Modeling Transport Phenomena of Microparticles
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Lecture – 40
Gel Electrophoresis

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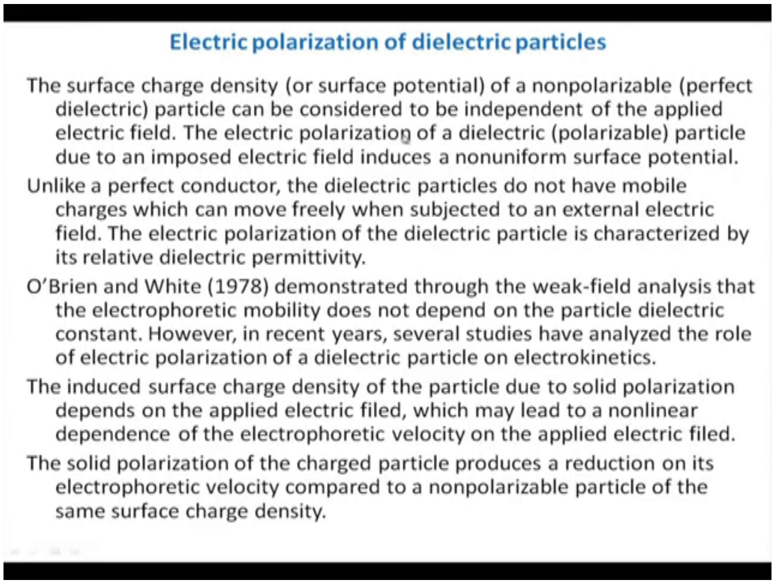

Electric polarization of dielectric particles

The surface charge density (or surface potential) of a nonpolarizable (perfect dielectric) particle can be considered to be independent of the applied electric field. The electric polarization of a dielectric (polarizable) particle due to an imposed electric field induces a nonuniform surface potential.

Unlike a perfect conductor, the dielectric particles do not have mobile charges which can move freely when subjected to an external electric field. The electric polarization of the dielectric particle is characterized by its relative dielectric permittivity.

O'Brien and White (1978) demonstrated through the weak-field analysis that the electrophoretic mobility does not depend on the particle dielectric constant. However, in recent years, several studies have analyzed the role of electric polarization of a dielectric particle on electrokinetics.

The induced surface charge density of the particle due to solid polarization depends on the applied electric filed, which may lead to a nonlinear dependence of the electrophoretic velocity on the applied electric filed.

The solid polarization of the charged particle produces a reduction on its electrophoretic velocity compared to a nonpolarizable particle of the same surface charge density.

Now in the previous cases we talked about the situation where the particles have a constant surface charge density or constant zeta potential. Now this kind of situation can only appear if the particle is either non conducting, perfectly non conducting perfectly dielectric or perfectly conducting. So in that case we can consider a constant surface potential but that surface potential is depends also on the external electric field.

Now if the particle is, even in the O'Brien-White analysis and all the permittivity of the electric permittivity of the particle was neglected and found it has got no effect on its electrophoresis. Electric polarization of the dielectric particle due to imposed electric field induces a non uniform surface potential. Now what happen if it is a dielectric particle like a conducting particle?

So it does not have any free charges so in that case there will be a electric field penetration of the inside the particle and there will be a formation of surface charge density which becomes a non uniform and it is a function of the external electric field. So O'Brien and White demonstrated through the weak field analysis that the electrophoretic mobility does not depend on the particle dielectric constant.

However in recent years there are several theoretical analysis and experimental result suggests that the role of electric polarization of a dielectric particle on electro-kinetics. Now this charge density that appears due to the electric polarization of the particle is we call as the induced surface charge density. So that is non uniform that is one problem another is depends on the applied electric field.

So in that case that means the electrophoretic velocity in that case becomes a nonlinear function of the applied electric field. So you cannot impose the mobility only on the, that means electrophoretic velocity depends nonlinearly on the electric field. So we cannot have a electrophoretic mobility that is linear variation no longer exist.

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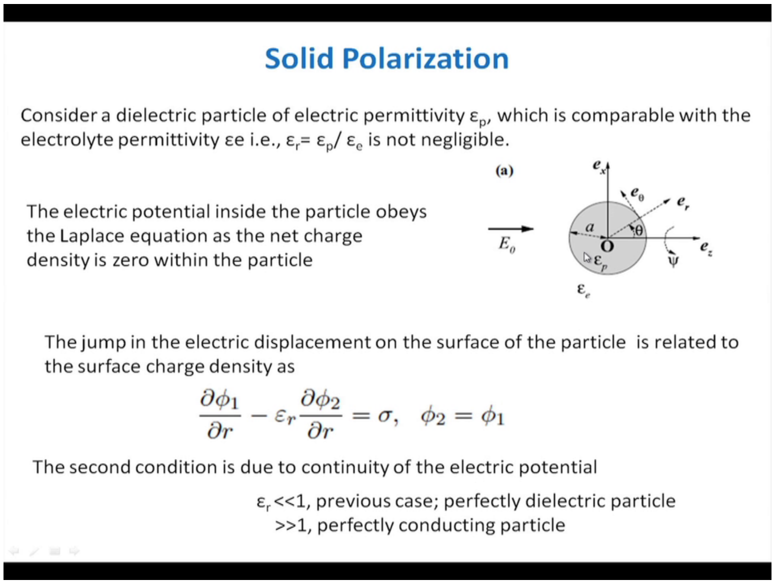

Solid Polarization

Consider a dielectric particle of electric permittivity ε_p, which is comparable with the electrolyte permittivity εe i.e., $\varepsilon_r = \varepsilon_p / \varepsilon_e$ is not negligible.

The electric potential inside the particle obeys the Laplace equation as the net charge density is zero within the particle

The jump in the electric displacement on the surface of the particle is related to the surface charge density as

$$\frac{\partial \phi_1}{\partial r} - \varepsilon_r \frac{\partial \phi_2}{\partial r} = \sigma, \quad \phi_2 = \phi_1$$

The second condition is due to continuity of the electric potential

ε_r <<1, previous case; perfectly dielectric particle
>>1, perfectly conducting particle

Now how to model this kind of situation? I will just give the overview to model a electrophoresis of a dielectric particle. So now the dielectric particle is characterized by the dielectric permittivity ratio given by this Epsilon r. This is the permittivity of the particle, relative permittivity of the particle and this is the liquid. So this ratio, now if this ratio is very low so that means the permittivity of Epsilon p is negligible.

So we can consider it is a non conducting and the previous analysis is old school. But if it is very large then also it is a perfectly conducting, so these are the two extreme situation. Now we are considering that where Epsilon r is not negligible. So that means we have a polarizable particle. If the particle does not contain any free charges within the within itself, so what we will have is the inside the particle so what we will have this.

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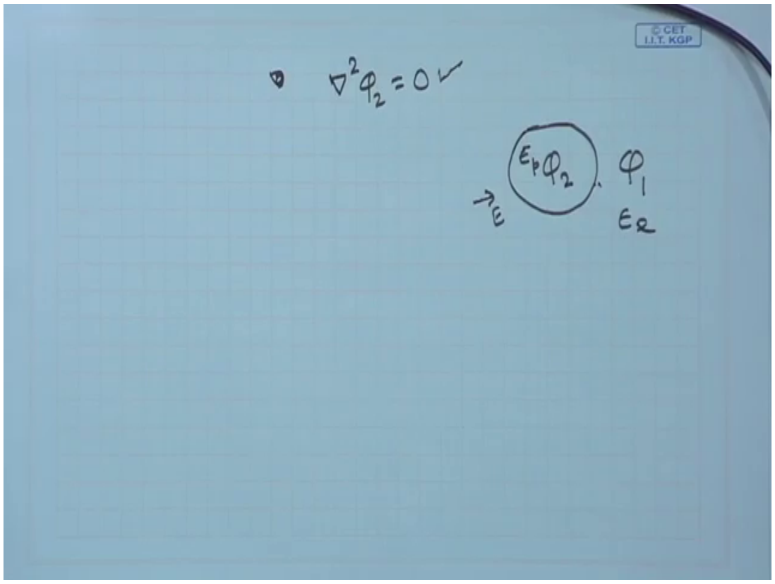

Del 2 Phi 2 = 0, so what are you doing is this is the electric field we are talking about. This electric potential inside the particle and this is Epsilon r and the dielectric permittivity Epsilon p and this is Epsilon e. So this is equation if there is no free charge within the there is no net charge within the particles. So Del 2 Phi 2 =0, but on the surface of the particle that is the electric displacement condition that we have derived in the very beginning will be governed by this.

This is what the continuity of the potential Phi 2 = Phi 1 and there is a electric displacement condition. So Phi 1 is the one which satisfy the Poisson equations and all this equation. So here we are outside the electrolyte medium this, the potential is governed by the superscript subscript 1. So it follows the same equation only thing is that it satisfies this condition at the surface governed by this.

And Epsilon r is the permittivity constant, so this is the only Del 2 Phi 2 = 0. So this is the only modifications which has to be taken into account that on the surface we cannot have a particle to have a constant potential or constant charge density. This is one aspect another aspect is that the particle velocity and surface charge density becomes a function of the electric field.

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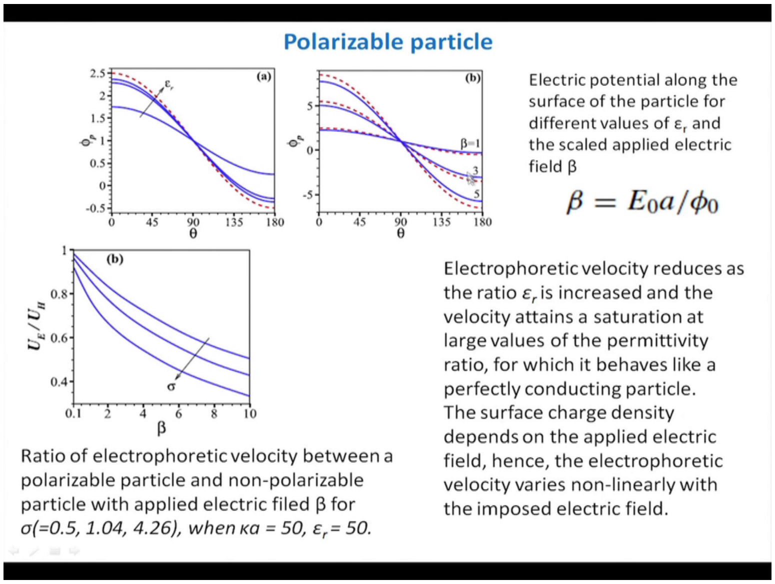

Polarizable particle

Electric potential along the surface of the particle for different values of ε_r and the scaled applied electric field β

$$\beta = E_0 a/\phi_0$$

Electrophoretic velocity reduces as the ratio ε_r is increased and the velocity attains a saturation at large values of the permittivity ratio, for which it behaves like a perfectly conducting particle. The surface charge density depends on the applied electric field, hence, the electrophoretic velocity varies non-linearly with the imposed electric field.

Ratio of electrophoretic velocity between a polarizable particle and non-polarizable particle with applied electric filed β for *σ(=0.5, 1.04, 4.26), when $\kappa a = 50$, $\varepsilon_r = 50$.*

Now in this case there is we considered a full computations, computation of model just highlight how it differs from the situations where a particle is taken to be a non conducting one. So if we consider the particle to be a polarizable particle, so the surface potential this can be obtained and governed by this following this curve is axisymmetric. So we have taken 0 to Phi. So what we find that as Epsilon r this one is the permittivity ratio.

So that means as Epsilon r is increasing the surface potential is following a nice Sin curve and it is approaching becoming independent also now beyond a certain value of Epsilon r that means the particle is behaving like a conducting particle. And also you see these from this figure the surface charge surface potential. Here Beta is the scaled electric field. E0 is the applied electric field and we define Beta as the scaled one given by this way.

So if I consider a high electric field, the large radiation in the surface potential is evident. If it is low than it is smaller compared to this, so obviously the surface potential strongly depends on E0. So this implies that the electrophoretic mobility will also be a function of E0. So that is why mobility is not used the term mobility is not used, the velocity is used. Now electrophoretic velocity is found to reduce.

Now there are several there are physical mechanisms used for reduction because as the surface become polarizable so the surface conduction effect becomes significant. So the surface contraction effect reduces the mobility electrophoretic velocity. That is what you find that the electrophoretic velocity reduces as the ratio Epsilon r is increased.

And velocity attains a is saturation at large value of the permittivity ratio for which the particle behaves like a perfectly conducting particle and also what you see is that the surface charge density depends on the applied electric field. Hence the electrophoretic velocity varies non-linearly with the imposed electric field. This result this is the showing the ratio of electrophoretic velocity between a polarizable particle and non-polarizable particle.

Non-polarizable means Epsilon r is very, very small. So what you find that this ratio is deviates. It deviates by a large extent and it is always less than 1. So that means this UE by UH is always less than 1. So this implies that the electrophoretic velocity is low when we considered a polarizable particle. Here we are taken Epsilon r and large at 50 and Debye length is large, k is large, so Debye length is low, small.

So smaller Debye length and larger Epsilon r for different charge of the surface charge density Sigma. In the beginning the particle have a service charge density Sigma and due to polarization there will be a additional surface charge formation, electric polarization and the what you find the a great deviation is occurring and the division is prominent where Sigma is large and electric field is large, this is the scaled electric field.

So as the electric field is becoming higher so what we find that the deviation is becoming significant between the non-polarizable, polarizable and non-polarizable particle. So which resolve these results precisely shows that the dielectric particle solid polarization is not a negligible effect when you have the permittivity ratio is order one and the electric field is strong.

So this kind of situations and another thing is that this nonlinear electrophoresis cannot be solved by the Henry model or even the first order perturbation has done by the O'Brien White, Weismann and other things. So in that case the non-linear situations one has to rely on the computations of the governing equations. Now next this is will be the our last topic on electrophoresis is gel electrophoresis.

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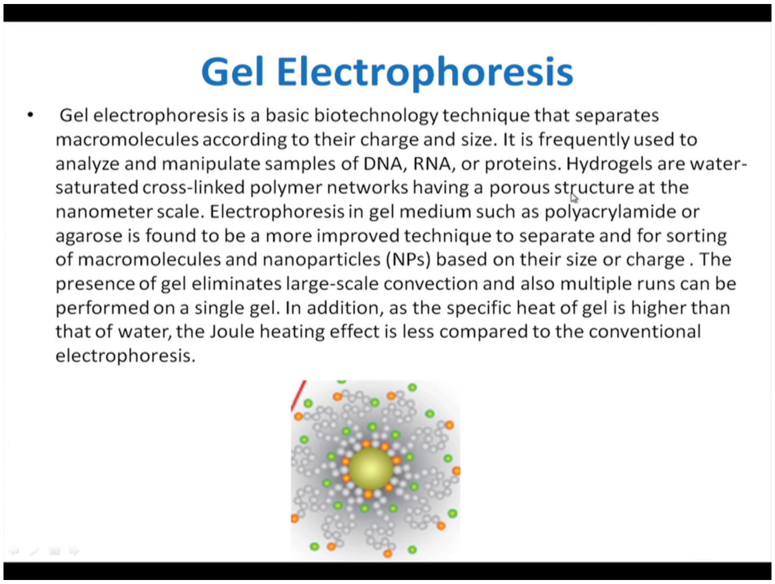

Gel Electrophoresis

- Gel electrophoresis is a basic biotechnology technique that separates macromolecules according to their charge and size. It is frequently used to analyze and manipulate samples of DNA, RNA, or proteins. Hydrogels are water-saturated cross-linked polymer networks having a porous structure at the nanometer scale. Electrophoresis in gel medium such as polyacrylamide or agarose is found to be a more improved technique to separate and for sorting of macromolecules and nanoparticles (NPs) based on their size or charge . The presence of gel eliminates large-scale convection and also multiple runs can be performed on a single gel. In addition, as the specific heat of gel is higher than that of water, the Joule heating effect is less compared to the conventional electrophoresis.

Now this Gel electrophoresis is a very important aspect in electrophoresis because through the gel electrophoresis the sorting of particles and DNA and other things can be done very nicely or efficiently and also gel has advantages that the gel can be used several times. Another thing is that the joulity effect is low in the hydro gel. Now joulity effect we have not discussed because of the joulity effect this all migrations and all, there will be generation of heat loss and that way the energy loss will arise.

So the aim will be to reduce amount of joulity. So which is good in gel electrophoresis and also the dispersion is low. So that is why gel electrophoresis is a very important technique for manipulation of DNA RNA and all these things in bio colloids and all. So we will give a little overview of the gel electrophoresis. Now what is the gel electrophoresis is that the particle the colloid particles are suspended in a hydro gel medium.

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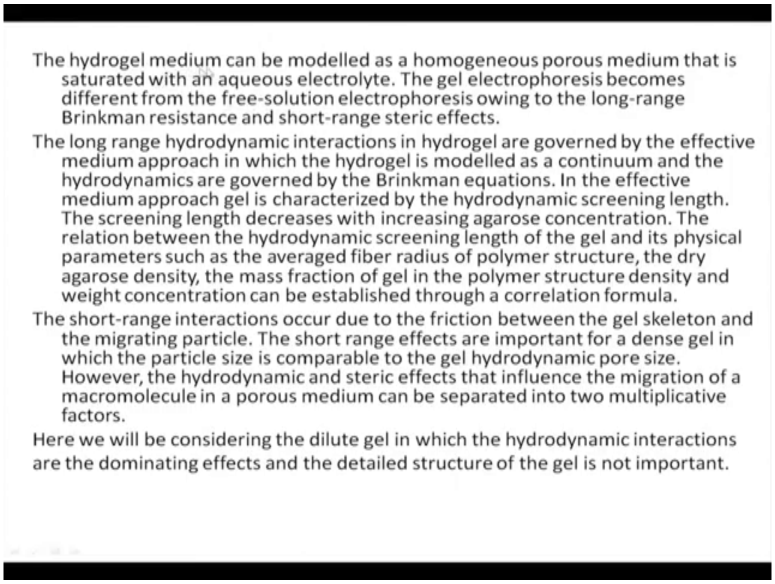

The hydrogel medium can be modelled as a homogeneous porous medium that is saturated with an aqueous electrolyte. The gel electrophoresis becomes different from the free-solution electrophoresis owing to the long-range Brinkman resistance and short-range steric effects.

The long range hydrodynamic interactions in hydrogel are governed by the effective medium approach in which the hydrogel is modelled as a continuum and the hydrodynamics are governed by the Brinkman equations. In the effective medium approach gel is characterized by the hydrodynamic screening length. The screening length decreases with increasing agarose concentration. The relation between the hydrodynamic screening length of the gel and its physical parameters such as the averaged fiber radius of polymer structure, the dry agarose density, the mass fraction of gel in the polymer structure density and weight concentration can be established through a correlation formula.

The short-range interactions occur due to the friction between the gel skeleton and the migrating particle. The short range effects are important for a dense gel in which the particle size is comparable to the gel hydrodynamic pore size. However, the hydrodynamic and steric effects that influence the migration of a macromolecule in a porous medium can be separated into two multiplicative factors.

Here we will be considering the dilute gel in which the hydrodynamic interactions are the dominating effects and the detailed structure of the gel is not important.

So this hydro gel medium which can be modeled as a homogeneous porous medium that is saturated with an aqua’s electrolyte. So the gel electrophoresis becomes different because now here we have the medium as a homogeneous porous medium instead of electrolyte medium that we have discussed in the previous cases. So now this creates some new phenomena compared to the previous one.

One is the long range hydrodynamic effect this is called the Brinkman resistance and there is a short range steric effect. Steric effects when there is a friction with the gel port and particle. Now this long range hydrodynamic introduction in hydro gel are governed by the effective medium approach in which hydro gel is modeled as I continue and the hydrodynamics are governed by the Brinkman equation.

So the effective medium approach what I do is hydro gel is modeled as a homogeneous porous medium and is characterized by a screening length parameter hydrodynamic screen length, screening length. This screening length is also related with the permeability of the porous medium. And also the short range introduction this is important when the gel port sizes are compatible with the particle size.

Now if I assumed the gel is highly permeable. So in that case the short range steric effects can be taken to be negligible. So and also there are several models through which the steric effect can be estimated. So in this one can assume that steric effect has not a significant importance when we have a hydrodynamic screening length of the gel is quite large compared to the particle size.

So if we considered a dilute gel, that means the screening length of permeability is high. So in that case this theory contractions can be neglected. Now we consider the electrophoresis under externally applied electric field E0 of a non conductive spherical particles of radius a with uniform service charge density Sigma submerged in an electrolyte saturated gel medium. And we model the gel medium as a effective Brinkman porous medium with screening length L.

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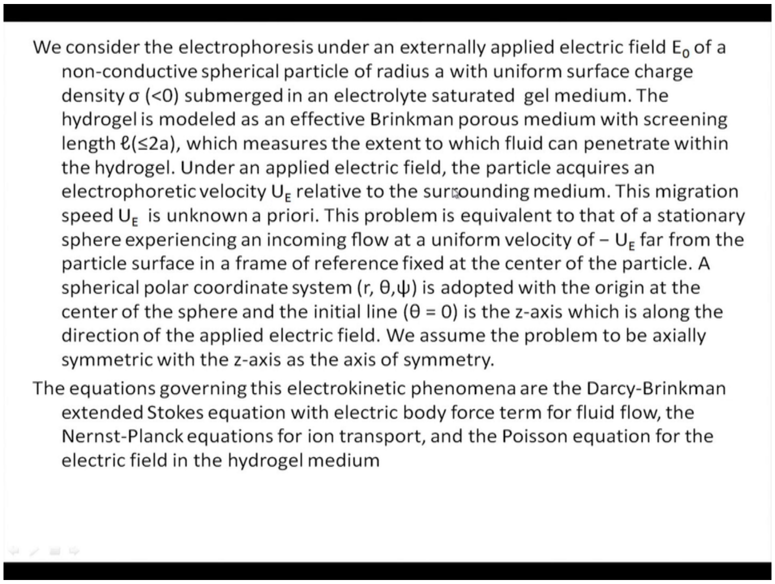

We consider the electrophoresis under an externally applied electric field E_0 of a non-conductive spherical particle of radius a with uniform surface charge density σ (<0) submerged in an electrolyte saturated gel medium. The hydrogel is modeled as an effective Brinkman porous medium with screening length ℓ(≤2a), which measures the extent to which fluid can penetrate within the hydrogel. Under an applied electric field, the particle acquires an electrophoretic velocity U_E relative to the surrounding medium. This migration speed U_E is unknown a priori. This problem is equivalent to that of a stationary sphere experiencing an incoming flow at a uniform velocity of $-U_E$ far from the particle surface in a frame of reference fixed at the center of the particle. A spherical polar coordinate system (r, θ,ψ) is adopted with the origin at the center of the sphere and the initial line (θ = 0) is the z-axis which is along the direction of the applied electric field. We assume the problem to be axially symmetric with the z-axis as the axis of symmetry.

The equations governing this electrokinetic phenomena are the Darcy-Brinkman extended Stokes equation with electric body force term for fluid flow, the Nernst-Planck equations for ion transport, and the Poisson equation for the electric field in the hydrogel medium

Which we assume to be lower than the diameter of the particle and the screening length is also measures to which extend it can penetrate within the hydro gel. Now the under the applied electric field particle acquires a electrophoretic velocity UE relative to the surrounding medium and this UE is to be obtained which is unknown priori.

Now the governing equations in this case to take into account the flow through porous media is accounted by the, that is the Brinkman equation. And the ion transport which is governed by the Nernst-Planck equation in the electrolyte and the Poisson equation which determines the electric field in the hydro gel medium. So these things are there only thing is that the gel hydrodynamic resistance has to be taken into account through the through some terms.

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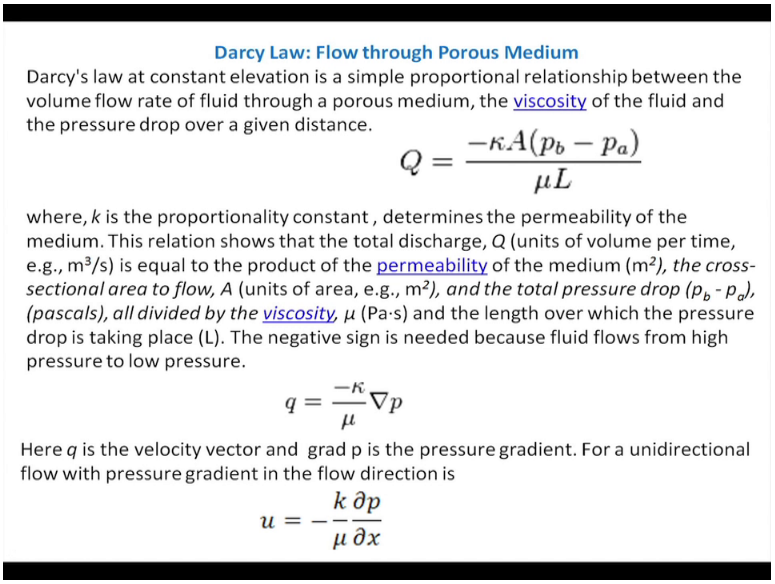

Darcy Law: Flow through Porous Medium

Darcy's law at constant elevation is a simple proportional relationship between the volume flow rate of fluid through a porous medium, the viscosity of the fluid and the pressure drop over a given distance.

$$Q = \frac{-\kappa A(p_b - p_a)}{\mu L}$$

where, *k* is the proportionality constant , determines the permeability of the medium. This relation shows that the total discharge, *Q* (units of volume per time, e.g., m^3/s) is equal to the product of the permeability of the medium (m^2*), the cross-sectional area to flow, A* (units of area, e.g., m^2*), and the total pressure drop* (p_b - p_a)*, (pascals), all divided by the viscosity,* μ (Pa·s) and the length over which the pressure drop is taking place (L). The negative sign is needed because fluid flows from high pressure to low pressure.

$$q = \frac{-\kappa}{\mu}\nabla p$$

Here *q* is the velocity vector and grad p is the pressure gradient. For a unidirectional flow with pressure gradient in the flow direction is

$$u = -\frac{k}{\mu}\frac{\partial p}{\partial x}$$

Now before we write the equation what is Darcy Law? Now Darcy law when there is a flow through a porous media under a pressure difference along a length scale pressure difference in a cross section area A, so the Darcy law through Q measures that the fluid discharge amount is related by this way where K is the proportionality constant which is the permeability. Which is referred as the permeability and this is the pressure drop along the length L.

A is the cross-sectional area; Mu is the viscosity of the medium. So now if I write it Q by A and all so the velocity if I write in terms of velocity and this is the pressure gradient. There is a negative side because the pressure increases velocity decrease negative side and fluid flows from high pressure to low pressure. So opposite direction and if I consider only unidirectional flow, so this can be simplified form is governed by this equation.

So in a porous medium the fluid flow can be determined by this equation. But this is not a complete equation particularly when you have the boundary effect is there and also the permeability is not permeability is high. So that means gel screening length is high. So in that case we cannot have a Darcy law is not sufficient.

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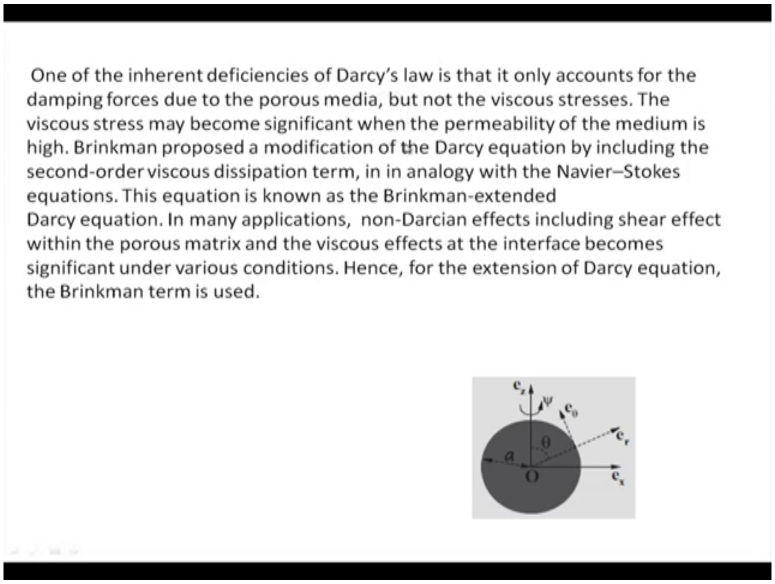

One of the inherent deficiencies of Darcy's law is that it only accounts for the damping forces due to the porous media, but not the viscous stresses. The viscous stress may become significant when the permeability of the medium is high. Brinkman proposed a modification of the Darcy equation by including the second-order viscous dissipation term, in in analogy with the Navier–Stokes equations. This equation is known as the Brinkman-extended Darcy equation. In many applications, non-Darcian effects including shear effect within the porous matrix and the viscous effects at the interface becomes significant under various conditions. Hence, for the extension of Darcy equation, the Brinkman term is used.

For that this Brinkman extended, Brinkman take into account extended or modified the Darcy equation by taking into account the viscous stress that gives the several simplification what is the this is a kind of analogues to the Navier-Stokes equation and if you have a interface, porous and fluid, so this Brinkman equation is works very nicely because the momentum equation have the viscous shear stress in both the Navier-Stokes equation as well as in the Brinkman terms.

And also if you have the permeability is high, so viscous shear stress becomes an important thing. So the governing equation in gel medium or the governing equation for free transport in a gel medium is governed by this equation. So this is as well this is Navier Stokes equation. So you have extra term here, this is the Darcy term.

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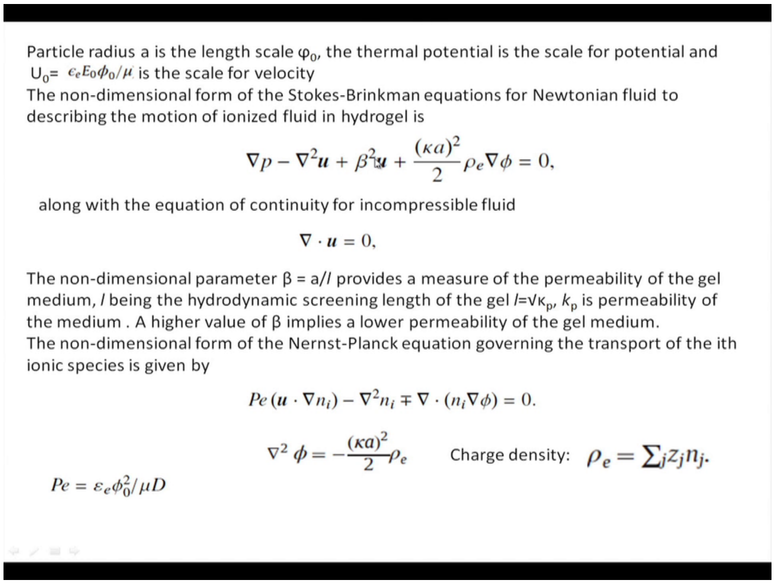

Particle radius a is the length scale φ_0, the thermal potential is the scale for potential and $U_0 = \epsilon_e E_0 \phi_0/\mu$ is the scale for velocity

The non-dimensional form of the Stokes-Brinkman equations for Newtonian fluid to describing the motion of ionized fluid in hydrogel is

$$\nabla p - \nabla^2 \boldsymbol{u} + \beta^2 \boldsymbol{u} + \frac{(\kappa a)^2}{2} \rho_e \nabla \phi = 0,$$

along with the equation of continuity for incompressible fluid

$$\nabla \cdot \boldsymbol{u} = 0,$$

The non-dimensional parameter $\beta = a/l$ provides a measure of the permeability of the gel medium, l being the hydrodynamic screening length of the gel $l = \sqrt{\kappa_p}$, k_p is permeability of the medium . A higher value of β implies a lower permeability of the gel medium.

The non-dimensional form of the Nernst-Planck equation governing the transport of the ith ionic species is given by

$$Pe\,(\boldsymbol{u} \cdot \nabla n_i) - \nabla^2 n_i \mp \nabla \cdot (n_i \nabla \phi) = 0.$$

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

Charge density: $\rho_e = \sum_j z_j n_j$.

$$Pe = \varepsilon_e \phi_0^2/\mu D$$

Beta square u this is the because of the electric body force and this is the shear stress, viscous shear stress. Mu is absent here because of the scaling. We have taken the velocity scale as this is a non-dimensional equation. So Mu is absorbed over here Rho is also absorbed in p. So this is scaled equation and this is equation for continuity as usual incompressible flow.

So we have electrolyte saturated porous media so the electric electrolyte flowing or the flow of the electrolyte is governed by these equation along with the continuity equation and this parameter. This measures the scale parameter for the porous permeability and defined by this way, so L is the hydrodynamic scaling length of the gel. L also can be written as root kp, kp is the permeability.

So higher value of beta implies a lower permeability of the gel medium and because this is inwards. Now the ion distribution within the electrolyte is governed by that Nernst-Planck equation. So if I write the z-z electrolyte because here we are triggered plus and minus. So our 1-1 electrolyte z is balance is taken to be mod z is 1. So I get the Nernst-Planck equation governed by this transport equation.

Again this is the convective transport of the ions, diffusion, electro-migration. So this balance and this is the Poisson equation for electric field. Rho is the charge density given by this way. So this set of equations are governing the electrophoresis in a hydro gel medium. So if we look back to the previous one so only difference what we find is the addition of this term Beta square u which was at the gel contribution of gel is coming through this Beta.

And Beta is determined through the permeability of the medium. So one need to study this set of equations, here of course you have taken the gel as uncharged, so that means the gel skeleton is uncharged. So that is why charge density of whatever appears in Rho e is because of the moment of the electrolyte within through the hydro gel medium.

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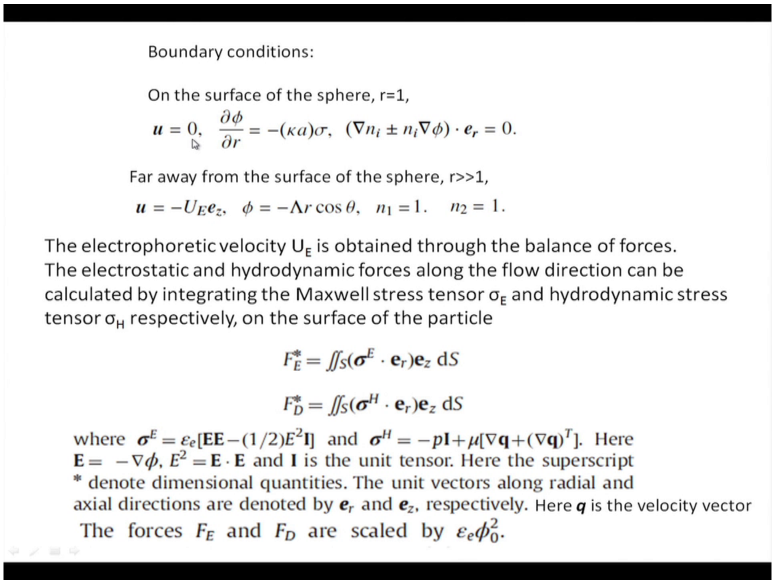

Boundary conditions:

On the surface of the sphere, r=1,

$$\boldsymbol{u} = 0, \quad \frac{\partial \phi}{\partial r} = -(\kappa a)\sigma, \quad (\nabla n_i \pm n_i \nabla \phi) \cdot \boldsymbol{e}_r = 0.$$

Far away from the surface of the sphere, r>>1,

$$\boldsymbol{u} = -U_E \boldsymbol{e}_z, \quad \phi = -\Lambda r \cos\theta, \quad n_1 = 1. \quad n_2 = 1.$$

The electrophoretic velocity U_E is obtained through the balance of forces. The electrostatic and hydrodynamic forces along the flow direction can be calculated by integrating the Maxwell stress tensor σ_E and hydrodynamic stress tensor σ_H respectively, on the surface of the particle

$$F_E^* = \iint_S (\boldsymbol{\sigma}^E \cdot \mathbf{e}_r)\mathbf{e}_z \, dS$$

$$F_D^* = \iint_S (\boldsymbol{\sigma}^H \cdot \mathbf{e}_r)\mathbf{e}_z \, dS$$

where $\boldsymbol{\sigma}^E = \varepsilon_e[\mathbf{EE} - (1/2)E^2\mathbf{I}]$ and $\boldsymbol{\sigma}^H = -p\mathbf{I} + \mu[\nabla\mathbf{q} + (\nabla\mathbf{q})^T]$. Here $\mathbf{E} = -\nabla\phi$, $E^2 = \mathbf{E}\cdot\mathbf{E}$ and $\mathbf{I}$ is the unit tensor. Here the superscript * denote dimensional quantities. The unit vectors along radial and axial directions are denoted by $\boldsymbol{e}_r$ and $\boldsymbol{e}_z$, respectively. Here $\boldsymbol{q}$ is the velocity vector The forces F_E and F_D are scaled by $\varepsilon_e\phi_0^2$.

Now the boundary conditions we can impose on the surface of the sphere r = 1, we have u = 0. This condition the surface charge density if you have a constant surface charge density is gone by this way and the no normal flux of the ions on the surface. So this is governed by this equation, no normal flux no ion penetration through the surface of the sphere. Far away from the surface of the sphere that means when r is many, many times greater than 1.

U is approaching to –UE, again we are taking the particle to be stationary and fluid is approaching towards the particle and Phi is becoming the imposed electric field and this are the bulk value. Because this is either away from the sphere the electrolyte is neutral so you have the same ionic concentration. So, it is scaled of course, so it is n0 is the bulk ionic number so it will be the n0.

And we need to find out the forces and through the force balance we can obtain the mobility or electrophoretic velocity. Both are the same in this case because here we are considered the linear situation, linear, which is with the electric field. So we need to find out the electric force and the hydrodynamic drag experienced by the particle.

Electric force again one can compute through the Maxwell stress and hydrodynamic drag from the shear stress and pressure drop and all these things.

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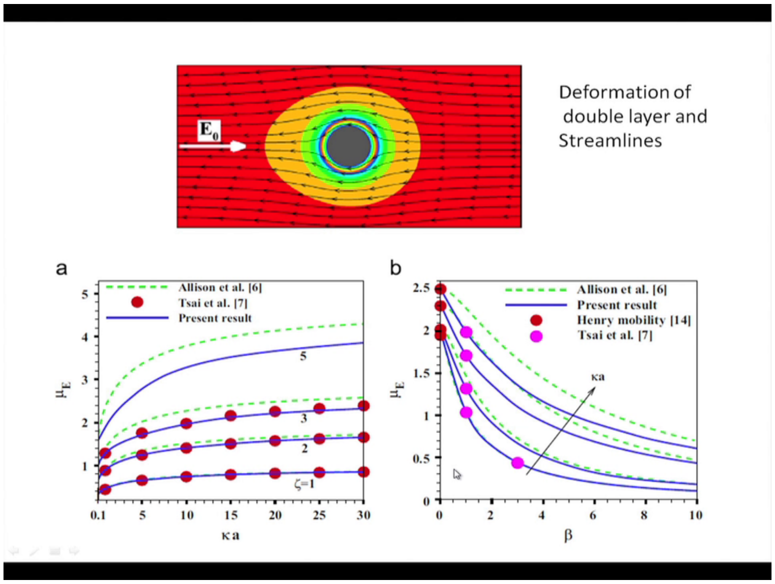

Deformation of double layer and Streamlines

So now I show some result. So this is a stimulant pattern for gel electrophoresis so what if ion here deformation of the double layer. So this is the counter and distribution. So here this is streamline so that means a electric field is applied and the fluid is moving along this direction where we keep the particle to be stationary.

And so the particle is kept to be stationary so in that case the fluid is approaching from the other side opposite side the proportion of the particle and the deformation of the double layer is quite evident because we have the particle to be moving this direction. So the ions attract downstream direction. So this direction will be downstream for the particle because particle is moving on the direction of the electric field positively charged.

So the mobility there are several authors have obtained the mobility, so best of the competitions of those nonlinear governing equations one can obtain the mobility. Some of the show with the experimental results and theoretical analysis we made a comparisons. Now what we find the electrophoretic mobility which is scaled of course is varies with the Debye length, so after certain value of Debye length so it attains a saturation a constant value.

So we get and this is the based on a perturbation analysis the Allison. So I find a large deviation particularly when zeta is large. And also this is mobility versus the permeability Beta, so the mobility is large when the permeability is high. So that is Beta is low means permeability is high because Beta was defined as a by l. So l is large and Beta is low, so permeability is high means the electrophoretic mobility is high.

So as permeability becoming low that means gel becomes dense. It is becoming it is decreasing and slowly becoming vanishing over there. So that is how the gel electrophoresis can be modeled. So in modeling the gel electrophoresis what we need to do is we have to extend the Navier Stokes equation to the Darcy Brinkman equation.

Where the Darcy terms which takes into account the hydro dynamic resistance provided by the gel skeleton and long range effect is good enough if we have the gel is quite dilute. If not then we have to consider the static effect. There are several correlation formulation for static effect which is available in the literature, so that I conclude for the electrophoresis portion. Thank you!