we had a similar, criteria that if $\nabla \times \mathbf{v}$ is equal to 0 then the flow is irrotational and. So, you can define a velocity field is equal to minus $\nabla \phi$, by the same token if $\nabla \times \mathbf{e}$ is equal to 0 $\nabla \times \mathbf{e}$ equal to 0 in this **in in the in** the context of this electric field or people who work with the pH lyricists who work with electric field they call this at in absence of a changing magnetic field. So, $\nabla \times \mathbf{e}$ equal to 0 means, changing magnetic field is absent. So, this the under this criteria you can define \mathbf{e} as equal to minus of $\nabla \phi$ where \mathbf{e} is referred as electric field and ϕ is referred as potential.

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The image shows handwritten mathematical derivations and a graph on a blue background. The derivations are as follows:

$$\nabla \cdot \mathbf{E} = \frac{\rho_{el}}{\epsilon}$$

$$-\nabla^2 \phi = \frac{\rho_{el}}{\epsilon}$$

$$\nabla^2 \phi(r) = \frac{2(Ze)c_0}{\epsilon k_B T} \phi(r)$$

$$= \frac{1}{\lambda_D^2} \phi(r)$$

$$\frac{d^2 \phi}{dz^2} = \frac{1}{\lambda_D^2} \phi(z)$$

$$\phi(z) = c_1 e^{z/\lambda_D} + c_2 e^{-z/\lambda_D}$$

Additional notes include:

- $\sin A(u) \approx u$ if $Ze\phi \ll k_B T$
- $\nabla^2 \phi(r) = \frac{2Ze c_0}{\epsilon} \sinh \left[\frac{Ze}{k_B T} \phi(r) \right]$
- A graph labeled "Zeta-potential" showing a curve of potential ϕ versus distance z .

So, with that understanding what you can write is then $\nabla \cdot \mathbf{e}$ is equal to ρ_e / ϵ_0 divide by ϵ_0 . $\nabla \cdot \mathbf{e}$ is equal to ρ_e / ϵ_0 . Do you remember what we had what we had for $\nabla \cdot \mathbf{v}$. What is $\nabla \cdot \mathbf{v}$ in fluid mechanics context continuity right $\nabla \cdot \mathbf{u} = \nabla_x v + \nabla_y w + \nabla_z \rho = 0$ or or change in density if you want to put it. So, here $\nabla \cdot \mathbf{e}$ is defined as ρ_e / ϵ_0 where ϵ_0 is constant no the the ϵ_0 is basically the what do you call it the permittivity right, ϵ_0 naught into $\epsilon_0 r$ you you got to brush up your understanding of this electric field. So, this $\nabla \cdot \mathbf{e}$ is equal to ρ_e / ϵ_0 , and then if ϵ_0 is equal to constant if this is constant then, this $\nabla \cdot \mathbf{e}$ can be written as minus of $\nabla^2 \phi$. So, that is equal to ρ_e / ϵ_0 , because that is exactly what we said $\nabla \cdot \mathbf{e}$ is equal to minus $\nabla^2 \phi$ $\nabla \cdot \mathbf{e}$ is equal to minus $\nabla^2 \phi$. So, you can write minus $\nabla^2 \phi$ is equal to ρ_e / ϵ_0 if ϵ_0 is constant. So, what you would be writing in that case, is now we have an expression for ρ_e / ϵ_0 you remember. We have an expression for ρ_e / ϵ_0 charge density which is this $2 z e C_0 \sinh$ hyperbolic this quantity this is an expression that we already have you must have already you might have written already on your notebook. So, if we use that what we end up with is. So, what you would be writing in that case is $\nabla^2 \phi = \rho_e / \epsilon_0$ I mean. for general position vector if that is what you would be writing that is equal to $2 z e C_0 \sinh$ again $z e$ divided by $k_B T$ ϕ into $k_B T$ into ϕ . So, that is what you get.

So, this is what you get for $\nabla^2 \phi = \rho_e / \epsilon_0$. Now if you **if you** take a Taylor expansion of these \sinh term. If you take a Taylor expansion of \sinh term and you can write \sinh of u is close to u . If $z e$ and the ϕ **right** corresponding ϕ divided by $k_B T$ or or or let us say $z e$ i write this as ζ I will explain what ζ is much less than $k_B T$. If this quantity is small; that means, this quantity the numerator is much less than the denominator in that case you can approximate this as $\sinh u$ is close to u . Now what is this why **why** do I write this as ζ and not ϕ what is the difference what what is new here. See if we try to plot ϕ versus z ϕ versus z if we if we plot ϕ versus z then you get a profile which is something like this. This is actually that stern layer that we had and then we see that the ϕ is decreasing like this and then at z is equal to infinity this will go down to 0 this particular value of ϕ this is referred as.

So, this is referred as ζ this this this this value of ϕ is referred as ζ . So, ϕ drop like this I have not come up with an expression for ϕ yet. So, I cannot I do not

know what functional form it has, but one thing I know is that if you solve this equation you can get, because this del square ϕ I this is basically I mean, in **in** other words it is del square ϕ I del z square for a one d system it is del square ϕ I del z square. So, if you integrate this two times you will get a functional form of ϕ I as you will get a ϕ I as a function of z, but before I before I solve before I solve this before I get in to that expression. I tell you that ϕ I versus z there exists form like this and at z is equal to 0 not exactly at z equal to 0 I mean, here it is there is a change I mean, here it would be like this I mean there is a very small layer which is practically negligible. I mean it is difficult to measure experimentally that what is the thickness of this layer there whatever potential is existing that we call that we are referring as zeta.

So, when it came to I mean, if somebody asks I mean, which ϕ I to take. If you if you want to ignore this then what ϕ I to take then ideally you should to take the maximum ϕ I that is possible maximum ϕ I is basically zeta. So, that is why you are **you are** writing it instead of writing any arbitrary ϕ I at any location at any this r basically the position. So, instead of picking up any z and write corresponding ϕ I you would be writing the maximum of it which is zeta. So, that is that is how we put the condition z e zeta which is much less than k B T. This zeta is referred as it **it** to has a very it is very famous in many ways, this is referred as zeta potential. Zeta potential and this thing can be measured I mean, the zeta potential can be measured this there are there are instruments to measure zeta potential, but that that is a different issue I mean, our **our** original aim is to find out what would be the velocity in this electro osmosis that **that** is what we are heading to. So, for that now we have this del square ϕ I is equal to rho e l by epsa and del square ϕ I k can written as in with proper the next step would be this and then sin h u can be can be approximated as u if this quantity is small that is what we take.

So, if that is so then the sin this would be replaced by this the sin h would be gone sin h u would be replaced by u. So, what do you get in that case you get del square ϕ I r that is equal to 2 z e whole square C 0 divided by epsa k B T into ϕ I of r this what you get. So, this is also referred as 1 divided by lambda d whole square ϕ I of r. What is lambda d in that case, lambda d would be lambda d whole square is this quantity one by lambda d whole square is this quantity.

So, then what is the idea here we have. So, we can write the square of the potential $\phi(z)$ is equal to $\frac{1}{\lambda_D^2} \phi(z)$ that is exactly what you can write. And if that is so then what would be the solution of this. Solution would be that $\phi(z)$ would be equal to $C_1 e^{-z/\lambda_D}$ plus $C_2 e^{z/\lambda_D}$ see from this point onwards we have introduced the small z which is different from the upper case z that we have been working. So, far this is upper case z we have worked. So, far is that valence in number and this small z , now is the distance away from the wall. So, mind in take it make note of it very carefully, and this small z that appears this **this** is a general solution for $\phi(z)$ this small z is basically the distance from the wall.

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Handwritten notes on a blue background showing the derivation of the potential distribution. The notes include:

- Boundary conditions: $\phi(\infty) = 0$ and $\phi(0) = \zeta$.
- The potential distribution: $\phi(z) = \zeta e^{-z/\lambda_D}$.
- The Debye length: $\lambda_D \equiv \text{Debye Length}$.
- The Poisson equation: $\rho_{el}(z) = -\epsilon \nabla^2 \phi(z)$.
- The charge density: $= -\frac{\epsilon \zeta}{\lambda_D^2} \exp\left(-\frac{z}{\lambda_D}\right)$.
- The final expression for the potential: $C_{\pm}(z) = C_0 \left[1 \mp \frac{z e \zeta}{k_B T} \exp\left(-\frac{z}{\lambda_D}\right) \right] \quad z > 0$.

The notes also include a diagram of a wall with positive charges (+++++) and negative charges (O-O-O) above it, and a graph of the potential $\phi(z)$ versus distance z showing an exponential decay from ζ at $z=0$ to 0 at $z \rightarrow \infty$. The NPTEL logo is visible in the bottom left corner.

So, now you have boundary conditions and what is the boundary conditions for for $\phi(z)$. You have $\phi(\infty)$ is equal to 0, that is understood. We said that add infinity there will not be any potential, because add infinity you have n a plus and C_1 minus in equal numbers. So, you do not have any potential gradient. So, $\phi(\infty)$ equal to 0. And you have the other boundary condition here is $\phi(0)$ is equal to ζ , that is already you have I mean, I said that we we referred this as as the zeta potential the potential existing at the wall.

So, with these two boundary conditions if you solve these equation. See moment I say that ϕ at infinity is equal to 0 now here, at infinity this term will blow up. So, this

term you cannot allow this to blow up. So, C_1 has to be equal to 0. So, you are ending up with this expression, and C_2 would be equal to simply zeta. So, you end up with this expression $\psi(z)$ is equal to zeta e^{-z/λ_D} . So, this is the expression that you have for $\psi(z)$. So, this is how the potential changes with z . e^{-z/λ_D} is a very neat expression you have very easy to handle, and more importantly now look at this λ_D term there is a name to this λ_D term. This λ_D is referred as Debye length. What is the importance of λ_D can somebody tell me I mean, can you think about it you think about it. You have $\psi(z)$ as a function of z and which is basically I mean, now we have now we do not consider the stern layer moment we said this boundary we said this boundary condition we are forcing it to be zeta at $z=0$. So, we are talking about a functional form of e^{-z/λ_D} . So, what is the importance of λ_D now where would this λ_D be.

Think about this Debye length is a very important term the zeta potential and Debye length I think you need to do some study, when you go back when you go back after the class you do some study you find out what is zeta potential and what is Debye length these two are very important concept. So, what does this Debye length mean in when have an expression for potential like this. So, this is the expression and then you have you have $\rho_e(z)$ in that case what is $\rho_e(z)$. $\rho_e(z)$ we had a we had talked about it what is that here we talked about $\rho_e(z)$. So, if we just multiply by $\epsilon_0 \epsilon_s$ and take the second derivative. So, if we if somebody wants to know what is $\rho_e(z)$ then what you will do is you will multiply these by $\epsilon_0 \epsilon_s$ into $\nabla^2 \psi(z)$ that is what it is that is what we are talking about. So, $\rho_e(z)$ would nothing, but minus $\epsilon_0 \epsilon_s \nabla^2 \psi(z)$; that means, what these term means, is basically $\nabla^2 \psi(z)$. This is $\nabla^2 \psi(z)$ a notation lot of physicists use $\nabla^2 \psi(z)$ this is basically $\nabla^2 \psi(z)$.

So, basically $\rho_e(z)$ is equal to nothing, but minus $\epsilon_0 \epsilon_s \nabla^2 \psi(z)$. And what would be $\nabla^2 \psi(z)$ if this is the $\psi(z)$ this is the expression for $\psi(z)$ then what would be $\nabla^2 \psi(z)$. You take the second derivative of it, you will be seeing this as minus $\epsilon_0 \epsilon_s zeta / \lambda_D^2$ because you are taking derivative two times exponential of

minus z by λd . So, basically it is $\epsilon \psi_0 \exp(-z/\lambda d)$ that is what you get.

Now, what we had earlier we have an expression for concentration profile as well. We had an expression for concentration profile which was like this in terms of ψ . Now if you bring this ψ here, and before that if you take this e to the power $e^{-z/\lambda d}$ this quantity if we expand it in Taylor series and if you put this ψ instead of ψ you put this ψ_0 into that quantity what you will be getting in that case is $c = c_0 \exp(-z/\lambda d)$ where z is the valence number e ψ_0 divided by $k_B T$ exponential of minus this is distance z by λd greater than 0.

So, this is $c = c_0 \exp(-z/\lambda d)$ the expression for concentration profile. And as a matter of fact as a matter of fact this concentration profile that we had obtained earlier. The concentration profile that we had I mean, not obtained I mean, we intuitively we said this is the type of profile we get. Now you can plot this using this expression using this expression you can plot that concentration profile. So, you have more or less you have some handle over these ψ_0 parameter. Now this ψ_0 I said that this is a potential. So, this ψ_0 is a property of the system that you are working with.

So, when you pick up a wall when you pick up an electrolyte I mean, it is ψ_0 is property of the system you have. This z is valence number whether you are working with n or c it would be one or two it depends on that k_B is a Boltzmann constant you figure out what that is T is the absolute temperature in absolute scale, exponential minus the distance away from the wall and λd is Debye length. Now Debye length we have where where did we bring in λd you remember when you go back to your notes, we were working with this expression. We said that $\sinh u$ is equal to u and we ended up with this expression and then suddenly from here I said this is equal to $1/\lambda d^2$. So, if somebody asks you what is λd then you have to write λd as square root of inverse of this quantity.

So, it would be square root of $\epsilon k_B T / 2 z e^2 C_0$ that entire thing under square root. So, you know what is ϵ it is the property of the system $k_B T$ all you note 2 is z is valence number e is the elemental charge whole square C_0 where

how much is the that this you see how much ions you start I mean, you started with all. So, this this is a C_0 that bulk concentration. So, bulk concentration of ions. So, it is **it is** **it is** very straight forward. So, you can find out what is the concentration profile. So, you know all the terms here. So, this is this is what this is what would be the concentration profile now we have solved for what we solved for just a wall just a wall is there, the wall for some reason has picked up some positive charge with it and it is pooling negative counter ions here. It is pooling counter ions. So, I developed. So, so you have developed a potential ϕ I as a function of z . You have developed a C_+ ion concentration as a function of z ; you have developed a C_- as a function of z . So, all these things you developed next to a wall. What is above the wall we do not know I mean we are just working with a one d system above the wall, but when we talked about a flow through a channel then there has to be another wall above it.

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Parallel plate geometry

$$\frac{d^2 \phi}{dz^2} = \frac{\phi}{\lambda_D^2}$$

$$\phi(z=0) = \zeta$$

$$\phi(z=\infty) = 0$$

$$\phi\left(\pm \frac{h}{2}\right) = \zeta$$

$$\frac{d\phi}{dz}(z=0) = 0$$

$$\frac{c_1}{\lambda_D} - \frac{c_2}{\lambda_D} = 0$$

$$\phi(z) = c_1 e^{z/\lambda_D} + c_2 e^{-z/\lambda_D}$$

$$\phi(z) = \zeta \frac{\cosh\left(\frac{z/\lambda_D}\right)}{\cosh\left(\frac{h/2}{\lambda_D}\right)}$$

$$\phi(z) = \zeta e^{-z/\lambda_D}$$

So, if you bring in that system that system here; that means, for parallel plate geometry. If we talk about parallel geometry where is where the change is going to be. This equation I do not have any doubt with this equation will remain same ϕ I divided by λ_D^2 . That was a governing equation right one by λ_D^2 into ϕ I this was the governing equation and this governing equation remains the same. Only problem only change would be in the boundary condition what the boundary condition was you had taken earlier. The boundary condition you have taken is ϕ I at z is equal to 0 is equal to ζ , and ϕ I at z is equal to infinity is equal to 0. This was the boundary

condition you have for a plate and one d case above it one d situation which is above the plate, but when you have two parallel plates then there exists a symmetry in between. So, instead of this boundary condition what you would be taking is ϕ at $z = \pm h/2$ is equal to ζ .

ϕ at $z = \pm h/2$ is equal to ζ . What is $h/2$? If there are 2 if this is the channel if these are the parallel plates this distance between two parallel plates if that is h . So, then your z starts from here, this is this is the place this is where the z starts from. So, this is equal to $z = h/2$ and this is equal to $z = -h/2$.

So, you will write ϕ instead of ϕ at $z = 0$ is ζ you will be writing ϕ at $z = \pm h/2$ is equal to ζ all right. understandable now if that is. So, then where where would be the change in this case you will have I mean what was the general solution we had ϕ at z is equal to $c_1 e^{z/\lambda d} + c_2 e^{-z/\lambda d}$ earlier we had this infinity and to satisfy that we said c_1 is equal to 0. Now that is not the case in that case you will have both c_1 and c_2 and what would be the values of those, if he impose this boundary condition I think what you will be getting is $c_1 e^{z/\lambda d} + c_2 e^{-z/\lambda d} = \zeta$ at $z = \pm h/2$. Am I right at well well well at $z = 0$, there is another boundary condition you there is a symmetry at the centre which I have not mentioned, due to symmetry at the centre ϕ at $z = 0$, d of that $d \phi/dz$ that has to be equal to 0, because there exists a symmetry at the centre.

So, this becomes another boundary condition another condition another boundary condition here. So, ϕ at $z = \pm h/2$ is equal to ζ that is at the o wall and at the centre there has to be a symmetry. So, this has to be satisfied. So, play with this see what c_1 and c_2 you get I mean, I can give you the final form see here, here since you have $e^{z/\lambda d}$ and $e^{-z/\lambda d}$ to the power something and $e^{-z/\lambda d}$ to the power minus something. So, you would be again ending up with instead of instead of $e^{-z/\lambda d}$ that you had earlier only you have this term right, only you have this term and c_2 was replaced by ζ . So, that is the only thing you had now you will have is ϕ at z would be equal to $\zeta \cos(\text{hyperbolic } z/\lambda d) / \cos(\text{hyperbolic } h/2/\lambda d)$ z starts from the centre and goes up there

And similarly, you have to you will get an expression for $\rho_e(z)$ all right. So, this is what you get as a new **new** 1. So, what did we what did we have when we had just a 1 single plate and we are concentrating z running from 0 at the wall to infinity that time was the $\phi(z)$. If I write it here what was the $\phi(z)$ at that time $\phi(z)$ is equal to $\zeta e^{-\lambda z}$ into $e^{-\lambda z}$ to the power minus z by λd all this z is distance from the wall here, the coordinate system changed the z starts from the centre, and the expression that we have is $\phi(z)$ is equal to $\zeta \cos(\lambda z)$ and $\cos(\lambda z)$ divided by λd .

So, look at look at the change now here this **this this this** is what we had earlier for simple situation. And this is what we have now, because of this boundary condition the governing equation remains same clear to everybody. So, the if this is. So, then you can you can come up with ρ_e once again and once we have ρ_e in this case I mean, you know what ρ_e is how ρ_e is related to ρ_e by $\epsilon_0 \nabla^2 \phi$. how it relates to $\nabla^2 \phi$. So, you have to take the second derivative of this ϕ , and relate that to ρ_e by $\epsilon_0 \nabla^2 \phi$ and get the ρ_e . And once you have this ρ_e then you can use this ρ_e in that navier stokes equation.

So, you you must have seen the third process here, you have defined a velocity potential you have to come up with a ρ_e , which is basically the charge density and then you introduce that in the body force term in navier stokes equation, and then only you can come up with a velocity expression for velocity. And then you can say this is the electro osmosis osmotic velocity this is the velocity you can expect in electro osmosis for two parallel channels. Two **two** parallel plates channel between channel form between two parallel plates. So, we will continue this discussion we have not yet gone to navier stokes we are just doing the preliminaries that is all for this class meet you next day.