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PARTICLE TRANSPORT BY DIFFUSIOPHORESIS IN POROUS MEDIA

by

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Chapter 1

Introduction

Colloid separation is essential to many industrial processes and applications that are essential to our daily lives, including water treatment, medicine production, disease diagnosis and prevention, personal care products, and food processing. Microfluidics has allowed for an increase in separation research over the past few decades since it makes fluids and particles easier to manipulate and visualize, facilitating both the discovery of novel separation processes as well as a greater knowledge of current systems. For microfluidic separations, colloidal particles must be moved relative to the flow by a variety of external forces. Available forces include electrostatic coulomb (electrophoresis), magnetic (magnetophoresis), dielectric (dielectrophoresis), thermal (thermophoresis), surface tension (tensiophoresis), osmotic (diffusiophoresis), acoustic (acoustophoresis), optical (optophoresis), and inertial forces (inertial migration). While each of these mechanisms has advantages and disadvantages for separation, diffusiophoresis stands out in particular when compared to electrical techniques, which are frequently used in biological and medicinal applications. Electrical separation methods such as electrophoresis and dielectrophoresis are invariably associated with electrodes, power supplies, and bulky peripherals, as well as the risk of inducing solvent electrolysis; diffusiophoresis is free of all of these drawbacks and thus potentially suitable for portable, wireless, and point-of-care diagnostics platforms.

Derjaguin discovered diffusiophoresis in the 1940s and Anderson and Prieve established it in the 1980s.

In addition to using "active diffusiophoresis" to enable self-propelled microswimmers to study active matter, there has been an increase in interest in "passive diffusiophoresis" over the past decade. In this technique, the motion of passive colloidal particles (such as homogeneous latex particles, liquid drops, proteins, DNAs, cells, and lipid vesicles) is induced by externally imposed solute gradients.

Diffusiophoresis has recently been found to be crucial to a number of processes, including bone fracture detection and healing, colloidal self-assembly, membrane fouling, pattern formation, fabric cleaning, cellular transport, and possibly the origin of life. These processes include colloid stratification during drying, colloidal self-assembly, membrane fouling, pattern formation, and fabric cleaning. Due to its promising properties in

separation processes, there have been quite a few diffusiophoresis investigations devoted to colloid separation in the past several years.

Chapter 2

Diffusiophoresis

2.1 Elettrochinetc theory

Microfluidics flow can be controlled by electrical fields and the science behind that mainly lies on electrokinetics which is basically a combination of electrostatics and hydrodynamics.

Electrokinetics refers to all the processes in which the boundary layer between one charge phase and another, is forced to undergo some sort of shearing process. The charge attached to one phase will move in one direction and that associated with the adjoining phase will move (more or less tangentially) in the opposite direction.

One of the important considerations of Electrokinetics is the formation of a charged layer close to the fluid solid interface. The question is first that what is this charged layer.

Most solid surfaces tend to acquire a net surface charge, positive or negative, when brought in contact with an aqueous (polar) solvent.

Various surface charging mechanisms are there like: ionization of covalently bonded surface groups or ion adsorption.

Aqueous solutions generally have dissolved ions. If the surface has a negative charge then in the fluid if there are positive charges, those are called Counterions. Counterions means ions charge opposite to the surface charge. If surface charge is positive, then negative charge in the fluid is Counterions.

Co-ions instead means ions having the same polarity of surface charge.

Charged surface will attracts Counterions because of Coulomb attraction and they will repel Co-ions.

The Ionization of Surface Groups explains that the magnitude of the surface charge depends on the acidic or basic strength of the surface groups and on the pH of the solution.

An example can be done considering a glass surface. This surface, due to ions absorption, has acquired some negative charge. The entire system being electrically neutral, it is aspect that all the positive charge,

whatever it is, will fall on the surface so that it will neutralise. The neutralization will not happen just like that, because all the ions would have fallen on this surface, provided the ions has no thermal energy. Since that ions have nonzero absolute temperature, ions have their own thermal energy and so a thermal motion, that will resist all the ions from falling on the top of the surface wall because there is a balance between Coulomb attraction and thermal interaction.

There will be some fixed layer of ions (some positive charges) which will be bound to the surface but these will not totally neutralize the charge wall and in the outer layer (in the bulk) there will be some positive ions as well as some negative ions but the positive ions dominates respect to negative ions.

The bulk plus subsurface, in totality, will neutralise the system.

The sum of these two layers (charged surface and Ion distributon) is called Electrical Doubel Layer (EDL). There are various theories of electrical double layer. A very simple model is called Guoy-Chapman model with Stern modification.

with neutral water pH glass surface will develop negative charge on the wall. The first layer that does not move is called as stern layer or helmholtz layer and this layer is few angstroms because basically represents one entity of ions diameter.

beyond the stern layer the ions are mobile. Advanced Research shows that in the stern layer, ions are not mobile provided there is no hydrophobic interaction, that means the wall is hydrophilic. There is a layer which is called diffuse layer in which there are both positive and negative ions and those ions are mobile that means if a field is applied, ions in this layer move.

There is an interface between the diffuse layer and the stern layer there called shear plane.

The distance to reach the potential approximately equal to zero is the span of the electrical double layer. Electrical double layer is a sort of analogous to boundary layer; just like outside boundary layer the effect of the viscous interaction between the wall and the fluid are not felt, similarly, outside the electrical double layer, the effect of surface charge is not felt.

The electrical double layer has a characteristic length scale which is called as Debye Length Λ .

In electrochemistry there is a very important terminology called as Zeta potential which is the electrical potential at the shear plane.

the shear plane is a very important location because in case of a hydrophilic surface, it can be seen that anything to the left of the shear plane is immobile; the shear plane effectively acts like a plane on which the non slip boundary condition is applied, not on the wall.

there are 4 primary electrokinetic effects which are considered in the literature:

Electroosmosis it refers to the relative movement of liquid over a stationary charge surface with an external electric field acting as an activator.

Streaming potential it refers to the electrical potential that is induced when a liquid, containing ions, is driven to flow along a stationary charge surface.

electrophoresis it refers to the movement of a charge surface relative to a stationary liquid due to the application of an external electric field.

sedimentation potential it refers to the potential that is induced when a charged particle moves relative to a stationary liquid.

2.1.1 Thermodynamics

Considering a system of different chemical entities, the system is in chemical equilibrium when there is no gradient in chemical potential, because the chemical potential is the driving force for a chemical change to take place.

If there is chemical potential gradient, there is a creation of a driving force and that will create a change. Equilibrium picture with chemical entities should have no gradient of chemical potential.

However, in the system that will be studied, it is not merely chemical entities but in the system there will be ions which are chemical entities but with charge, so the chemical potential must be augmented with electrical effects and that is called as electrochemical potential.

First of all, an expression for the electrochemical potential within the electrical double layer must be established and for that a refer to the chemical potential must be done and then a referment to the thermodynamic issues must be done.

Considering a system with some heat transfer δQ and with some work obtained δW ; the first law of thermodynamics for the system tells that

$$\delta Q = dE + \delta W \quad (2.1)$$

where dE includes internal energy plus kinetic energy plus potential energy.

Very often in thermodynamic processes, the change in internal energy is much more important as compared to changes in kinetic and potential energy, and then, dE will approximate to dU .

Importantly, it is not the kinetic energy and potential energy that are small but changes in kinetic energy and potential energy are small.

Assuming that the system is a simple compressible substance undergoing a quasi-equilibrium process or a quasi-static process. If the system is a simple compressible substance, means that the changes in pressure, volume and temperature are much more significant as compared to other effects like electrical effect, magnetic effect and so on.

For a quasi-equilibrium process, δW is equal to pdV . The quasi-equilibrium process is also one type of internally reversible process. A process is reversible when, once having taken place, it can be reversed, but in doing so, it leaves no change in the system and in the surroundings. When the system comes back to its original state, there is no net change in the surroundings.

This kind of process can be realised by a very slow expansion of gas in a piston cylinder arrangement and then, that makes sure that internally it is a reversible process, but external irreversibility cannot be precluded. The reason of this is because there could be a finite temperature difference between the system and the surrounding across which the heat transfer can take place; that will make it externally irreversible. A process is reversible if it is both externally and internal reversible. For a reversible process, an additional modification of the equation is done, writing in place of δQ TdS and the equation becomes:

$$TdS = dU + pdV \quad (2.2)$$

where T typically represents the temperature of the system boundary, across which the heat transfer is taking place.

Dividing the equation by the mass yields:

$$Tds = du + pdv \quad (2.3)$$

once this equation is derived, it can be used to calculate the change in entropy for any process. The integration has to be carried over a reversible path but once the integration has been evaluated, the change in entropy can be used to evaluate the change in entropy for any process (also irreversible) that connects the two end state points.

By using the definition of enthalpy $u = h - pv$, eq.(2.3) can be written as:

$$Tds = dh - p\cancel{dv} - vdp + p\cancel{dv} \quad (2.4)$$

For the chemical potential explanation it is important to know two other functions: the Gibbs function (or the Gibbs free energy) or the helmholtz function (or the helmholtz free energy).

The Gibbs free energy is defined as follows:

$$g = h - Ts \quad (2.5)$$

this represent the energy that is freely available for a chemical change to take place.

Writing the differential form of eq.(2.5) and inserting eq.(2.4) yields:

$$dg = dh - Tds - sdT = vdp - sdT \quad (2.6)$$

The chemical potential of a pure component (substance) is $\mu = \bar{g} = \frac{G}{n}$. When the bar is used, it means molar quantity per mole (n represent the number of moles).

Eq.(2.6) is written on a mass basis but can be easily write it on a molar basis, in terms of unit mole:

$$\bar{d}g = \bar{v}dp - \bar{s}dT \quad (2.7)$$

$d\bar{g}$ can be written at constant T ($dT = 0$):

$$\bar{d}g_T = \bar{v}dp \quad (2.8)$$

Considering an ideal gas, \bar{v} is equal to $\frac{\bar{R}T}{p}$, where \bar{R} is the universal gas constant equal to $8.31446 \frac{J}{molK}$ and the eq.(2.8) can be written as:

$$d\mu_T^* = \bar{R}Td(\ln(p^*)) \quad (2.9)$$

in which the symbol " *" means that ideal gas quantities are used.

For a substance which is not ideal gas, the eq.(2.9) is not true.

Instead of using the pressure as a quantity, a different quantity which is a pseudo pressure is used, that means it becomes pressure only when the state of the substance corresponds to an ideal gas state. This pseudo pressure is known as fugacity.

For any generic substance the following equation can be written:

$$d\mu_T = \bar{R}Td(\ln(f)) \quad (2.10)$$

in which $\lim_{p \rightarrow 0} \frac{f}{p} = 1$.

All this treatment is done for a single component system.

For a multi-component system, in the following for semplicity it is considered that in the mixture there are just two components A and B, a generic extensive properties is a function of :

$$X = X(T, p, n_A, n_B) \quad (2.11)$$

where n_A and n_B are the number of moles of A and B respectively.

Doing the differential of eq.(2.11):

$$dX = \left. \frac{\partial X}{\partial T} \right|_{p, n_A, n_B} dT + \left. \frac{\partial X}{\partial p} \right|_{T, n_A, n_B} dp + \left. \frac{\partial X}{\partial n_A} \right|_{T, p, n_B} dn_A + \left. \frac{\partial X}{\partial n_B} \right|_{T, p, n_A} dn_B \quad (2.12)$$

in which the term $\left. \frac{\partial X}{\partial n_A} \right|_{T, p, n_B}$ is called as partial molar property of A and it is defined as \bar{X}_A . Partial molar property, only refers to extensive property it does not refer to any intensive property.

Since that \bar{X}_A is a property, it should depends on composition. When the changing of n_A is allowed, that will change the composition.

It is assumed that an infinitesimal number of moles of A is either added or taken away. The change in number of moles is infinitesimal. Practically it is not infinitesimal, but practically considering the total number of moles which are present in the system, the actual change in number of moles may be very insignificant as

compared to that. Practically it does not change the composition of the system.

$$dX_{T,p} = \bar{X}_A dn_A + \bar{X}_B dn_B \quad (2.13)$$

and integrating yields

$$X_{T,p} = \bar{X}_A n_A + \bar{X}_B n_B \quad (2.14)$$

because the partial molar properties are constant and can be put outside the integral because changing the number of moles they will not change.

The eq.(2.14) can be used for the Gibbs function in this way:

$$G_{T,p} = \bar{G}_A n_A + \bar{G}_B n_B = \mu_A n_A + \mu_B n_B \quad (2.15)$$

In the generic case, considering a component i in the mixture:

$$\mu_i = \bar{G}_i = \left. \frac{\partial G}{\partial n_i} \right|_{T,p,n_j(j \neq i)} \quad (2.16)$$

Drawing an analogy with the fugacity f of a pure substance, the fugacity of a component i in the mixture is defined as:

$$d\mu_{iT} = d\bar{G}_{iT} = \bar{R}T d(\ln(\bar{f}_i))_T \quad (2.17)$$

with $\lim_{p \rightarrow 0} \frac{\bar{f}_i}{y_i p} = 1$ where y_i is the mole fraction of component i in the mixture.

When two chemical entities are mixed, from their individual constituent state to a mixture state, there are changes in various properties and one of the very important properties is the volume.

$$G = G(T, p, n_A, n_B) \quad (2.18)$$

$$dG = \left. \frac{\partial G}{\partial T} \right|_{p,n_A,n_B} dT + \left. \frac{\partial G}{\partial p} \right|_{T,n_A,n_B} dp + \left. \frac{\partial G}{\partial n_A} \right|_{T,p,n_B} dn_A + \left. \frac{\partial G}{\partial n_B} \right|_{T,p,n_A} dn_B \quad (2.19)$$

$$dG_{T,n_B} = \left. \frac{\partial G}{\partial p} \right|_{T,n_A,n_B} dp + \left. \frac{\partial G}{\partial n_A} \right|_{T,p,n_B} dn_A \quad (2.20)$$

Looking the eq.(2.19) the last two terms are the multicomponent terms. The pure substance will have just the first two terms and looking for the analogy of the definition of dG in the eq.(2.6), $\left. \frac{\partial G}{\partial T} \right|_{p,n_A,n_B} = -S$ and

$\left. \frac{\partial G}{\partial p} \right|_{T,n_A,n_B} = V$ and the eq.(2.6) can be rewritten as

$$dG_{T,n_B} = V dp + \bar{G}_A dn_A \quad (2.21)$$

In differential calculus the differential of a function of two variables can be written as:

$$dz = Mdx + Ndy = \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy \quad (2.22)$$

and for continuity in the second order partial derivative $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$. This is also called Marxwell's cross-relation. This can be applied to eq.(2.22) yielding

$$\left. \frac{\partial V}{\partial n_A} \right|_{T,p,n_B} = \left. \frac{\partial \bar{G}_A}{\partial p} \right|_{T,n_A,n_B} \quad (2.23)$$

in which $\left. \frac{\partial V}{\partial n_A} \right|_{T,p,n_B} = \bar{V}_A = \left. \frac{\partial \bar{G}_A}{\partial p} \right|_{T,n_A,n_B}$ For a pure component, in place of partial molar property it will be molar property:

$$\bar{v}_A = \left. \frac{\partial \bar{g}_A}{\partial p} \right|_T \quad (2.24)$$

for the pure component, n_A and n_B are anyway fixed.

The volume before mixing is the individual some of the volumes:

$$V_{Before} = n_A \bar{v}_A + n_B \bar{v}_B \quad (2.25)$$

The volume after mixing is:

$$V_{After} = n_A \bar{V}_A + n_B \bar{V}_B \quad (2.26)$$

The change in volume due to mixing is the difference between the two equations:

$$\Delta V_{Mix} = n_A(\bar{V}_A - \bar{v}_A) + n_B(\bar{V}_B - \bar{v}_B) \quad (2.27)$$

Using eq.(2.17) and eq.(2.23) yields:

$$d\mu_{AT} = d\bar{G}_{AT} = \bar{R}Td(\ln(\bar{f}_A))_T = \bar{V}_A dp \quad (2.28)$$

Similarly, can be written the mole Gibbs free energy of the pure component A :

$$d\bar{g}_{AT} = \bar{R}Td(\ln(f_A))_T = \bar{v}_A dp \quad (2.29)$$

where f_A is the fugacity of the pure component A .

Subtracting eq.(2.28) and eq.(2.29) the following can be calculated:

$$(\bar{V}_A - \bar{v}_A)dp = \bar{R}Td\left(\ln\left(\frac{\bar{f}_A}{f_A}\right)\right)_T \quad (2.30)$$

Integrating eq.(2.30) from low pressure p^* to a generic pressure p at constant T , where p^* means ideal gas state. Remembering that the fugacity for a pure component at ideal gas state is equal to the same pressure p^* , the following is obtained:

$$\int_{p^*}^p (\bar{V}_A - \bar{v}_A) dp = \bar{R}T \int_{p^*}^p d \left(\ln \left(\frac{\bar{f}_A}{f_A} \right) \right) = \bar{R}T \left[\ln \left(\frac{\bar{f}_A}{f_A} \right) - \ln \left(\frac{y_A p^*}{p^*} \right) \right] = \bar{R}T \ln \left(\frac{\bar{f}_A}{y_A f_A} \right) \quad (2.31)$$

The change in volume due to mixing is zero when $\bar{f}_A = y_A f_A$ and similarly $\bar{f}_B = y_B f_B$. The fugacity of the component in the mixture is related with the fugacity of the pure component through the mole fraction.

It can be shown that for the ideal gas also the same thing is obeyed, that means, ideal gas is a special case of an ideal solution.

Ideal solution is a more general case. The definition of ideal solution is when the changing in volume due to mixing is equal to zero.

Integrating eq.(2.28) from p^* to p remembering to keeping T constant:

$$\bar{G}_A = \bar{G}_A^* + \bar{R}T \ln \left(\frac{\bar{f}_A}{y_A p^*} \right) \quad (2.32)$$

For an ideal gas the definition of the Gibbs free energy is:

$$G^* = H^* - TS^* \quad (2.33)$$

and differentiating all the terms with respect to n_A by keeping T, p, n_B fixed, the following is obtained:

$$\bar{G}_A^* = \bar{H}_A^* - T \bar{S}_A^* \quad (2.34)$$

From the definition of entalpy

$$H^* = n_A c_{pA} T + n_B c_{pB} T \quad (2.35)$$

it is possible to calculate

$$\bar{H}_A^* = \left. \frac{\partial H^*}{\partial n_A} \right|_{T, p, n_B} = c_{pA} T = \bar{h}_A^* \quad (2.36)$$

also for the entropy will be done the same procedure. Using eq.(2.4) , valid for a pure component, if it is written in molar quantities, it is possible to calculate ds , remembering that for an ideal gas $d\bar{h} = \bar{c}_p dT$

$$ds = \frac{\bar{c}_p dT}{T} - \frac{\bar{R} dp}{p} \quad (2.37)$$

Ideal gas means that $c_p = c_p(T)$ if instead $c_p = \text{const}$, this a specif case of ideal gas called calorically perfect gas.

Considering the assumption of calorically perfect gas, integrating gives

$$s - s_0 = \bar{c}_p \ln \left(\frac{T}{T_0} \right) - \bar{R} \ln \left(\frac{p}{p_0} \right) \quad (2.38)$$

$$S^* - S_0^* = n_A \left[\bar{c}_{pA} \ln \left(\frac{T}{T_0} \right) - \bar{R} \ln \left(\frac{y_A p^*}{p_0} \right) \right] + n_B \left[\bar{c}_{pB} \ln \left(\frac{T}{T_0} \right) - \bar{R} \ln \left(\frac{y_B p^*}{p_0} \right) \right] \quad (2.39)$$

where S_0^* is an hypothetical reference state because the second law based expressions talk about change in entropy and not the absolute value of entropy.

$$\bar{S}_A^* = \left. \frac{\partial S^*}{\partial n_A} \right|_{T, p, n_B} = \bar{c}_{pA} \ln \left(\frac{T}{T_0} \right) - \bar{R} \ln \left(\frac{y_A p^*}{p_0} \right) \quad (2.40)$$

For the pure component in unit number of mole, instead

$$\bar{s}_A^* - s_{A0}^* = \bar{c}_{pA} \ln \left(\frac{T}{T_0} \right) - \bar{R} \ln \left(\frac{p^*}{p_0} \right) \quad (2.41)$$

Subtracting eq.(2.40) and eq.(2.41), considering the reference state $s_{A0}^* = 0$, yields

$$\bar{S}_A^* - \bar{s}_A^* = -\bar{R} \ln(y_A) \quad (2.42)$$

Inserting eq.(2.36) and eq.(2.42) into eq.(2.34) yields

$$\bar{G}_A^* = \bar{h}_A^* - T(\bar{s}_A^* - \bar{R} \ln(y_A)) \quad (2.43)$$

Replacing eq.(2.43) into eq.(2.32), knowing that $\bar{g}_A^* = \bar{h}_A^* - T\bar{s}_A^*$, yields

$$\begin{aligned} \bar{G}_A &= \bar{h}_A^* - T(\bar{s}_A^* - \bar{R} \ln(y_A)) + \bar{R} T \ln \left(\frac{\bar{f}_A}{y_A p^*} \right) = \bar{g}_A^* + \bar{R} \ln(y_A) + \bar{R} T \ln \left(\frac{\bar{f}_A}{y_A p^*} \right) = \\ &= \bar{g}_A^* + \bar{R} T \ln \left(\frac{\bar{f}_A}{p^*} \right) \end{aligned} \quad (2.44)$$

Referring to a state called standard state, which is a reference state, designated with a subscript 0, of a pure component A (not mixture), eq.(2.10) can be integrated to obtain the following

$$\mu_A^0 = \mu_A^* + \bar{R} T \ln \left(\frac{f_A^0}{p_0^*} \right) \quad (2.45)$$

Subtracting eq.(2.45) and eq.(2.44) yields

$$\mu_A = \mu_A^0 + \bar{R} T \ln \left(\frac{\bar{f}_A}{f_A^0} \right) \quad (2.46)$$

where the ratio $\frac{\bar{f}_A}{f_A^0}$ is known as activity of the component A in the solution a_A . If an ideal solution is considered at standard state, the activity correspond to the mole fraction y_A , because for an ideal solution $\bar{f}_A = y_A f_A$. For the general case, non-ideal behaviour, the activity of the substance A can be expressed as $a_A = y_A \gamma_A$, where γ_A is the activity coefficient, that for the ideal behaviour is equal to 1. Instead, y_A is the number of moles of A by the total number of moles (molar fraction, that is fixed).

One mole of ions at standard state will contain Avogadro number of ions. For each ion, the expression must be divided by the Avogadro number, remembering that $\frac{\bar{R}}{N_A} = k_B$ Boltzmann constant, so, it is basically to transform from one mole to a single entity.

For each ion, the chemical potential of the ion is:

$$\mu_i = \mu_i^0 + k_B T \ln(n_i) \quad (2.47)$$

where n_i is the molar concentration, but in the logarithm, n_i must be divided by the standard molar concentration that is usually 1 mol/L in such a way the argument of the logarithm is dimensionless.

Chemical species have charges and so becomes ions. When the total potential of the system is described, a Chemical potential plus Electrical potential is needed, because the chemical entities have charges. In totality this is called Elettrochemical potential. The Elettrochemical potential of ions of type i is defined as:

$$\bar{\mu}_i = \mu_i + z_i e \psi \quad (2.48)$$

where z_i is the valency (charge) of ions of type i and e is the charge of proton, so the total charge of the i species is $z_i e$. ψ is the potential within the electrical double layer that is a function of the y -direction.

The system to be in equilibrium must have the gradient of the Elettrochemical potential equal to 0. Considering just the y -direction $\frac{d\bar{\mu}_i}{dy} = 0$ must be guaranteed or, for a generic direction $d\bar{\mu}_i = 0$, that yields

$$d\bar{\mu}_i = k_B T \frac{dn_i}{n_i} + z_i e d\psi = 0 \quad (2.49)$$

and integrating it yields

$$k_B T \int_{n_i^0}^{n_i} \frac{dn_i}{n_i} + z_i e \int_0^\psi d\psi = 0 \quad (2.50)$$

Infinity means not literally at infinity but that distance from the plate where the surface charging effect of the plate is not felt, that means the potential has dropped to 0.

When the potential is dropped to 0 the concentration is the bulk concentration n_i^0 and when the concentration is n_i , the potential is the generic ψ . Solving the integral, the following solution is obtained

$$n_i = n_i^0 e^{-\frac{z_i e \psi}{k_B T}} \quad (2.51)$$

This is called Boltzmann Distribution and describes the ion distribution under equilibrium.

The following equation can be derived also from the species conservation equation:

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0 \quad (2.52)$$

in which is the sum of the unsteady term and the divergence of the flux.

The flux is related to fluid flow, the number density and the gradient of the Electrochemical potential as follows

$$\mathbf{J}_i = n_i \mathbf{u} - b_i n_i \nabla \bar{\mu}_i^M \quad (2.53)$$

where the upper script M means molar quantity, because the expression is written for one mole of a system. b_i is called as ionic mobility and it is defines as

$$b_i = \frac{D_i}{RT} \quad (2.54)$$

where D_i is the diffusivity. To derive the diffusivity, can be assumed a sphere (ion) that is moving in a fluid. There will be a drag force on the ion $F_{Drag} = f v$ where f is the friction coefficient and v is the relative velocity of the ion. If the Stoke's law is valid, then $f = 6\pi\eta R$ and the velocity scales as $v \sim \frac{l}{t}$. The work done to overcome the drag force is $F_{Drag}l$ and by work due to thermal energy ($k_B T$), the particle can get sufficient energy to overcome the drag. The velocity times the length is the diffusion coefficient and so $fD \sim k_B T$ where $D \sim \frac{k_B T}{f}$ is obtained that is the Stoke-s Einstein relation.

$$\bar{\mu}_i^M = N_A(\mu_i^0 + k_B T \ln(n_i) + z_i e \psi) \quad (2.55)$$

$$\nabla \bar{\mu}_i^M = N_A k_B T \frac{\nabla n_i}{n_i} + N_A z_i e \nabla \psi \quad (2.56)$$

$$n_i \nabla \bar{\mu}_i^M = N_A k_B T \nabla n_i + N_A n_i z_i e \nabla \psi \quad (2.57)$$

$$b_i n_i \nabla \bar{\mu}_i^M = \frac{D_i}{RT} \nabla n_i + \frac{D_i}{RT} N_A n_i z_i e \nabla \psi = D_i \nabla n_i + D_i \frac{n_i z_i e}{k_B T} \nabla \psi \quad (2.58)$$

If an electric field is applied or if there is an induced electric field, ions will have an additional transport beyond advection and diffusion because of the action of the electric field and this is called as Electromigration of the ion species.

Inserting eq.(2.58) into eq.(2.53) and making the divergence of the flux yields

$$\nabla \cdot \mathbf{J}_i = \nabla \cdot (n_i \mathbf{u}) - \nabla \cdot (D_i \nabla n_i) - \nabla \cdot \left(D_i \frac{n_i z_i e}{k_B T} \nabla \psi \right) \quad (2.59)$$

and inserting it into eq.(2.52) yields

$$\underbrace{\frac{\partial n_i}{\partial t}}_{\text{transient}} + \underbrace{\nabla \cdot (n_i \mathbf{u})}_{\text{advection}} = \underbrace{\nabla \cdot (D_i \nabla n_i)}_{\text{diffusion}} + \underbrace{\nabla \cdot \left(D_i \frac{n_i z_i e}{k_B T} \nabla \psi \right)}_{\text{electromigration}} \quad (2.60)$$

Inside this equation there is the assumption of considering the system as an ideal solution because is inside the definition of $\bar{\mu}_i^M$. This definition is more general respect to the Boltzmann distribution because that considered a special case nthat the system is in equilibrium. The eq.(2.60) is a transport and is considering a flow field that can also have unsteadiness. This equation includes the effects of advection and transient. This differential equation is called Nearst-Planck equation.

The Boltzmann distribution can be recovered from eq.(2.60) considering advection and diffusioin equal to 0. Some major assumptions behind the Bolthzmann distribution: Ions are considered to be point charges. When ions are considered to be point charges there is no theoretical upper limit of the number of charges which can occupy a surface. however, because of the finite size of the ionic species, there will be a restricted number density of ions on a particular surface.

The system is in equilibrium with no macroscopic advection/diffusion of ions.

The solid surface is microscopically homogeneous. If there is in-homogeneity, then there will be a dependence on x also. The consideration done instead is that the electrical double layer phenomenon is dependent solely on y .

The charged surface is in contact with an infinitely large liquid media, that means the first stream boundary condition can be applied. At y tends to Infinity, ψ tends to zero.

When the Boltzmann distribution is used, the electrical double layer film is considered, that is the electric field within the electrical double layer because of the electrical double layer phenomenon. Considering a typical electric double length thickness of $10nm$ and a surface potential of $100mV$. The potential gradient is $\frac{100-0}{10} = 10^7 V/m$. An electric field on the x axis is applied. Typical axial electric field that is applied for the Electrosmosis is like of the order of $10^4 V/m$. The field within and due to electrical double layer is much more over weighing as compared to the field that is externally applied in the axial direction. It is only considered the electric double layer potential for the Boltzmann distribution.

In the Boltzmann distribution the number density of ions is related with the potential, but this does not solve the number of density or the potential because one is related to the other and another equation involving these two terms, to close the system, must be need. This equation is given by the Gauss'law. The Gauss'Law in integral form is the following

$$\epsilon_0 \oint_S \mathbf{E} \cdot d\mathbf{S} = \int_V \rho_{e,total} dV \quad (2.61)$$

where $\rho_{e,total}$ is the total volumetric charge density and ϵ_0 is the permittivity of a free space.

Converting the contour integral into volume integral by using the divergence theorem yields the differential

for of the Gauss'Law

$$\epsilon_0 \nabla \cdot \mathbf{E} = \rho_{e,total} = \underbrace{\rho_e}_{\text{free}} + \underbrace{\rho_{e,bound}}_{= -\nabla \cdot \mathbf{P}} \quad (2.62)$$

where \mathbf{P} is the polarization density vector (dipole moment per unit volume) that originates due to gradients in local dipole densities within the medium The constitutive relationship between the electric field and the polarization density vector is the following

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (2.63)$$

Inserting it inside eq.(2.62) yields

$$\begin{aligned} \epsilon_0 \nabla \cdot \mathbf{E} &= \rho_e - \nabla \cdot (\epsilon_0 \chi \mathbf{E}) \Rightarrow \\ \Rightarrow \nabla \cdot \left[\underbrace{\epsilon_0 (1 + \chi)}_{\epsilon_r} \mathbf{E} \right] &= \rho_e \end{aligned} \quad (2.64)$$

where ϵ is the permittivity of the medium and ϵ_r is the relative permittivity.

The eq.(2.64) is the Poisson equation.

As boundary conditions: Continuity in E_t that is the tangential electric field, to the interface

Jump in normal flux is in term of the interface $\epsilon_1 E_{n1} - \epsilon_2 E_{n2} = \sigma_e$.

Since that $\mathbf{E} = -\nabla\psi$, the Poisson equation becomes

$$\nabla \cdot (\epsilon \nabla \psi) = -\rho_e \quad (2.65)$$

where

$$\rho_e = F \sum z_i n_i = e N_A \sum z_i n_i \quad (2.66)$$

Assuming that there are two types of ions, one is z_+ an the other one is z_- . For a symmetric electrolyte ($z:z$) $z_+ = z$ and $z_- = -z$ and so utilizing also the Boltzmann distribution (eq.(2.51)), eq.(2.66) becomes

$$\rho_e = ze N_A n_+ - ze N_A n_- = ze N_A \left[n_0 e^{-\frac{ze\psi}{k_B T}} - n_0 e^{\frac{ze\psi}{k_B T}} \right] = -2n_0 ze N_A \sinh \left(\frac{ze\psi}{k_B T} \right) \quad (2.67)$$

As can be seen, now eq.(2.65) is expressed only in terms of ψ and so it is a governing equation for ψ . The Poisson-Boltzmann equation is

$$\nabla \cdot (\epsilon \nabla \psi) = 2n_0 ze N_A \sinh \left(\frac{ze\psi}{k_B T} \right) \quad (2.68)$$

For a 1D problem, eq.(2.68) becomes

$$\frac{d}{dy} \left(\epsilon \frac{d\psi}{dy} \right) = 2n_0 ze N_A \sinh \left(\frac{ze\psi}{k_B T} \right) \quad (2.69)$$

doing the order-of-magnitude analysis, considering ϵ as a constant, yields

$$\frac{d}{dy} \left(\epsilon \frac{d\psi}{dy} \right) \sim \frac{\epsilon \zeta}{\lambda^2}$$

$$2n_0 z e N_A \sinh \left(\frac{ze\psi}{k_B T} \right) \sim 2n_0 z e \frac{ze\zeta}{k_B T}$$

and from these two, implies that

$$\lambda \sim \sqrt{\frac{\epsilon k_B T}{2n_0 z^2 e^2 N_A}} \quad (2.70)$$

The Debye length is expressed standard unit of measure but can be expressed also using in Gaussian units, knowing that $4\pi\epsilon_0 = 1$, and so the Debye length can be expressed in this way

$$\lambda = \sqrt{\frac{\epsilon_r k_B T}{8\pi(z e)^2 N_A n_0}}, \text{ where } \epsilon_r = \frac{\epsilon}{\epsilon_0} \text{ is the relative permittivity.}$$

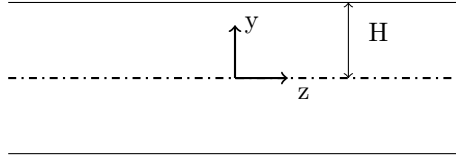
Now, let's find the solution of the Poisson-Boltzmann equation in 1D.

The Poisson-Boltzmann equation is a non-linear equation due to the presence of the $\sinh()$ term. To simplify the problem, a linearization of that function is done, called Debye-Huckel linearization, considering that $\frac{ze\psi}{k_B T} \ll 1$ (at least less than 0.1 or the same thing if the magnitude of $\zeta < 25mV$), $\sinh \left(\frac{ze\psi}{k_B T} \right) \approx \frac{ze\psi}{k_B T}$ and this yields

$$\frac{d^2\psi}{dy^2} = \frac{2n_0 z^2 e^2 N_A}{\epsilon k_B T} \psi = \frac{1}{\lambda^2} \psi \quad (2.71)$$

Electric potential solution for a slit microchannel for low ζ

Considering a straight channel in which the reference frame is placed at the center line of the channel, as can be seen in the following figure



The solution of eq.(2.71) is of the type

$$\psi(y) = A_1 e^{\frac{y}{\lambda}} + A_2 e^{-\frac{y}{\lambda}} \quad (2.72)$$

The boundary conditions imposed for ψ are: at $y = 0$, $\frac{d\psi(y)}{dy} = 0$ that is the condition of symmetry of the channel in which far away from (at the center of the channel) the the wall the potential is 0, and at $y = H$, $\psi(y) = \zeta$. Inserting these BC's, the solutions is

$$\psi(y) = \zeta \frac{\cosh \left(\frac{y}{\lambda} \right)}{\cosh \left(\frac{H}{\lambda} \right)} \quad (2.73)$$

This boundary condition is not completely true because $y = H$ is the solid boundary of the channel and the zeta potential is for the shear plane. Since that the shear plane and the solid boundary are located at few Armstrong this approximation is well valid.

This is one type of boundary condition when the surface potential is specified. There are some cases in which will be easier to set the surface charge density as boundary conditions.

Electroneutrality condition says that the surface charge on a wall, must be equal and opposite to the total unbalance charge in the electrical double layer, near the wall, because in totality as to be electrically neutral.

For this reason the following can be written

$$\sigma|_{y=H} = - \int_0^H \rho_e dy = \int_0^H \epsilon \frac{d^2 \psi}{dy^2} dy = \left[\epsilon \frac{d\psi}{dy} \right]_{y=H} - \left[\epsilon \frac{d\psi}{dy} \right]_{y=0} \quad (2.74)$$

Similarly,

$$\sigma|_{y=-H} = - \left[\epsilon \frac{d\psi}{dy} \right]_{y=-H} \quad (2.75)$$

Solving the Poisson-Boltzmann equation, with the Debye-Huckel linearization and including eq.(2.74) and eq.(2.75) yields

$$\psi(y) = \frac{\sigma \lambda}{\epsilon} \frac{\cosh\left(\frac{y}{\lambda}\right)}{\cosh\left(\frac{H}{\lambda}\right)} \quad (2.76)$$

There are some limitations to obtain the potential profile. First of all in the EDL overlap is not considered. The overlap of the electrical double layer occurs when typically $\lambda > H$. In general it was seen that the result obtain is good for $K = \frac{H}{\lambda} > 4$. The center line condition in which $\psi = 0$ is no longer valid for values less then 4, because the Debye length becomes important.

Also Steric effects are neglected, in which finite size effects of the ionic physics are neglected. In the Poisson-Boltzmann descriptions, ions are assumed to be point charges and they are assumed to be non-interacting.

Electric potential solution for a fixed plate wall for low value of ζ

To solve eq.(2.71), a method can be multiply both sides by $2 \frac{d\psi}{dy}$

$$2 \frac{d\psi}{dy} \frac{d^2 \psi}{dy^2} = \frac{2}{\lambda^2} \psi \frac{d\psi}{dy} \Rightarrow \frac{d}{dy} \left(\frac{d\psi}{dy} \right)^2 = \frac{1}{\lambda^2} 2\psi \frac{d\psi}{dy} \quad (2.77)$$

and then integrating with respect to y , from some point in the bulk solution (in which $\psi = 0$) up to a point in the double layer

$$\left(\frac{d\psi}{dy} \right)^2 = \frac{1}{\lambda^2} \psi^2 \Rightarrow \frac{d\psi}{dy} = \pm \frac{1}{\lambda} \psi \Rightarrow \frac{d\psi}{dy} = -\frac{1}{\lambda} \psi \quad (2.78)$$

The negative sign of the right hand side is chosen because when ψ is positive, the potential will decrease to zero in the bulk.

Applying the separation of variables of eq.(2.78) and integrating

$$\int \frac{d\psi}{\psi} = -\frac{1}{\lambda} \int dy \Rightarrow \psi(y) = \zeta e^{-y/\lambda} \quad (2.79)$$

Electric potential solution for a fixed plate wall for any value of ζ

Eq.(2.69) can be solved also analytically. To do that, dimensionless variables must be introduced.

$\psi^* = \frac{Ze\psi}{k_B T}$ and $y^* = \frac{y}{\lambda}$ are the dimensionless potential and coordinate respectively. The equation is simplified in this way

$$\frac{k_B T}{ze\lambda^2} \frac{d^2\psi^*}{dy^{*2}} = \frac{2zeN_A n_0}{\epsilon} \sinh(\psi^*) \Rightarrow \frac{d^2\psi^*}{dy^{*2}} = \sinh(\psi^*) \quad (2.80)$$

To solve eq.(2.80), let's multiply both side by $\frac{d\psi^*}{dy^*}$:

$$\begin{aligned} \frac{d\psi^*}{dy^*} \frac{d^2\psi^*}{dy^{*2}} &= \sinh(\psi^*) \frac{d\psi^*}{dy^*} \Rightarrow \frac{1}{2} \frac{d}{dy^*} \left(\left(\frac{d\psi^*}{dy^*} \right)^2 \right) = \frac{d}{dy^*} (\cosh(\psi^*)) \\ \Rightarrow \left(\frac{d\psi^*}{dy^*} \right)^2 &= 2\cosh(\psi^*) + c_1 \end{aligned} \quad (2.81)$$

When $y^* \rightarrow \infty$, $\psi^* \rightarrow 0$ and $\frac{d\psi^*}{dy^*} \rightarrow 0$ and so settings these boundary conditions the constant of integration is $c_1 = -\frac{2}{\lambda^2}$.

Eq.(2.81) becomes:

$$\begin{aligned} \left(\frac{d\psi^*}{dy^*} \right)^2 &= 2(\cosh(\psi^*) - 1) = 2 \left(2 \sinh^2 \left(\frac{\psi^*}{2} \right) \right) = 4 \sinh^2 \left(\frac{\psi^*}{2} \right) \Rightarrow \\ \frac{d\psi^*}{dy^*} &= \pm 2 \sinh \left(\frac{\psi^*}{2} \right) \end{aligned} \quad (2.82)$$

Considering a negative charged wall, $\psi < 0$ and so the potential increase from the negative zeta potential (ζ) to 0 at infinity that means $\frac{d\psi}{dy} > 0$ and so a negative sign of the equation must be used. To solve that differential equation an integration by parts must be done:

$$\begin{aligned} \int_{\frac{ze\zeta}{k_B T}}^{\psi^*} \frac{1}{2 \sinh(\frac{\psi^*}{2})} d\psi^* &= - \int_0^{y^*} dy^* \Rightarrow \\ \ln \left[\tanh \left(\frac{\psi^*}{4} \right) \right] - \ln \left[\tanh \left(\frac{ze\zeta}{4k_B T} \right) \right] &= -y^* \Rightarrow \\ \psi^* &= 4 \tanh^{-1} \left[e^{-y^*} \tanh \left(\frac{ze\zeta}{4k_B T} \right) \right] \end{aligned} \quad (2.83)$$

and coming back to the denationalize equation, the following solution is obtained:

$$\psi = \frac{4k_B T}{ze} \tanh^{-1} \left[e^{-y/\lambda} \tanh \left(\frac{ze\zeta}{4k_B T} \right) \right] \quad (2.84)$$

It must be notice that if a Taylor expansion stopped at the first order of eq.(2.84) is done, eq.(2.79) is obtained.

Electric potential solution for a slit microchannel for any value of ζ

In the case in which the Debye Hunkel approximation is not applied, eq.(2.69) must be solved.

That equation can be written in the following dimensionless form

$$\frac{d^2\bar{\psi}}{d\bar{y}^2} = K^2 \sinh(\bar{\psi}) \quad (2.85)$$

where $\bar{y} = y/H$, $K = H/\lambda$ and $\bar{\psi} = \frac{ze\psi}{k_B T}$. Considering that at the center of the channel the electric potential is not 0 but is equal to ψ_c . Multipling both sides of the equation by $\frac{d\bar{\psi}}{d\bar{y}}$ and then inserting the condition in which at $y = 0$, $\bar{\psi} = \bar{\psi}_c \Rightarrow \frac{d\bar{\psi}}{d\bar{y}} = 0$ yields

$$\frac{d\bar{\psi}}{d\bar{y}} = \pm \sqrt{2K^2(\cosh(\bar{\psi}) - \cosh(\bar{\psi}_c))} \quad (2.86)$$

Since it is consider the upper half of the channel, the positive sign is adopted.

The following problem is difficult to solve it analytical but an analytical solution can be found putting $\bar{\psi}_c = 0$

Solving this differential equation separating the variables

$$\begin{aligned} \int_1^{\bar{y}} d\bar{y} &= \int_{\bar{\zeta}}^{\bar{\psi}} \frac{1}{\sqrt{2K^2(\cosh(\bar{\psi}) - 1)}} d\bar{\psi} \Rightarrow \\ \bar{y} &= 1 - \frac{\ln\left(e^{\frac{\bar{\psi}}{2}} + 1\right) - \ln\left(e^{\frac{\bar{\psi}}{2}} - 1\right) - \ln\left(e^{\frac{\bar{\zeta}}{2}} + 1\right) + \ln\left(e^{\frac{\bar{\zeta}}{2}} - 1\right)}{K} \end{aligned} \quad (2.87)$$

and the solution of this equation is

$$\bar{\psi}(\bar{y}) = 2 \ln \left(\frac{e^{\frac{\bar{\zeta}}{2}} + e^{\frac{\bar{\zeta}}{2} + K(\bar{y}-1)} - e^{K(\bar{y}-1)} + 1}{e^{\frac{\bar{\zeta}}{2}} - e^{\frac{\bar{\zeta}}{2} + K(\bar{y}-1)} + e^{K(\bar{y}-1)} + 1} \right) \quad (2.88)$$

Electric potential solution of a spherical particle for low value of ζ

The governing equation for the EDL potential around a spherical particle is written for a spherical coordinate system

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = -\frac{\rho_e}{\epsilon} \quad (2.89)$$

in which

$$\rho_e = zeN_A(n_+ - n_-) = zeN_A \left[n_0 e^{-\frac{ze\psi}{k_B T}} - n_0 e^{\frac{ze\psi}{k_B T}} \right] = -2n_0 zeN_A \sinh \left(\frac{ze\psi}{k_B T} \right)$$

and so the equation becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = - \frac{2n_0 z e N_A \sinh \left(\frac{ze\psi}{k_B T} \right)}{\epsilon} \quad (2.90)$$

Applying the Debye-Huckel linearization

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = - \frac{2n_0 z^2 e^2 N_A}{\epsilon k_B T} = \frac{\psi}{\lambda^2} \quad (2.91)$$

To solve this equation, a transformation is done considering

$$w = r\psi \Rightarrow \psi = \frac{w}{r}, \quad \frac{d\psi}{dr} = \frac{1}{r} \frac{dw}{dr} - \frac{w}{r^2}, \quad r^2 \frac{d\psi}{dr} = r \frac{dw}{dr} - w$$

$$\frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \cancel{\frac{dw}{dr}} + r \frac{d^2 w}{dr^2} - \cancel{\frac{dw}{dr}}, \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{1}{r} \frac{d^2 w}{dr^2}$$

An the governing equation becomes

$$\frac{d^2 w}{dr^2} - \frac{w}{\lambda^2} = 0 \quad (2.92)$$

in which the solution is of the form

$$w = c_1 e^{\frac{r}{\lambda}} + c_2 e^{-\frac{r}{\lambda}} \quad (2.93)$$

The BC are that at $r \rightarrow \infty, \psi \rightarrow 0 \Rightarrow w$ finite $\Rightarrow c_1 = 0$. The second BC is that at $r = R, \psi = \zeta \Rightarrow w = R\zeta \Rightarrow c_2 = \frac{R\zeta}{e^{-\frac{R}{\lambda}}}$. The potential field w is equal to

$$w = \frac{R\zeta}{e^{-\frac{R}{\lambda}}} e^{-\frac{r}{\lambda}} \Rightarrow \psi = \frac{R\zeta}{r} \frac{e^{-\frac{r}{\lambda}}}{e^{-\frac{R}{\lambda}}} = \frac{R\zeta}{r} e^{-\frac{(r-R)}{\lambda}} \quad (2.94)$$

The total charge on the surface of the sphere is equal to minus the charge in the EDL because the total charge in the system is electrically neutral.

$$Q_{EDL} = \int_R^\infty \rho_e 4\pi r^2 dr = -4\pi\epsilon \int_R^\infty \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) r^2 dr = 4\pi\epsilon R^2 \frac{d\psi}{dr} \Big|_R \quad (2.95)$$

from eq.(2.94) is possible to calculate

$$\frac{d\psi}{dr} = \frac{R\zeta}{e^{-\frac{R}{\lambda}}} \left[-\frac{1}{\lambda} \frac{e^{-\frac{r}{\lambda}}}{r} - \frac{e^{-\frac{r}{\lambda}}}{r^2} \right] \quad (2.96)$$

$$\frac{d\psi}{dr} \Big|_R = -\zeta \left[\frac{1}{\lambda} + \frac{1}{R} \right] \quad (2.97)$$

$$Q_{EDL} = -4\pi\epsilon\zeta R^2 \left[\frac{1}{\lambda} + \frac{1}{R} \right] \quad (2.98)$$

$$Q_{surface} = 4\pi\epsilon\zeta R^2 \left[\frac{1}{\lambda} + \frac{1}{R} \right] \quad (2.99)$$

2.1.2 Electromagnetic Force

Considering a channel in which an electrical voltage across the channel is applied. Because the surface has a net negative charge, the bulk fluid will have some net positive charge and because of the application of an external electric field along the axial direction, the net positive charge will preferentially move and this phenomenon is called electrophoresis.

Since that ions will move, they will drag the liquid water along with that and the water will also start moving. To understand this mechanism an additional body force is represented into the Navier-Stokes equations. The body force comes from a continuity of an electrical force, which is expressed in form of an equivalent stress which is called Electrical Stress or Maxwell Stress which is beyond the hydrodynamic stress and also a quantity called Osmotic Pressure. The Electrosmosis is the combination of the electrical stress and osmotic pressure gradient.

The Gauss law for electricity in vacuum is

$$\nabla \cdot \mathbf{E} = \frac{\rho_e}{\epsilon_0} \quad (2.100)$$

The Gauss law for magnetism is

$$\nabla \cdot \mathbf{B} = 0 \quad (2.101)$$

The Maxwell-Faraday law

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2.102)$$

The Ampere's law with Maxwell addition

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (2.103)$$

The total force in the generalized electromagnetic framework, called also Lorenz force, is

$$\begin{aligned} \mathbf{F} &= \rho_e \mathbf{E} + \mathbf{J} \times \mathbf{B} = \rho_e \mathbf{E} + [\sigma(\mathbf{E} + \mathbf{v} \times \mathbf{B})] \times \mathbf{B} = \\ &= \rho_e \mathbf{E} + \sigma \mathbf{E} \times \mathbf{B} + \sigma(\mathbf{v} \times \mathbf{B}) \times \mathbf{B} \end{aligned} \quad (2.104)$$

Gauss Law describes the relationship between a static electric field, and the electrical charges that cause it. The static electric field, points away from positive charges and towards negative charges.

In the field line description, electric field lines begin only at positive electric charges and end only at negative electric charges.

Counting the number of field lines, passing through a closed surface, yields to the total charge enclosed by the surface divided by the dielectricity of the free space. All the four Maxwell's equations were written for the free space and not for any general medium. The Gauss Law for magnetism says that there are no magnetic charges analogous to electrical charges. The magnetic field due to the materials, is generated by a configuration called dipole. Magnetic dipoles are represented as loops of current, but resemble positive and negative magnetic charges inseparably bound together, having no net magnetic charge. Any magnetic field line that enters the given volume must somewhere exit that volume. And in more technical terms that some total magnetic flux to any Gaussian surface is zero, Electric field is proper vector but magnetic field is a pseudo vector. Vectors will transform with rotation in a proper way. Under rotation, a pseudo vector will transform in the same way as the original vector but under deflection, it will flip its sign. In mechanics, for example, angular momentum is a pseudo vector.

Maxwell-Faraday's equation is a version of the Faraday's law, which says how a time magnetic field, create an electric field.

Ampere's law with Maxwell's addition states that magnetic field can be generated in two ways: by electrical current (original Ampere's law) and by changing electric field (Maxwell's addition).

If inside eq.(2.104) the Gauss Law and the Ampere's law are used, yields

$$\mathbf{F} = \epsilon_0(\nabla \cdot \mathbf{E})\mathbf{E} + \left(\frac{\nabla \times \mathbf{B}}{\mu_0} - \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \times \mathbf{B} = \epsilon_0(\nabla \cdot \mathbf{E})\mathbf{E} + \frac{\nabla \times \mathbf{B}}{\mu_0} \times \mathbf{B} - \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \times \mathbf{B} \quad (2.105)$$

Since that

$$\frac{\partial}{\partial t}(\mathbf{E} \times \mathbf{B}) = \frac{\partial \mathbf{E}}{\partial t} \times \mathbf{B} + \mathbf{E} \times \frac{\partial \mathbf{B}}{\partial t}$$

inserting it inside eq.(2.105)

$$\mathbf{F} = \epsilon_0(\nabla \cdot \mathbf{E})\mathbf{E} + \frac{\nabla \times \mathbf{B}}{\mu_0} \times \mathbf{B} - \epsilon_0 \frac{\partial}{\partial t}(\mathbf{E} \times \mathbf{B}) + \epsilon_0 \mathbf{E} \times \frac{\partial \mathbf{B}}{\partial t} \quad (2.106)$$

Using Maxwell's law

$$\mathbf{F} = \epsilon_0(\nabla \cdot \mathbf{E})\mathbf{E} + \frac{\nabla \times \mathbf{B}}{\mu_0} \times \mathbf{B} - \epsilon_0 \frac{\partial}{\partial t}(\mathbf{E} \times \mathbf{B}) - \epsilon_0 \mathbf{E} \times (\nabla \times \mathbf{E}) \quad (2.107)$$

Using the identity

$$(\nabla \times \mathbf{B}) \times \mathbf{B} = (\nabla \cdot \mathbf{B})\mathbf{B} - \mathbf{B} \times (\nabla \times \mathbf{B})$$

$$\mathbf{F} = [\epsilon_0(\nabla \cdot \mathbf{E})\mathbf{E} - \epsilon_0\mathbf{E} \times (\nabla \times \mathbf{E})] + \frac{(\nabla \cdot \mathbf{B})\mathbf{B} - \mathbf{B} \times (\nabla \times \mathbf{B})}{\mu_0} - \epsilon_0 \frac{\partial}{\partial t}(\mathbf{E} \times \mathbf{B}) \quad (2.108)$$

For the vector identity

$$\mathbf{A} \times (\nabla \times \mathbf{A}) = \frac{\nabla A^2}{2} - (\mathbf{A} \cdot \nabla)\mathbf{A}$$

The following is obtained

$$\mathbf{F} = [\epsilon_0(\nabla \cdot \mathbf{E})\mathbf{E} - \epsilon_0(\mathbf{E} \cdot \nabla)\mathbf{E}] + \frac{1}{\mu_0} ((\nabla \cdot \mathbf{B})\mathbf{B} + \epsilon_0(\mathbf{B} \cdot \nabla)\mathbf{B}) - \frac{1}{2}\nabla \left(\epsilon_0 E^2 - \frac{B^2}{\mu_0} \right) - \epsilon_0 \frac{\partial}{\partial t}(\mathbf{E} \times \mathbf{B}) \quad (2.109)$$

The eq.(2.109) can be written as a divergence pf a tensor which is also known as Maxwell stress tensor. In a steady state

$$F_i = \frac{\partial \tau_{ij}^M}{\partial x_j} = \bar{\mathbf{T}} = \epsilon_0 \left(\mathbf{E} \otimes \mathbf{E} - \frac{1}{2}\bar{\mathbf{I}}(\mathbf{E} \cdot \mathbf{E}) \right) + \frac{1}{\mu_0} \left(\mathbf{B} \otimes \mathbf{B} - \frac{1}{2}\bar{\mathbf{I}}(\mathbf{E} \cdot \mathbf{E}) \right) \quad (2.110)$$

Neglecting magnetic effects, and considering inside the medium. the Maxwell Stress tensor becomes

$$\bar{\mathbf{T}} = \epsilon \left(\mathbf{E} \otimes \mathbf{E} - \frac{1}{2}\bar{\mathbf{I}}(\mathbf{E} \cdot \mathbf{E}) \right) \quad (2.111)$$

$$\begin{aligned} \mathbf{F}_E &= \nabla \cdot \bar{\mathbf{T}} = \epsilon \nabla \cdot (\mathbf{E} \otimes \mathbf{E}) - \epsilon \frac{1}{2} \nabla \cdot (\bar{\mathbf{I}}(\mathbf{E} \cdot \mathbf{E})) \\ &= \epsilon \mathbf{E}(\nabla \cdot \mathbf{E}) + \epsilon(\mathbf{E} \cdot \nabla)\mathbf{E} - \epsilon \frac{1}{2} \nabla(\mathbf{E} \cdot \mathbf{E}) \\ &= \epsilon \mathbf{E}(\nabla \cdot \mathbf{E}) + \epsilon(\mathbf{E} \cdot \nabla)\mathbf{E} - \epsilon \frac{1}{2} 2\mathbf{E} \cdot \nabla \mathbf{E} \\ &= \epsilon \mathbf{E}(\nabla \cdot \mathbf{E}) \end{aligned} \quad (2.112)$$

\mathbf{E} is the total electrical field and is expressed as $\mathbf{E} = -\nabla\varphi$. Therefore, the force due to electrical stress is

$$\mathbf{F}_E = \epsilon \nabla \varphi \nabla^2 \varphi \quad (2.113)$$

2.2 Osmosis without a membrane

The geometry taken in consideration, is a solid surface along which a solute gradient, or more generally a thermodynamic force (an electric field, a temperature gradient) is imposed.

Under an electric field, the fluid will be pushed by the net electric forces present at the diffuse interface next to the solid, creating an electro-osmosis flow for the solvent.

A solute gradient ∇c^∞ parallel to the surface, however, can also produce fluid motion whose amplitude is proportional to $u_{DO} \propto \nabla c^\infty$ and this phenomena is called diffusio-osmosis. The phenomena shares some basic similarities with Marangoni effects, in which a gradient of surface tension at a contact may promote fluid (or, conversely, particle) motion as $u_f \propto \nabla \gamma_{LV}$. Although it is not immediately obvious how to apply Marangoni flows to solid-fluid interfaces, but Derjaguin noted that the diffuse character of the interface might allow the fluid to slip over the solid surface under a concentration gradient. Therefore, diffusio-osmosis is an interfacially driven flow that originates in the solute's interfacial structure close to the solid surface, in the initial few nanometers close to the surface.

Electro-osmosis Force

Electro-osmosis is the fluid flow created by an applied electric field adjacent to a solid surface. A solution with ions will form a "electric double layer" (EDL) next to any charged surface because the surface charge attracts counter-ions and repels co-ions. The charged surface is balanced by a density of charge $\rho_e = e(c_+ - c_-)$, assuming monovalent ions for illustration, the difference between the density of positive and negative ions is defined. The resulting double layer has a finite width and is diffuse. There is a net charge density in the fluid within the EDL, and anytime an external electric field is applied to the fluid (parallel to the surface), this will produce a net bulk force $\rho_e E_x$.

Considering a semi permeable membrane in which there is a concentration difference across that. On the left hand side there is a low concentration instead on the right hand side there is a high concentration. In effort to equilibrate the concentration, the high concentration solute goes to the low concentration solute or another possibility is that solvent can go from low solute to high solute concentration, that means that the solvent will make the high concentration solute more diluted and this phenomenon is called osmosis.

When there is osmosis, there is a driving pressure gradient that drives this transport and this pressure, which is the minimum pressure that is necessary to achieve equilibrium is called osmotic pressure.

Considering a channel in which at the wall there is the electrical double layer formation and so there will be a potential $\psi(y)$ and along the x direction there is a potential field $\phi_0(x)$ which is a function of x .

writing the momentum equation along the y direction with low Reynolds number and fully developed flow

$$0 = -\frac{d\Pi}{dy} + \rho_e E_y \quad (2.114)$$

where Π is the osmotic pressure. The viscous terms are zero because the velocity is negligibly small in the y direction.

In the generic direction it can be written

$$0 = -\nabla\Pi + \rho_e \mathbf{E}_{EDL} \quad (2.115)$$

Since that there a the electrical double layer, there will be a concentration gradient along the y direction, there for there must be an osmotic pressure acting in the y direction.

Remembering that $\mathbf{E}_{EDL} = -\nabla\psi$ and $\rho_e = -\epsilon\nabla^2\psi$, the equation becomes

$$\nabla\Pi = \epsilon\nabla^2\psi\nabla\psi \quad (2.116)$$

The same expression can be get using the electrochemistry consideration.

The Osmotic Pressure is defined as

$$\Pi = nk_B T \quad (2.117)$$

where $n = n_+ + n_-$. Remembering the Boltzmann distribution, is it possible to calculate the gradient of n in the following way

$$\begin{aligned} n_{\pm} &= n_0 e^{\mp \frac{ze\psi}{k_B T}} \\ \Rightarrow \ln(n_{\pm}) &= \ln(n_0) \mp \frac{ze\psi}{k_B T} \\ \Rightarrow \frac{\nabla n_{\pm}}{n_{\pm}} &= \mp \frac{ze\nabla\psi}{k_B T} \end{aligned} \quad (2.118)$$

and so the Force due to Osmotic Pressure is

$$\begin{aligned} \mathbf{F}_o &= -\nabla\Pi = -k_B T \nabla(n_+ + n_-) \\ &= -k_B T \left(-\frac{ez}{k_B T} n_+ + \frac{ez}{k_B T} n_- \right) \nabla\psi \\ &= ez(n_+ + n_-) \nabla\psi = -\epsilon\nabla^2\psi\nabla\psi \end{aligned} \quad (2.119)$$

The electroosmosis force is the some of the electrical force plus the osmotic force

$$\mathbf{F}_{Eo} = \mathbf{F}_E + \mathbf{F}_o = \epsilon\nabla\phi\nabla^2\phi - \epsilon\nabla^2\psi\nabla\psi \quad (2.120)$$

The total field is $\phi = \phi_0 + \psi$ and so $\nabla^2\phi = \nabla^2\phi_0 + \nabla^2\psi$.

Since that the applied field must satisfy the Laplace equation, $\nabla^2\phi_0 = 0$. The induce field instead will satisfy the Poisson equation. The equation becomes

$$\mathbf{F}_{Eo} = \underbrace{\epsilon \nabla^2 \psi}_{-\rho_{e,free}} \underbrace{\nabla \phi_0}_{-\mathbf{E}_{ext}} = \rho_{e,free} \mathbf{E}_{ext} \quad (2.121)$$

Considering a parallel plate channel and an axial electric field E_x is applied, pointing on the right because on the left of the channel there is a positive plate and on the right of the channel there is negative plate. The surfaces of the wall have a negative charge and so there is the electric double layer phenomenon at the surface.

The x -momentum equation assuming a hydrodinamically fully developed flow. The left hand side is 0 because fully developed flow and we are assuming also that there is no additional pressure gradient acting on the system in the x direction. For fully developed flow the velocity is function of y only

$$0 = \mu \frac{d^2 u}{dy^2} + \rho_e E_x \quad (2.122)$$

using the Poisson equation, the equation becomes

$$0 = \mu \frac{d^2 u}{dy^2} - \epsilon E_x \frac{d^2 \psi}{dy^2} \quad (2.123)$$

Assuming that u_s is the scale of the velocity u and y_s the length scale of y (if there is just one plate the Debye length can be used as a length scale), the order of magnitude of ψ is the zeta potential ζ because is the biggest one, doing the order of magnitude analysis

$$\mu \frac{d^2 u}{dy^2} \sim \mu \frac{u_s}{y_s^2}, \quad \epsilon E_x \frac{d^2 \psi}{dy^2} \sim \epsilon E_x \frac{\zeta}{y_s^2}$$

Since that in the equation there are just two terms, they must be of the same order, and this yields

$$u_s \sim \frac{\epsilon \zeta E_x}{\mu} \quad (2.124)$$

The order of magnitude does not take care of the sign. For a negative wall charge $\zeta < 0$, but the electric field is positive. Since that in the bulk there are some positive and negative charge, but positive charge dominates (because the system must be electrical neutral), the positive charges will move in the same direction of the applied electric field (because attracted from the negative surface on the right) and that will drag the water along the positive direction. Finally, since that the velocity is positive but the right hand side of 2.124 is negative, a negative sign in the equation must be added, to yield

$$u_s \sim -\frac{\epsilon \zeta E_x}{\mu} \quad (2.125)$$

This velocity scale in electroosmosis is the well known Helmholtz-Smoluchowski velocity scale.

This velocity was just obtained doing the order of magnitude, but solving the x momentum equation integrating ones

$$\mu \frac{du}{dy} - \epsilon E_x \frac{d\psi}{dy} = c_1 \quad (2.126)$$

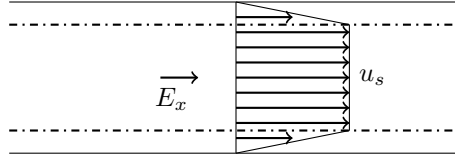
at the center line of the channel $\frac{du}{dy} = 0$ and $\psi = 0 \Rightarrow \frac{d\psi}{dy} = 0$ and this implies that $c_1 = 0$. Integrating once more

$$\mu u - \epsilon E_x \psi = c_2 \quad (2.127)$$

and since that at the wall $\psi = \zeta$ and $u = 0$ yields that $c_2 = -\epsilon E_x \zeta$ and finally the velocity is

$$u = -\frac{\epsilon \zeta E_x}{\mu} \left(1 - \frac{\psi}{\zeta} \right) \quad (2.128)$$

Since that outside the electric Double layer ($y \rightarrow \infty$) ψ will become 0, the velocity is constant and equal to the Helmholtz-Smoluchowski velocity scale (slip velocity).



The uniform velocity profile will be distorted if there is a gradient of the zeta potential (zeta potential not uniform on the wall) because that will induce a pressure gradient axially

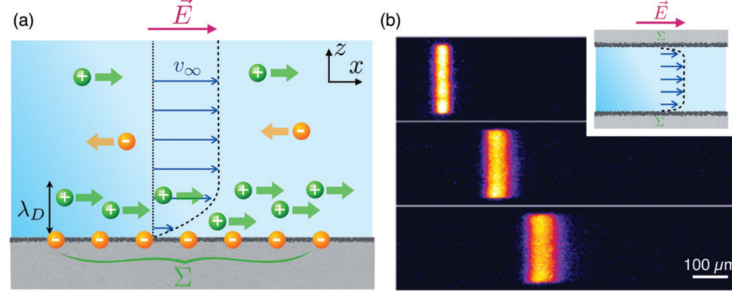


Figure 2.1: Electro-osmosis. (a) An electrical double layer normally arises in the presence of a surface charge S and extends over a distance determined by the Debye length λ_D . Due to the unbalanced charge within the electric double layer, a net electric force develops under an applied electric field E that is parallel to the surface. It induces a solvent flow that extends as a flat flow profile into the bulk and is parallel to the surface. (b) The displacement of (neutral) tagged molecules allows for the visualization of electroosmotic flow in a capillary. The electroosmotic flow profile resembles a plug flow in contrast to the parabolic Poiseuille flow.

Since the electro-osmotic flow originates at the very few nanometers near to the boundary, molecular details such as hydrodynamic slippage, nanoscale roughness, pollution, dielectric inhomogeneities, etc., can have a significant impact on it.

2.2.1 Elettro-phoresis force on a spherical particle

If the radius of the particle is $R \ll \lambda$, particle like a point mass, the Stokes drag can be applied and so

$$\begin{aligned} Q_{surface} E &= 6\pi\mu u_{sp} R \Rightarrow 4\pi\epsilon\zeta R^2 \left[\frac{1}{\lambda} + \frac{1}{R} \right] E = 6\pi\mu u_{sp} R \Rightarrow \\ \Rightarrow u_{sp} &= \frac{2}{3} \frac{\epsilon\zeta E}{\mu} \left[1 + \frac{R}{\lambda} \right] \approx \frac{2}{3} \frac{\epsilon\zeta E}{\mu} \quad (\text{Huckel Equation}) \end{aligned} \quad (2.129)$$

If $R \gg \lambda$, called thin Debye-Layer approximation, the curvature of the particle cannot be neglected. For large radius of curvature, each region of the surface of the particle can be considered as a localized flat plate, with the local perpendicular and parallel velocity components. The perpendicular velocity must be 0 due to no penetration instead the parallel velocity is a function of the applied Electric parallel field.

Since that the particle is like a flat plate, the parallel velocity can be written as $\frac{\epsilon\zeta E_{||}}{\mu}$ the problem is that $E_{||}$ is not known. The potential of the applied electric field is distributed over the surface of the sphere, such that, at each local of the surface a different $E_{||}$ is felt. There must be a governing equation in the (r, θ) coordinate system to solve for the potential distribution. This is not the EDL potential distribution but is the potential distribution due to the applied electric field.

The induced electrical field due to the EDL satisfy the Poisson Boltzmann equation but the field, due to the applied potential, satisfy the Laplace equation (for property of the potential).

$$\begin{aligned} \mathbf{E} &= -\nabla\phi \quad (\text{Represent electric field by potential}) \\ \nabla \cdot \mathbf{E} &= \frac{\rho_e}{\epsilon} \quad (\text{Poisson equation}) \\ \rho_e &= 0 \quad (\text{No free charges present}) \\ \nabla^2\phi &= 0 \quad (\text{Laplace equation}) \end{aligned} \quad (2.130)$$

The extended Laplace equation in (r, θ) coordinate system is

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \phi}{\partial \theta} \right) \quad (2.131)$$

The BC's are that at $r = R$ there should not be penetration, that means $\hat{\mathbf{n}} \cdot \nabla\phi = 0$ (i.e. $\frac{\partial \phi}{\partial n} = 0$) and at far-stream, $\phi = \phi_\infty$ (corresponded to unperturbed electric field far away from the particle). The Laplace equation is solvable with the method of separation of variables. Let's say that

$$\phi = G(r)H(\theta)$$

$$\frac{\partial \phi}{\partial r} = G' H, \quad r^2 \frac{\partial \phi}{\partial r} = r^2 G' H$$

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) = H \frac{d}{dr} (r^2 G')$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \phi}{\partial \theta} \right) = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta G H')$$

and so the Laplace equation becomes

$$\begin{aligned} H \frac{d}{dr} (r^2 G') + \frac{G}{\sin \theta} \frac{d}{d\theta} (\sin \theta H') &= 0 \Rightarrow \\ \frac{1}{G} \frac{d}{dr} (r^2 G') + \frac{1}{H \sin \theta} \frac{d}{d\theta} (\sin \theta H') &= 0 \end{aligned} \quad (2.132)$$

Since that the first term is a function of r only and the second term is a function of θ only and they must be the same but with opposite sign, the only possibility is that the two terms are equal to a constant k that must be determined. The problem to solve is split in two equations that are not partial differential equation but ordinary differential equations

$$\begin{aligned} \frac{1}{G} \frac{d}{dr} (r^2 G') &= k \\ - \frac{1}{H \sin \theta} \frac{d}{d\theta} (\sin \theta H') &= k \end{aligned} \quad (2.133)$$

First of all let's solve the first equation

$$\begin{aligned} \frac{1}{G} \frac{d}{dr} \left(r^2 \frac{dG}{dr} \right) &= k \Rightarrow \\ \frac{d}{dr} \left(r^2 \frac{dG}{dr} \right) &= kG \end{aligned} \quad (2.134)$$

The standard form of this equation is recovered by replacing $k = n(n+1)$, so another parameter n is introduced. Let say that the solution of the equation is of the form

$$\begin{aligned} G &= r^\alpha \\ \frac{dG}{dr} &= \alpha r^{\alpha-1}, \quad r^2 \frac{dG}{dr} = \alpha r^{\alpha+1}, \quad \frac{d}{dr} \left(r^2 \frac{dG}{dr} \right) = \alpha(\alpha+1) r^\alpha \end{aligned} \quad (2.135)$$

and from the eq.(2.138) is possible to write

$$\alpha(\alpha+1)r^\alpha = n(n+1)r^\alpha$$

and this justify that the form of the solution choose is correct.

From that α can be calculated

$$\begin{aligned}
\alpha^2 + \alpha - n^2 - n &= 0 \\
\alpha^2 + [(n+1) - n]\alpha - n(n+1) &= 0 \\
\alpha[\alpha + (n+1)] - n[\alpha + (n+1)] &= 0 \\
\Rightarrow \alpha = -(n+1), \alpha = n
\end{aligned} \tag{2.136}$$

The second differential equation to solve is

$$\begin{aligned}
-\frac{1}{H \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dH}{d\theta} \right) &= k = n(n+1) \Rightarrow \\
\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dH}{d\theta} \right) + n(n+1)H &= 0
\end{aligned} \tag{2.137}$$

Making a substitution, calling

$$\cos \theta = w$$

$$\begin{aligned}
\frac{dH}{d\theta} &= \frac{dH}{dw} \frac{dw}{d\theta} = -\sin \theta \frac{dH}{dw} \\
\sin \theta \frac{dH}{d\theta} &= -\sin^2 \theta \frac{dH}{dw} = -(1-w^2) \frac{dH}{dw} \\
\frac{d}{d\theta} \left(\sin \theta \frac{dH}{d\theta} \right) &= -\frac{d}{dw} \left[(1-w^2) \frac{dH}{dw} \right] = \frac{d}{dw} \left[(1-w^2) \frac{dH}{dw} \sin \theta \right] \\
\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dH}{d\theta} \right) &= \frac{d}{dw} \left[(1-w^2) \frac{dH}{dw} \right]
\end{aligned}$$

and the equation becomes

$$\frac{d}{dw} \left[(1-w^2) \frac{dH}{dw} \right] + n(n+1)H = 0$$

The solution of this differential equation can be expressed in terms of the Legendre polynomial

$$H = P_n(w) = P_n(\cos \theta)$$

where different values of n will give different Legendre polynomials The total solution is

$$\phi = G(r)H(\theta) = r^\alpha P_n(\cos \theta) \tag{2.138}$$

This is a linear differential equation and the resultant solution is a linear superposition of the solution for the two values of α .

$$\phi = \sum A_n r^n P_n(\cos \theta) + \sum B_n r^{-(n+1)} P_n(\cos \theta) \tag{2.139}$$

Let's impose the BC's. Remembering that the electric field is applied along x direction and that the $x = r \cos \theta$, the first BC is

$$\phi = -E_\infty r \cos\theta \quad \text{at } r \rightarrow \infty$$

Inserting it inside eq.(2.139) the only possibility to have that value is to remove the first summation because that one will spread the solution at $r \rightarrow \infty$ and is not correct. So the conclusion of inserting this boundary condition is that $A_1 = -E_\infty$ and $A_n = 0$ for $n = 0$ and $\forall n \geq 2$, and so the solution becomes

$$\phi = -E_\infty r \cos\theta + \sum B_n r^{-(n+1)} P_n(\cos\theta) \quad (2.140)$$

Expanding the summation, the following can be written

$$\phi = -E_\infty r \cos\theta + \frac{B_0}{r} P_0(\cos\theta) + \frac{B_1}{r^2} P_1(\cos\theta) + \dots \quad (2.141)$$

Remembering that the Legendre polynomial Let's imposing the second BC that guaranteed the non penetration. Calculating the derivative of ϕ with respect to r knowing that $P_0(\cos\theta) = 1$ and $P_1(\cos\theta) = \cos\theta$ yields

$$\frac{\partial\phi}{\partial r} = -E_\infty \cos\theta - \frac{B_0}{r^2} - 2\frac{B_1}{r^3} \cos\theta - \dots \quad (2.142)$$

and evaluating it at $r = R$

$$\left. \frac{\partial\phi}{\partial r} \right|_{r=R} = -E_\infty \cos\theta - \frac{B_0}{R^2} - 2\frac{B_1}{R^3} \cos\theta - \dots = 0 \quad (2.143)$$

yields the following constant $B_0 = 0, B_1 = \frac{1}{2} A_1 R^3 = -\frac{1}{2} E_\infty R^3$ and $B_n = 0 \quad \forall n \geq 2$.

Therefore, the electric potential distribution on the surface of the sphere can be expressed as function of θ in this way

$$\phi = -E_\infty r \cos\theta - \frac{1}{2} E_\infty R^3 \frac{\cos\theta}{r^2} = -E_\infty \cos\theta \left(r + \frac{R^3}{2r^2} \right) \quad (2.144)$$

note that

$$E_{||} = -\frac{1}{r} \frac{\partial\phi}{\partial\theta} \Big|_{r=R} = -\frac{3}{2} E_\infty \sin\theta, \quad E_\perp = 0 \quad (2.145)$$

Diffusio-osmosis Force with electrolytes

Diffusio-osmotic motion takes place under the gradient of a solute, $\frac{\partial c^\infty}{\partial x}$, close to a solid surface, whereas electro-osmosis relates to interfacially driven fluid motion under an external electric field. The precise interaction of the solute with the surface, which takes place within a diffuse layer of finite thickness, is a crucial component, similar to electro-osmosis.

There are two methods by which a tangential gradient of a dissociating electrolyte causes fluid to flow along

a charged solid surface. The first is based in the excess osmotic pressure within the interaction layer due to the attraction of counterions. The local solute gradients can thus induce interfacial fluid flow by the osmotic pressure gradient (chemiosmotic effect), and the second is based on the macroscopic electric field produced because the tangential diffusive fluxes of the two electrolyte ions are not equal (electroosmotic effect).

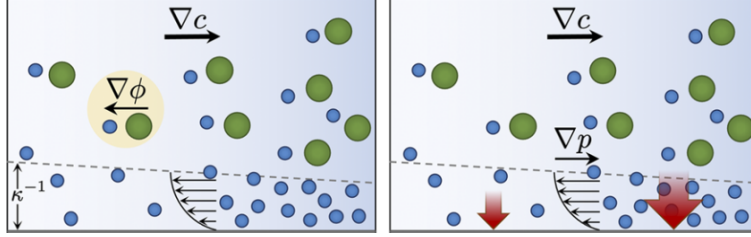


Figure 2.2: On the left hand side is shown the phenomena of Electro-osmosis and on the right hand side the phenomena of chemical-osmosis

The ionic concentrations n_+ and n_- in the fluid, are not uniform in both tangential (x) and normal (y) directions, and their gradients in the tangential direction can give rise to a “diffusion current” distribution. The negative and positive ions, diffuse from high concentration to low concentration and this give rise to two current in the same direction but unequal diffusion fluxes, and therefore tend to create a diffusion current. The corresponding ion fluxes $\mathbf{J}_+ = -D_+ \nabla n_+$ and $\mathbf{J}_- = -D_- \nabla n_-$ are different due to the difference in the diffusion coefficients of cations (D_+) and anions (D_-) (e.g. Cl^- diffuses slightly faster than Na^+). To prevent a continuous separation of the counterions and co-ions, an electric field distribution \mathbf{E} along the tangential direction arises spontaneously in the electrolyte solution to produce another electric current distribution which exactly balances the diffusion current, in such way to speed up the positive ion. This induced electric field generates an electroosmotic flow of the fluid parallel to the planewall, in addition to the chemiosmotic flow caused by the electrolyte gradient directly.

The flux of either ionic species can be expressed by the Nernst-Planck eq.(2.53) but adding the flux contribution due to the spontaneous electric field (for the principle of superposition for the electric potential) in the x direction yields

$$J_{\pm,x} = -D_{\pm} \left[\frac{\partial n_{\pm}}{\partial x} \pm \frac{ze}{k_B T} n_{\pm} \left(\frac{\partial \psi}{\partial x} - E \right) \right] + n_{\pm} u \quad (2.146)$$

in which $n_{\pm} = n_{\pm}(x, y)$ due to the fact that the concentration in the y direction is due to the charged wall and so caused by the EDL and there is also a dependency on the x direction because there is a concentration gradient applied on that direction. Also the potential $\psi = \psi(x, y)$, for the same reason of the concentration. The velocity of the fluid is not zero because due to the fact that the ions are moving, they will transport also the fluid due to viscosity (drag) and so the fluid from rest will start to move.

Imposing no flux along the y direction, the only two terms that are present are the diffusion of ions due to EDL and the potential aroused from the EDL. Balancing these two bring back to the Boltzmann distribution.

Diffusio-osmosis of an electrolyte solution in a slit nanochannel

The electric field can be calculated imposing that the local axial cationic and anionic fluxes are equal to each other. This condition is true when an isolated nanochannel bounded by insulating end walls are considered and the end effects are neglected. In real applications there are some nanochannels/nanocapillaries that are not isolated, but are connected to microchannel reservoirs. In such cases, it must be imposed that the total current across the entire nanochannel cross section should be zero, where $y = \pm h$ are the top and bottom wall, which yields

$$I_{net} = \int_{-h}^h (J_{+,x} - J_{-,x}) dy = 0 \Rightarrow$$

$$D_+ \int_{-h}^h \left\{ \left[\frac{\partial n_+}{\partial x} + \frac{ze}{k_B T} n_+ \left(\frac{\partial \psi}{\partial x} - E \right) \right] + n_+ u \right\} dy = D_- \int_{-h}^h \left\{ \left[\frac{\partial n_-}{\partial x} - \frac{ze}{k_B T} n_- \left(\frac{\partial \psi}{\partial x} - E \right) \right] + n_- u \right\} dy \quad (2.147)$$

Since that the variation of the concentration follows the Boltzmann distribution $n_{\pm} = n^{\infty} e^{\mp \frac{ze\psi}{k_B T}}$, doing the derivative respect to x

$$\frac{\partial n_+}{\partial x} = \frac{dn^{\infty}}{dx} e^{-\frac{ze\psi}{k_B T}} - n^{\infty} \frac{ze}{k_B T} e^{-\frac{ze\psi}{k_B T}} \frac{\partial \psi}{\partial x}$$

$$\frac{\partial n_-}{\partial x} = \frac{dn^{\infty}}{dx} e^{\frac{ze\psi}{k_B T}} + n^{\infty} \frac{ze}{k_B T} e^{\frac{ze\psi}{k_B T}} \frac{\partial \psi}{\partial x}$$

and plug it inside eq.(2.147) yields

$$\frac{zen^{\infty}}{k_B T} E \int_{-h}^h \left(D_+ e^{-\frac{ze\psi}{k_B T}} + D_- e^{\frac{ze\psi}{k_B T}} \right) dy = \int_{-h}^h \left[2un^{\infty} \sinh \left(\frac{ze\psi}{k_B T} \right) + \frac{dn^{\infty}}{dx} \left(D_+ e^{-\frac{ze\psi}{k_B T}} - D_- e^{\frac{ze\psi}{k_B T}} \right) \right] dy \quad (2.148)$$

Considering $\beta = \frac{D_+ - D_-}{D_+ + D_-}$, it is possible to write D_+ and D_- in function of $(D_+ + D_-)$ in this way

$$\beta = \frac{D_+ - D_-}{D_+ + D_-} \Rightarrow (D_+ - D_-) = \beta(D_+ + D_-) \quad (2.149)$$

Adding and subtracting D_+ to eq.(2.149)

$$D_+ - D_- + D_+ - D_+ = \beta(D_+ + D_-) \Rightarrow 2D_+ - (D_+ + D_-) = \beta(D_+ + D_-) \Rightarrow$$

$$D_+ = \frac{1}{2}(D_+ + D_-)(1 + \beta) \quad (2.150)$$

instead, adding and subtracting D_- to eq.(2.149) yields

$$D_+ - D_- + D_- - D_- = \beta(D_+ + D_-) \Rightarrow -2D_- + (D_+ + D_-) = \beta(D_+ + D_-) \Rightarrow$$

$$D_- = \frac{1}{2}(D_+ + D_-)(1 - \beta) \quad (2.151)$$

Plugging eq.(2.150) and eq.(2.151) inside eq.(2.148) and calling $\bar{\psi} = \frac{ze\psi}{k_B T}$, the induced electric field is obtained

$$E = \frac{4k_B T}{ze(D_+ + D_-)} \frac{\int_{-h}^h u \sinh(\bar{\psi}) dy}{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] dy} + \frac{k_B T}{zen^\infty} \frac{dn^\infty}{dx} \frac{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} - (1 - \beta)e^{\bar{\psi}}] dy}{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] dy}$$

$$\Rightarrow E = \frac{k_B T}{zen^\infty} \frac{dn^\infty}{dx} \left\{ \frac{4n^\infty}{(D_+ + D_-)} \left(\frac{dn^\infty}{dx} \right)^{-1} \frac{\int_{-h}^h u \sinh(\bar{\psi}) dy}{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] dy} + \frac{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} - (1 - \beta)e^{\bar{\psi}}] dy}{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] dy} \right\} \quad (2.152)$$

Defining the characteristic value of the diffusioosmotic velocity and the Peclet number

$$U^* = \frac{2k_B T N_A}{\eta \kappa^2} \frac{dn^\infty}{dx}, \quad Pe = \frac{4n^\infty U^*}{(D_+ + D_-) \frac{dn^\infty}{dx}} = \frac{8k_B T N_A n^\infty}{(D_+ + D_-) \eta \kappa^2}$$

where κ is the inverse of the Debye-length, eq.(2.152) finally can be written as

$$E = \frac{k_B T}{zen^\infty} \frac{dn^\infty}{dx} \left\{ \frac{\int_{-h}^h Pe \sinh(\bar{\psi}) \frac{u}{U^*} dy}{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] dy} + \frac{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} - (1 - \beta)e^{\bar{\psi}}] dy}{\int_{-h}^h [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] dy} \right\} \quad (2.153)$$

Considering steady state flow ($\frac{\partial u}{\partial t} = 0$), fully developed ($\frac{\partial u}{\partial x} = 0 \Rightarrow \frac{\partial^2 u}{\partial x^2} = 0$, the velocity is constant in x direction) and uni-directional in the axial direction flow, the Navier-Stokes in x and y direction is respectively

$$\eta \frac{\partial^2 u}{\partial y^2} = \frac{\partial p}{\partial x} - zeN_A(n_+ - n_-) \left(E - \frac{\partial \psi}{\partial x} \right) \quad (2.154)$$

$$\frac{\partial p}{\partial y} + zeN_A(n_+ - n_-) \frac{\partial \psi}{\partial y} \quad (2.155)$$

Inside the conservation of mass is included the transient term of the velocity and so the velocity, if the concentration vary with time, will also vary.

The concentration applied externally varies linearly in the x direction and so this implies that the gradient of the applied concentration is constant both in space and time and so the velocity will not depend on time.

The concentration depends on $n = n(x, y)$ in which the dependency also on y is due to the fact that is also considering a Debye layer, instead the concentration in the bulk just depends on x , $n^\infty = n^\infty(x)$ because the Debye layer is not finished. Since that the Debye length depends on the bulk of the concentration, this implies that $\lambda = \lambda(x)$. Since that the electric potential depends how far away it is from the wall (y direction) and also from λ , at the end $\psi = \psi(x, y)$.

Applying the Boltzmann distribution eq.(2.155) can be rewritten as

$$\frac{\partial p}{\partial y} = 2n^\infty z e N_A \sinh(\bar{\psi}) \frac{\partial \psi}{\partial y} = 2n^\infty k_B T N_A \sinh(\bar{\psi}) \frac{\partial \bar{\psi}}{\partial y} \quad (2.156)$$

Integrating eq.(2.156) respect to y and remembering the Integration by substitution

$$\int_a^b f(g(y))g'(y)dy = \int_{g(a)}^{g(b)} f(t)dt$$

in which $t = \bar{\psi}(x, y)$, $dt = \frac{\partial \bar{\psi}(x, y)}{\partial y} dy$ and the extreme of integration becomes $b = y \Rightarrow g(b) = \bar{\psi}(x, y)$, $a \rightarrow \infty \Rightarrow g(a) = \bar{\psi}(x, \infty) = 0$, yields the pressure profile

$$p(x, y) = p^\infty + 2n^\infty k_B T N_A [\cosh(\bar{\psi}(x, y)) - 1] \quad (2.157)$$

where p^∞ is the pressure far away from the wall, which is constant in absence of applied pressure gradient. The term in the squared brackets is an even function and always positive that means $p(x, y) > p^\infty$ within the double layer.

If the bulk concentration n^∞ changes gradually enough along a parallel to the surface, p deepens on x .

Deriving eq.(2.157) respect to x

$$\frac{\partial p}{\partial x} = 2k_B T N_A \frac{dn^\infty}{dx} [\cosh(\bar{\psi}) - 1] + 2n^\infty k_B T N_A \sinh(\bar{\psi}) \frac{\partial \bar{\psi}}{\partial x} \quad (2.158)$$

and substituting inside eq.(2.154) using also the Boltzmann distribution, yields

$$\eta \frac{\partial^2 u}{\partial y^2} = 2k_B T N_A \frac{dn^\infty}{dx} [\cosh(\bar{\psi}) - 1] + 2n^\infty z e N_A \sinh(\bar{\psi}) E \quad (2.159)$$

As it can be seen the velocity of the flow $u = u(y)$ due to parabolic profile.

Considering the dimensionless quantities $\bar{u} = u/U^*$, $\bar{x} = x/L$ and $\bar{y} = y/h$ and substituting eq.(2.153) into eq.(2.159) yields

$$\frac{\partial^2 \bar{u}}{\partial \bar{y}^2} = K^2 [\cosh(\bar{\psi}) - 1] + K^2 \sinh(\bar{\psi}) \left\{ \frac{\int_{-1}^1 Pe \sinh(\bar{\psi}) \bar{u} d\bar{y}}{\int_{-1}^1 [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] d\bar{y}} + \frac{\int_{-1}^1 [(1 + \beta)e^{-\bar{\psi}} - (1 - \beta)e^{\bar{\psi}}] d\bar{y}}{\int_{-1}^1 [(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}] d\bar{y}} \right\} \quad (2.160)$$

where $K = \kappa h = h/\lambda$. Eq.(2.160) is an integro-differential equation that can be solved numerically.

The boundary conditions of the equations are

$$(\bar{u})_{\bar{y}=1} = 0, \quad \left(\frac{\partial \bar{u}}{\partial \bar{y}} \right)_{\bar{y}=0} = 0$$

Solution of the velocity field for a flat plate

Assuming now that the end effects are neglected, the condition to be imposed is that the ions flux must be the same, and so the electric field eq.(2.152) can be written without integrals and the integro-differential equation becomes just a differential equation

$$\frac{\partial^2 \bar{u}}{\partial \bar{y}^2} = K^2 [\cosh(\bar{\psi}) - 1] + K^2 \sinh(\bar{\psi}) \left\{ \frac{Pe \sinh(\bar{\psi}) \bar{u}}{(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}} + \frac{(1 + \beta)e^{-\bar{\psi}} - (1 - \beta)e^{\bar{\psi}}}{(1 + \beta)e^{-\bar{\psi}} + (1 - \beta)e^{\bar{\psi}}} \right\} \quad (2.161)$$

Considering the case in which $\kappa y \rightarrow \infty$ (that means far away from the Debye length), then $\psi \rightarrow 0$ and the induced electric field reduces to its bulk-phase quantity

$$E^\infty = \frac{k_B T}{ze n^\infty} \beta \frac{dn^\infty}{dx} \quad (2.162)$$

Inserting this electric field inside eq.(2.159) gives

$$\eta \frac{\partial^2 u}{\partial y^2} = 2k_B T N_A \frac{dn^\infty}{dx} [\cosh(\bar{\psi}) - 1 + \beta \sinh(\bar{\psi})] \quad (2.163)$$

The same equation can be rewritten in dimensionless form. Defining $\bar{y} = \frac{y}{\lambda}$ and considering $\bar{u} = \frac{u}{U^*}$, the equation can be rewritten in this way

$$\frac{\partial^2 \bar{u}}{\partial \bar{y}^2} = \cosh(\bar{\psi}) - 1 + \beta \sinh(\bar{\psi}) \quad (2.164)$$

To solve this differential equation, the equation is separated in two terms; the first one that is the chemicalphoresis term $(\cosh(\bar{\psi}) - 1)$ and the second one that is the electrophoresis term $\sinh(\bar{\psi})$.

Gouy-Chapman model for the electric potential in the case of a charged flat plate is used.

$$\frac{\partial \bar{u}}{\partial \bar{y}} = \int \left\{ \cosh \left[2 \ln \left(\frac{1 + \tanh \left(\frac{ze\zeta}{4k_B T} \right) e^{-\bar{y}}}{1 - \tanh \left(\frac{ze\zeta}{4k_B T} \right) e^{-\bar{y}}} \right) \right] - 1 \right\} d\bar{y} \quad (2.165)$$

just for simplification, let's define

$$\gamma = \tanh \left(\frac{ze\zeta}{4k_B T} \right)$$

First of all applying linearity the integral can be separated in two integrals

$$\frac{\partial \bar{u}}{\partial \bar{y}} = \int \cosh \left[2 \ln \left(\frac{1 + \gamma e^{-\bar{y}}}{1 - \gamma e^{-\bar{y}}} \right) \right] dy - \int 1 dy \quad (2.166)$$

In the first integral, the \cosh function can be written using exponentials and knowing that $e^{2 \ln(x)} = e^{\ln(x^2)} = x^2$ and $e^{-2 \ln(x)} = e^{\ln(x^{-2})} = \frac{1}{x^2}$

$$\begin{aligned} \int \cosh \left[2 \ln \left(\frac{1 + \gamma e^{-\bar{y}}}{1 - \gamma e^{-\bar{y}}} \right) \right] dy &= \int \frac{\frac{(1 + \gamma e^{-\bar{y}})^2}{(1 - \gamma e^{-\bar{y}})^2} + \frac{(1 - \gamma e^{-\bar{y}})^2}{(1 + \gamma e^{-\bar{y}})^2}}{2} dy \\ &= \frac{1}{2} \int \frac{(1 + \gamma e^{-\bar{y}})^2}{(1 - \gamma e^{-\bar{y}})^2} dy + \frac{1}{2} \int \frac{(1 - \gamma e^{-\bar{y}})^2}{(1 + \gamma e^{-\bar{y}})^2} dy \end{aligned} \quad (2.167)$$

since that $(1 - \gamma e^{-\bar{y}})^2 = (\gamma e^{-\bar{y}} - 1)^2$ the following yields

$$= \frac{1}{2} \int \frac{(\gamma e^{-\bar{y}} + 1)^2}{(\gamma e^{-\bar{y}} - 1)^2} dy + \frac{1}{2} \int \frac{(\gamma e^{-\bar{y}} - 1)^2}{(\gamma e^{-\bar{y}} + 1)^2} dy \quad (2.168)$$

the attention is focused on the first integral of eq.(2.168) an multiplying numerator and denominator by $(e^{\bar{y}})^2$

$$\int \frac{(\gamma e^{-\bar{y}} + 1)^2}{(\gamma e^{-\bar{y}} - 1)^2} dy = \int \frac{(e^{\bar{y}} + \gamma)^2}{(\gamma - e^{\bar{y}})^2} dy = \int \frac{(e^{\bar{y}} + \gamma)^2}{(e^{\bar{y}} - \gamma)^2} dy \quad (2.169)$$

Substituting $v = e^{\bar{y}} \rightarrow dv = e^{\bar{y}} d\bar{y}$ the integral becomes

$$= \int \frac{(v + \gamma)^2}{v(v - \gamma)^2} dv \quad (2.170)$$

let's simplify the fraction with the method of the partial fraction

$$\frac{(v + \gamma)^2}{v(v - \gamma)^2} = \frac{A_1}{v} + \frac{A_2}{(v - \gamma)^2} \quad (2.171)$$

Multiplying both sides by $v(v - \gamma)^2$

$$(v + \gamma)^2 = A_1(v - \gamma)^2 + A_2 v \quad (2.172)$$

The roots of $v(v - \gamma)^2$ are $v = 0$ and $v = \gamma$; substituting these roots inside eq.(2.171) the constant are $A_1 = 1$ and $A_2 = 4\gamma$ and the integral simplified becomes

$$\int \frac{(v + \gamma)^2}{v(v - \gamma)^2} dv = 4\gamma \int \frac{1}{(v - \gamma)^2} dv + \int \frac{1}{v} dv = -\frac{4\gamma}{v - \gamma} + \ln(v) \quad (2.173)$$

and plug $v = e^{\bar{y}}$ yields

$$\int \frac{(\gamma e^{-\bar{y}} + 1)^2}{(\gamma e^{-\bar{y}} - 1)^2} dy = \bar{y} - \frac{4\gamma}{e^{\bar{y}} - \gamma} \quad (2.174)$$

Solving the second integral of eq.(2.168) with the same method yield

$$\int \frac{(\gamma e^{-\bar{y}} - 1)^2}{(\gamma e^{-\bar{y}} + 1)^2} d\bar{y} = \bar{y} + \frac{4\gamma}{e^{\bar{y}} + \gamma} \quad (2.175)$$

plug eq.(2.174) and eq.(2.175) inside eq.(2.168) gives

$$\int \cosh \left[2 \ln \left(\frac{1 + \gamma e^{-\bar{y}}}{1 - \gamma e^{-\bar{y}}} \right) \right] d\bar{y} = \frac{2\gamma}{e^{\bar{y}} + \gamma} - \frac{2\gamma}{e^{\bar{y}} - \gamma} + \bar{y} \quad (2.176)$$

at the end, the integral of eq.(2.165) is

$$\frac{\partial \bar{u}}{\partial \bar{y}} = \frac{2\gamma}{e^{\bar{y}} + \gamma} - \frac{2\gamma}{e^{\bar{y}} - \gamma} + C_1 = -\frac{4\gamma^2}{e^{2\bar{y}} - \gamma^2} + C_1 \quad (2.177)$$

Integrating again eq.(2.177)

$$\bar{u} = \int \left(C_1 - \frac{4\gamma^2}{e^{2\bar{y}} - \gamma^2} \right) d\bar{y} = C_1 \int 1 d\bar{y} - 4\gamma^2 \int \frac{1}{e^{2\bar{y}} - \gamma^2} d\bar{y} \quad (2.178)$$

The second integral can be solve doing the following substitution $t = -2\bar{y} \rightarrow dt = -2d\bar{y}$ and the integral becomes

$$\int \frac{1}{e^{2\bar{y}} - \gamma^2} d\bar{y} = -\frac{1}{2} \int \frac{1}{e^{-t} - \gamma^2} dt \quad (2.179)$$

multiplying numerator and denominator by e^t yields

$$= \int \frac{e^t}{1 - \gamma^2 e^t} dt \quad (2.180)$$

calling $w = (1 - \gamma^2 e^t) \rightarrow dw = -\gamma^2 e^t dt$

$$= -\frac{1}{\gamma^2} \int \frac{1}{w} dw = -\frac{\ln(w)}{\gamma^2} \quad (2.181)$$

where eq.(2.179) becomes

$$\int \frac{1}{e^{2\bar{y}} - \gamma^2} d\bar{y} = \frac{\ln(1 - \gamma^2 e^t)}{2\gamma^2} = \frac{\ln(1 - \gamma^2 e^{-2\bar{y}})}{2\gamma^2} \quad (2.182)$$

and finally eq.(2.178) becomes

$$\bar{u} = C_1 \bar{y} - 2 \ln(1 - \gamma^2 e^{-2\bar{y}}) + C_2 \quad (2.183)$$

To find the two constant, the BC must be set. At far away from the wall the gradient of the velocity is 0 ($\bar{y} \rightarrow \infty, \frac{\partial \bar{u}}{\partial \bar{y}} = 0$) and plugging this condition in eq.(2.177) yield that $C_1 = 0$. The second BC is that the velocity at the wall must be 0 for the non slip condition ($\bar{y} = 0, \bar{u} = 0$) and plugging this condition inside eq.(2.177) yields that $C_2 = 2 \ln(1 - \gamma^2)$.

The velocity profile along the \bar{y} direction becomes

$$\bar{u} = -2\ln(1 - \gamma^2 e^{-2\bar{y}}) + 2\ln(1 - \gamma^2) \quad (2.184)$$

The velocity far away from the wall (the constant slip velocity) can be ordained

$$\bar{u}_\infty = \lim_{\bar{y} \rightarrow \infty} \bar{u} = 2\ln(1 - \gamma^2) = 2\ln\left(1 - \tanh^2\left(\frac{ze\zeta}{4k_B T}\right)\right) \quad (2.185)$$

This is the component of the velocity due to chemicalphoresis.

Now the elettrophoresis component must be calculated.

$$\frac{\partial \bar{u}}{\partial \bar{y}} = \int \beta \sinh\left[2\ln\left(\frac{1 + \gamma e^{-\bar{y}}}{1 - \gamma e^{-\bar{y}}}\right)\right] dy \quad (2.186)$$

deriving one times gives

$$\frac{\partial \bar{u}}{\partial \bar{y}} = -\frac{4\gamma\beta e^{\bar{y}}}{e^{2\bar{y}} - \gamma^2} + C_1 \quad (2.187)$$

and deriving ones again

$$\bar{u} = 2\beta\ln(|e^{\bar{y}} + \gamma|) - 2\beta\ln(|e^{\bar{y}} - \gamma|) + C_1\bar{y} + C_2 \quad (2.188)$$

The same boundary condition must be set, from wich the constant are $C_1 = 0$ and $C_2 = 2\beta\ln\left(\frac{1-\gamma}{1+\gamma}\right)$ The velocity becomes

$$\bar{u} = 2\beta\ln(|e^{\bar{y}} + \gamma|) - 2\beta\ln(|e^{\bar{y}} - \gamma|) + 2\beta\ln\left(\frac{1-\gamma}{1+\gamma}\right) \quad (2.189)$$

$$\bar{u}_\infty = \lim_{\bar{y} \rightarrow \infty} \bar{u} = 2\beta\ln\left(\frac{1-\gamma}{1+\gamma}\right) \quad (2.190)$$

It is possible to write the far away elettrophoresis velocity in another way. Since that

$$\begin{aligned} \frac{1 + \tanh(x)}{1 - \tanh(x)} &= \frac{1 + \frac{\sinh(x)}{\cosh(x)}}{1 - \frac{\sinh(x)}{\cosh(x)}} = \frac{\frac{\cosh(x) + \sinh(x)}{\cosh(x)}}{\frac{\cosh(x) - \sinh(x)}{\cosh(x)}} = \frac{\cosh(x) + \sinh(x)}{\cosh(x) - \sinh(x)} = \\ &= \frac{\frac{1}{2}(e^x + e^{-x}) + \frac{1}{2}(e^x - e^{-x})}{\frac{1}{2}(e^x + e^{-x}) - \frac{1}{2}(e^x - e^{-x})} = \frac{e^x + \cancel{e^{-x}} + e^x - \cancel{e^{-x}}}{\cancel{e^x} + e^{-x} - \cancel{e^x} + e^{-x}} = \frac{2e^x}{2e^{-x}} = e^{2x} \\ \bar{u}_\infty &= 2\beta\ln\left(e^{-2\frac{ze\zeta}{4k_B T}}\right) = -\beta\frac{ze\zeta}{k_B T} \end{aligned} \quad (2.191)$$

The sum of the two contribution is

$$\bar{u}_\infty = -\beta \frac{ze\zeta}{k_B T} + 2 \ln \left(1 - \tanh^2 \left(\frac{ze\zeta}{4k_B T} \right) \right) \quad (2.192)$$

$$u_\infty = -\frac{\epsilon}{\eta} \frac{k_B T}{ze} \left[\beta \zeta - 2 \frac{k_B T}{ze} \ln \left(1 - \tanh^2 \left(\frac{ze\zeta}{4k_B T} \right) \right) \right] \frac{d}{dx} (\ln(n^\infty)) \quad (2.193)$$

This velocity represent the tangential velocity, diffusioosmosis velocity, (x component) of the fluid with respect to the fixed wall.

It is possible to define the diffusio-osmosis mobility that has the unit of a diffusion coefficient

$$\Gamma_{DO} = -\frac{\epsilon}{\eta} \frac{k_B T}{ze} \left[\beta \zeta - 2 \frac{k_B T}{ze} \ln \left(1 - \tanh^2 \left(\frac{ze\zeta}{4k_B T} \right) \right) \right] \quad (2.194)$$

2.3 Diffusio-phoresis of particles

The previous sections demonstrated how the diffusio-osmotic phenomena causes fluid motion in the presence of solute gradients. Gradients of solute will cause motion in a particle that is suspended in a quiescent fluid. The same osmotic driving forces, present in the interfacial layer at the particle boundary, are responsible for this motion, known as "diffusio-phoresis."

The physical process at play is depicted in Fig. 18: the solute gradient at the solute surface causes a fluid's diffusioosmotic slip velocity (relative to the solid particle) across the interfacial diffuse layer; the particle is moved to perfectly negate the corresponding velocity. The value of the mobility Γ_{DP} of the spherical particle, coincides with minus the equivalent diffusio-osmotic mobility.

$$\Gamma_{DP} = -\Gamma_{DO} \quad (2.195)$$

and the diffusio-phoresis velocity of the partficle is

$$U = \frac{\epsilon}{\eta} \frac{k_B T}{ze} \left[\beta \zeta - 2 \frac{k_B T}{ze} \ln \left(1 - \tanh^2 \left(\frac{ze\zeta}{4k_B T} \right) \right) \right] \frac{d}{dx} (\ln(n^\infty)) \quad (2.196)$$

This is true when the Debye length is negligibly small compared to the particle diameter ($(\kappa a)^{-1} \rightarrow 0$). The particle diffusiophoretic mobility is different from the diffusio-osmotic mobility when the particle size is comparable with or smaller than the Debye length ($(\kappa a)^{-1} \leq 1$). As can be seen, the diffusiphoresis velocity is independent from the size of the colloidal particle.

2.3.1 Diffusio-phoretic velocity for $(\kappa a)^{-1} \ll 1$

When the thickness of the Debye layer κ^{-1} becomes comparable to the size of the colloidal particle, the ion concentration, electrostatic potential and velocity fields are expressed as a regular power-series expansion in

the smallest parameter $(\kappa a)^{-1}$, denoted by λ .

An asymptotic expansion is done:

$$u = u_0 + \lambda u_1 + O(\lambda^2) \quad (2.197)$$

In general, u depends on the ζ_p, β and Pe .

The diffusio-phoretic velocity becomes size dependent and it is expressed in this way:

$$U = \frac{\epsilon}{2\mu} \left(\frac{k_B T}{ze} \right)^2 [u_0 + \lambda u_1] \frac{d \ln C_\infty}{dx} \quad (2.198)$$

In fact, when $\kappa a \rightarrow \infty$, that means that $\kappa^{-1} \rightarrow 0$ (or $\lambda \rightarrow 0$), the only terms that remains is u_0 that is the lowest order contribution and the velocity of the particle is the same of eq.(??).

The lowest order terms in defined as:

$$u_0 = 2\beta\bar{\zeta} - 4 \ln \left(1 - \tanh^2 \left(\frac{ze\zeta_p}{4k_B T} \right) \right) \quad (2.199)$$

Where $\bar{\zeta} = \frac{Ze\zeta_p}{k_B T}$ is the dimensionless zeta potential.

If $|\bar{\zeta}|$ is restricted to small values, a regular expansion on power series of $\bar{\zeta}$ can be done to obtain:

$$u_1 = -6\beta\bar{\zeta} - \frac{21}{8}\bar{\zeta}^2 + O(\bar{\zeta}^3) \quad (2.200)$$

If instead the zeta potential is larger, u_1 is valuated in this way:

$$u_1 = F_0 + \beta F_1 + Pe [F_2 + \beta(F_3 + F_5) + \beta^2 F_4] \quad (2.201)$$

and all the coefficients are calculated in this way:

$$\begin{aligned} F_0 &= -\frac{21}{8}\bar{\zeta}^2 + O(\bar{\zeta}^4) & F_1 &= -6\bar{\zeta} + O(\bar{\zeta}^3) \\ F_2 &= -\frac{1}{3}\bar{\zeta}^4 + O(\bar{\zeta}^6) & F_3 &= -\frac{5}{48}\bar{\zeta}^4 + O(\bar{\zeta}^7) \\ F_4 &= -\frac{7}{12}\bar{\zeta}^4 + O(\bar{\zeta}^6) & F_5 &= -2\bar{\zeta}^3 + O(\bar{\zeta}^5) \end{aligned} \quad (2.202)$$

where the Peclet number is $Pe = \frac{\epsilon}{2\mu D_s} \left(\frac{k_B T}{ze} \right)^2$.

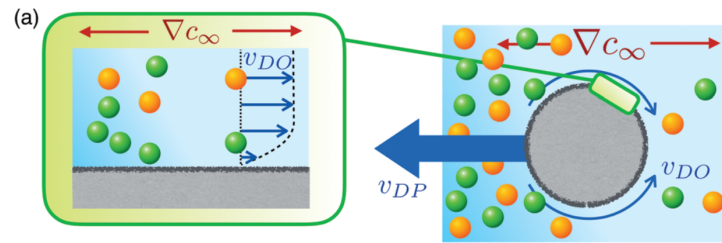


Figure 2.3: (a) Diffusio-osmosis at the surface of a particle causes it to move when subjected to a concentration gradient.

2.4 General solution of the diffusio-osmotic velocity field in a slit nanochannel

The end effects are neglected and the electric potential at the center of the micro-channel is ψ_c . The attention is focused only on the top half part of the channel. The pressure distribution can be written as

$$p(x, y) = p^\infty + 2n^\infty k_B T N_A [\cosh(\bar{\psi}(x, y)) - \cosh(\bar{\psi}_c)] \quad (2.203)$$

where now p^∞ is the centerline pressure and is constant if there is no applied pressure force.

Doing the derivative of eq.(2.203) with respect to x and substituting inside eq.(2.154) using also the Boltzmann distribution, yields

$$\eta \frac{\partial^2 u}{\partial y^2} = 2k_B T N_A \frac{dn^\infty}{dx} [\cosh(\bar{\psi}) - \cosh(\bar{\psi}_c)] + 2n^\infty z e N_A \sinh(\bar{\psi}) E \quad (2.204)$$

The following equation can be dimensionless calling $\bar{u} = u/U^*$, $\bar{y} = y/H$ $K = H/\lambda$ and $\bar{E} = E/E^\infty$, which yield

$$\frac{\partial^2 \bar{u}}{\partial \bar{y}^2} = K^2 [\cosh(\bar{\psi}) - \cosh(\bar{\psi}_c) + \beta \bar{E} \sinh(\bar{\psi})] \quad (2.205)$$

where the BC's are

$$(\bar{u})_{\bar{y}=1} = -\bar{b} \left(\frac{\partial \bar{u}}{\partial \bar{y}} \right)_{\bar{y}=1}, \quad \left(\frac{\partial \bar{u}}{\partial \bar{y}} \right)_{\bar{y}=0} = 0$$

where $\bar{b} = b/H$ is the dimensionless slip length.

Integrating with respect to \bar{y} from the centerline to an arbitrary point and then integrating the resultant equation once more from the wall to an arbitrary place, the dimensionless velocity is obtained

$$\bar{u} = K^2 \left[\int_1^{\bar{y}} \int_0^{\bar{y}} (\cosh(\bar{\psi}) - \cosh(\bar{\psi}_c) + \beta \bar{E} \sinh(\bar{\psi})) d\bar{y} d\bar{y} - \bar{b} \int_0^1 (\cosh(\bar{\psi}) - \cosh(\bar{\psi}_c) + \beta \bar{E} \sinh(\bar{\psi})) d\bar{y} \right] \quad (2.206)$$

As it can be seen, the electric field is coupled with the velocity field and to solve this problem an iterative method is needed.

When the potential ψ is low, a Taylor expansion of $\beta \bar{E}$ up to the second term can be done.

Remembering the Taylor expansion of the exponential, and hyperbolic sine and hyperbolic cosine, centered at $x = 0$ respectively

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \mathcal{O}(x^2)$$

$$\sinh(x) = \sum_{n=0}^{\infty} \frac{x^{2n+1}}{(2n+1)!} = x + \mathcal{O}(x^3)$$

$$\cosh(x) = \sum_{n=0}^{\infty} \frac{x^{2n}}{(2n)!} = 1 + \frac{x^2}{2!} + \mathcal{O}(x^4)$$

Doing the Taylor expansion of the second term of the electric field yield

$$\frac{(1+\beta) \left(1 - \bar{\psi} + \frac{\bar{\psi}^2}{2}\right) - (1-\beta) \left(1 + \bar{\psi} + \frac{\bar{\psi}^2}{2}\right)}{(1+\beta) \left(1 - \bar{\psi} + \frac{\bar{\psi}^2}{2}\right) + (1-\beta) \left(1 + \bar{\psi} + \frac{\bar{\psi}^2}{2}\right)} = \frac{2\beta - 2\bar{\psi} + \beta\bar{\psi}^2}{2 - 2\beta\bar{\psi} + \bar{\psi}^2} \quad (2.207)$$

Calling a and b the coefficients of the Taylor expansion of the numerator and denominator respectively, to calculate the coefficients c of the division, the Cauchy product of two series is applied

$$c_n = \frac{a_n - \sum_{i=0}^{n-1} c_i b_{n-i}}{b_0}$$

$$\begin{aligned} \bar{\psi}^0 : c_0 &= \frac{a_0}{b_0} = \frac{2\beta}{2} = \beta \\ \bar{\psi}^1 : c_1 &= \frac{a_1}{b_0} - \frac{b_1}{b_0} c_0 = \frac{-2}{2} - \frac{-2\beta}{2} \beta = \beta^2 - 1 \\ \bar{\psi}^2 : c_2 &= \frac{a_2}{b_0} - \frac{b_2}{b_0} c_0 - \frac{b_1}{b_0} c_1 = \frac{\beta}{2} - \frac{1}{2} \beta - \frac{-2\beta}{2} (\beta^2 - 1) = \beta(\beta^2 - 1) \end{aligned}$$

and doing the Taylor expansion of the first term of the electric field

$$\frac{Pe \bar{\psi} \bar{u}}{(1+\beta) \left(1 - \bar{\psi} + \frac{\bar{\psi}^2}{2}\right) + (1-\beta) \left(1 + \bar{\psi} + \frac{\bar{\psi}^2}{2}\right)} = \frac{Pe \bar{\psi} \bar{u}}{2 - 2\beta\bar{\psi} + \bar{\psi}^2} \quad (2.208)$$

$$\begin{aligned} \bar{\psi}^0 : c_0 &= \frac{a_0}{b_0} = 0 \\ \bar{\psi}^1 : c_1 &= \frac{a_1}{b_0} - \frac{b_1}{b_0} c_0 = \frac{Pe \bar{u}}{2} \\ \bar{\psi}^2 : c_2 &= \frac{a_2}{b_0} - \frac{b_2}{b_0} c_0 - \frac{b_1}{b_0} c_1 = \frac{\beta Pe \bar{u}}{2} \end{aligned}$$

Putting all together yield

$$\beta \bar{E} = \frac{Pe \bar{u}}{2} \left(\bar{\psi} + \beta \bar{\psi}^2 \right) + \beta + (\beta^2 - 1) \bar{\psi} + \beta(\beta^2 - 1) \bar{\psi}^2 \quad (2.209)$$

Since that the electric potential is low, the solution of the potential field for a slit microchannel was alrady done in eq.(2.74) in which in dimensionless form can be written as

$$\bar{\psi}(\bar{y}) = \bar{\zeta} \frac{\cosh(\bar{y}K)}{\cosh(K)} \quad (2.210)$$

Doing the Taylor expansion of the hyperbolic cosine, imposing that $\bar{\psi}_c = 0$ (that means the potential at the center of the channel is 0) and plugging (2.210) and (2.209) into eq.(2.205), neglecting all the terms of the power 3, yield the following differential equation

$$\begin{aligned} \frac{\partial^2 \bar{u}}{\partial \bar{y}^2} = & K^2 \left\{ 1 + \frac{\bar{\zeta}^2 \cosh^2(\bar{y}K)}{2 \cosh^2(K)} - 1 + \beta \bar{\zeta} \frac{\cosh(\bar{y}K)}{\cosh(K)} + \beta \bar{\zeta}^3 \frac{\cosh^3(\bar{y}K)}{\cosh^3(K)} + \beta^2 \bar{\zeta}^2 \frac{\cosh^2(\bar{y}K)}{\cosh^2(K)} - \bar{\zeta}^2 \frac{\cosh^2(\bar{y}K)}{\cosh^2(K)} + \right. \\ & \left. + \beta^3 \bar{\zeta}^3 \frac{\cosh^3(\bar{y}K)}{\cosh^3(K)} - \beta \bar{\zeta}^3 \frac{\cosh^3(\bar{y}K)}{\cosh^3(K)} + \frac{Pe \bar{\zeta}^2 \cosh^2(\bar{y}K)}{2 \cosh^2(K)} \bar{u} + \frac{\beta Pe \bar{\zeta}^3 \cosh^3(\bar{y}K)}{2 \cosh^3(K)} \bar{u} \right\} \Rightarrow \\ \frac{\partial^2 \bar{u}}{\partial \bar{y}^2} - \frac{K^2 Pe \bar{\zeta}^2 \cosh^2(\bar{y}K)}{2 \cosh^2(K)} \bar{u} = & \frac{K^2}{2} \left\{ (2\beta^2 - 1) \bar{\zeta}^2 \frac{\cosh^2(\bar{y}K)}{\cosh^2(K)} + 2\beta \bar{\zeta} \frac{\cosh(\bar{y}K)}{\cosh(K)} \right\} \end{aligned} \quad (2.211)$$

The solution of this differential equation can be done numerically. To have an analytical expression of the velocity profile, advection contribution to the electric field may be ignored. This can be imposed putting $Pe = 0$. Considering also no slip velocity at the walls of the channel ($\bar{b} = 0$) the following solution is obtained

$$\bar{u} = \frac{\zeta \left((2\beta - 1) (\cosh^2(Ky) + K^2 (y - 1)(y + 1) - \cosh^2(K)) \zeta + 8 \cosh(K) \beta (\cosh(Ky) - \cosh(K)) \right)}{8 \cosh^2(K)} \quad (2.212)$$

2.5 1-D Diffusion equation

The diffusion equation is a partial differential equation that is described by the following equation:

$$\frac{\partial c}{\partial t} = D_s \frac{\partial^2 c}{\partial x^2} \quad (2.213)$$

imposing a Dirichlet boundary conditions, that specify the concentration $c(x, t)$ at the boundary of the channel. The Dirichlet BC guaranteed the flux inside or outside the boundary and since that the value at the boundary is constant, this means that the boundary are like connected to a huge reservoir that allows to have a constant concentration at the boundary.

The boundary conditions are $c(0, t) = c(L, t) = 0$ and an initial condition that is $c(x, 0) = f(x)$ at $t = 0$, where $f(x)$ is an initial concentration profile.

To find a solution, the concentration profile $c(x, t)$, that is a function of two variable, is separated in two individual functions:

$$c(x, t) = F(x)G(t) \quad (2.214)$$

and substituting this solution in the partial differential equation:

$$F(x)G'(t) = D_s F''(x)G(t) \quad (2.215)$$

grouping together all the same therms:

$$\frac{1}{D_s} \frac{G'(t)}{G(t)} = \frac{F''(x)}{F(x)} \quad (2.216)$$

it can be seen that everything on the left hand side is a function of t only and on the right hand side is a function of x only. The only way that these two things are equal is that both of them are equal to a constant k . The constant k can take any value and there will be three specific cases.

Solving the equation on the right hand side, the boundary conditions now becomes $F(x) = F(L) = 0$.

Assuming that $k > 0$ e.g. $k = 1$ the differential equation to solve is:

$$\frac{d^2 F(x)}{dx^2} - F(x) = 0 \quad (2.217)$$

Postulating a solution of the type $F(x) = Ae^{\lambda x}$, differentiating it two times and substituting in the eq.(3.8), the following is obtained:

$$\begin{aligned} \lambda^2 Ae^{\lambda x} - Ae^{\lambda x} &= 0 \\ Ae^{\lambda x}(\lambda^2 - 1) &= 0 \end{aligned} \quad (2.218)$$

ignoring the trivial solution $Ae^{\lambda x} = 0$, the characteristic equation is obtained:

$$\lambda^2 - 1 = 0 \quad (2.219)$$

Where the two eigenvalues are $\lambda = \pm 1$ In conclusion, the solution of the differential equation is:

$$F(x) = A_1 e^x + A_2 e^{-x} \quad (2.220)$$

Substituting the two boundary conditions inside, the two constant are $A_1 = A_2 = 0$ and so the trivial solution $F(x) = 0$ is obtained.

The second case is when $k = 0$ and the following differential equation is:

$$\frac{d^2 F(x)}{dx^2} = 0 \quad (2.221)$$

where the solution is obtained integration twice and a linear function is obtained:

$$F(x) = A_1 x + A_2 \quad (2.222)$$

and applying the boundary condition, one again the two constant are zero and a trivial solution is obtained.

The case three is when $k < 0$ and the following equation must be solved:

$$\frac{d^2 F(x)}{dx^2} + kF(x) = 0 \quad (2.223)$$

Doing the same procedure of the case one, the eigenvalues now are $\lambda = \pm\sqrt{-k}$ and the solution is of the form:

$$F(x) = A_1 e^{\sqrt{-k}x} + A_2 e^{-\sqrt{-k}x} \quad (2.224)$$

Using the Euler Identity:

$$e^{\pm\sqrt{-k}x} = \cos(\sqrt{-k}x) \pm \sin(\sqrt{-k}x) \quad (2.225)$$

Substituting into the eq.(3.15), the solution it can be seen as a sum of sinusoidal:

$$\begin{aligned} F(x) &= A_1 [\cos(\sqrt{-k}x) + \sin(\sqrt{-k}x)] + A_2 [\cos(\sqrt{-k}x) - \sin(\sqrt{-k}x)] \\ F(x) &= (A_1 + A_2)\cos(\sqrt{-k}x) + (A_1 - A_2)\sin(\sqrt{-k}x) \\ F(x) &= B_1\cos(\sqrt{-k}x) + B_2\sin(\sqrt{-k}x) \end{aligned} \quad (2.226)$$

Substituting the boundary conditions, for $F(0) = 0$ the value of the constant is $B_1 = 0$, instead for $F(L) = 0$, $B_2\sin(\sqrt{-k}L) = 0$ and to do not get the trivial solution in which $B_2 = 0$, the following must be guarantied

$\sin(\sqrt{-k}L) = 0$. Generally, $\sin(x) = 0$ when $x = n\pi$ for $n \in \mathbb{Z}/\{0\}$ and so $k = -\frac{n^2\pi^2}{L^2} < 0, n = 1, 2, 3, \dots$

In this situation, the solution is:

$$F(x) = b_n \sin\left(\frac{n\pi x}{L}\right) \quad (2.227)$$

where b_n is a constant that might change depending on the value of n selected. Now, solving the left hand side of the eq.(3.7) using the constant k calculated:

$$\frac{1}{D_s} \frac{G'(t)}{G(t)} = -\frac{n^2\pi^2}{L^2} \quad (2.228)$$

Integrating this equation both sides respect to t and bringing D_s from the other side:

$$\begin{aligned} \ln(G(t)) &= -\frac{n^2\pi^2 D_s t}{L^2} + \alpha \\ G(t) &= B e^{-\frac{n^2\pi^2 D_s t}{L^2}} \end{aligned} \quad (2.229)$$

Combining eq.(3.18) and eq.(3.20) the general solution for $n = 1, 2, 3, \dots$ is:

$$c(x, t) = B_n \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2\pi^2 D_s t}{L^2}} \quad (2.230)$$

For each value of n , there will be a solution of the partial differential equation and since that the equation is linear, also the sum of more solutions is a solution and so the general solution of the equation is:

$$c(x, t) = \sum_{n=1}^{\infty} B_n \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2\pi^2 D_s t}{L^2}} \quad (2.231)$$

The condition that is not satisfied in the eq.(3.22) is the initial condition $c(x, 0) = f(x)$ and this will help to find the value of the coefficient B_n .

At $t = 0$, $c(x, 0) = f(x)$ and so:

$$f(x) = \sum_{n=1}^{\infty} B_n \sin\left(\frac{n\pi x}{L}\right) \quad (2.232)$$

the given initial concentration distribution is expressed as a infinity sum series.

In Fourier terms, the coefficient B_n can be calculated as follows:

$$B_n = \frac{2}{L} \int_0^L f(x) \sin\left(\frac{n\pi x}{L}\right) dx \quad (2.233)$$

Another type of boundary condition is called Neumann boundary conditions, in which is specified the rate

of change of concentration at the end of the channel.

Imposing the Neumann BC $c_x(0, t) = c_x(L, t) = 0$, it can be seen that $D_s c_x(0, t) = J(0, t) = 0$ and this represent the flux, the same thing is for $c_x(L, t)$. Imposing a Neumann BC equal to 0 means that there is no flux that can enter or exit from the boundary and so there is a conservation of mass inside the domain.

An example can be done imposing an initial linear distribution of concentration $f(x) = \frac{x}{L}(c_i - c_0) + c_0$.

As previous, the solution when the constant $k > 0$, gives trivial solution $F(x) = 0$.

The second case, in which $k = 0$, gives the normal mode solution $c(x, t) = 1$. The important one is when $k < 0$, where the solution is the same of eq.(3.17).

Inserting the BC's and the initial condition, the following solution is obtained:

$$c(x, t) = \frac{A_0}{2} + \sum_{n=1}^{\infty} A_n \cos\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2 \pi^2 D_s t}{L^2}} \quad (2.234)$$

where the coefficients are calculated in this way:

$$A_n = \frac{2}{L} \int_0^L f(x) \cos\left(\frac{n\pi x}{L}\right) dx \quad (2.235)$$

$$\frac{A_0}{2} = \frac{1}{L} \int_0^L f(x) dx \quad (2.236)$$

Applying the Neumann BC's and the initial condition, the following solution is obtained:

$$c(x, t) = \frac{c_0 + c_i}{2} + \sum_{n=1}^{\infty} \frac{2(c_i - c_0)(\cos(n\pi) - 1)}{n^2 \pi^2} \cos\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2 \pi^2 D_s t}{L^2}} \quad (2.237)$$

Since that for a Neumann BC no material is living the domain, the area below the concentration profile at time $t = 0$ must be equal at each time. When the time $t \rightarrow \infty$ an equilibrium is reached, the exponential goes to 0 and remain just the $\frac{A_0}{2}$ that represent the average of the function at time $t = 0$.

Another type of BC is called Mixed BC in which is imposed both Dirichlet and Neumann BC. This kind of BC is used for the application of the dead-end-pore.

An example can be done imposing that in all the dead-end-pore, there is a constant initial concentration $f(x) = c_i$ for $0 < x \leq L$ at $t = 0$. At the boundary $c(0, t) = c_0$ and $c_x(L, t) = 0$ and this means that at $x = L$ no mass can enter or exit, and at $x = 0$ the mass can exit and the concentration is imposed equal to the concentration in the main channel, that basically represents the huge reservoir. The initial function distribution represents a step function.

To solve this problem, since that the BC's are non-homogeneous, the solution must be divide in a transient solution $\omega(x, t)$ plus a steady-state solution $v(x)$:

$$c(x, t) = \omega(x, t) + v(x) \quad (2.238)$$

the steady-state solution is when $t \rightarrow \infty$, the transient solution is 0, $\frac{\partial c(x, t)}{\partial t} = 0$ and so the following equation must be solved:

$$\begin{aligned} D_s \frac{\partial^2 c(x, t)}{\partial x^2} &= 0 \\ \Rightarrow \frac{d^2 v(x)}{dx^2} &= 0 \end{aligned} \quad (2.239)$$

Integrating twice eq.(2.239), the following solution is obtained $v(x) = c_1 x + c_2$ and applying BC's the steady-state solution is $v(x) = c_0$.

Now the transient concentration must be solved and the equation is:

$$\frac{\partial \omega(x, t)}{\partial t} = D_s \frac{\partial^2 \omega(x, t)}{\partial x^2} \quad (2.240)$$

The BC's and the initial condition for the transient are:

$$\begin{aligned} \omega(0, t) &= c(0, t) - v(0) = c_0 - c_0 = 0 \\ \omega_x(L, t) &= c_x(L, t) - v'(L) = 0 - 0 = 0 \\ \omega(x, 0) &= c(x, 0) - v(x) = f(x) - c_0 \end{aligned}$$

as can be seen, the BC's are now homogeneous and so the problem to solve is already done. The solution is looked for the third case in which $k < 0$ the solution is the same of eq.(3.17).

Imposing the BC's $F(0) = 0$ and $F'(L) = 0$, it is obtained $B_1 = 0$ and $\sqrt{-k} B_2 \cos(\sqrt{-k} L) = 0$ and to do not get the trivial solution in which $B_2 = 0$, the following must be guaranteed $\cos(\sqrt{-k} L) = 0$. In general, $\cos(x) = 0$ when $x = \frac{2n+1}{2} \pi$ for $n \in \mathbb{Z}$ and so $k = -\left(\frac{2n+1}{2L} \pi\right)^2 < 0, n = 0, 1, 2, 3, \dots$. In this situation, the solution is:

$$F(x) = b_n \sin\left(\frac{2n+1}{2L} \pi x\right) \quad (2.241)$$

Now, solving the left hand side of the eq.(2.240) using the constant k calculated, the solution is obtained:

$$G(t) = B e^{-\left(\frac{2n+1}{2L} \pi\right)^2 D_s t} \quad (2.242)$$

Combining eq.(2.241) and eq.(2.242) the general solution for $n = 0, 1, 2, 3, \dots$ is:

$$\omega(x, t) = \sum_{n=0}^{\infty} B_n \sin\left(\frac{2n+1}{2L} \pi x\right) e^{-\left(\frac{2n+1}{2L} \pi\right)^2 D_s t} \quad (2.243)$$

Applying initial condition:

$$\omega(x, 0) = \sum_{n=0}^{\infty} B_n \sin\left(\frac{2n+1}{2L}\pi x\right) = f(x) - c_0 \quad (2.244)$$

the coefficient B_n is:

$$B_n = \frac{2}{L} \int_0^L (f(x) - c_0) \sin\left(\frac{2n+1}{2L}\pi x\right) dx \quad (2.245)$$

and using superposition principle, the general solution is:

$$c(x, t) = c_0 + \sum_{n=0}^{\infty} B_n \sin\left(\frac{2n+1}{2L}\pi x\right) e^{-\left(\frac{2n+1}{2L}\pi\right)^2 D_s t} \quad (2.246)$$

Since that $f(x) = c_i$, the final solution is obtained:

$$c(x, t) = c_0 + 4(c_i - c_0) \sum_{n=0}^{\infty} \frac{1}{(2n+1)\pi} \sin\left(\frac{2n+1}{2L}\pi x\right) e^{-\left(\frac{2n+1}{2L}\pi\right)^2 D_s t} \quad (2.247)$$

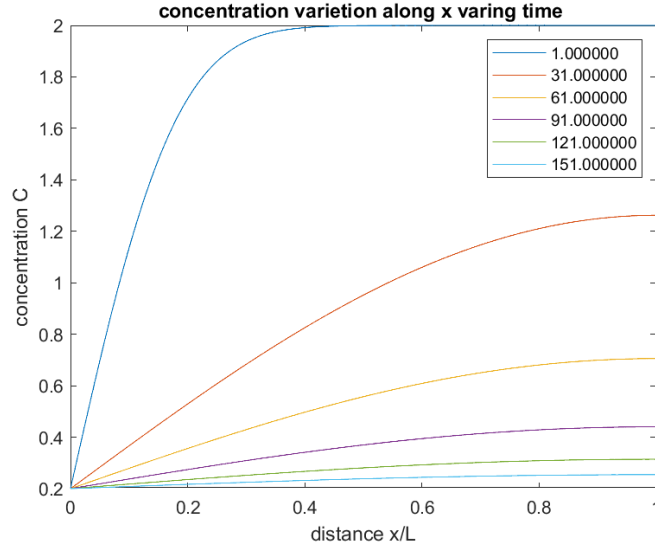


Figure 2.4: plot of eq.(2.247) in which at time $t=0$ the concentration has a step function and when the time increase the concentration decays up to c_0 . Length of dead-end-pore $L = 4 \cdot 10^{-4}m$, $c_i = 2$, $D_s = 1.607 \cdot 10^{-9}m^2/s$ and $c_0 = 2 \cdot 10^{-1}$

To obtain the particle velocity, the derivative of the logarithm of eq.(2.247) must be done.

$$\frac{\partial}{\partial x} \ln(c(x, t)) = \frac{\frac{\partial}{\partial x} c(x, t)}{c(x, t)} = \frac{\frac{2}{L}(c_i - c_0) \sum_{n=1}^{\infty} \cos\left(\frac{2n+1}{2L}\pi x\right) e^{-\left(\frac{2n+1}{2L}\pi\right)^2 D_s t}}{c_0 + 4(c_i - c_0) \sum_{n=0}^{\infty} \frac{1}{(2n+1)\pi} \sin\left(\frac{2n+1}{2L}\pi x\right) e^{-\left(\frac{2n+1}{2L}\pi\right)^2 D_s t}}$$

For simplicity of calculation, the series at the numerator will start from 0 and instead to have n , $(n + 1)$ is substituted:

$$\frac{\partial}{\partial x} \ln(c(x, t)) = \frac{\frac{\partial}{\partial x} c(x, t)}{c(x, t)} = \frac{\frac{2}{L}(c_i - c_0) \sum_{n=0}^{\infty} \cos\left(\frac{2n+3}{2L}\pi x\right) e^{-\left(\frac{2n+3}{2L}\pi\right)^2 D_s t}}{c_0 + 4(c_i - c_0) \sum_{n=0}^{\infty} \frac{1}{(2n+1)\pi} \sin\left(\frac{2n+1}{2L}\pi x\right) e^{-\left(\frac{2n+1}{2L}\pi\right)^2 D_s t}} \quad (2.248)$$

It was observed that the eq.(2.248) implemented in MATLAB does not work and so the gradient of the logarithmic of the concentration of salt was solved in MATLAB numerically, using eq.(2.247).

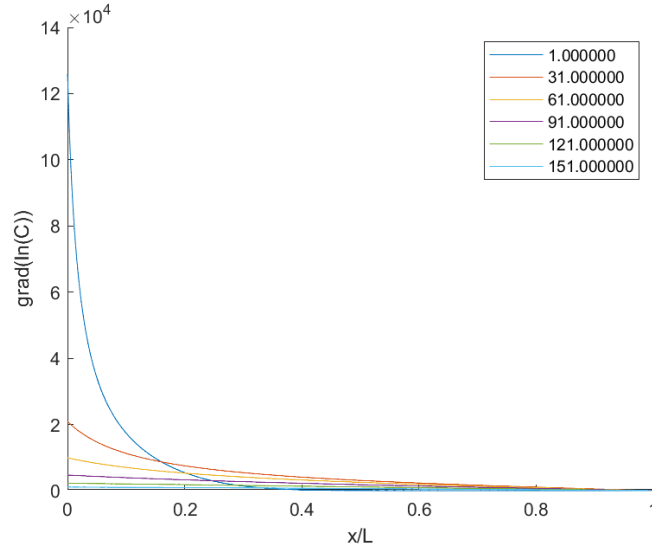


Figure 2.5: the results are obtained using a length of channel $L = 4 \cdot 10^{-4}m$, initial concentration of salt $c_i = 2$ and fixed concentration at the boundary $c_0 = 2 \cdot 10^{-1}$

2.6 Lubrication theory

Consider a 2-D planar geometry flow in a narrow gap where $h = h(x)$ and one of the boundary is moving related with the other. h_0 is the characteristic length scale along y and l_c is the characteristic length scale along x .

The condition to be satisfied are:

- 1) $h(x)$ vary slowly along x ;
- 2) $h_0 \ll l_c$.

The basic idea in general, is the analysis of flow when there are at least two distinctive length and velocity scales involved with the flow. One each of the velocity and length scales are much larger than the other. Therefore, there is a dominant length scale and a dominant direction of flow.

In boundary layer theory it is considered a flat plat and close to the wall there is a region where velocity gradients exist because of viscous effects. Outside that region, there is in-viscid flow.

The boundary layer is a layer adhering to the solid boundary in which viscous effects are failed and the thickness of boundary layer depends on the Reynolds number. If the Reynolds number is large, then the thickness of the layer is very small and on the other hand if Reynolds number is small, viscous effects are so highly penetrating that the fluid which is even located at a very far stream, feels the effect of the solid boundary explicitly. So, boundary layer thickness can be anything from very small to infinitely large but, for the case where the boundary layer thickness is infinitely large, the boundary layer theory cannot be applied. Boundary layer theory is only valid for high Reynolds number flows, provided there is no boundary layer separation.

In boundary layer theory there are two different scales and can be applied only if $\delta \ll L$.

There is a similarity of boundary layer theory and lubrication theory but the physics of these two problems are completely different.

In the lubrication theory, inertial effects are usually negligible (at least in the leading order), as long as Reynolds number is not very high. In microfluidics concepts the Reynolds number is very small.

For notation applications, the " * " symbol is used for dimensional quantities and without asterisk the dimensionless quantities.

The confinement is made up of two boundaries (walls). There is bottom wall and s top wall. The top wall moves with arbitrary velocity $\mathbf{V}^* = U^* \mathbf{e}_x + V^* \mathbf{e}_y$ related to the bottom wall, both along x and y . The ratio $\epsilon = \frac{h_0}{l_c} \ll 1$. The x -velocity is of the order of u_c ($u^* \sim u_c$). u_c is not known and it depends on the physics that governs the problem. The y -velocity is of the order of v_c ($v^* \sim v_c$), the Reynolds number is $Re = \frac{\rho u_c l_c}{\mu}$

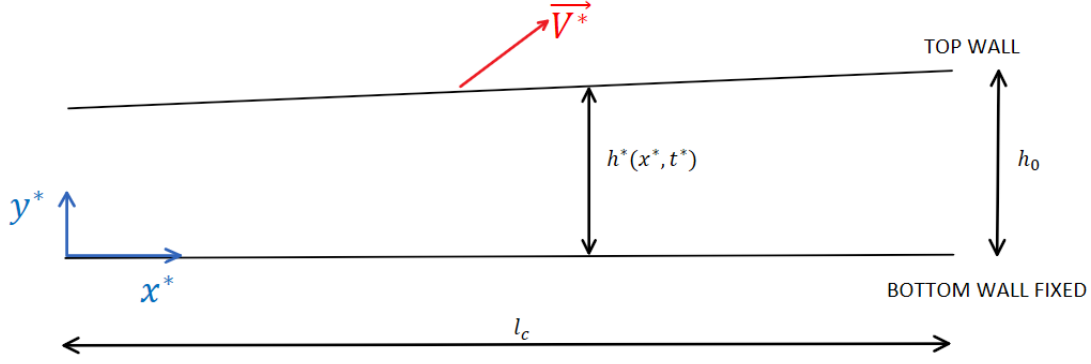


Figure 2.6

The 2-D continuity equation for incompressible flow is:

$$\frac{\partial u^*}{\partial x^*} + \frac{\partial v^*}{\partial y^*} = 0 \quad (2.249)$$

where $\frac{\partial u^*}{\partial x^*} \sim \frac{u_c}{l_c}$ and $\frac{\partial v^*}{\partial y^*} \sim \frac{v_c}{h_0}$. If the top plate velocity is the dominant influence, than its velocity along the x is the characteristic scale u_c . At this state u_c is totally arbitrary. They must have the same scale so that the net effective is 0, so this means:

$$\begin{aligned} \frac{u_c}{l_c} &\sim \frac{v_c}{h_0} \\ \Rightarrow v_c &\sim u_c \epsilon \end{aligned} \quad (2.250)$$

Since that ϵ is small, there is one dominant flow direction that is u_c .

The x -momentum equation is:

$$\rho \left[\frac{\partial u^*}{\partial t^*} + u^* \frac{\partial u^*}{\partial x^*} + v^* \frac{\partial u^*}{\partial y^*} \right] = -\frac{\partial p^*}{\partial x^*} + \mu \left(\frac{\partial^2 u^*}{\partial x^{*2}} + \frac{\partial^2 u^*}{\partial y^{*2}} \right) + F_x^* \quad (2.251)$$

To non-denationalize the eq.(2.251), the following dimensionless quantities are defined:

$$u = \frac{u^*}{u_c}, \quad v = \frac{v^*}{v_c}, \quad x = \frac{x^*}{l_c}, \quad y = \frac{y^*}{h_0}, \quad p = \frac{p^*}{p_c}, \quad F_x = \frac{F_x^*}{F_{xc}}, \quad t = \frac{t^*}{t_c}$$

There are different possibilities of choosing the time scale t_c like advective time scale, diffusive time scale, forcing base time scale. An appropriate choose could be advection base time scale and is $t_c = \frac{l_c}{u_c}$ Inserting them into the equation:

$$\rho \left[\frac{u_c}{t_c} \frac{\partial u}{\partial t} + \frac{u_c^2}{l_c} u \frac{\partial u}{\partial x} + \frac{v_c u_c}{h_0} v \frac{\partial u}{\partial y} \right] = -\frac{p_c}{l_c} \frac{\partial p}{\partial x} + \mu \left(\frac{u_c}{l_c^2} \frac{\partial^2 u}{\partial x^2} + \frac{u_c}{h_0^2} \frac{\partial^2 u}{\partial y^2} \right) + F_x F_{xc}$$

inserting t_c and knowing from continuity equation that $\frac{v_c}{h_0} = \frac{u_c}{l_c}$ the equation becomes:

$$\rho \left[\frac{u_c^2}{l_c} \frac{\partial u}{\partial t} + \frac{u_c^2}{l_c} u \frac{\partial u}{\partial x} + \frac{u_c^2}{l_c} v \frac{\partial u}{\partial y} \right] = -\frac{p_c}{l_c} \frac{\partial p}{\partial x} + \mu \left(\frac{u_c}{l_c^2} \frac{\partial^2 u}{\partial x^2} + \frac{u_c}{h_0^2} \frac{\partial^2 u}{\partial y^2} \right) + F_x F_{xc}$$

$$\rho \frac{u_c^2}{l_c} \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = -\frac{p_c}{l_c} \frac{\partial p}{\partial x} + \mu \frac{u_c}{h_0^2} \left(\frac{h_0^2}{l_c^2} \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + F_x F_{xc}$$

multiplying both sides by $\frac{h_0^2}{\mu u_c}$

$$\rho \frac{u_c^2}{l_c} \frac{h_0^2}{\mu u_c} \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = -\frac{p_c}{l_c} \frac{h_0^2}{\mu u_c} \frac{\partial p}{\partial x} + \left(\epsilon^2 \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + F_x F_{xc} \frac{h_0^2}{\mu u_c} \quad (2.252)$$

The order of magnitude of various terms depends on how the terms are non denationalized. There is a key difference between normalizing with appropriate scale and any non denationalization.

For example in this problem, one it could non denationalize $y = \frac{y^*}{l_c}$ as well, because l_c is also a length but that is not a proper scaling based normalization since that y^* is ranging from 0 to h_0 and not from 0 to l_c . If one variable is normalized with its range, then the dimensionless parameters are constrain to be within 0 to 1 in terms of order. All the derivatives then are also constrain to be within 0 and 1.

After this discussion, it can be seen that $\frac{\partial^2 u}{\partial y^2} \sim 1$ and $\epsilon^2 \frac{\partial^2 u}{\partial x^2} \sim \epsilon^2$. It can be concluded that $\epsilon^2 \frac{\partial^2 u}{\partial x^2}$ is asymptotically smaller then $\frac{\partial^2 u}{\partial y^2}$.

When there is a competition between viscous force and force due to pressure gradient and an appropriate choice of the pressure scale should be such that $\frac{p_c}{l_c} \frac{h_0^2}{\mu u_c} \sim 1$ and so $p_c = \frac{\mu u_c l_c}{h_0^2} = \frac{\mu u_c}{\epsilon^2 l_c}$.

$\rho \frac{u_c^2}{l_c} \frac{h_0}{\mu u_c} = \frac{\rho u_c l_c}{\mu} \left(\frac{h_0}{l_c} \right)^2 = Re \epsilon^2$ and $\frac{h_0^2}{\mu u_c} = \frac{\epsilon^2 l_c^2}{\mu u_c}$. Inserting this into eq.(2.252) the following is obtained:

$$Re \epsilon^2 \left[\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right] = -\frac{\partial p}{\partial x} + \left(\epsilon^2 \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + F_x F_{xc} \frac{\epsilon^2 l_c^2}{\mu u_c} \quad (2.253)$$

The terms that multiply ϵ^2 are negligible but the last term on the right hand side cannot be said that is negligible because the scale of F_{xc} is not known and u_c is also not known.

The asymptotic expansion can be done if there are two important constrains that are obeyed: 1) ϵ is small; 2) the parameters $\alpha_1, \alpha_2, \alpha_3, \dots$ are constrain to be within 1. This condition is ensure by considering appropriate scale for normalization. That why the equations are dimensionless.

$$u = u_0 + \epsilon u_1 + \epsilon^2 u_2 + \dots$$

$$v = v_0 + \epsilon v_1 + \epsilon^2 v_2 + \dots$$

$$p = p_0 + \epsilon p_1 + \epsilon^2 p_2 + \dots$$

At the end, inserting the expansion, the final leading order x -momentum equation is obtained:

$$0 = -\frac{\partial p_0}{\partial x} + \frac{\partial^2 u_0}{\partial y^2} + F_x F_{xc} \frac{\epsilon^2 l_c^2}{\mu u_c} \quad (2.254)$$

and if no body force is present, the last term is 0:

$$\frac{\partial p_0}{\partial x} = \frac{\partial^2 u_0}{\partial y^2} \quad (2.255)$$

The viscous stress μ^* is of the order of $\mu \frac{u_c}{h_0}$ but $h_0 = \epsilon l_c$ and so the viscous stress scales with $\frac{1}{\epsilon}$. The pressure instead scales as $\frac{1}{\epsilon^2}$ and so the pressure is dominating respect to the viscous stress.

Now the y -momentum equation is written:

$$\rho \left[\frac{\partial v^*}{\partial t^*} + u^* \frac{\partial v^*}{\partial x^*} + v^* \frac{\partial v^*}{\partial y^*} \right] = -\frac{\partial p^*}{\partial y^*} + \mu \left(\frac{\partial^2 v^*}{\partial x^{*2}} + \frac{\partial^2 v^*}{\partial y^{*2}} \right) + F_y^* \quad (2.256)$$

Using the suitable scaling parameters to non desensitize the equation:

$$v = \frac{v^*}{v_c}, u = \frac{u^*}{u_c}, x = \frac{x^*}{l_c}, y = \frac{y^*}{h_0}, p = \frac{p^*}{p_c}, F_x = \frac{F_y^*}{F_{yc}}, t = \frac{t^*}{t_c}$$

Since that the pressure is just a scalar, the same pressure scale has to be considered $p_c = \frac{\mu u_c}{\epsilon^2 l_c}$

$$\rho \frac{u_c v_c}{l_c} \left[\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right] = -\frac{p_c}{h_0} \frac{\partial p}{\partial y} + \mu \frac{v_c}{h_0^2} \left(\frac{h_0^2}{l_c^2} \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + F_y F_{yc}$$

and multiplying both sides by $\frac{h_0^2}{\mu v_c}$

$$\rho \frac{u_c v_c h_0^2}{\mu l_c v_c} \left[\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right] = -\frac{\mu u_c h_0^2}{\epsilon^2 l_c h_0 \mu v_0} \frac{\partial p}{\partial y} + \left(\epsilon^2 \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + F_y F_{yc} \frac{h_0^2}{\mu v_c}$$

knowing that $\frac{u_c v_c h_0^2}{\mu l_c v_c} = \frac{\rho u_c \epsilon^2 l_c}{\mu} = Re \epsilon^2$, $\frac{\mu u_c h_0^2}{\epsilon^2 l_c h_0 \mu v_0} = \frac{1}{\epsilon^2}$ and $\frac{h_0^2}{\mu v_c} = \frac{l_c^2 \epsilon^2}{\mu u_c \epsilon} = \frac{l_c^2 \epsilon}{\mu}$ and multiplying both sides by ϵ^2 the following is obtained:

$$Re \epsilon^4 \left[\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right] = -\frac{\partial p}{\partial y} + \left(\epsilon^4 \frac{\partial^2 v}{\partial x^2} + \epsilon^2 \frac{\partial^2 v}{\partial y^2} \right) + F_y F_{yc} \frac{\epsilon^3 l_c^2}{\mu u_c} \quad (2.257)$$

and making the asymptotic expansion, the final leading order y -momentum equation, considering no body force, is obtained:

$$\frac{\partial p_0}{\partial y} = 0 \quad (2.258)$$

From eq.(2.258) it can be seen that the pressure do not depends on y and so the governing equation, in absence of body force, can be written in this way:

$$\frac{\partial^2 u_0}{\partial y^2} = \frac{dp_0}{dx} \quad (2.259)$$

The continuity equation in the leading order is:

$$\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} = 0 \quad (2.260)$$

2.6.1 Problem of dead-end-pore

In the dead-end-pore, where there is a sale concentration, the walls of the channel are negative charged and this cause the slip velocity at the two walls due to diffusiosmosis. The slip velocity generate a flow field v_f that can be calculated using the lubrication theory.

The dead-end-pore in of constant length L and the high of the channel is $2h$, where $L \gg 2h$. The reference system is placed at the center of the channel.

To solve the problem, the eq.(2.259) and eq.(2.260) must be used with the appropriate boundary conditions.

Integrating twice the x -momentum equation with respect to y

$$\begin{aligned}\frac{\partial^2 u_0}{\partial y^2} &= \frac{dp_0}{dx} \\ \frac{\partial u_0}{\partial y} &= \frac{dp_0}{dx} y + c_1(x) \\ u_0 &= \frac{dp_0}{dx} \frac{y^2}{2} + c_1(x)y + c_2(x)\end{aligned}\tag{2.261}$$

The first boundary condition is due to symmetry of velocity profile with respect to the axis of the channel and so at $y = 0$, $\frac{\partial u_0}{\partial y} = 0$ and from this, the constant $c_1(x) = 0$.

The second boundary condition is due to velocity slip at the two walls, where the velocity is equal to $u_0 = -\Gamma_w \frac{d \ln c(x)}{dx}$ at $y = h$ and from this the constant $c_2(x) = -\frac{dp_0}{dx} \frac{h^2}{2} - \Gamma_w \frac{d \ln c(x)}{dx}$.

Inserting these two constant the following is obtained:

$$u_0 = \frac{dp_0}{dx} \left[\frac{y^2}{2} - \frac{h^2}{2} \right] - \Gamma_w \frac{d \ln c(x)}{dx}\tag{2.262}$$

Derivating eq.(2.262) with respect to x :

$$\frac{\partial u_0}{\partial x} = \frac{d^2 p_0}{dx^2} \left[\frac{y^2}{2} - \frac{h^2}{2} \right] - \Gamma_w \frac{d^2 \ln c(x)}{dx^2}\tag{2.263}$$

and using continuity equation, eq.(2.260)

$$\frac{\partial v_0}{\partial y} = -\frac{d^2 p_0}{dx^2} \left[\frac{y^2}{2} - \frac{h^2}{2} \right] + \Gamma_w \frac{d^2 \ln c(x)}{dx^2}\tag{2.264}$$

Integrating eq.(2.264) with respect to y :

$$v_0 = -\frac{d^2 p_0}{dx^2} \left[\frac{y^3}{6} - \frac{h^2}{2} y \right] + \Gamma_w \frac{d^2 \ln c(x)}{dx^2} y + c_3(x)\tag{2.265}$$

The third boundary condition is to not have fluid penetration at the wall, that at $y = h$, $v_0 = 0$ and the coefficient $c_3(x) = -\frac{d^2 p_0}{dx^2} \frac{h^3}{3} - \Gamma_w \frac{d^2 \ln c(x)}{dx^2} h$.

Inserting the constant the following is obtained:

$$v_0 = -\frac{d^2 p_0}{dx^2} \left[\frac{y^3}{6} - \frac{h^2}{2} y + \frac{h^3}{3} \right] - \Gamma_w \frac{d^2 \ln c(x)}{dx^2} (h - y)\tag{2.266}$$

The fourth boundary condition is also no fluid penetration at the other wall, at $y = -h$, $v_0 = 0$ and inserting this into the eq.(2.266) the following equation can be obtained:

$$\frac{d^2 p_0}{dx^2} = -3\Gamma_w \frac{d^2 \ln c(x)}{dx^2} \frac{1}{h^2} \quad (2.267)$$

Inserting eq.(2.267) into eq.(2.266) the velocity is obtained:

$$v_0 = \frac{\Gamma_w}{2} \frac{d^2 \ln c(x)}{dx^2} \left[y \left(\left(\frac{y}{h} \right)^2 - 1 \right) \right] \quad (2.268)$$

Integrating eq.(2.267):

$$\frac{dp_0}{dx} = -3\Gamma_w \frac{d \ln c(x)}{dx} \frac{1}{h^2} + c_4(x) \quad (2.269)$$

Imposing that at $x = L$, $\frac{dp_0}{dx} = 0$ and knowing that $\Gamma_w \frac{d \ln c(L)}{dx} = 0$, the constant $c_4(x) = 0$ and so, inserting eq.(2.269) inside eq.(2.262) the following velocity is obtained:

$$u_0 = -\frac{\Gamma_w}{2} \frac{d \ln c(x)}{dx} \left[3 \left(\frac{y}{h} \right)^2 - 1 \right] \quad (2.270)$$

2.7 1-D advection-diffusion equation with constant coefficients

The advection diffusion equation is a second-order partial differential equation and for an incompressible flow, since that $\nabla \cdot \mathbf{v} = 0$, the equation is written in non-conservative form:

$$\frac{\partial n}{\partial t} = D_p \frac{\partial^2 n}{\partial x^2} - v \frac{\partial n}{\partial x} \quad (2.271)$$

where D_p and v are constant. For simplicity, the eq.(2.271) is written using subscription notation:

$$n_t = D_p n_{xx} - v n_x \quad (2.272)$$

eq.(2.272) is valid within the following boundaries:

$$0 < x < L, \quad 0 < t < \infty$$

and the initial condition is that the concentration n of colloids at time $t = 0$, as an initial distribution $n(x, 0) = f(x)$.

To solve eq.(2.271), the basic idea is to transform it into a diffusion equation where the solution is well known. This can be done, assuming that $n(x, t)$ can be rewritten as:

$$n(x, t) = A(x, t)g(x, t) \quad (2.273)$$

The function $A(x, t)$ must be found imposing the condition that the convection term vn_x of eq.(2.272) disappears.

Substituting eq.(2.273) into eq.(2.272), with the respective derivatives, leads to:

$$A_t g + A g_t = D_p (A_{xx} g + 2A_x g_x + A g_{xx}) - v (A_x g + A g_x) \quad (2.274)$$

than dividing by A and rearranging the equation will result in:

$$g_t = D_p g_{xx} + \left(2D_p \frac{A_x}{A} - v \right) g_x + \left(-v \frac{A_x}{A} + D_p \frac{A_{xx}}{A} - \frac{A_t}{A} \right) g \quad (2.275)$$

to obtain the diffusion equation, the two brackets on the right and side must be 0:

$$\begin{aligned} 2D_p \frac{A_x}{A} - v &= 0 \\ -v \frac{A_x}{A} + D_p \frac{A_{xx}}{A} - \frac{A_t}{A} &= 0 \end{aligned} \quad (2.276)$$

The first condition is a differential equation and the solution is:

$$A = C(t) e^{\frac{v}{2D_p} x} \quad (2.277)$$

To find the coefficient $C(t)$, (2.277) must be inserted inside the second condition of eq.(2.276). Before do that, all the derivatives of (2.277) must be done:

$$\begin{aligned} A_t &= C_t e^{\frac{v}{2D_p}x} = \frac{C_t}{C} A \\ A_x &= C \frac{v}{2D_p} e^{\frac{v}{2D_p}x} = \frac{v}{2D_p} A \\ A_{xx} &= C \frac{v^2}{4D_p^2} e^{\frac{v}{2D_p}x} = \frac{v^2}{4D_p^2} A \end{aligned}$$

multiplying the second condition of eq.(2.276) by A and substituting:

$$\frac{C_t}{C} A = D_p \frac{v^2}{4D_p^2} A - v \left(\frac{v}{2D_p} A \right) \quad (2.278)$$

Putting in evidence the function A leads to:

$$\left(\frac{C_t}{C} - \frac{v^2}{4D_p} + \frac{v^2}{2D_p} \right) A = 0 \quad (2.279)$$

and to not get the trivial solution, in which A=0, the brackets must be 0 and rearranging it, the following differential equation is obtained:

$$\frac{C_t}{C} + \frac{v^2}{4D_p} = 0 \quad (2.280)$$

and the solution of eq.(2.279) is:

$$C(t) = A_0 e^{-\frac{v^2}{4D_p}t} \quad (2.281)$$

inserting (2.281) inside (2.277):

$$A = A_0 e^{-\frac{v^2}{4D_p}t} e^{\frac{v}{2D_p}x} \quad (2.282)$$

the transformation of the advection-diffusion equation, is valid for all values of the constant A_0 . To simplify the problem let's impose that $A_0 = 1$ and substitution (2.282) into (2.273) leads to:

$$n(x, t) = e^{-\frac{v^2}{4D_p}t} e^{\frac{v}{2D_p}x} g(x, t) \quad (2.283)$$

The problem now to solve is the following partial differential equation (diffusion equation):

$$g_t = D_p g_{xx} \quad (2.284)$$

The initial condition that are given for the $n(x, t)$ function, must be adjusted for the $g(x, t)$ function in this way:

$$\begin{aligned}
n(x, 0) &= A(x, 0)g(x, 0) = e^{\frac{v}{2D_p}x} g(x, 0) = f(x) \\
\Rightarrow g(x, 0) &= e^{-\frac{v}{2D_p}x} f(x)
\end{aligned} \tag{2.285}$$

Imposing an homogeneous Dirichlet boundary condition in which $n(0, t) = n(L, t) = 0$, using eq.(2.283), the corresponding boundary conditions for the $g(x, t)$ function are $g(0, t) = g(L, t) = 0$.

The solution of this problem was already done and the solution is found in eq.(3.22).

The general solution for the function $n(x, t)$ is:

$$n(x, t) = e^{-\frac{v^2}{4D_p}t} e^{\frac{v}{2D_p}x} \sum_{n=1}^{\infty} B_n \sin\left(\frac{n\pi x}{L}\right) e^{-\frac{n^2\pi^2 D_p t}{L^2}} \tag{2.286}$$

and B_n is calculated as (3.24).

2.8 2D channel diffusiophoresis

In the following section, the phenomenon of diffusiophoresis is simulated using OpenFOAM. A straight channel geometry is used and doing a 1D simulation (along the x axis). The total length of the channel is $L = 400 \cdot 10^{-6}m$ and is fully filled with a uniform salt concentration. The geometry used is a dead-end-channel, the right boundary is closed, the left hand side is open. The salt, due to difference of concentration at the inlet boundary, tends to diffuse toward the left direction.

When a salt is putted in a water, tend to dissolve and release cation and anions. To understand the movement of the ions, the Nerst Planck equation eq.(2.60) is used. To do not avoid confusion between salt and colloidal particles concentration, the letter c is used for the concentration of the salt, instead n for the concentration of colloidal particles.

Considering $NaCl$ dissolved in water. The molar mass of $NaCl$ is $58.44g/mol$. The number of moles of a substance is the ratio of its mass to its molar mass:

$$\text{Number of molar of a substance} = \frac{\text{Mass in g}}{\text{Molar mass in g/mol}} \quad (2.287)$$

The Molar concentration is the number of moles of a substance (solute) that can dissolve in 1L of solution (water). The molar concentration is often referred to its molarity:

$$\text{Molarity (mol/L)} = \frac{\text{Amount of solute (in mol)}}{\text{Volume of solution (in L)}} \quad (2.288)$$

$NaCl$ is a strong electrolyte, therefore it will dissociate completely into its constituent ions. Therefore one formula unit of $NaCl$ will dissociate to give one Na^+ ion and one Cl^- ion; in total two ions. Remembering that 1 mole of a species contains $6.022 \cdot 10^{23}$ number of atoms/molecules/ions/any other species.

For the case of binary salt like 1:1 ($NaCl$, KI), 2:2 (CaS , MgO),... in which $z_+ = -z_- = z$, the concentration of cation and anions is the same $c_+ = c_- = c$, because the number of ions of the anion and cation are the same. In the case of a binary salt like 2:1, 4:1,..., the concentration of anions and cations is different because the valence of each ion is different, and so the number of ions created in the dissociation of the salt are different for cation and anion due to the fact that the electroneutrality of the solution must be guaranteed. What remain constant is the ratio of the concentration to the number of ions produced by the dissociation of one molecule of electrolyte (called ν) and so $c = \frac{c_+}{\nu_+} = \frac{c_-}{\nu_-}$. The equation of transport of salt can be written as

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{u}) = \nabla \cdot (D_i \nabla c) + \nabla \cdot \left(D_i \frac{cz_i e}{k_B T} \nabla \psi \right) \quad (2.289)$$

Subtracting the Nerst-Planck equation of the anion from the cation the following is obtained:

$$(D_+ - D_-)\nabla^2 c + (D_+ z_+ - D_- z_-) \frac{e}{k_B T} \nabla \cdot (c \nabla \psi) = 0 \Rightarrow \nabla \cdot (c \nabla \psi) = \frac{(D_- - D_+) \nabla^2 c}{(D_+ z_+ - D_- z_-)} \frac{k_B T}{e} \quad (2.290)$$

Substituting this relation in the Nerst Planck equation of cation (or anion), yield

$$\begin{aligned} \frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{u}) &= D_+ \nabla^2 c + D_+ z_+ \frac{(D_- - D_+) \nabla^2 c}{(D_+ z_+ - D_- z_-)} \\ &= \left(\frac{\cancel{D_+^2 z_+} - D_+ D_- z_- + D_+ D_- z_+ - \cancel{D_+^2 z_+}}{D_+ z_+ - D_- z_-} \right) \nabla^2 c = D_s \nabla^2 c \end{aligned} \quad (2.291)$$

where $D_s = \frac{D_+ D_- (z_+ - z_-)}{D_+ z_+ - D_- z_-}$ is the diffusion coefficient of the generic binary salt.

For a binary salt like *NaCl* instead $D_s = \frac{2D_+ D_-}{D_+ + D_-}$. In case of absence of flow, eq.(2.291) reduces to the diffusion equation of the concentration c of salt

$$\frac{\partial c}{\partial t} = D_s \nabla^2 c \quad (2.292)$$

The colloidal particles instead are injected from the left side of the channel. The colloidal particles density is n and the equation that govern the transport of these particles is the advection diffusion equation. Denoting $\mathbf{v} = \mathbf{u}_p + \mathbf{u}$ the total velocity composed by diffusiohoresis velocity of the particle and velocity of the fluid, yield

$$\frac{\partial n}{\partial t} = D_p \nabla^2 n - \nabla \cdot (\mathbf{v} n) \quad (2.293)$$

where D_p is the diffusion coefficient of the colloidal particles $D_p = \frac{k_B T}{6\pi\eta R}$, and R is the radius of the particle.

Chapter 3

Flow Through Porous Media

3.1 Introduction

The properties that we are interested in are averaged over a Representative elementary volume (REV). It is not interested what happen at the pore scale but what happens at continuum scale where in the REV properties are continuous and uniform. For flow through porous media there is mass and momentum that is conserved.

The Representative elementary volume (REV) is the smallest volume over which a measurement can be made, that will yield a value representative of the whole volume.

Supposing to calculate the porosity of a porous media that is represented in the following picture

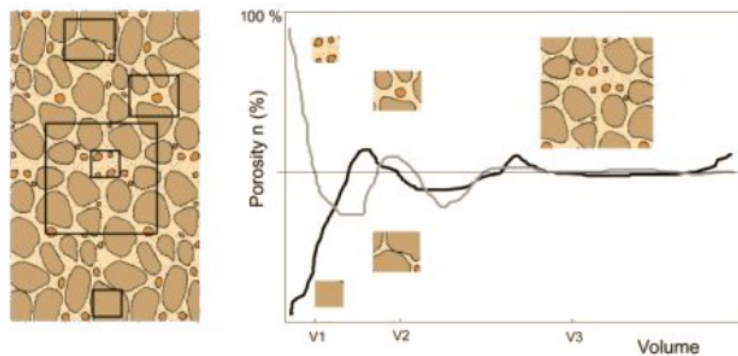


Figure 3.1

Depending on the place or location of the measurement, different values of the porosity are obtained. In the picture is plotted the porosity vs size of the window.

As can be seen in the figure, if the window at the bottom is used, since that the majority of that window is

covered by the solid phase, the porosity is very low. If the same window (V1) is placed in another place, the porosity will increase since that in that window the majority is covered by the void space. If the window is large enough (V3), the same value of the porosity is obtained no matter the window is placed.

A porous material is a material containing pores (voids). The skeleton portion of the material often called the "matrix". The pores are typically filled with fluid.

The porosity is the measure of the void or empty spaces inside a material. It can vary from 0 to 1 (or in percentage 0 to 100). If V_{void} is the volume of the void and V_{total} is the total volume of the material, then the porosity is defined by

$$\phi = \frac{V_{void}}{V_{total}} \quad (3.1)$$

The void space of the material is occupied by liquids or gases. The permeability is the measure of ease with which the fluid can move inside the porous material. The S.I. unit of permeability is m^2 .

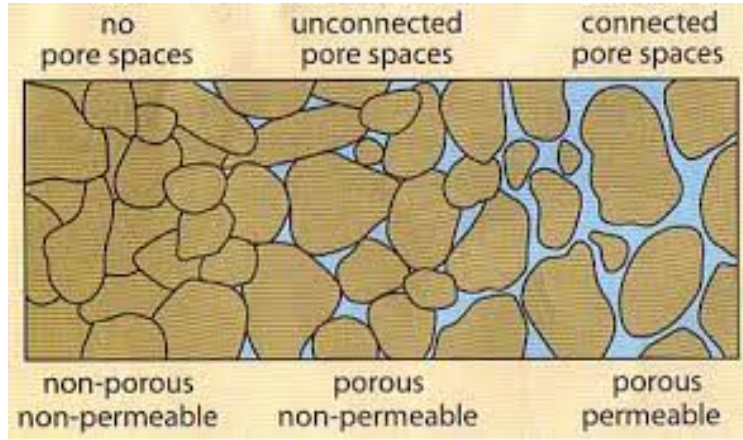


Figure 3.2

Permeability depends on the distribution or connectivity of the pores. It is an empirical relation between permeability and porosity of the porous medium that is the Carman-Kozeny hydraulic radius theory

$$K = \frac{D_p^2 \phi^3}{180(1 - \phi)^2} \quad (3.2)$$

where K is the permeability of the porous medium and D_p is the mean grain diameter and ϕ is the porosity of the medium.

For isotropic porous material permeability is the same (equal) in all the directions. For isotropic porous material, the permeability is constant.

'Aniso' is the property of being directionally dependent which implies different properties in different directions. Anisotropy mainly occurs due to the orientation of the particles or grains or pores in different

directions.

In 2D, the anisotropic porous media permeability is a symmetric matrix of the form

$$\mathbf{K} = \begin{pmatrix} K_{xx} & K_{xy} \\ K_{xy} & K_{yy} \end{pmatrix}$$

where K_{ij} means along i^{th} plane j^{th} direction.

Considering a pipe filled with particles as can be seen in the figure

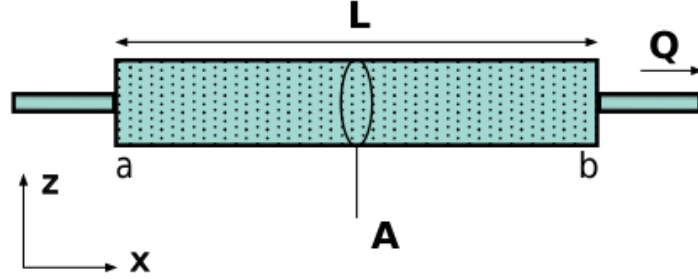


Figure 3.3

Darcy's law is an equation that describes the flow of a fluid through a porous medium. Darcy initially discovered Darcy's law empirically, but it has since been derived from the Navier-Stokes equations using homogenization techniques.

Morris Muskat's revised version of Darcy's law states that in the absence of gravitational forces and in a homogeneously permeable material, the connection between the instantaneous flux $q = \frac{Q}{A}$ through a porous medium, the permeability K of the medium, the dynamic viscosity of the fluid μ , and the pressure drop Δp over a given distance in the form

$$q = -\frac{KA}{\mu} \left(\frac{p_b - p_a}{L} \right) \quad (3.3)$$

In a more general notation it leads to

$$q = -\frac{K}{\mu} \nabla p \quad (3.4)$$

If the particles are arranged in a sparse, way there will be a force acting on the surface of the particles that is different from the case in which the particles are dense. For this reason Brinkman's modified the Darcy's law to take into account this problem. For the case in which the permeability is constant (isotropic case), the equation becomes

$$\nabla p = -\frac{\mu}{K}\mathbf{v} + \mu'\nabla^2\mathbf{v} \quad (3.5)$$

there is a viscous term that will contribute as a surface force (damping force). μ' is the effective viscosity of the fluid inside the porous medium and typically is different from the dynamic viscosity of the fluid (outside the porous media) μ .

In the case of anisotropic, the permeability in 2D will be a matrix (in 3D a tensor) and the equation becomes

$$\nabla p = -\mu\mathbf{K}^{-1}\mathbf{v} + \mu'\nabla^2\mathbf{v} \quad (3.6)$$

When $K_{xy} = 0, K_{xx} = K_{yy} = K$, one may get the corresponding isotropic situation

$$\mathbf{K} = \begin{pmatrix} K & 0 \\ 0 & K \end{pmatrix}$$

Flow in a horizontal channel filled with porous medium

The continuity equation $\nabla \cdot \mathbf{v} = 0$ and Brinkman equation must be satisfied.

The flow is bounded by two plates (impermeable walls) and there is a porous packing inside.

Assuming unidirectional flow $\mathbf{v} = (u, 0)$. The continuity equation becomes $\frac{\partial u}{\partial x} = 0$ and this implies that $u = u(y)$.

The corresponding x-momentum equation is

$$-\frac{\partial p}{\partial x} + \mu'\frac{\partial^2 u}{\partial y^2} = \frac{\mu u}{K} \quad (3.7)$$

and from the y-momentum

$$-\frac{\partial p}{\partial y} = 0 \Rightarrow p = p(x) \quad (3.8)$$

As can be seen in the x-momentum equation there is an additional force on the right hand side due to porous packing. If $K \rightarrow \infty$, the equation reduces to Stokes's equation.

For simplicity in this study it is assumed that $\mu = \mu'$. At the impermeable boundary, no slip condition is imposed (at $y = H, u = 0$). For symmetry of the channel at $y = 0, \frac{du}{dy} = 0$.

Since that u is function of y only, and p is a function of x only, it is possible to rewrite the x-momentum equation in this way

$$\mu\frac{d^2 u}{dy^2} - \frac{\mu u}{K} = \frac{dp}{dx} = \text{const} \quad (3.9)$$

The mean velocity is given by

$$\bar{u} = \frac{1}{H} \int_0^H u dy \quad (3.10)$$

Introducing the following non-dimensionalization, since that there just one length scale involved (H), the variables becomes

$$x = \frac{x}{H}, \quad y = \frac{y}{H}, \quad u = \frac{u}{\bar{u}}, \quad p = \frac{p}{\mu \bar{u}/H}, \quad Da = \frac{K}{H^2} \quad (3.11)$$

where Da is a dimensionless parameter called Darcy number which represents the percolation inside the porous medium.

Introducing these inside eq.(3.9) and multiplying all by $\frac{H^2}{\mu \bar{u}}$ yields

$$\frac{d^2 u}{dy^2} - \frac{H^2}{K} u = \frac{dp}{dx} \Rightarrow \frac{d^2 u}{dy^2} - \alpha^2 u = \frac{dp}{dx} \quad (3.12)$$

where $\alpha^2 = \frac{H^2}{K} = \frac{1}{Da}$. The BC's becomes at $y = 1, u = 0$, at $y = 0, \frac{du}{dy} = 0$ and the volumetric flow rate is $1 = \int_0^1 u dy$.

The solution of eq.(3.12) is

$$u(y) = -\frac{1}{\alpha^2} \frac{dp}{dx} + c_1 \cosh(\alpha y) + c_2 \sinh(\alpha y) \quad (3.13)$$

Imposing the BC's, one may get

$$c_1 = \frac{1}{\alpha^2} \frac{dp}{dx} \frac{1}{\cosh(\alpha)}, \quad c_2 = 0 \quad (3.14)$$

The pressure gradient can be found from the volumetric flow rate condition and is given by

$$\frac{dp}{dx} = -\alpha^3 \left(\frac{\cosh(\alpha)}{\alpha \cosh(\alpha) - \sinh(\alpha)} \right) \quad (3.15)$$

Hence, the velocity solution profile is

$$u(y) = \frac{\alpha(\cosh(\alpha) - \cosh(\alpha y))}{\alpha \cosh(\alpha) - \sinh(\alpha)} \quad (3.16)$$

For $Da \rightarrow \infty$ or rather $\alpha \rightarrow 0$, the flow behaves like clear channel flow.

If $\alpha \ll 1$ is it possible to do asymptotic analysis

$$\begin{aligned} \cosh(\alpha) &\sim 1 + \frac{\alpha^2}{2!} + O(\alpha^4) \\ \sinh(\alpha) &\sim \alpha + \frac{\alpha^3}{3!} + O(\alpha^5) \\ \cosh(\alpha y) &\sim 1 + \frac{(\alpha y)^2}{2!} + O(\alpha^4) \end{aligned} \quad (3.17)$$

and plug into the velocity equation yields the Plane Poiseuille flow inside plane channel

$$u(y) = \frac{3}{2} (1 - y^2) \quad (3.18)$$

The velocity increase with the Darcy number near the center (due to less viscosity) and decrease near the boundary (due to significant viscous effects) to retain the volume flux balance.

Flow in a cylindrical tube filled with porous medium

Has it was done for the horizontal channel, the continuity and the Brinkman equation must be satisfied.

Is it possible to write the momentum equation in cylindrical coordinates

$$\begin{aligned} \text{r-component: } & -\frac{\partial p}{\partial r} + \mu \left(\nabla^2 u_r - \frac{u_r}{r^2} - \frac{2}{r^2} \frac{\partial u_\theta}{\partial \theta} \right) = \frac{\mu}{K} u_r \\ \theta\text{-component: } & -\frac{1}{r} \frac{\partial p}{\partial \theta} + \mu \left(\nabla^2 u_\theta - \frac{u_\theta}{r^2} - \frac{2}{r^2} \frac{\partial u_r}{\partial \theta} \right) = \frac{\mu}{K} u_\theta \\ \text{z-component: } & -\frac{\partial p}{\partial z} + \mu \nabla^2 u_z = \frac{\mu}{K} u_z \end{aligned} \quad (3.19)$$

Assuming fully developed flow in the z-direction, $\mathbf{u} = (0, 0, u_z)$ The continuity equation, under this assumption, is $\frac{\partial u_z}{\partial z} = 0 \Rightarrow u_z = u_z(r, \theta)$. Since that the flow is axial-symmetrical, $\frac{\partial}{\partial \theta} = 0 \Rightarrow u_z = u_z(r)$ Under these assumptions, the momentum equation reduces to

$$\begin{aligned} \text{r-component: } & -\frac{\partial p}{\partial r} = 0 \\ \theta\text{-component: } & -\frac{1}{r} \frac{\partial p}{\partial \theta} = 0 \\ \text{z-component: } & -\frac{\partial p}{\partial z} + \mu \nabla^2 u_z = \frac{\mu}{K} u_z \end{aligned} \quad (3.20)$$

The r and θ components of the momentum equation implies that $p = p(z)$.

The governing equation reduces to

$$-\frac{dp}{dz} + \mu \left(\frac{d^2 u_z}{dr^2} + \frac{1}{r} \frac{du_z}{dr} \right) = \frac{\mu}{K} u_z \quad (3.21)$$

No slip condition at the impermeable wall, at $r = a, u_z = 0$ and regularity condition at the center of the tube at $r = 0, \frac{du_z}{dr} = 0$. The mean flow velocity inside the tube is

$$\bar{u} = \frac{\int_A u dA}{A} = \frac{\int_0^a \int_0^{2\pi} u r dr d\theta}{\pi a^2} = \frac{2\pi}{\pi a^2} \int_0^a u r dr = \frac{2}{a^2} \int_0^a u r dr \quad (3.22)$$

Introducing the following non-dimensionalization

$$r = \frac{r}{a}, \quad z = \frac{z}{a}, \quad u = \frac{u_z}{\bar{u}}, \quad p = \frac{p}{\mu \bar{u} / a}, \quad Da = \frac{K}{a^2} \quad (3.23)$$

The equation becomes

$$-\frac{dp}{dz} + \left(\frac{d^2u}{dr^2} + \frac{1}{r} \frac{du}{dr} \right) = \frac{1}{Da} u \quad (3.24)$$

and the BC's becomes: at $r = 1, u = 0$ and at $r = 0, \frac{du}{dr} = 0$. The corresponding flow rate is $1 = 2 \int_0^1 u r dr$

The solution of the above equation can be given as

$$u(r) = -\frac{1}{\alpha^2} \frac{dp}{dz} + c_1 I_0(\alpha r) + c_2 K_0(\alpha r) \quad (3.25)$$

where I_n, K_n are the modified Bessel functions of first and second kind of order n respectively.

From Regularity condition $c_2 = 0$, instead from no-slip $c_1 = \frac{1}{\alpha^2 I_0(\alpha)} \frac{dp}{dz}$.

The solution of the velocity profile is

$$u(r) = -\frac{1}{\alpha^2} \frac{dp}{dz} \left(1 - \frac{I_0(\alpha r)}{I_0(\alpha)} \right) \quad (3.26)$$

The pressure gradient can be found using the volumetric flow rate condition

$$\frac{dp}{dz} = -\frac{\alpha^3 I_0(\alpha)}{\alpha I_0(\alpha) - 2I_1(\alpha)} \quad (3.27)$$

and finally, the velocity is

$$u(r) = \frac{\alpha(I_0(\alpha) - I_0(\alpha r))}{\alpha I_0(\alpha) - 2I_1(\alpha)} \quad (3.28)$$

3.2 Multi-scale Homogenization of Stokes equation

Homogenization is the study of macroscopic and/or bulk behavior of solutions to partial differential or other type of equations posed on a heterogeneous domain/media, where the heterogeneity are present at microscopic scale ϵ .

The heterogeneities can be in the form of fine mixing of two or more materials with different physical properties in the domain or due to singularities in the domain in the form of pores, granules, etc.

Homogenization has many applications in:

- 1) the study of properties (structural, electro-magnetic, thermal, ...) of composites;
- 2) study of flow in porous media (flow of oil, water through subsurface, pollution of ground water, ...);
- 3) analysis of vibrations in thin structures.

The problem posed on the heterogeneous domain has a unique solution.

Heterogeneity cause the solution to develop high frequency oscillations.

So a direct numerical study will not be able to capture either the bulk behavior or the oscillations presents in the solution which are at a microscopic level.

Considering a porous material. For each ϵ there should be a different PDE (a family of PDE). Do an asymptotic analysis as $\epsilon \rightarrow 0$, a PDE on the homogeneous media is obtained (limiting behavior of that family of PDE). Basically, it is trying to approximate the solution u_ϵ corresponding to the heterogeneous domain, for small $\epsilon > 0$, by the solution of the homogenized problem in which the small parameter do not appear.

The mathematical problem is:

- 1) to identify the homogenized equation;
- 2) to prove convergence of u_ϵ corresponding to the heterogeneous equation to that of the homogeneous equation as $\epsilon \rightarrow 0$;
- 3) to capture the oscillations in u_ϵ (known as corrector in the literature);
- 4) the solution together with the corresponding corrector can be used (and also can be computed numerically) to get good approximation to the original solution.

Darcy's Law is a constitutive equation that describes how a fluid moves slowly through a porous media.

Homogenization approach and the indices notation are used to derive Darcy's Law from the Stokes equation. Let Ω be the periodic cell domain, which consists of a fluid phase Ω_F , a solid phase Ω_S , and a piece-wise continuous liquid-solid interface $\Gamma = \Gamma_S \cup \Gamma_F$ where Γ_S and Γ_F are the solid and liquid phase borders, respectively.

A slow fluid flow, a stationary solid, and a viscous incompressible fluid are assumed such that the Stokes equations may be used

$$\nabla \cdot \mathbf{v} = 0 \quad \text{in } \Omega_F \quad (3.29a)$$

$$-\nabla p + \mu \nabla^2 \mathbf{v} + \mathbf{f} = \mathbf{0} \quad \text{in } \Omega_F \quad (3.29b)$$

$$\mathbf{v} = \mathbf{0} \quad \text{in } \Gamma_S \quad (3.29c)$$

where a no-slip condition is assumed at the solid boundary Γ_S ; μ is the dynamic viscosity; \mathbf{v} is the velocity; p is the pressure and \mathbf{f} is a source term.

It is supposed that the diameter of the cylinders, $a = 2r$, is tiny in comparison to a macroscopic scale length L , which can be the length of a long pipe; i.e., if $\epsilon = a/L$, then $\epsilon \ll 1$

Assuming \mathbf{x} is a macroscopic variable, then the microscopic variable (or stretched coordinate) is $\mathbf{y} = \mathbf{x}/\epsilon$.

The dynamic viscosity coefficient μ is assumed fixed and independent of ϵ .

As it can be seen in the picture there is a reference cell, microscopic, that is repeated periodically inside the domain. The configuration in which $\epsilon \rightarrow 0$ is the macroscopic scale that is homogenized (basically a zoom out is done and is observed that the macroscopic domain is homogeneous).

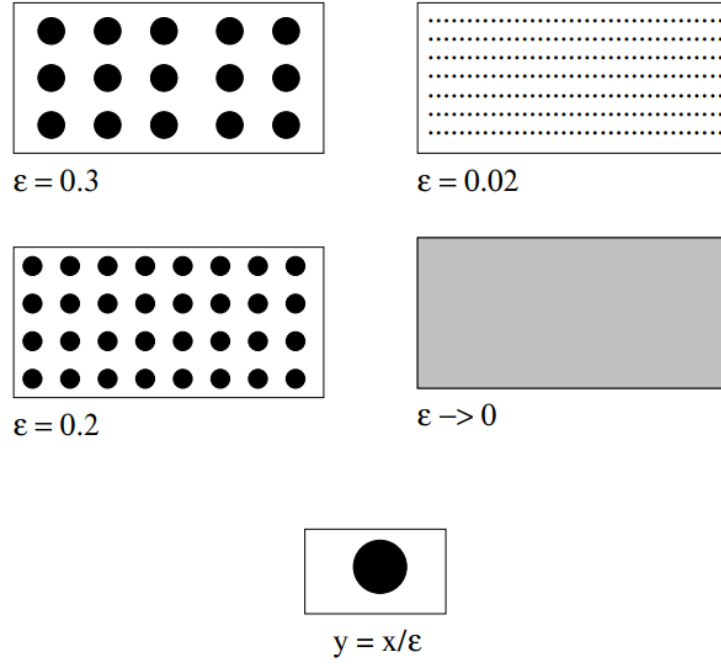


Figure 3.4

Instead of having a microscopic cell that has a circular grain is possible to have different shapes, the important thing is that that cell is repeated periodically, as is shown in the following picture

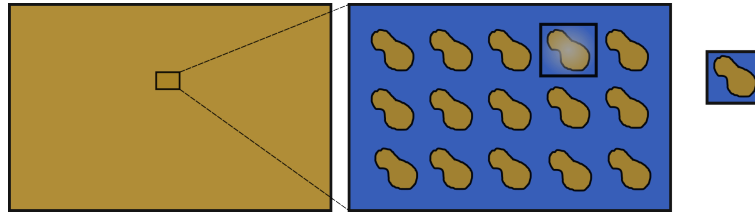


Figure 3.5

Where the dimension of the macroscopic homogenized domain is L and the dimension of the single cell is l such that $\epsilon = l/L \ll 1$. Is it possible to have more shapes inside the microcell.

This coefficient ϵ is then used for two asymptotic expansions in powers of ϵ for \mathbf{v} and p , in an analysis known as multi-scale analysis

$$\mathbf{v} = \epsilon^\alpha (\mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) \quad (3.30a)$$

$$p = \epsilon^\beta (p^0(\mathbf{x}, \mathbf{y}) + \epsilon p^1(\mathbf{x}, \mathbf{y}) + \dots) \quad (3.30b)$$

where \mathbf{v}^i and p^i are Ω -periodic in \mathbf{y} and α and β are nonzero parameters that produce a physically relevant solution. The choice of α and β gives multiple macroscopic models, and in this instance, α and β are chosen in such a way to yield a nonzero macroscopic first-order pressure and a second order velocity, which can lead to Darcy's Law.

Since that velocity and pressure are function of two variable and \mathbf{y} is expressed in function of \mathbf{x} , the derivative of these two functions should be calculated using the chain rule

$$\frac{d}{dx_j} = \frac{\partial}{\partial x_j} + \frac{\partial}{\partial y_j} \frac{dy_j}{dx_j} = \frac{\partial}{\partial x_j} + \frac{1}{\epsilon} \frac{\partial}{\partial y_j}, \quad j = 1, 2, 3 \quad (3.31)$$

and since that $\frac{d}{dx_j}$ is a function of \mathbf{x} and \mathbf{y} with \mathbf{y} is expressed in function of \mathbf{x} , the chain rule can be applied again but this time to the first derivative

$$\begin{aligned} \frac{d^2}{dx_j^2} &= \frac{d}{dx_j} \left(\frac{d}{dx_j} \right) = \frac{\partial}{\partial x_j} \left(\frac{\partial}{\partial x_j} + \frac{1}{\epsilon} \frac{\partial}{\partial y_j} \right) + \frac{1}{\epsilon} \frac{\partial}{\partial y_j} \left(\frac{\partial}{\partial x_j} + \frac{1}{\epsilon} \frac{\partial}{\partial y_j} \right) \\ &= \frac{\partial^2}{\partial x_j^2} + \frac{1}{\epsilon} \frac{\partial^2}{\partial x_j \partial y_j} + \frac{1}{\epsilon} \left(\frac{\partial^2}{\partial y_j \partial x_j} + \frac{1}{\epsilon} \frac{\partial^2}{\partial y_j^2} \right) \\ &= \frac{1}{\epsilon^2} \frac{\partial^2}{\partial y_j^2} + \frac{1}{\epsilon} \left(\frac{\partial^2}{\partial x_j \partial y_j} + \frac{\partial^2}{\partial y_j \partial x_j} \right) + \frac{\partial^2}{\partial x_j^2} \end{aligned} \quad (3.32)$$

The Laplacian of the velocity field becomes

$$\begin{aligned} \nabla^2 \mathbf{v} &= \mathbf{v}_{,jj} = \left(\frac{d^2 v_1}{dx_j^2}, \frac{d^2 v_2}{dx_j^2}, \frac{d^2 v_3}{dx_j^2} \right) \\ &= \left(\frac{1}{\epsilon^2} \frac{\partial^2 v_1}{\partial y_j^2} + \frac{1}{\epsilon} \left(\frac{\partial^2 v_1}{\partial x_j \partial y_j} + \frac{\partial^2 v_1}{\partial y_j \partial x_j} \right) + \frac{\partial^2 v_1}{\partial x_j^2}, \right. \\ &\quad \frac{1}{\epsilon^2} \frac{\partial^2 v_2}{\partial y_j^2} + \frac{1}{\epsilon} \left(\frac{\partial^2 v_2}{\partial x_j \partial y_j} + \frac{\partial^2 v_2}{\partial y_j \partial x_j} \right) + \frac{\partial^2 v_2}{\partial x_j^2}, \\ &\quad \left. \frac{1}{\epsilon^2} \frac{\partial^2 v_3}{\partial y_j^2} + \frac{1}{\epsilon} \left(\frac{\partial^2 v_3}{\partial x_j \partial y_j} + \frac{\partial^2 v_3}{\partial y_j \partial x_j} \right) + \frac{\partial^2 v_3}{\partial x_j^2} \right) \\ &= \frac{1}{\epsilon^2} \left(\frac{\partial^2 v_1}{\partial y_j^2}, \frac{\partial^2 v_2}{\partial y_j^2}, \frac{\partial^2 v_3}{\partial y_j^2} \right) + \\ &\quad \frac{1}{\epsilon} \left(\frac{\partial^2 v_1}{\partial x_j \partial y_j} + \frac{\partial^2 v_1}{\partial y_j \partial x_j}, \frac{\partial^2 v_2}{\partial x_j \partial y_j} + \frac{\partial^2 v_2}{\partial y_j \partial x_j}, \frac{\partial^2 v_3}{\partial x_j \partial y_j} + \frac{\partial^2 v_3}{\partial y_j \partial x_j} \right) + \\ &\quad \left(\frac{\partial^2 v_1}{\partial x_j^2}, \frac{\partial^2 v_2}{\partial x_j^2}, \frac{\partial^2 v_3}{\partial x_j^2} \right) \\ &= \frac{1}{\epsilon^2} \nabla_y^2 \mathbf{v} + \frac{1}{\epsilon} \nabla_{xy}^2 \mathbf{v} + \nabla_x^2 \mathbf{v} \end{aligned} \quad (3.33)$$

Remembering that

$$\frac{d^2 v_1}{dx_j^2} = v_{1,jj} = \sum_{j=1}^3 \frac{d^2 v_1}{dx_j^2}$$

The continuity equation become easily

$$\nabla \cdot \mathbf{v} = \frac{dv_j}{dx_j} = \frac{\partial v_j}{\partial x_j} + \frac{1}{\epsilon} \frac{\partial v_j}{\partial y_j} = \nabla_x \cdot \mathbf{v} + \frac{1}{\epsilon} \nabla_y \cdot \mathbf{v} = 0 \quad (3.34)$$

and the Stokes equation becomes

$$-\nabla_x p - \frac{1}{\epsilon} \nabla_y p + \mu \left(\frac{1}{\epsilon^2} \nabla_y^2 \mathbf{v} + \frac{1}{\epsilon} \nabla_{xy}^2 \mathbf{v} + \nabla_x^2 \mathbf{v} \right) + \mathbf{f} = \mathbf{0} \quad (3.35)$$

Substituting (3.30a,b) in the continuity and Stokes equations yields

$$\nabla_x \cdot (\epsilon^\alpha \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon^{\alpha+1} \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \frac{1}{\epsilon} \nabla_y \cdot (\epsilon^\alpha \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon^{\alpha+1} \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) = 0 \quad (3.36)$$

$$\begin{aligned} & -\nabla_x (\epsilon^\beta p^0(\mathbf{x}, \mathbf{y}) + \epsilon^{\beta+1} p^1(\mathbf{x}, \mathbf{y}) + \dots) - \frac{1}{\epsilon} \nabla_y (\epsilon^\beta p^0(\mathbf{x}, \mathbf{y}) + \epsilon^{\beta+1} p^1(\mathbf{x}, \mathbf{y}) + \dots) + \\ & \mu \frac{1}{\epsilon^2} \nabla_y^2 \epsilon^\alpha (\mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \frac{\mu}{\epsilon} \nabla_{xy}^2 \epsilon^\alpha (\mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \\ & \mu \nabla_x^2 \epsilon^\alpha (\mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \mathbf{f} = \mathbf{0} \end{aligned} \quad (3.37)$$

It is important to find the correct coefficient to guarantied a physical sense of the equations. It was found that the correct coefficients are $\alpha = 2$ and $\beta = 0$. Substituting them into the continuity and Stokes equation yields

$$\nabla_x \cdot (\epsilon^2 \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon^3 \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \nabla_y \cdot (\epsilon \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon^2 \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) = 0 \quad (3.38)$$

$$\begin{aligned} & -\nabla_x (p^0(\mathbf{x}, \mathbf{y}) + \epsilon p^1(\mathbf{x}, \mathbf{y}) + \dots) - \nabla_y (\epsilon^{-1} p^0(\mathbf{x}, \mathbf{y}) + p^1(\mathbf{x}, \mathbf{y}) + \dots) + \\ & \mu \nabla_y^2 (\mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \mu \nabla_{xy}^2 (\epsilon \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon^2 \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \\ & \mu \nabla_x^2 (\epsilon^2 \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \epsilon^3 \mathbf{v}^1(\mathbf{x}, \mathbf{y}) + \dots) + \mathbf{f} = \mathbf{0} \end{aligned} \quad (3.39)$$

The coefficients of the right hand side (that are all 0) must them agree with the coefficients of the left hand side because Taylor series are unique. By collecting the terms of the same order, a series of continuity and Stokes equations of order ϵ^n are obtained, with $n = 1, \dots$ for the continuity equation and $n = -1, 0, \dots$ for the Stokes equation. Since that ϵ is small, power of it are not considered

$$\epsilon^1 : \nabla_y \cdot \mathbf{v}^0(\mathbf{x}, \mathbf{y}) = 0 \quad (3.40a)$$

$$\epsilon^{-1} : \nabla_y p^0(\mathbf{x}, \mathbf{y}) = 0 \quad (3.40b)$$

$$\epsilon^0 : -\nabla_x p^0(\mathbf{x}, \mathbf{y}) - \nabla_y p^1(\mathbf{x}, \mathbf{y}) + \mu \nabla_y^2 \mathbf{v}^0(\mathbf{x}, \mathbf{y}) + \mathbf{f} = \mathbf{0} \quad (3.40c)$$

From the second equation is possible to notice that p^0 does not depends on the microscopic variable \mathbf{y} but depends only on the macroscopic variable \mathbf{x}

$$p^0 = p^0(\mathbf{x})$$

Remembering that also the body force is only a function of the macroscopic variable

$$\mathbf{f} = \mathbf{f}(\mathbf{x})$$

The non slip boundary condition on the grain should be respected and so imposing (3.30a) equal to 0 yield

$$\mathbf{v}^0 = 0 \quad \text{on } \Gamma_S$$

Since the domain is assumed to be periodic, we introduce a Hilbert space of Ω -periodic functions:

$$H(\omega) = \{\omega = (\omega_1, \omega_2, \omega_3) \in (H^1(\Omega_F))^3 : \omega \text{ is } \Omega\text{-periodic}, \omega = 0 \text{ on } \Gamma_S, \text{ and } \nabla_y \cdot \omega = 0\}$$

with scalar product

$$(\mathbf{w}, \omega)_{H(\Omega)} = \int_{\Omega_F} \frac{\partial w_j}{\partial y_k} \frac{\partial \omega_j}{\partial y_k} dy$$

Equation (3.40a) can be rewritten in index notation

$$-\frac{\partial p^1}{\partial y_i} + \mu \frac{\partial^2 v_i^0}{\partial y_j^2} + f_i - \frac{\partial p^0}{\partial x_i} = 0$$

To obtain a weak form, the equation is multiplied by a test function $\omega_i \in H(\Omega)$ and integrate it on all the volume of the fluid Ω_F

$$-\int_{\Omega_F} \omega_i \frac{\partial p^1}{\partial y_i} dy + \mu \int_{\Omega_F} \omega_i \frac{\partial^2 v_i^0}{\partial y_j^2} dy - \int_{\Omega_F} \omega_i \frac{\partial p^0}{\partial x_i} dy + \int_{\Omega_F} \omega_i f_i dy = 0 \quad (3.41)$$

Applying now the integration by part in higher dimensions of the two first terms, is possible to transfer the derivatives to the test function that is differentiable and remembering that at the boundary the test function is 0, yields

$$\begin{aligned}
-\int_{\Omega_F} \omega_i \frac{\partial p^1}{\partial y_i} dy &= \int_{\Omega_F} p^1 \frac{\partial \omega_i}{\partial y_i} dy \\
\mu \int_{\Omega_F} \omega_i \frac{\partial^2 v_i^0}{\partial y_j^2} dy &= -\mu \int_{\Omega_F} \frac{\partial v_i^0}{\partial y_j} \frac{\partial \omega_i}{\partial y_j} dy
\end{aligned}$$

$$\int_{\Omega_F} p^1 \frac{\partial \omega_i}{\partial y_i} dy - \mu \int_{\Omega_F} \frac{\partial v_i^0}{\partial y_j} \frac{\partial \omega_i}{\partial y_j} dy - \left(\frac{\partial p^0}{\partial x_i} - f_i \right) \int_{\Omega_F} \omega_i dy = 0$$

and since that the divergence of the test function is $\frac{\partial \omega_i}{\partial y_i} = 0$ yields

$$\mu \int_{\Omega_F} \frac{\partial v_i^0}{\partial y_j} \frac{\partial \omega_i}{\partial y_j} dy = \left(f_i - \frac{\partial p^0}{\partial x_i} \right) \int_{\Omega_F} \omega_i dy$$

and using the definition of the inner product yields

$$\mu(\mathbf{v}^0, \omega)_{H(\Omega)} = (\mathbf{f} - \nabla_x p^0) \cdot \int_{\Omega_F} \omega dy \quad (3.42)$$

Instead of solving (3.40a,b,c), the variational problem (3.42) must be solved. The problem is to find $\mathbf{v}^0 \in H(\Omega)$ that satisfy that equation.

Applying the linearity property, it is possible to write the solution velocity of the macroscopic field

$$\mathbf{v}^0(\mathbf{x}, \mathbf{y}) = \frac{1}{\mu} \left(f_i - \frac{\partial p^0}{\partial x_i} \right) \mathbf{u}^i(\mathbf{y}) \quad (3.43)$$

where now the problem is to find $\mathbf{u}^i(\mathbf{y}) \in H(\Omega)$ such that

$$(\mathbf{u}^i, \omega)_{H(\Omega)} = \int_{\Omega_F} \omega_i dy \quad (3.44)$$

Substituting (3.43) inside (3.40a,c) and inside the boundary condition, considering that \mathbf{f} and $\nabla_x p^0$ are constant, yields

$$\begin{aligned}
\nabla_y \cdot \mathbf{u}^i &= 0 && \text{in } \Omega_F \\
-\nabla_y q^i + \nabla_y^2 \mathbf{u}^i + \mathbf{e}^i &= 0 && \text{in } \Omega_F \\
\mathbf{u}^i &= 0 && \text{on } \Gamma
\end{aligned} \quad (3.45)$$

where $q^i(\mathbf{y}) = \frac{p^1(\mathbf{x}, \mathbf{y})}{\left(f_i - \frac{\partial p^0}{\partial x_i} \right)}$ and \mathbf{e}^i is the unitary vector in the direction of the y_i axis, $i = 1, 2, 3$ (basis vector). These are the incompressible flow equations in the micro-domain. Solving these equations is possible to

obtain the characteristic functions \mathbf{u}^i and q^i (that are Ω -periodic) and use \mathbf{u}^i to compute the permeability, because the permeability depends only on the microscopic geometry properties.

Multiplying both members of (3.43) by the inverse of the total volume of the cell $\Omega = \Omega_S + \Omega_F$ and integrating it respect to Ω_F

$$\frac{1}{\Omega} \int_{\Omega_F} \mathbf{v}^0(\mathbf{x}, \mathbf{y}) dy = \frac{1}{\mu} \left(f_i - \frac{\partial p^0}{\partial x_i} \right) \frac{1}{\Omega} \int_{\Omega_F} \mathbf{u}^i(\mathbf{y}) dy \quad (3.46)$$

which represent the volume average value

$$\langle \mathbf{v}^0 \rangle = \frac{1}{\mu} \left(f_i - \frac{\partial p^0}{\partial x_i} \right) \langle \mathbf{u}^i \rangle \quad (3.47)$$

or in indices notation

$$\langle v_j^0 \rangle = \frac{1}{\mu} \left(f_i - \frac{\partial p^0}{\partial x_i} \right) \langle u_j^i \rangle \quad (3.48)$$

where $\langle u_j^i \rangle$ is the permeability tensor which depends on the geometry of the periodic domain Ω .

This equation is the Darcy's Law. A common whay to write it is the following

$$\mathbf{q} = -\frac{\mathbf{k}}{\mu} (\nabla p - \mathbf{f}) \quad (3.49)$$

where the permeability is

$$k_{ij} = \langle \mathbf{u}^i \rangle = \frac{1}{\Omega} \int_{\Omega_F} u_j^i dy \quad (3.50)$$