Modeling Transport Phenomena of Microparticles
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Lecture – 39
Electrophoresis of charged colloids – Part II

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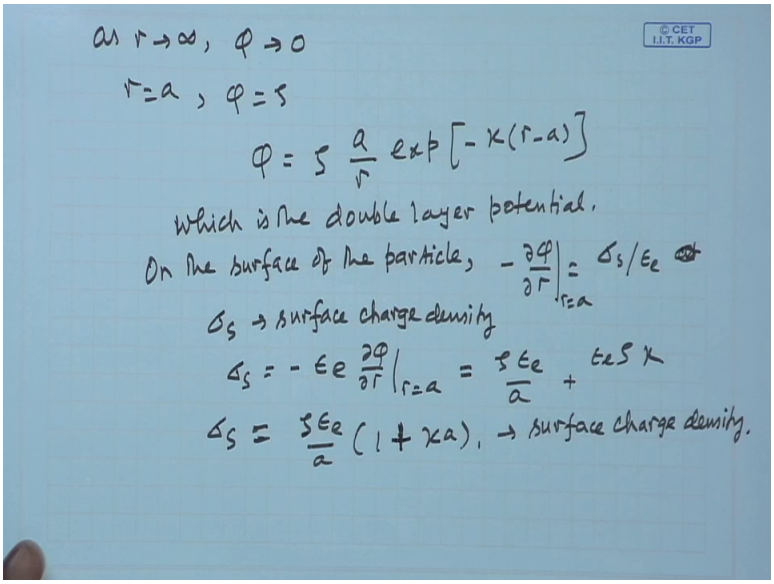

So the surface charge density is governed by this way here what we have assumed is no deformation of the double layer as I said before and ions follow the Boltzmann distribution. Now if I assume that k is very small, so this surface charge density Sigma E can be approximately written as Zeta by a.

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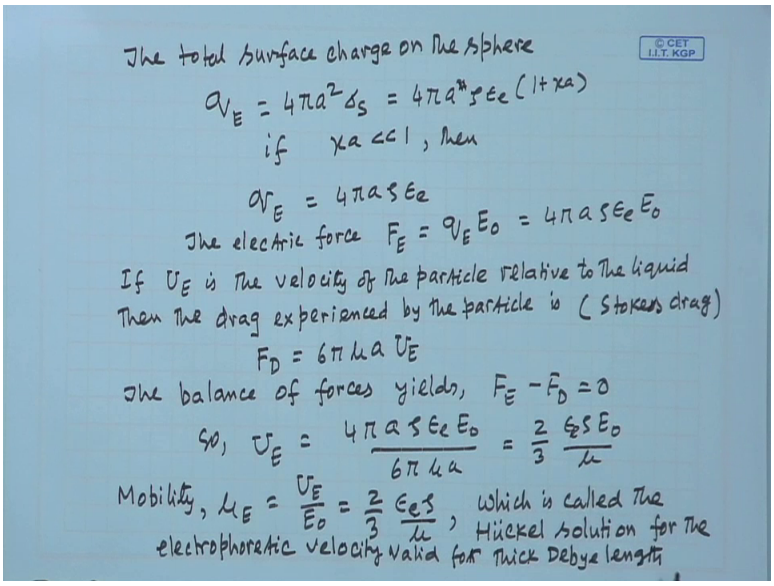

Now the total surface charge of the sphere, so let us call qe, this is equal to 4 Phi a square sigma s, so 4 Phi a square Zeta so a got canceled Zeta Epsilon e 1 + Kappa a. So under the assumption this is if this then what I get is then qe becomes 4 Phi a Zeta Epsilon e. So the electric force in that case becomes Fe = qe E0, E0 is applied electrical because which is along the direction of the propulsion.

So what I get this becomes 4 Phi a Zeta Epsilon e E0. Now if UE is the velocity of the particle relative to the liquid, then the drag experienced by the particle is FD = 6 Phi Mu a UE. We can call this is as the Stokes drag basically because only this simple form will get under the linear Stokes flow if there is a flow separation and recirculation formation, then this no longer valid. So here fluid velocity UE is quite small.

That means Reynolds number basically has to be lower than one. So which have considered the electrophoretic situation? So Stokes drag one can assume this for formula. So the balance of forces balance of forces yields Fe - FD = 0. So what I get is UE is basically 4 Phi a Zeta Epsilon Ee E0 by 6 Phi Mu a. So that means this become 2/3rd Epsilon Zeta Epsilon E, of course, Epsilon E. This is electric permittivity of the fluid, Zeta E0 by Mu.

And the mobility what we have already defined is equal to, let us call this as Mu E is UE by E0 power unit electric field. So this become 2/3rd Epsilon e Zeta by Mu, so this limit which is called

the Huckel solution, Huckel solution for the electrophoretic velocity, velocity valid for Thick Debye length. So now here we have not talked about anything, about the migration of ions and movement of ions, electro-migration of ions other kind of things.

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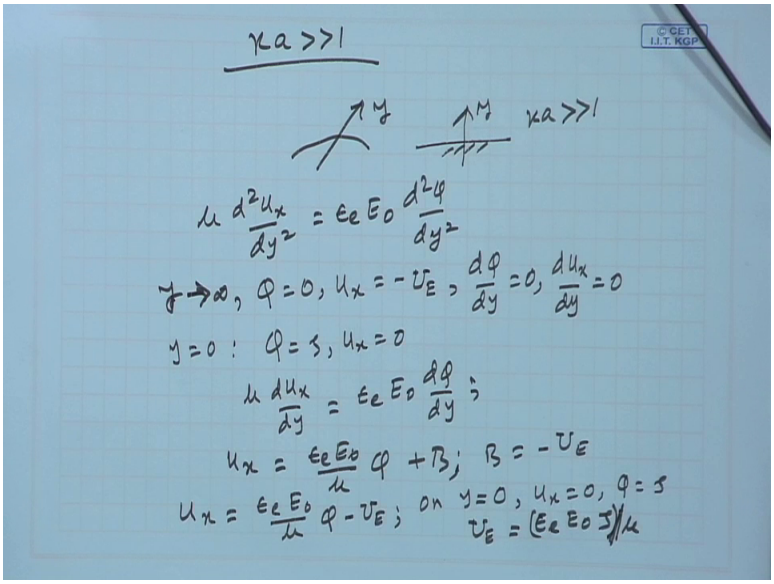

Similar manner we can also have a electrophoresis for thin Debye length. So now when we come to the situations for thin Debye layer, so there what I can talk about that instead of Debye length Lambda which is k inverse.

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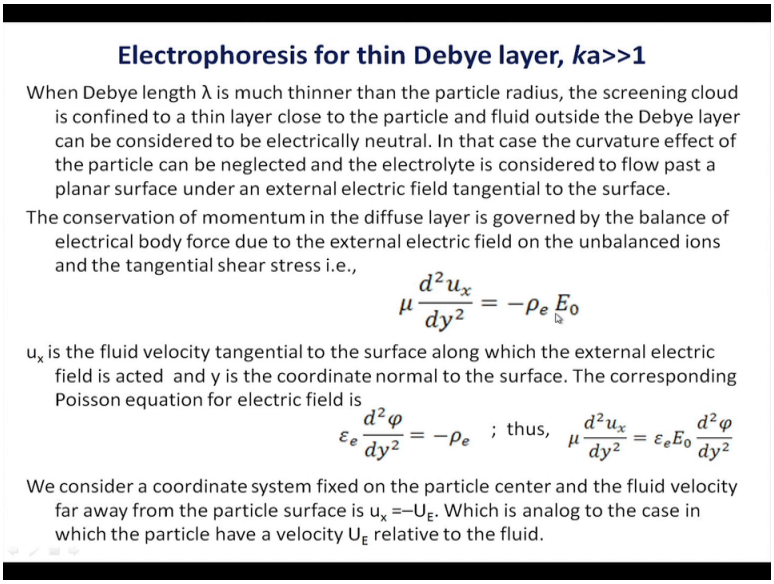

So we can talk about a flat surfaces, the curvature may not come into picture because just outside the Debye layer the flow field is just the balance of the shear stress and the electric force. So screening cloud is confined to a thin layer close to the particle and the fluid outside the Debye layer can be considered to be electrically neutral. In that case the curvature effect of the particle can be neglected.

The electrolyte is considered to flow past a planar surface under an external electric field tangential to the surface. So the conservation of momentum is basically the shear stress and the electric body force and the Poisson equations can also be written as y is of course is the normal direction. So that means we have say this is the particle, so let us talk about y. In this case of course here we have taken this is the surface as flat.

So, because of k is very, very thin, so locally we can say that only the normal gradient is important. So the Poisson equations can be reduced to this, Epsilon e d2 Phi dy2 = - Rho e. So if we know right from here that Mu d2u dx2 by dy2, so that means we are writing d2u okay, x direction y2 = Epsilon e E0 d2 Phi dy2 from this momentum equation, I just.

So again we assume that the fluid velocity far away from the particle surface ux = - UE, which is analog to the case in which the particle have a velocity UE relative to the fluid. So that means we are assuming the fluid particle is stationary and fluid is approaching the particle with a velocity – UE.

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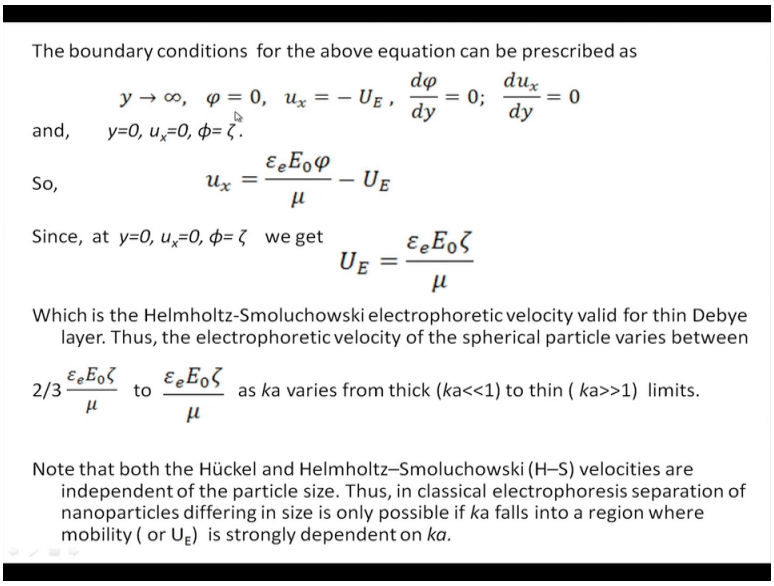

So I can impose the boundary conditions as this y tends to infinity that is far away from the surface of the particle. Y tends to infinity when we are away from the surface of the particle that is well within the electrically neutral fluid. We should have Phi = 0, Ux is coming to a -UE because this is the opposite direction fluid velocity you have taken. No gradient for Phi, no gradient for U and on surface of the particle we should have Phi = Zeta and Ux = 0.

Now if we integrate this equation so what we get is Mu integrate with respect to y, so dUx dy = Epsilon Ee E0 d Phi dy and we apply the infinity condition, this conditions, this two conditions should get the constant out, so the constant is 0. Now further integration we get Epsilon e E0 by Mu Phi + B. Now what we have is y tends to infinity so Ux = - U and Phi = 0, so this implies B = - UE.

So that means what a get is Ux = Epsilon e E0 by Mu Phi - UE by the Infinity condition. Now on the particle surface on y = 1 or y = 0 we are assuming the measuring this y from the surface. So y = 0 what we have is Ux is zero and Phi = Zeta. So this gives you UE = Epsilon Ee E0 Zeta by Mu. So which is nothing but the Smoluchowski velocity. So Epsilon e E0 Zeta by Mu which is the Smoluchowski velocity that is the usual electro-osmotic velocity.

When you have a thin double layer is formed. So what we found is that the electrophoretic velocity of the particle varies from 2/3rd Epsilon e E0 Zeta by Mu to Epsilon e E0 Zeta by Mu as

in the limiting situation. This is for the very thin or thick Debye length, where k is very small and this becomes for the thin situations and there electrophoretic mobility or here velocity. It does not depend this in this limiting cases are independent of the Debye length.

And also note that both Huckel and the Smoluchowski velocities are independent of the particle size. So thus in classical electrophoretic separation nano particle differing in size is only possible if the Debye length falls into a region where Debye length is in order 1.

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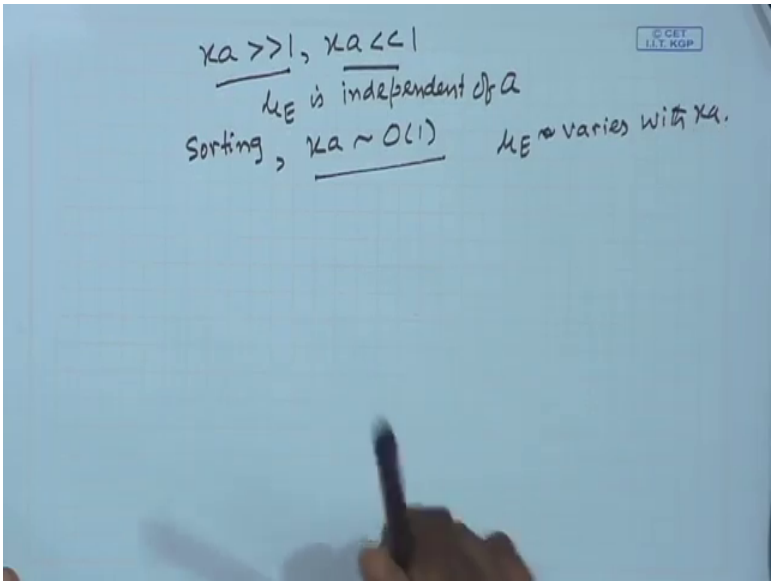

So that is why what it says this from the limiting situations that when ka is less than 1 or ka is Debye length is thin or thick, you have the Mu E is independent of size a. So for sorting on the basis of particle size ka should be of order 1. So that means ka should be of some comfortable well. So that is why we need now a formula or a expression for Mu E which depends on the, which varies with ka.

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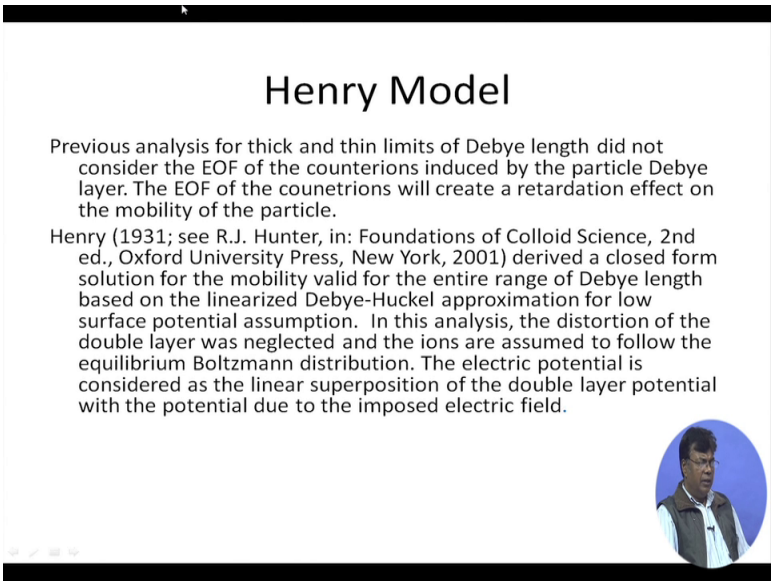

So to do that the first analysis was by Henry back in 1931. So Henry's model is very simple situation. So Henry assumed that the ions are obeying of a Boltzmann distribution and also the Debye-Huckel approximation and through that a closed form solution was obtained. The distortion of the double layer was neglected and the electric potential assumed to be a linear superposition of the external electric field and the double layer potential that arise due to the movement of the ions under the equilibrium Boltzmann distribution.

So this Henry model are discussed in some articles or books. One of this is Hunter which is a very fundamental books, so I am not going into details of that.

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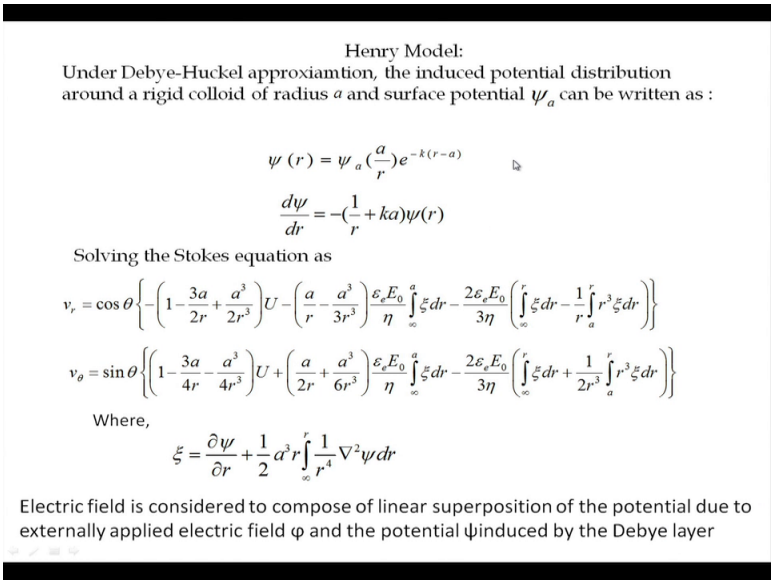

So basic idea is that you divide the electric potential into 2,1 is the double layer potential, Psi is another the external electric potential Phi. Okay now the Psi satisfy the Boltzmann rather Poisson-Boltzmann equation. So under Debye-Huckel approximation one can obtain that form like this and this is why the assuming that the ions are obeying the Boltzmann distribution.

So we get a form of this Psi governed by this way and this Stokes equation which describe the fluid motion. If you take the curl of that and get rid of the pressure and all so through some simplification one can obtain the velocity component governed by this integral form Electric integral form where Zeta is given by this way, this is the thing.

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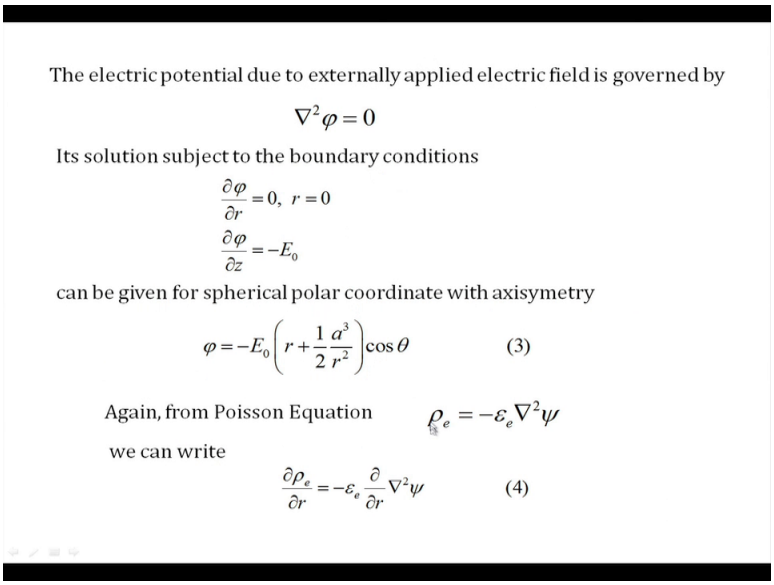

So electric external electric field if I call it is in a reverse way. Now here Phi is the in this portion we have taken Phi as the electric potential imposed due to the externally imposed electric field should satisfy the Laplace equation. If I the insulated particle that means you have a constant electric potential on the surface of the particle. So you have Del Phi Del r = 0 and at the far end it approach the Del Phi Del z approach the -E0 the imposed electric field.

If I solve this we get the form of Phi is given by this way okay. Now the Poisson equation for the Debye layer potential is governed by this equations.

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The Hydrodynamic force experienced by the fluid on the particle may be written as :

$$F_h = 2\pi a^2 \int_0^{\pi} [-\tau_{rr} Cos\theta + \tau_{r\theta} Sin\theta]_{r=a} Sin\theta \; d\theta$$

With $\tau_{rr} = -p + 2\eta \frac{\partial v_r}{\partial r}$

$$\tau_{r\theta} = \eta[\frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} + \frac{1}{r}\frac{\partial v_r}{\partial \theta}]$$

The electric force experienced by the charged particle

$$F_e = \int_s \sigma E_z \; ds$$

Where the surface charge density σ is given by $\sigma = -\varepsilon_e \frac{\partial \psi}{\partial r}\Big|_{r=a}$

The electric field along the direction of propulsion is $E_z = -E_\theta \, Sin\theta + E_r \, Cos\theta$

$$E_z = \frac{1}{r}\frac{\partial \phi}{\partial \theta} Sin\theta - \frac{\partial \psi}{\partial r} Cos\theta$$

So now if you do some careful manipulations and all so one can obtain the force component Fh, the hydro dynamic force and Fe the electrostatic body force and the which is the surface charge density which can be obtained by the from the Psi and electric field which are the Z along the direction along the Z basically direction of the particle motion or which is the same as the electric field direction.

So can be written as E Theta Sin Theta Er Cos Theta., so since the E Theta is no component for Psi only Phi we will have and Psi only function of r. So you get this Z this manner and with some manipulation and all.

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A closed form solution for the electrophoretic velocity is obtained as

$$U_E = \frac{2\varepsilon_e E_0 \zeta}{3\mu} f(\kappa a) \quad \text{, where}$$

$$f(\kappa a) = 1 + \frac{1}{16}(\kappa a)^2 - \frac{5}{48}(\kappa a)^3 - \frac{1}{96}(\kappa a)^4 + \frac{1}{96}(\kappa a)^5 + \frac{1}{8}(\kappa a)^4 e^{\kappa a}\left(1 - \frac{(\kappa a)^2}{12}\right)\int_{\kappa a}^{\infty}\left(\frac{e^{-t}}{t}\right) dt$$

The function f(κa) refers as the Henry function which depends on the Debye layer thickness. This particular form of the electrophoretic velocity is valid for weakly charged particle in which the electric potential is governed by the linearized Poisson-Boltzmann equation.

The electrophoretic mobility of the particle can be defined as velocity per unit applied electric field, i.e., $\mu_E = U_E/E_0$

Henry come to the, a closed form solution for the electrophoretic velocity governed by this way where if Kappa a is the called the Henry function. Now obviously this UE is depending on the Debye length Kappa a, there is no doubt about it. And this Kappa if Kappa a is governed by this way so this is referred as the Henry function.

Now the electrophoretic mobility is Mu E E0. Now if we plot this if Kappa a for low to high Kappa a values so we will find that if it is low it is becoming 1. And so that means you get back the Huckel limit, and if it is high Kappa a is very large you get 3 y 2. So that means you get the Smoluchowski limit.

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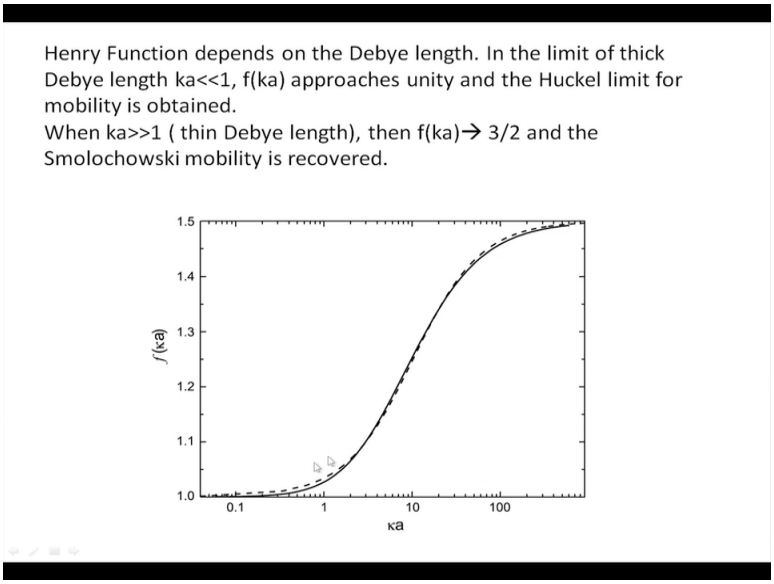

So basically if Kappa a takes this form. So that means it is 1 close to 1, when Kappa a is very small and it is asymmetrically merging into 3/2. So that means we get back the limits that is this here this is the Smoluchowski velocity, electrophoretic velocity, and this is the Huckel value, Huckel solution for thick Debye length. So this is the Henry model and it varies with the remaining portion, this if Kappa a is depending on the Kappa a.

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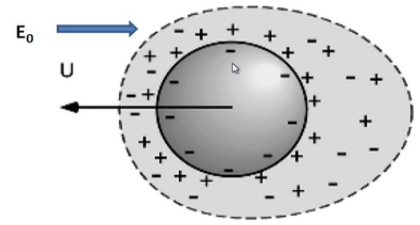
- Henry Model is based on the equilibrium Boltzmann distribution of ions under Debye-Huckel approximation. Thus, it is valid for weak applied field for which the electro-migration of ions are negligible and low charge density of the particle for which Debye-Huckel approximation is valid.
- Henry Model does not account for the double layer polarization (DLP) by convection and electromigration of ions, relaxation by the molecular diffusion of ions and their interactions with the background electroosmotic flow.



Now in the Henry model as stated before is assumed that the ions not have no electric osmotic flow of the ions neglected. Deformation of the Debye layer around the particle is not considered. Ions are obeying the equilibrium Boltzmann distribution. That means the electro-migration and convection effects are not taken into account. So this are the drawbacks of the Henry model.

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First-order Perturbation Analysis: O'Brien and White (Electrophoretic mobility of a spherical colloidal particle, J. Chem. Soc., Faraday Trans. 2 74, 1607 1978

Under the assumption of a weak applied electric field compared to the double layer potential, the double layer around the particle is assumed to slightly distorted from equilibrium i.e.,

$$n_i(r) = n_i^0 + \delta n_i(r)$$

$$\psi(r) = \psi^0 + \delta\psi(r)$$

$$\mu_i(r) = \mu_i^0 + \delta\mu_i(r)$$

$$\rho_{el}(r) = \rho_{el}^0 + \delta\rho_{el}(r)$$

Where the quantity with '0' refer to those at equilibrium

In equilibrium, the concentration distribution of the ionic species follows the Boltzmann distribution

$$n_i^0 = n_0 \exp\left(\frac{-z_i e\psi^0(r)}{k_B T}\right)$$

Now the second remedy was made by the several other authors. One of these in a very systematic way is O'Brien and White in 1978. So one the way of solving the electrophoretic problem is by the Perturbation analysis, so Perturbation analysis based on the weak applied electrical applied

electric field is taken to be very weak enough, so that you have a very first order negligible distortion of the double layer.

So that means this is zero superscript zero is the equilibrium and due to this applied electric field you have a distortion, this is the next step. So now if you substitute in the equation and neglect the higher orders for this approximation or this error terms, so deviation terms so you get a series of ordinary differential equation. So this ordinary differential equations and of course this is zero are governed based on the small Boltzmann distribution of ions.

Can be assumed for the zeros and it obeys Boltzmann distribution because we assume an equilibrium situation for the in the beginning and a first order distortion.

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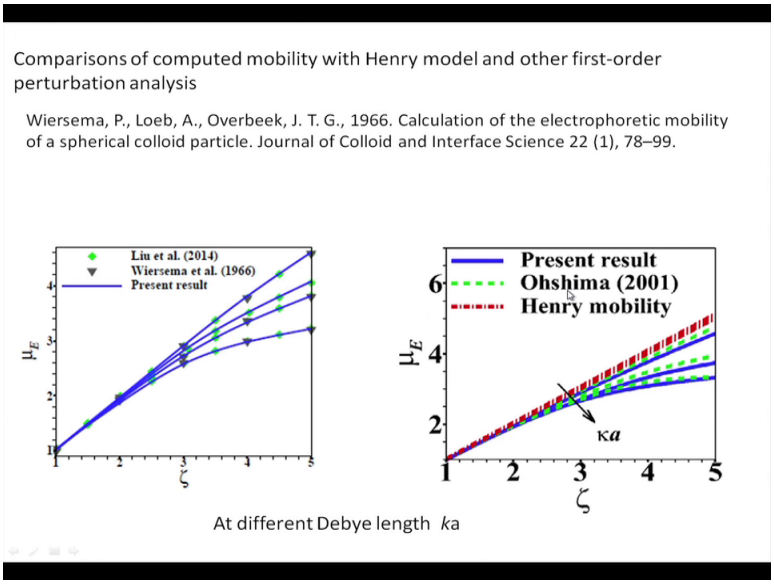

So through that the solutions was obtained and that solution differs from the Henry mobility by a large extent particularly when the Zeta potential becomes high. That means where the Debye-Huckel no longer valid and also when the Debye length is thick. So that means Debye length is not thin. So that means ka is of order 1, so in that case the deformation of the double layer or the double layer polarization become very important.

So here is the comparison with the computed solutions and all this model solution. Henry, Oshima is another model, then Wasserman, Wasserman is the similar as the O'Brien and White.

So this results: Wasserman, O'Brien-White are pretty accurate with the computed solution that in solving the full set of governing equations as discussed in the very beginning. But over the Henry model which is the linear model that deviates to a large extent particularly when Debye length become thick and Zeta potential is high.

Now the when the Debye is not thin then the deformation or the Debye layer polarization become very important aspects. See how which way we have define is that the so which way we have discussed is this Debye layer polarization is that see if the Debye length is not thin. So what will happen is that the ions as we move away from the particle will be loosely connected because the shielding effect is not strong as we go away from the particle, surface of the particle.

So this loosely connected ions, imbalanced ions when there will be an applied electric field, so it will move in the opposite direction to the direction the particle is moving. So it is negatively so there will be a negative ions will be surplus and that will move. Another positive ions will be surplus here so these particles ions will move and then in that process there will be a electro-osmotic flow and as well as the due to the movement of the particle so there will be a wave formation.

So the ions will be pushed backwards in the downstream direction. So in that process there will be a oppositely directing electric field will be developed. So these introductions of the double layer polarization and also the relaxation effect which is important when Zeta potential is high and their interaction with the Electroosmotic flow of the imbalanced ions become very important.

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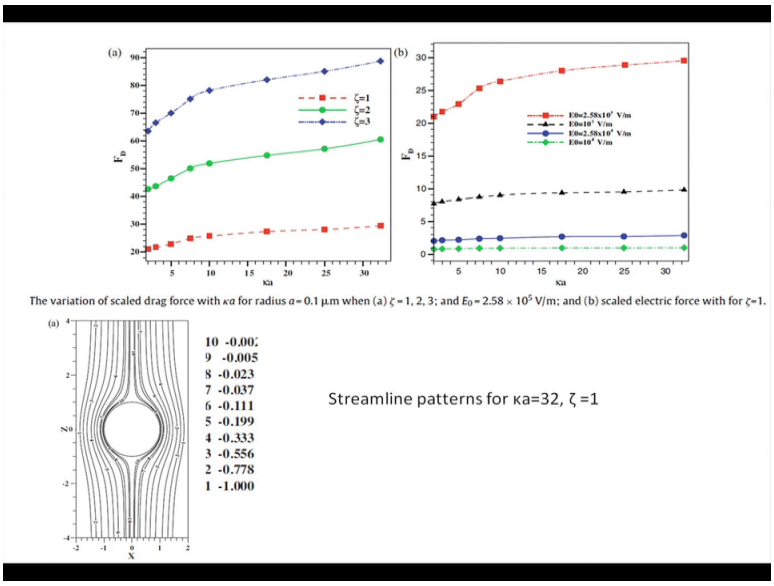

And that is only possible to capture through the model based on the Navier Stokes equation without doing any neglecting the charts neglecting some effects like in the first order perturbation analysis where the only rate is not complete the neglected but it is taken only up to the first order aspect. Now most cases for finding the electrophoretic velocity and all the first analysis found to be quiet okay.

But when you add a precise measurement of the force and flow pattern and all, so and also we will talk in the next lecture about the electric polarization. So in those cases the first order perturbation analysis is not good enough. Though here you see the force variation of the electric force or drag which are the same. So with the Debye length now see there is a all of a sudden there is a formation of a kind of kink or pattern change.

That is because of the Debye layer polarization at this kind of values of Kappa a. So and also see the Zeta potential of the particle surface potential is increasing the electric force as well as drag is also increasing and also the electric field radiation with the electric field which is somewhat linear up to this range of electric field and the form of the drag is showing. But the pattern, the variation of k Kappa a different electric field may not be same.

This is stream line pattern no doubt it is looks like a Stokes flow. So the stream lines forming a linear Stokes flow kind of things, no separations and a deformation.

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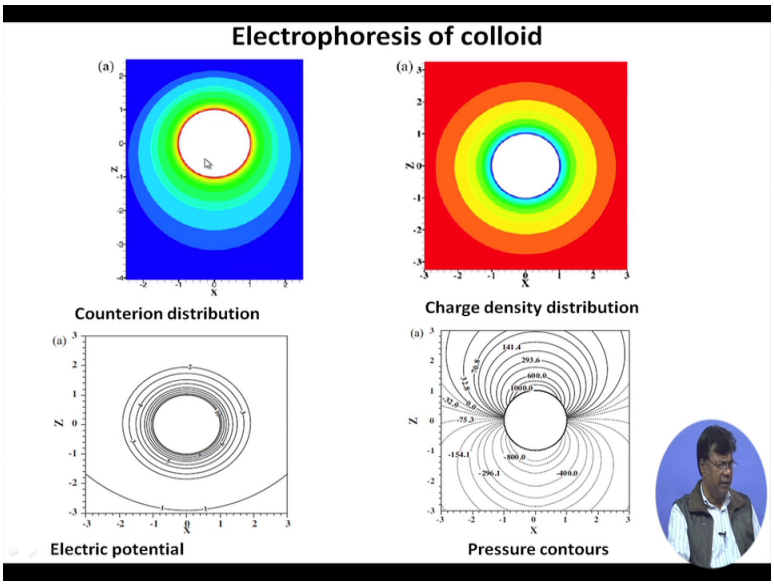

And this is the showing the counter on distribution, so this is negatively charged. So positive ion distribution around the particles so this is a particle. So what we can is is the deformation of the double layer is quite evident and this is the charge density distribution. So that means here Rho E, basically the scaled Rho E, this is near the particle. So if we move away from the particle Rho E is zero, so that is why no contours.

So Rho E is non zero on linearity close to the particle. And this is electric potential ion again its a ring structure is forming, there is a pressure contours. So particle is moving so induced pressure is developed near the particle surface. So we will continue to the next lecture on induced electric field formation when the particle is considered to be a dielectric particle. Thank you.