

Flow of electrolytes in a porous medium

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1. Basic equations.

We consider a binary electrolyte, i.e. a solution (not necessarily an aqueous solution) containing one type of cations and one type of anions.

For fairly well diluted mixtures, the exchange of momentum between the solvent and the dissolved components is described by the Stokes law

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \mu \Delta \mathbf{v} + \mathbf{E} \sum_{i=\pm} \frac{q_i \rho_i}{m_i} + \rho \mathbf{g}. \quad (1)$$

Here ρ is the density of the medium, \mathbf{v} is the velocity of the mixture, μ is the viscosity, m_i is the molecular weight of the ion, p is the pressure, ρ_+ (ρ_-) is the mass density of the positive (negative) ions, q_i is the ion charge, \mathbf{E} is the electrical field, \mathbf{g} is the acceleration due to gravity, $q_i = z_i e$ is the ion charge, e is an elementary charge, z_i is the ion valency, and $c_i = \rho_i / m_i$ is the concentration, i.e. the number of ions in a unit volume.

The equilibrium ion distribution obeys the Nernst law

$$0 = -\frac{\rho_i q_i}{m_i} d\psi - \frac{kT}{m_i} d\rho_i, \quad \mathbf{E} = -\nabla \psi, \quad (2)$$

where ψ is the potential of the field \mathbf{E} , k is the Boltzmann constant, and T is the temperature.

Equality (2) means that the contacting phases , being in equilibrium, have identical chemical potentials.

In the dynamic case, Eq. (2) is generalized to the force-balance equation as follows

$$\rho_i \frac{\partial \mathbf{v}_i}{\partial t} = \mu_i \Delta \mathbf{v}_i - \alpha_i \nabla p + \frac{\rho_i q_i}{m_i} \mathbf{E} - \frac{kT}{m_i} \nabla \rho_i + \frac{\gamma_i \rho_i}{m_i} (\mathbf{v} - \mathbf{v}_i) + \rho_i \mathbf{g}, \quad (3)$$

where the resistance coefficient γ_i is defined by the Stokes-Einstein-Sutherland formula

$$\gamma_i = \frac{kT}{D_i}. \quad (4)$$

Here \mathbf{v}_i is the ion velocity, μ_i is the viscosity of the i -th ion component, and α_i is the bulk concentration ($\alpha_1 + \alpha_2 \leq 1$). The fifth term in the right hand side of (3) is a diffusion term, and D_i is the coefficient of diffusion.

In what follows, we neglect the ion viscosities μ_i and the terms $\alpha_i \nabla p$ since both α_1 and α_2 are small.

The Poisson equation of charge conservation has the form

$$\operatorname{div} \mathbf{D} = 4\pi \sum_{\pm} \frac{\rho_i q_i}{m_i}, \quad \mathbf{D} = \varepsilon_f \mathbf{E}, \quad \mathbf{E} = -\nabla \psi, \quad (5)$$

where \mathbf{D} is the electric induction vector and ε_f is the dielectric permittivity of the electrolyte. As the mixture is assumed to be incompressible, the laws of conservation of mass of the mixture and individual components are set as follows :

$$\operatorname{div} \mathbf{v} = 0, \quad \rho = \text{const}, \quad \frac{\partial \rho_i}{\partial t} + \operatorname{div} (\rho_i \mathbf{v}_i) = 0. \quad (6)$$

Inside the solid dielectric, the electrical field obeys the equations

$$\operatorname{div} \mathbf{D} = 0, \quad \mathbf{D} = \varepsilon_s \mathbf{E}, \quad \mathbf{E} = -\nabla \psi,$$

where ε_s is the dielectric permittivity of the dielectric material.

2. One dimensional flows.

Our study is motivated by the electrolyte flow through a membrane of thickness l when the inflow pressure p_- (on the left) is greater than the outflow pressure p_+ . It is the pressure gradient $(p_+ - p_-)/l \equiv -\alpha$ which mainly controls the flow. It is also possible that the flow is due to the external electrical field $E = -(\psi^+ - \psi^-)/l \equiv -\beta$. Commonly, an inflow density ρ_i^- of the i -th ion is prescribed.

As a model problem, we consider a steady flow of the electrolyte in an infinite horizontal layer of thickness L consisting of N horizontal thin slits $a_n < z < b_n$ of the same thickness h_l separated by layers $b_n < z < a_{n+1}$ of a solid dielectric of identical thickness h_s . At the central points d_n of the liquid domain $a_n < z < b_n$, the ion densities ρ_i acquire prescribed values ρ_i^- , which correspond to imposing input concentrations in the case of a finite-thickness membrane. Let Q_f and Q_s stand for fluid and solid domain

$$Q_f = \{x, z : -\infty < x < +\infty, z \in \Omega_f\}, \quad Q_s = \{x, z : -\infty < x < +\infty, z \in \Omega_s\},$$

$$\Omega_f = \bigcup_{n=0}^{N-1} \{a_n < z < b_n\}, \quad \Omega_s = \bigcup_{n=0}^{N-1} \{b_n < z < a_{n+1}\},$$

$$\Omega = \Omega_f \cup \Omega_s \equiv \{0 < z < L\},$$

$$a_n = n(h_l + h_s), \quad b_n = a_n + h_l, \quad d_n = a_n + h_l/2.$$

In the fluid domain Ω_f , the solution of equations (1)-(6) is sought in the form

$$\mathbf{v} = (v(z), 0, 0), \mathbf{v}_i = (v_i(z), 0, 0), \rho_i = \rho_i(z), p = \alpha x + P(z), \psi = \beta x + \varphi(z),$$

where $\alpha = \text{const}$ and $\beta = \text{const}$.

In this case, system (1)-(6) becomes

$$\mu v_{zz} - \alpha - \beta \sum_{\pm} c_i q_i = 0, \quad c_i = \frac{\rho_i}{m_i}, \quad (7)$$

$$-P_z - \varphi_z \sum_{\pm} c_i q_i - \rho g = 0, \quad (8)$$

$$-\beta c_i q_i + \frac{k T c_i}{D_i} (v - v_i) = 0, \quad (9)$$

$$-c_i q_i \varphi_z - k T c_{iz} - g c_i m_i = 0, \quad (10)$$

$$\varepsilon_f \varphi_{zz} = -4\pi \sum_{\pm} c_i q_i. \quad (11)$$

In the solid domain Ω_s , the potential φ satisfies the equation

$$\varepsilon_s \varphi_{zz} = 0. \quad (12)$$

The conditions of continuity of the potential φ and induction D have the form

$$\text{for } z = a_n \text{ and } z = b_n : [\varphi] = [\varepsilon\varphi_z] = 0, \quad \text{for } z = d_n : c_i = c_i^-, \quad (13)$$

where $n = 1, \dots, N - 1$ and $[\varphi]|_{z=z_0}$ stands for the jump of the discontinuous function φ at the discontinuity point z_0 :

$$[\varphi]|_{z=z_0} = \lim_{\sigma \rightarrow 0} (\varphi(z_0 + \sigma) - \varphi(z_0 - \sigma)).$$

The no-slip conditions can be written as

$$\text{for } z = a_n \text{ and } z = b_n : v = 0, \quad \text{where } n = 0, \dots, N. \quad (14)$$

The external boundary conditions of the potential φ are assumed to be given

$$\varphi|_{z=0} = \zeta_0, \quad \varphi|_{z=L} = \zeta_L. \quad (15)$$

Thus, one-dimensional flows are governed by equations (7)-(12) and conditions (13)-(15). Let us derive some consequences of the above formulation. We introduce a discontinuous function of dielectric permittivity

$$\varepsilon = \begin{cases} \varepsilon_l, & z \in \Omega_f, \\ \varepsilon_s, & z \in \Omega_s, \end{cases}$$

which is extended periodically for all values of z .

To eliminate the concentrations c_i , we write Eq. (10) in the form

$$\frac{d}{dz}(q_i \varphi + kT \ln c_i + m_i g z) = 0.$$

Integrating this equation from d_n to $z \in (a_n, b_n)$, we obtain

$$c_i = c_i^- \exp \left[\frac{q_i}{kT} (\varphi(d_n) - \varphi(z)) + \frac{g m_i}{kT} (d_n - z) \right]. \quad (16)$$

Hence, the potential φ solves in each liquid domain (a_n, b_n) the Poisson-Boltzmann equation

$$\varepsilon_f \varphi_{zz} = -4\pi \sum_{\pm} c_i^- q_i \exp \left[\frac{q_i}{kT} (\varphi(d_n) - \varphi(z)) + \frac{g m_i}{kT} (d_n - z) \right]. \quad (17)$$

We introduce the function $[z]_e$ which takes the value of the integer part of the number z . Then, for $a_n < z < a_{n+1}$, the functions

$$H_a(z) = h\left[\frac{z}{h}\right]_e, \quad H_d(z) = \frac{h_l}{2} + h\left[\frac{z}{h}\right]_e, \quad H_b(z) = h_l + h\left[\frac{z}{h}\right]_e, \quad h \equiv h_l + h_s, \quad (18)$$

take the constant values a_n , d_n , and b_n .

Let χ be the characteristic function of the liquid domain Ω_f . Thus to define φ on the whole interval $0 < z < L$, we have to solve the equation

$$(\varepsilon\varphi_z)_z = -4\pi\chi(z) \sum_{\pm} c_i^- q_i \exp\left[\frac{q_i}{kT}(\varphi(H_d(z)) - \varphi(z)) + \frac{gm_i}{kT}(H_d(z) - z)\right],$$

with the conditions (13) and (15). Note that the function $\xi_d = H_d(z) - z$ is periodic, and $\xi_d = h_l/2 - z$ on the periodicity interval $0 < z < h$.

3. Transition to dimensionless quantities and comparison of parameters.

We look for an asymptotic solution of problem (7)-(15) assuming that the ratio

$$\frac{h}{L} = \frac{1}{N} = \delta$$

is small (N is a natural number). Within the framework of the homogenization method, the entire interval $\Omega = \{0 < z < L\}$ is fixed and δ varies in $(0, 1)$. In this case, we obtain

$$h(\delta) = \delta L, \quad h_f = \delta \bar{h}_f, \quad h_s = \delta \bar{h}_s, \quad \bar{h}_f + \bar{h}_s = L, \quad \Phi := \bar{h}_f/L,$$

where Φ is the porosity.

In addition to the slow variable $z \in \Omega$, we introduce the fast variable $y = z/(\delta L)$. For small values of δ , the periodic functions $\varepsilon(z)$ and $\chi(z)$ oscillate strongly and they can be represented as functions of the fast variable

$$\varepsilon(z) = \tilde{\varepsilon}\left(\frac{z}{\delta L}\right), \quad \chi(z) = \tilde{\chi}\left(\frac{z}{\delta L}\right),$$

where

$$\tilde{\varepsilon}(y) = \begin{cases} \varepsilon_f, & 0 < y < \Phi, \\ \varepsilon_s, & \Phi < y < 1, \end{cases} \quad \text{and} \quad \tilde{\chi}(y) = \begin{cases} 1, & 0 < y < \Phi, \\ 0, & \Phi < y < 1, \end{cases}$$

are periodic functions with a period equal to unity.

The functions

$$\tilde{\xi}_a(y) = -Ly, \quad \tilde{\xi}_d(y) = L(\Phi/2 - y), \quad \tilde{\xi}_b(y) = L(\Phi - y), \quad 0 < y < 1,$$

are extended periodically. The functions $H_a(z)$, $H_d(z)$, and $H_b(z)$ defined in (18) can be written as

$$H_a(z) = z + \delta\tilde{\xi}_a\left(\frac{z}{\delta L}\right), \quad H_d(z) = z + \delta\tilde{\xi}_d\left(\frac{z}{\delta L}\right), \quad H_b(z) = z + \delta\tilde{\xi}_b\left(\frac{z}{\delta L}\right).$$

With the above notations, the function $\varphi(z)$ solves on the interval $0 < z < L$ the problem

$$\left(\tilde{\varepsilon}\left(\frac{z}{\delta L}\right)\varphi_z\right)_z = f(\varphi), \quad (19)$$

$$f = -4\pi\tilde{\chi}\left(\frac{z}{\delta L}\right) \sum_{\pm} c_i^- q_i \exp\left(\frac{q_i}{kT} \{\varphi(z + \delta\tilde{\xi}_d\left(\frac{z}{\delta L}\right)) - \varphi(z)\} + \frac{\delta g m_i}{kT} \tilde{\xi}_d\left(\frac{z}{\delta L}\right)\right),$$

with the boundary conditions (15).

As the fluid domain Ω_f depends on δ , we write Ω_f^δ instead of Ω_f and Ω_s^δ instead of Ω_s . It follows from (7) and (11) that the bulk velocity satisfies the equation

$$z \in \Omega_f^\delta : \quad \mu v_{zz} + \frac{\beta \varepsilon_f}{4\pi} \varphi_{zz} = \alpha; \quad z \in \partial\Omega_f^\delta : \quad v = 0. \quad (20)$$

With c_i given by (16), the ion velocity solves the problem

$$z \in \Omega_f^\delta : \quad -\beta c_i q_i + \frac{kT c_i}{D_i} (v - v_i) = 0. \quad (21)$$

Let us perform scaling, using the bar-sign \bar{f} for a reference value of the variable f and the prime-sign f' for a dimensionless value of f , i.e. $f = \bar{f} f'$. We use the following notations :

$$z = Lz', \quad x = Lx', \quad c_i = \bar{c} c'_i, \quad q_i = \bar{q} q'_i, \quad v = \bar{v} v', \quad v_i = \bar{v} v'_i, \quad D_i = \bar{D} D'_i, \\ \alpha = \bar{\rho} \alpha' / L \equiv \bar{\rho} \rho'_{x'} / L, \quad \beta = \bar{\varphi} \beta' / L \equiv \bar{\varphi} \psi'_{x'} / L, \quad H_d(z) = L H'_d(z').$$

The quantity

$$l_d = \left(\frac{\varepsilon_l kT}{2\bar{c}\bar{q}^2} \right)^{1/2} \quad (22)$$

has a dimension of length and is known as the Debye length.

In dimensionless variables, equations (7)-(11) in the fluid domain take the form

$$\left(\frac{\mu\bar{v}/L^2}{\bar{\rho}/L}\right)_4 v'_{z'z'} + \frac{\beta'}{\pi} \left(\frac{l_d^2}{L^2}\right)_2 \left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1 \left(\frac{\bar{q}\bar{\varphi}\bar{c}}{\bar{\rho}}\right)_3 \varphi'_{z'z'} = \alpha',$$

$$-\beta' q'_i D'_i \left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1 + \left(\frac{\bar{v}L}{\bar{D}}\right)_5 (v' - v'_i) = 0,$$

$$\left(\frac{l_d^2}{L^2}\right)_2 \left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1 \varphi'_{z'z'} =$$

$$-2\pi \sum_{\pm} c'_i q'_i \exp\left(q'_i \left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1 \{\varphi'(H'_d(z')) - \varphi'(z')\} + \left(\frac{gm_i L}{kT}\right)_7 (H'_d(z') - z')\right).$$

In the solid domain, equation (12) reads $(\varepsilon_s)_6 \varphi'_{z'z'} = 0$.

Assuming that the dimensionless quantities $(\cdot)_i$ satisfy the equalities

$$(\cdot)_i = \delta^{ni}, \quad i = 1, \dots, 6, \quad (\cdot)_7 = 0,$$

we obtain a hierarchy of problems to study. In this study, we consider only the case when all the powers n_i are equal to zero, i.e. $(\cdot)_i = O(1)$.

The equality $(\cdot)_1 = O(1)$ means that the electroosmotic forces and the thermal forces are of the same order. Note that the relation $(\cdot)_1 = O(1)$ holds, for example, for an aqueous solution of a symmetric electrolyte (where $z_+ = z_-$ and $c_+^- = c_-^-$) at $T = 298K$, $z = 1$, and value of the ζ -potential equal to 25 mV. when the parameter $(\cdot)_1$ is not small, the Debye-Hückel linearization of the Poisson-Boltzmann equation is inapplicable.

For $(\cdot)_1 = O(1)$, the Debye length l_d can be large, as compared with the electrical double layer; in this case the double layers may overlap. Indeed, it is commonly assumed that $l_d = 9.6/(z\sqrt{\bar{c}})$. For the above-mentioned electrolyte with a molar concentration of counter-ions $\bar{c} = 0,01$ mmole, the Debye length is $l_d = 100[nm]$, whereas the characteristic thickness of the electrical double layer is only several nanometers, and the pore size in nanocapillary membranes is 15 [nm]. For such cases, the assumption $(\cdot)_2 = O(1)$ is fairly natural. The hypothesis $(\cdot)_3 = O(1)$ means that the horizontal pressure gradient and the horizontal electric field are commensurable in the order of magnitude.

The relation $(\cdot)_4 = O(1)$ is satisfied if the viscous forces are comparable with the pressure gradient applied. As the dimensionless parameter $(\cdot)_5$ is the Peclet number (Pe), the equality $Pe = O(1)$ means that convection and diffusion are quantities of the same order. If the electric concentration \bar{c} in water is small, then the hypothesis $(\cdot)_6 = O(1)$, i.e. $\varepsilon_s/\varepsilon_f = O(1)$, is valid. As the mass m_i can be neglected, in what follows we assume that $(\cdot)_7 = 0$.

The Debye-Hückel approach to the analysis of the Poisson-Boltzmann equation (17) in the single layer $z > 0$ with the boundary conditions $\varphi \rightarrow 0$ and $\varphi_z \rightarrow 0$ as $z \rightarrow \infty$ and $\varphi|_{z=0} = \zeta_0$ implies the following. For a symmetric electrolyte, the linearized equation (17) in the SI system of units where 4π is substituted by 1) acquires the form $l_d^2 \varphi_{zz} = -\varphi$, because the nonlocal term $\varphi(d)$ disappears as $d \rightarrow \infty$. In this case, the solution is given by the formula $\varphi = \zeta_0 e^{-z/l_d}$, which implies that the Debye length is determined by Eq. (22).

4. Asymptotic analysis of the Poisson-Boltzmann equation.

We pass back to dimensional variables. Using the method of two-scale expansions, we seek for the solution of Eq. (19) in the form of a series

$$\varphi(z) = \sum_0^{\infty} \delta^k \varphi^k(z, y)|_{y=z/(\delta L)}, \quad (23)$$

where the functions $\varphi^k(z, y)$ for each $z \in \Omega$ are periodic in the y direction with a period equal to unity. We introduce the flux

$$F(z) = \tilde{\varepsilon} \left(\frac{z}{\delta L} \right) \frac{d}{dz} \varphi(z), \quad \frac{d}{dz} F = f(\varphi), \quad (24)$$

and present it as a series

$$F(z) = \sum_0^{\infty} \delta^k F^k(z, y)|_{y=z/(\delta L)}, \quad (25)$$

where $F^k(z, y)$ are functions periodic in the y direction for all $z \in \Omega$.
Using the formula

$$\frac{d}{dz} \varphi^k(z, \frac{z}{\delta L}) = \varphi_z^k(z, \frac{z}{\delta L}) + \frac{1}{\delta L} \varphi_y^k(z, \frac{z}{\delta L})$$

and substituting series (23) and (25) into the first equality of (24), we obtain

$$\sum_{-1}^{\infty} \delta^k (\cdot)_k = 0.$$

Thus, for all $k = -1, 0, 1, \dots$, we have $(\cdot)_k = 0$. In particular, three first equalities can be written as

$$\varphi_y^0(z, y) = 0, \quad F^0(z, y) = \tilde{\varepsilon}(y)(\varphi_y^0(z, y) + \varphi_y^1(z, y)/L), \quad (26)$$

$$F^1(z, y) = \tilde{\varepsilon}(y)(\varphi_y^1(z, y) + \varphi_y^2(z, y)/L). \quad (27)$$

Substituting series (23) and (25) into the second equality of (24) and retaining only the powers δ^{-1} and δ^0 , we obtain

$$\frac{\partial}{\partial y} \left(\tilde{\varepsilon}(y)(\varphi_y^0(z, y) + \varphi_y^1(z, y)/L) \right), \quad (28)$$

$$\begin{aligned} & \frac{\partial}{\partial z} \left(\tilde{\varepsilon}(y)(\varphi_z^0(z, y) + \varphi_y^1(z, y)/L) \right) + \frac{1}{L} \frac{\partial}{\partial y} \left(\tilde{\varepsilon}(y)(\varphi_z^1(z, y) + \varphi_y^2(z, y)/L) \right) \\ & = -4\pi\chi(y) \sum_{\pm} c_i^- q_i. \end{aligned} \quad (29)$$

Equations (28) and (29) allow the functions $\varphi^0(z, y)$, $\varphi^1(z, y)$, and $\varphi^2(z, y)$ to be uniquely determined. Indeed, it follows from the first relation of system (26) that the function $\varphi^0(z, y)$ is independent of the variable y . For a given function $\varphi^0(z)$, Eq. (28) for $\varphi^1(z, y)$ can be solved by the method of separation of variables under the assumption that there exists a certain function $w_1(y)$, such that $\varphi^1(z, y) = \varphi^0(z)w_1(y)$. Substituting this presentation into Eq. (28), we obtain $w_1(y)$, which is a periodic solution of the problem

$$\frac{d}{dy} \left(\tilde{\varepsilon}(y) \left(1 + \frac{1}{L} \frac{dw_1}{dy} \right) \right) = 0, \quad \int_0^1 w_1(y) dy = 0. \quad (30)$$

Obviously, w_1 is found uniquely, and

$$\tilde{\varepsilon}(y) \left(1 + \frac{1}{L} \frac{dw_1}{dy} \right) = \varepsilon_h(\Phi) = \text{const}, \quad \varepsilon_h(\Phi) = \frac{1}{\Phi/\varepsilon_f + (1-\Phi)/\varepsilon_s}. \quad (31)$$

Integrating equality (29) with respect to y , we obtain an equation for $\varphi^0(z)$:

$$\varepsilon_h(\Phi) \varphi_{zz}^0 = -4\pi\Phi \sum_{\pm} c_i^- q_i, \quad \varphi^0(0) = \zeta_0, \quad \varphi^0(L) = \zeta_L. \quad (32)$$

For known functions $\varphi^0(z)$ and $\varphi^1(z, y) = \varphi_z^0(z)w_1(y)$, Eq. (29) for $\varphi^2(z, y)$ can also be solved by the method of separation of variables under the assumption that there exists a function $w_2(y)$, such that $\varphi^2(z, y) = \varphi_{zz}^0(z)w_2(y)$. Substituting this presentation into Eq. (29), we obtain $w_2(y)$, which is a periodic solution of the equation

$$\varepsilon_h \varphi_{zz}^0 + \frac{1}{L} \varphi_{zz}^0 \frac{d}{dy} \left(\tilde{\varepsilon}(y) \left(w_1(y) + \frac{1}{L} w_2(y) \right) \right) = -4\pi\chi(y) \sum_{\pm} c_i^- q_i. \quad (33)$$

For $\int_0^1 w_2(y) dy = 0$, Eq. (33) has a unique solution. Note that the presentation for the macroscopic parameter ε_h coincides with the known Maxwell formula for a mixture of two dielectrics.

5. Asymptotic analysis of velocity.

Integrating Eq. (20), we obtain the following formula for velocity in each fluid domain $a_n < z < b_n$:

$$\mu v(z) = \frac{1}{b_n - a_n} \int_{a_n}^z dr \int_{a_n}^{b_n} ds \int_s^r G(\lambda) d\lambda, \quad G = \alpha - \frac{\beta \varepsilon f}{4\pi} \varphi_{zz}. \quad (34)$$

We extend the function v by zero to the solid domain Ω_s^δ , using $\hat{v}(z)$ to denote this extension. It follows from Eq. (34) that, for any $z \in \Omega$,

$$\mu \hat{v}(z) = \frac{\tilde{\chi}(\frac{z}{\delta L})}{\delta h_j^*} \int_{z+\delta \tilde{\xi}_a(\frac{z}{\delta L})}^z dr \int_{z+\delta \tilde{\xi}_a(\frac{z}{\delta L})}^{z+\delta \tilde{\xi}_b(\frac{z}{\delta L})} ds \int_s^r G(\lambda) d\lambda, \quad G = \alpha - \frac{\beta \varepsilon f}{4\pi} \varphi_{zz}. \quad (35)$$

Having in mind that $\varphi(z)$ is given by the expansion (23), we seek for $\hat{v}(z)$ in the form

$$\hat{v}(z) = \sum_2^{\infty} \delta^k v^{k-2}(z, y)|_{y=z/(\delta L)}, \quad (36)$$

where the functions $v^k(z, y)$ are periodic in y and $v^k(z, y) = 0$, for $0 < y < \Phi$.

After simple calculations we have

$$\int_{z+\delta\tilde{\xi}_a(\frac{z}{\delta L})}^z dr \int_{z+\delta\tilde{\xi}_a(\frac{z}{\delta L})}^{z+\delta\tilde{\xi}_b(\frac{z}{\delta L})} ds \int_s^r \alpha d\lambda = \frac{\delta^3 \alpha \bar{h}_l}{2} \tilde{\xi}_a(\frac{z}{\delta L}) \tilde{\xi}_b(\frac{z}{\delta L}).$$

Using the properties of the functions $\varphi_z^0(z, y)$, $\varphi_z^1(z, y)$, and $\varphi_z^2(z, y)$ we obtain

$$\varphi(\lambda) = \varphi^0(z) + \delta\varphi_z^0(z)w_1(y) + \delta^2\varphi_{zz}^0(z)w_2(y) + \dots, \quad z = \lambda, \quad y = \frac{\lambda}{\delta L},$$

$$\varphi''(\lambda) = \left\{ \frac{\varphi_z^0(z)w_1''(y)}{\delta L^2} + \varphi_{zz}^0 \left(1 + \frac{2w_1'(y)}{L} + \frac{w_2''(y)}{L^2} \right) \right\} \Big|_{z=\lambda, y=\frac{\lambda}{\delta L}} + \delta(\cdot). \quad (37)$$

Due to the multiplier $\tilde{\chi}$ in the right hand side of formula (35), we can assume that $z \in (H_a(z), H_b(z))$ in this formula. In this case, the variables r and s also belong to this interval. As λ is between r and s , hence,

$$0 < \frac{\lambda}{\delta L} - \left[\frac{\lambda}{\delta L} \right]_e < \Phi,$$

the derivatives $w_1''(y)$ and $w_2''(y)$ in (37) are well defined.

Moreover, it follows from (29) and (31) that, for $0 < y < \Phi$, the functions $w_1(y)$ and $w_2(y)$ satisfy the equalities

$$w_1''(y) = 0,$$

and

$$\varphi_{zz}^0 \varepsilon_f \left(1 + \frac{2}{L} w_1'(y) + \frac{1}{L^2} w_2''(y) \right) = -4\pi \sum_{\pm} c_i^- q_i.$$

Thus

$$\varphi''(\lambda) = -\frac{4\pi}{\varepsilon_l} \sum_{\pm} c_i^- q_i + \delta(\cdot). \quad (38)$$

Substituting formulas (36) and (38) into (35) and considering only the power δ^2 , we can show that $v^0(z, y)$ does not depend on the variable z and has the form

$$\mu v^0(y) = \frac{1}{2} \tilde{\chi}(y) \tilde{\xi}_a(y) \tilde{\xi}_b(y) (\alpha + \beta \sum_{\pm} c_i^- q_i). \quad (39)$$

Integrating equality (39) over the periodicity cell, we obtain a macroscopic equation for velocity

$$V \equiv \int_0^1 v^0(y) dy = -\lambda_{11} \alpha - \lambda_{12} \beta, \quad (40)$$

where the hydrodynamic and electrochemical mobilities are given by the formulas

$$\lambda_{11} = \frac{L^2 \Phi^3}{12\mu}, \quad \lambda_{12} = \frac{L^2 \Phi^3}{12\mu} \sum_{\pm} c_i^- q_i.$$

6. Asymptotic analysis of ion velocity.

As $Pe = O(1)$ and $v = O(\delta^2)$, we assume that $D_i = \delta^2 \tilde{D}_i$. Let \hat{v}_i denote the zero extension of v_i to Ω_s^δ . Then it follows from (21) that

$$\hat{v}_i(z) = \hat{v}(z) - \frac{\beta q_i \delta^2 \tilde{D}_i \chi(z)}{kT}.$$

If \hat{v}_i admits the representation formula

$$\hat{v}_i(z) = \sum_2^{\infty} \delta^k v_i^{k-2}(z, y)|_{y=z/(\delta L)},$$

we obtain

$$v_i^0(z, y) = v^0(y) - \frac{\beta q_i \tilde{D}_i \chi(y)}{kT}. \quad (41)$$

Let us consider the total electric current

$$j = \sum_{\pm} c_i q_i \hat{v}_i, \quad j(z) = \sum_0^{\infty} \delta^k j^k(z, y)|_{y=z/(\delta L)}.$$

As it follows from (41) that

$$j^0(z, y) = \sum_{\pm} c_i^- q_i v_i^0(y), \quad (42)$$

the macroscopic electric current is

$$J \equiv \int_0^1 j^0(y) dy = -\lambda_{21}\alpha - \lambda_{22}\beta, \quad (43)$$

where

$$\lambda_{21} = \frac{L^2 \Phi^3}{12\mu} \sum_{\pm} c_i^- q_i, \quad \lambda_{22} = \frac{L^2 \Phi^3}{12\mu} \left(\sum_{\pm} c_i^- q_i \right)^2 + \frac{\Phi}{kT} \sum_{\pm} q_i^2 \tilde{D}_i c_i^-. \quad (44)$$

7. Macroscopic electroosmotic mobilities.

The macroscopic laws of electroosmotic

$$V = -\lambda_{11}p_x - \lambda_{12}\psi_x, \quad J = -\lambda_{21}p_x - \lambda_{22}\psi_x, \quad (45)$$

satisfy an following important condition : the mobilities λ_{ij} obey the Onsager condition $\lambda_{12} = \lambda_{21}$, known in nonequilibrium thermodynamics. Equations (45) explain the effect of electroosmosis and allow the difference in the water levels in the tubes to be calculated.

Indeed, the total velocity in the equilibrium state equals 0, and the pressure gradient p_x can be obtained by the equality

$$p_x = -\frac{\lambda_{12}}{\lambda_{11}}\psi_x.$$

Equations (45) also explain why the flow through the membrane induces an electrical field. For neutral electrolytes we have $J = 0$; therefore the second equation of (45) implies that the pressure gradient p_x induces an electrical field such that

$$\psi_x = -\frac{\lambda_{21}}{\lambda_{22}}p_x. \quad (46)$$

The induced electrical field reduces hydrodynamic permeability. Because of (46), the first equation in (45) implies that

$$p_x = -\lambda_{ef}\psi_x, \quad \lambda_{ef} = \lambda_{11} - \lambda_{12}^2/\lambda_{22}.$$

Observe, that the mobilities λ_{ij} do not depend on the ζ - potentials ζ_0 and ζ_L though these potentials control the macroelectrical field.

8. Conclusions.

We have proposed a two-scale one-dimensional model for osmotic nanoflows in thin horizontal slits under the action of a pressure gradient and an external electric field. The model is obtained by using two scales and applying the method of homogenization to the Stokes equation for the flow of ion components and the Poisson-Boltzmann equation for the induced electric field. Introducing a fast variable and using two-scale asymptotic expansions, we managed to derive macroequations with the coefficients calculated on the basis of microequations.

The averaged model is the generalization of the Darcy equation and the Boltzmann-Smoluchowski equation. In this model, the mean hydrodynamic flow and the mean electric current depend linearly on the pressure gradient and external electric field, and the coefficients obey the Onsager conditions of symmetry.