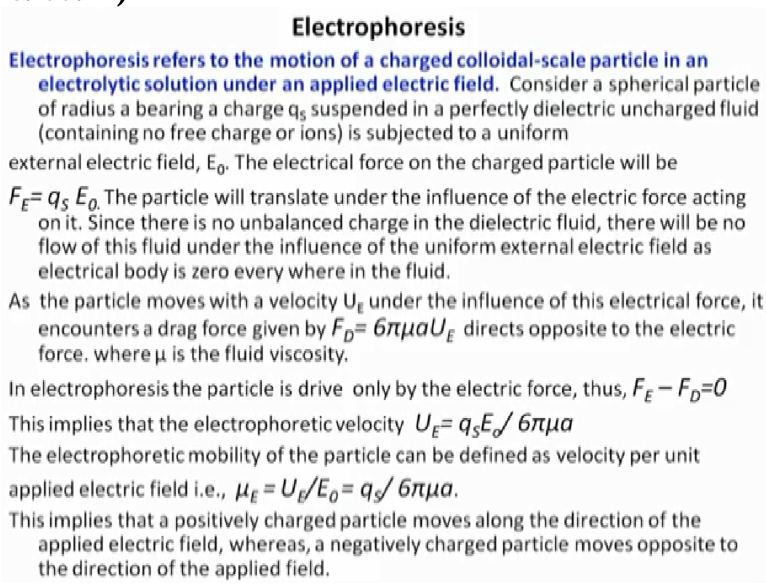
Modeling Transport Phenomena of Microparticles
Prof. Somnath Bhattacharyya
Department of Mathematics
Indian Institute of Technology - Kharagpur

Lecture - 38
Electrophoresis of Charged Colloids

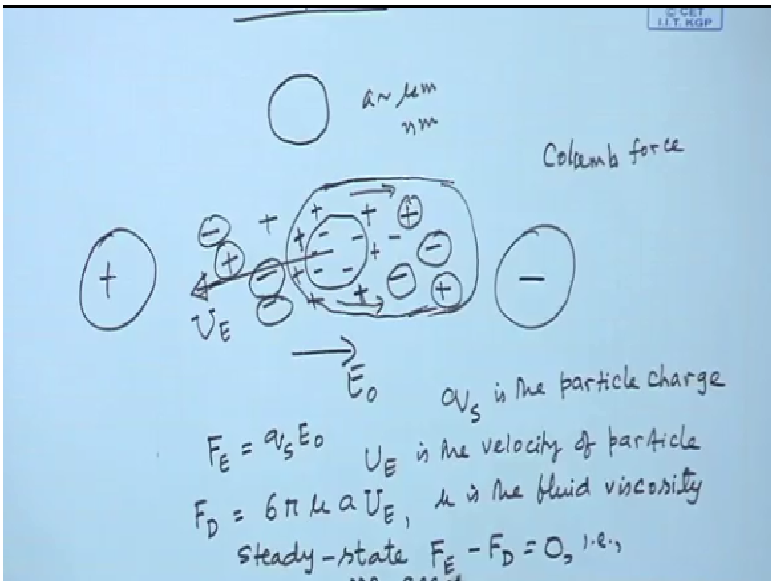
Now we will talk about the electrophoresis of colloid particles.

(Refer Slide Time: 00:24)



Now electrophoresis is basically.

(Refer Slide Time: 00:34)



The Electrokinetics transport of charged particles in a electrolyte media on or polar medium so that is the thing will be considered now how this electrophoresis occurs, now we can define the electrophoresis refers to the motion of a charged colloidal particle in an electrolyte solution under an applied electric field now when a charged particle maybe let us take it as a sphere.

Now basically this colloid particles means his side will be of approximately some micrometer order on the order of some micrometers few micrometer or maybe even a nanometre scale so this kind of particle, so whether we consider it is a spherical we can treat this kind of rigid particles as a spherical particle so there is not a big harm, on the form of the surface is not going to make much difference because of the small scale size of the particle.

So we can treat it as a spherical particle that is for the sake of convenience of our theoretical analysis now what will happen if when we place a charged particle in a situation say in a charged particle we place it in a negatively charged particle so the particle have a negative charge and we apply a say electric field like this so the particle will be in a electrolyte medium so there are charges, free charges.

So since the particle is negatively charged so positive charge will be attracted close to the particle, so there will be a formation of Debye layer and these negative ions positive ions all will be in the electrolyte which may be very close to this particle, so there will be a imbalance of ions but as we move away from the particle so these ions are all balanced now when you apply and externally applied electric field say let us call it constant electrically E0.

So what will happen this particle will be attracted to the since it is negatively charged so it will be attracted to other positive electrodes sure it will acquire a velocity propulsion velocity Q, so now know this because of these are now this because of the free ions around the particle so things becomes big complicated now these ions all so let's get a Coulomb force due to this applied electric field and they will also migrate and another thing is that the particle is moving.

So there will be a wake formation so the fluid will be drag downwards so that means along with that ions so that will be pushed backward, so downstream motion will be occurred in addition the ions which are imbalanced ions will acquire Coulomb force and they will be dragged towards the electrodes to the respective electrodes and in a process they will also drag the fluid because these arms are dissolved in the liquid medium, so that way there will be a complicated situation will arise okay.

So our intention is to model this kind of situations that means what we have is a charged particle colloid particles that means the particle of micro size or nanometre size is submerged in a polar medium where there are ions, are ionic solutions it is dissolved in an ionic solution and subjected to an applied electric field, so this kind of situations we would like to study now for a simple situation.

Suppose if I forget about the medium as let us assume that is a perfectly dielectric no free charge, no ions are containing so on and the particle have a charge Qs is the particle charge and the electric field applied is E0. So the electric force which will be experienced by the particle is Qs E0 okay. Now Qs E0 provided we are considering that surrounding the medium in which the particle is suspended have no free charge or free ions imbalance ions.

So the electric field is E0 and charges Qs show it experience electric force a Fe so because of that the particle will move say let the particle you is a velocity of the particle velocity of the particle of the particle so now since the particle is moving. So let us assume the particle is moving with a Stokes velocity, so it will experience a drag the particle is moving in a medium so it will experience a drag.

And let us call that drag is the Stokes drag is given by 6 by Mu a Ue, Mu is the viscosity of the medium the fluid viscosity, now if the electric field is the only mechanism so then at steady state what we should have if there is steady propulsion. These forces will be balanced so at steady state situation that is Fe - Fd should be 0 net force will be 0. Because there is no acceleration so that is the thing we have stated here more clearly.

So this is the particle experiencing a electric force, particle will translate under the influence of the electric force acting on it since there is no unbalanced charge in the dielectric fluid there will be no flow of discrete under the increase of uniform external electrical. That means the Coulomb force is zero no Electroosmotic flow occurs as the electric body force is zero everywhere in the fluid.

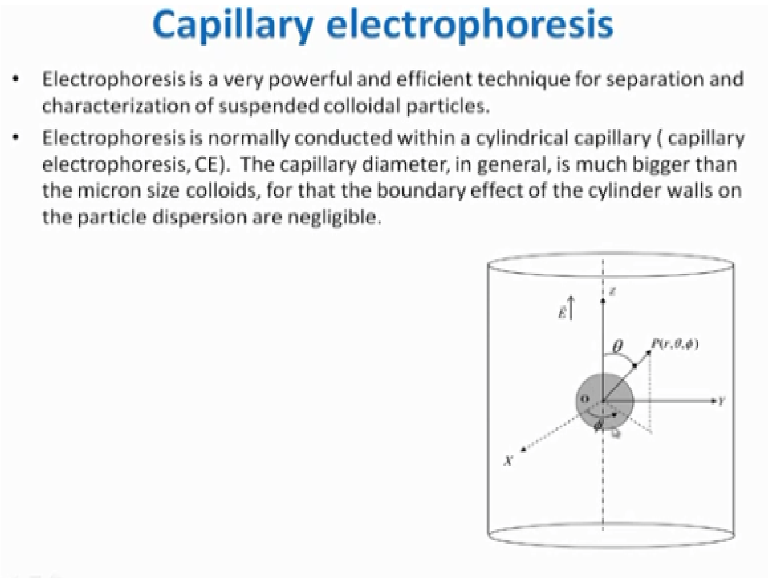
So the particle is moving with a velocity ue sure it will experience a drag since we are assuring that velocities very low velocity that is really the regime so this Stokes drag can be expressed as given by this way 6 Phi Mu a Ue, a is the radius of the particle sure there is no acceleration so these electric force. And the Stokes drag will be balanced and it will be given by Fe - Fd = 0.

And from here we can find out the velocity ue the propulsion velocity of the particle which is given by charge containing the charge amount of charge containing by the particle the external electric field and this 6 Phi Mu a Ue. Now one another important parameter or important measurement, we make is the electrophoretic mobility, so that means the electrophoretic mobility is defined as we electrophoretic velocity per unit electric field.

So that means Mu e is defined by Ue by E0 is the applied electric field so that becomes = qs by 6 PHI Mu a, this implies that about positively charged particle moves along the direction of the applied electrical charge qs is positive, so it will move in the along the direction of the applied electric field E0. And if qs negative so it will have a opposite direction depending on the qs charge it will move only along or reverse direction of the electric field.

So this is the simple situation where we have taken the surrounding or the medium has no free charges now when there is a free charge in the medium so then things becomes complicated.

(Refer Slide Time: 11:02)



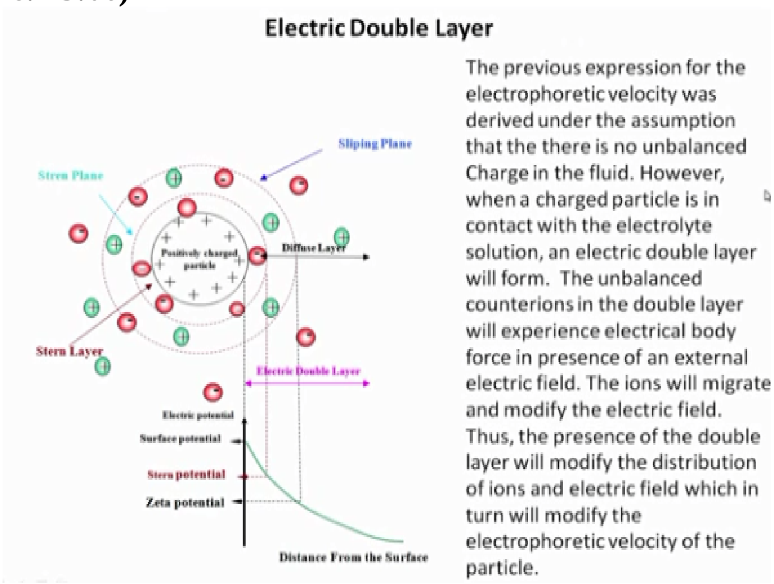
Now this capillary electrophoresis that is normally is used for shorting and characterizing the particle so basically what it is done in a capillary tube filled with electrolyte or other mediums later on we will talk about gel medium also so in which the particle is suspended and the electric field is applied across this capillary and a electrophoretic velocity is developed and of course as we could see from the previous one you see.

These depending on the charge or the radius velocity will define so now we can short the particle in terms of their loss in terms of the size charge density, so this kind of feature this kind of technique can be applied in capillary electrophoresis or so it is very helpful also the extra mentally one can measure the electrophoretic velocity and through that one can find out the charge, what is the electrostatic characteristics of the particle?

So that means we know the particle electrophoretic velocity through that we can get a expression for the charge density it got dreads and there are the realtor kinetic properties of the colloid particles which are also come on sometimes very important in biomedical application. So normally these capillary wall are quite far up say like it will be like 25 micrometer or 50 micro meters radius.

So if I consider a particle of size even if it is the one micro meters radius so that means these distance quite large so wall effect is negligible, now if I do the mathematical model for that.

(Refer Slide Time: 13:06)



So now before that the previous expression whatever we have derived for the electroplating velocity was derived under the assumption. That there is no unbalanced charge in the fluid however when a charged particle is in contact with in with the electrolyte solution an electric double layer will form, the unbalanced counter ions in the double layer will experience electric body force in presence of an external electric field.

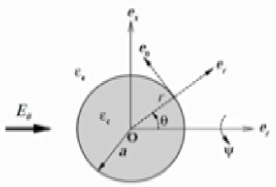
That is the Coulomb force what effect the ions will migrate and modify the electrical now the distribution will be distorted. And in that way there will be another induced electric field and that will go the opposite direction, so they are mostly this will be the retardation effect okay, thus the presence of the double layer will modify the distribution of ions an electric field which in turn will modify the electrophoretic velocity of the particle.

So schematic diagram is shown like this way sure if we have a diffused layer so that means imbalanced ions, so when there will be an electric field is applied. So this imbalanced ions will acquire a net body force and it will drag the fluid and also the ions distribution will be distorted and that creates an induced electric field and so whatever the formula we have developed in previous slide is no longer valid.

(Refer Slide Time: 14:46)

The governing equations in non-dimensional form in a spherical polar coordinate with origin at the center of the sphere and the direction of the applied electric field as the initial line is considered.

$$Re\frac{\partial \mathbf{u}}{\partial t} - \nabla^2\mathbf{u} + \nabla p + \frac{(\kappa a)^2}{2}\rho_e\nabla\phi = 0$$



$$\nabla\mathbf{u} = 0$$

$$Pe_i\frac{\partial n_i}{\partial t} + Pe_i(\mathbf{u}.\nabla n_i) = \nabla^2 n_i + \frac{z_i}{Z}\nabla.(n_i\nabla\phi)$$

$$\nabla^2\phi = -(\kappa a)^2\rho_e$$

A z-z symmetric electrolyte is considered with z_1=-z_2=Z.
The radius of the sphere a is the length scale, $U_0 = \varepsilon_e E_0 \varphi_0/\mu$ is the velocity scale, φ_0 is scale for potential and. $\Lambda = E_0\, a/\varphi_0$ is the scaled external applied electric field. Re is the Reynolds number and $Pe_i = \varepsilon_e\phi_0^2/\mu D_i$ is the Peclet number
On the surface of the particle (r=a) zero velocity and ion impermeability conditions are imposed. Particle can have either a uniform ζ-potential or surface charge density. Particle is considered to be non-conductive.
Far away from the particle i.e., r=R (>>a) $u.e_z = -U_E$, $\phi = -\Lambda R\cos\theta$ and $n_i = 1$ is imposed.

Now if I want to do the full mathematical situation so I can write the equations whatever we have already derived this is the Navier-Stokes equations modified with the electric body force so Rho e the charge density at any point within the fluid so within the electrolyte in this case because we are taking a ionized grid, so there is a we have scaled the variables so we get a Navier-Stokes equations of this for incompressible.

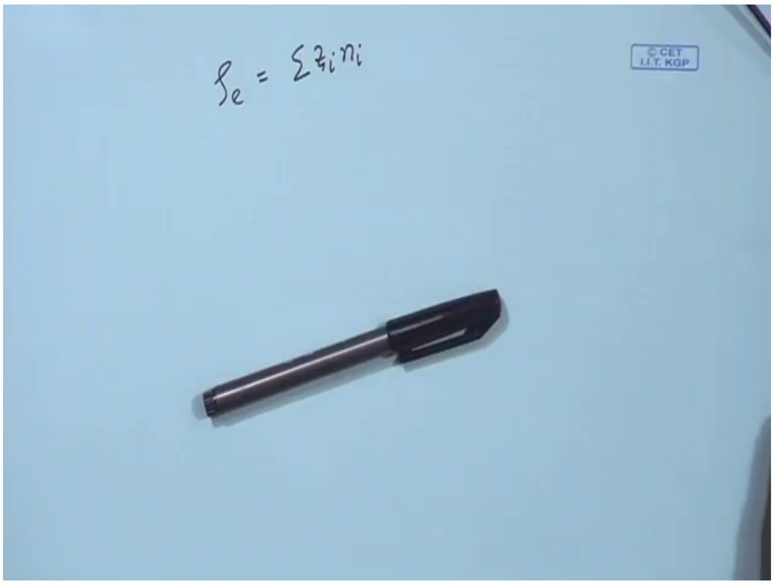
So this is the continuity question and this is the Nernst-Planck equation corresponding to the ith ionic species sure pi is the Peclet number depending on the diffusivity of the ion and this is the convective transport diffusion of ions electromigration Phi is the electrical now this electric field contributed in both ways by external as well as the redistribution of the ions, so this electric field satisfy this equation Laplace equation.

Which comes to the Gauss law given by this way now the external electric field always satisfied Delta Phi external electric field if I call sigh sure it will be always take Del 2 Phi = 0, so that means to describe mathematically the electrophoresis of the particle in a electrolyte medium. So we need to can we described by this set of equations so we need to compute or fog this set of equations.

So these equations are coupled now depending on the coordinate system if it is a spherical particle, so you can use a spherical coordinate system and will have three components and also three components for the momentum equation and then three the depending on the number of ions so if it is z-z symmetric electrolyte. So we will have two ions species so we will get two equations for the ions transferred again it is coupled with the velocity field.

And of course the velocity field is coupled with the electric field Phi and charge density Rho e as you know is the net charge density.

(Refer Slide Time: 17:29)



So Rho e = Sigma zi ni whatever we have already discussed before. So this set of equations need to be solved, if we have to describe the motion now here the scaling we can take the scale velocity scale given by this one this is thee well known that Smulzchochi velocity if Phi 0 is a potential, so Phi 0 is the thermal potential RT by F.

And the electric field is scaled by this manner capital Lambda and there are two parameters appearing one is a Reynolds number although it will be very small so one can neglect they are and Reynolds number situation in fact we have neglected here the convective terms in the inertia terms is already neglected. So the Reynolds number is based on the velocity u0 the viscosity of the medium and the length scale a.

And I will use the Reynolds number and Peclet number, now the boundary conditions so we can put on the surface of the particle the boundary condition as zero velocity. And I am empowered me already condition that means flux of ions is 0, Grad i is 0 over there imposed particle can have either a uniform Zeta potential either I can say if i= 0 or Del Phi del R = Sigma after the Epsilon e Del Phi Del R = -Sigma.

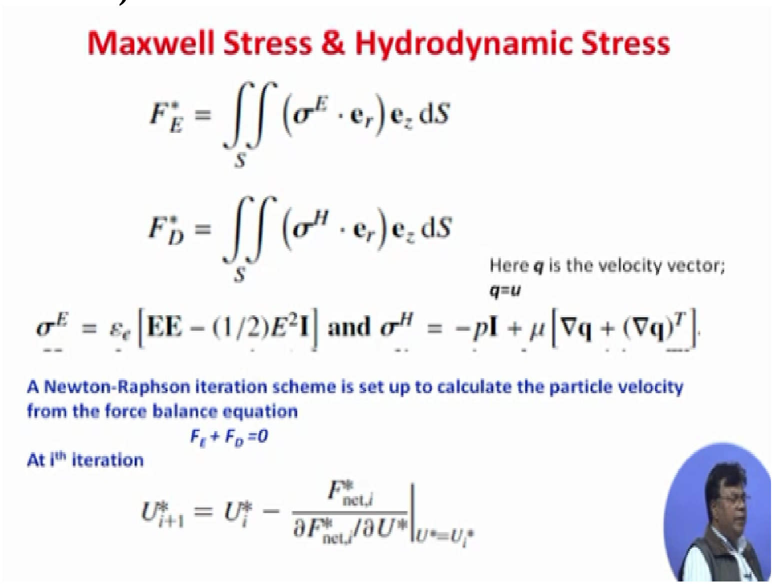
That form already we have described show these conditions either in terms of constant deter potential or constant surface charge density. And far away from the particle that means where the presence of the particle are no longer important we can impose the condition that fluid is moving with a velocity ue and Phi the electric field is marched with the external electric field Lambda R cos Theta.

R is the radius at which we are measuring and ni = 1, now here what we did is here basically we keep the particle stationary that means we have taken a relative coordinate system that means the particle is kept stationary and fluid is assumed to move forward move towards the particle with a velocity ue.

So that is why this condition –ue, so this is analogous to the situation. So basically the situation is the particle is moving with a velocity ue, now if I consider the moving frame of reference which becomes a mathematically complicated so that is why what we did is we kept the origin or we consider the origin at the centre of the particle and we consider the particle is stationary and the fluid is allowed to move with the velocity –ue.

From the far away distance, this two is the equivalent way of present.

(Refer Slide Time: 21:10)



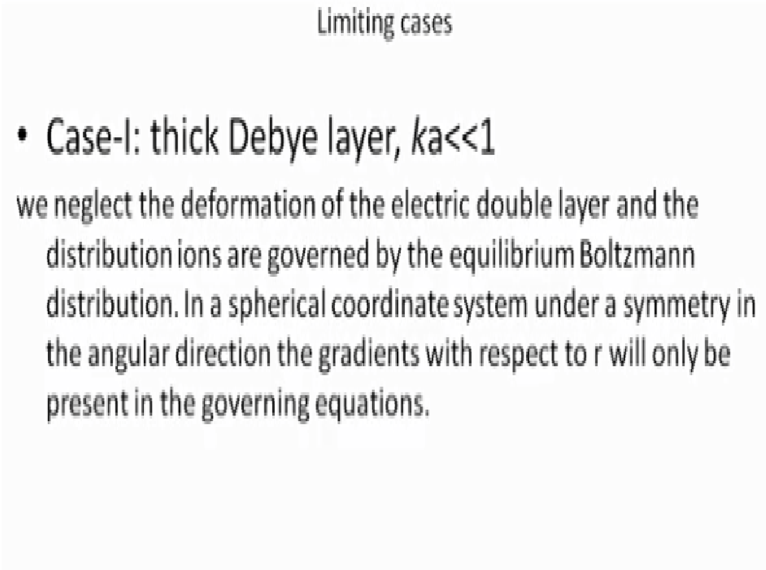
Now what it is by solving the velocity and charge density and all and the electric field what I need is the force balance now forces are electric force at the drag so electric force are given by the Maxwell stress tensor given this equation and the drag the Hydrodynamic drag that is due to the viscous force at the pressure drop, so that is governed by that Sigma h, so the Maxwell stress tensor so can be expressed in the form has written over here.

And the drag is due to this pressure and surface pressure and viscous shear stress, so once you have the electric field and the velocity and pressure so one can theoretically obtain the electric force at the drag so for a stationary situation where the particle is moving or translating or under the action of electric field. So what will have this Fe + Fd to be zero, Fe + Fd should be balanced.

So now what procedure normally is done is that is Ue we cannot put here the boundary condition is not known, so what you do is it is unknown, so what I do with iterative process so that means you solve this iteratively by this manner, start with initial approximation for the electrophoretic velocity you some initial guess and through that we compute the Fe Fd then calculate the next iteration iterated value by this manner.

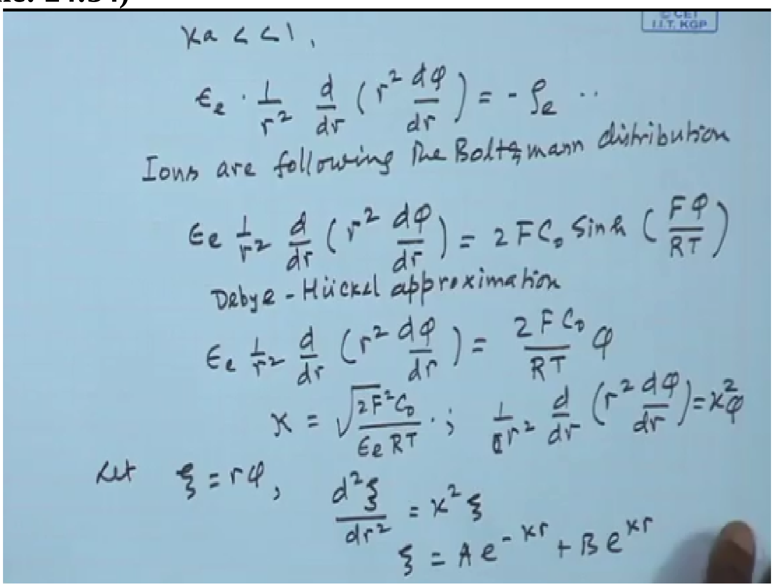
And then again go back solve the nearest equation, Nernst-Plank equations and the electric field equations all coupled manner to get the modified velocity and then calculate the drag say if we have established zero then stop the iteration otherwise we proceed further, so this is the general form to find out the velocity which obviously undoubtedly every complicated.

(Refer Slide Time: 23:57)



I would not say very complicated because through the computer simulations can be done so it is been done for several authors, so one can do that now first let's talk about the limiting situation, so that means in the case that Debye layer very thick, so Debye layer is very thick, so in that case what you can assume that limiting case is.

(Refer Slide Time: 24:34)



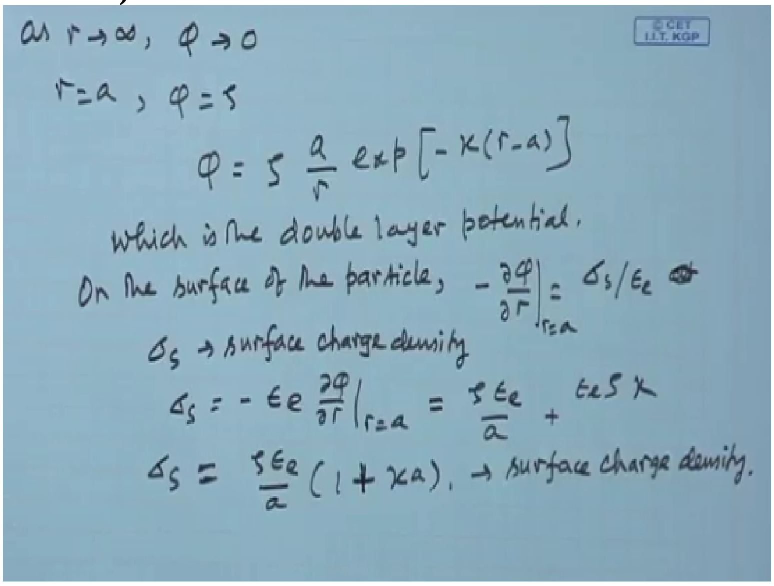
So k is very, very low thick Debye layer, so if we neglect the deformation of the electric double layer in this case then under cemetery condition in the angular direction in spherical polar co-ordinate so that means what we considered is only be dependent variable is only independent variable r is the only with radial direction then the Poisson equation for electric field can be expressed as Epsilon e into 1 by r square d dr of r square d Phi d r = - Rho e.

If answer so this is a form of the equation now if they ions are assume to obey the Boltzmann distribution, so assume that ions are followint the Boltzmann distribution so what I get is so in that case we can write is a Epsilon e this kind of equations we have already done several occasions, so I can straight away right this is becoming to 2FC0 Sin hyperbolic F Phi by RT, if I apply the Debye-Huckel approximation.

And the sketch show that means this nonlinear equation, we linearized so this can be written as Epsilon e square 1 by r square d dr of r square d Phi dr = 2FC0 by RT Phi, so lets us define the Debye length as 2F square C0 by Epsilon e RT so what you get this equation is becomes 1 by r square d dr of r square d Phi dr K square Phi. Let Jedi = r Phi, so what I get if I substitute now.

What I get is d2 Jedi d r2 = k square Jedi so solution is very simple, we can write Jedi = A e power – Kappa r + B e power Kappa r. Now what are the boundary conditions so the boundary conditions what we have is.

(Refer Slide Time: 27:58)



We can say that as r tends to infinity, Phi is tending to 0, that means here Phi is the equilibrium double layer potential, so Phi is tending to 0, so this implies that is 1 and r = A, you have Phi = Zeta, so with that we get the expression as Zeta a by r exp of - Kappa (r-a) this is a double layer potential, so this which is the double layer potential of course here we assume that will explain this week, Now the surface on the surface of the particle – Del Phi Del r = Sigma s by Epsilon e and at r = a, Sigma s is the surface charge density.

So what you get is from here Sigma s = - Epsilon e Del Phi Del r at r = a and so this can be obtained from here, so this becomes Sigma s becomes if I do little algebra at r = a one can find out that I am skipping this Epsilon e a + Epsilon e Zeta Kappa, so the Sigma s is basically can we obtain as Zeta Epsilon e a into 1+Kappa a, so this is the surface charge density. Okay, now will continue into the next class.