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FLOW OF ELECTROLYTES IN A POROUS MEDIUM

V. V. Shelukhin[1] **and Yu. Amirat**[2]

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A two-scale model of ion transfer in a porous medium is obtained for one-dimensional horizontal flows under the action of a pressure gradient and an external electric field by the method of homogenization. Steady equations of electroosmotic flows in flat horizontal nano-sized slits separated by thin dielectric partitions are averaged over a small-scale variable. The resultant macroequations include Poisson's equation for the vertical component of the electric field and Onsager's relations between flows and forces. The total horizontal flow rate of the fluid is found to depend linearly on the pressure gradient and external electric field, and the coefficients in this linear relation are calculated with the use of microequations.

Key words: *filtration of electrolytes, two-scale expansions, homogenization, nanoscale, nonlocal Poisson–Boltzmann equation.*

Introduction. The electroosmosis phenomenon discovered by Reuss [1] implies that the levels of water in a U-shaped tube with sand on the bottom become different if differently charged electrodes are placed into the tube (Fig. 1). In 1859, Quincke discovered the opposite effect: a filtration flow through a membrane induces a potential difference on the latter [1]. An explanation of these effects was found within the framework of the theory of an electrical double layer arising on the interface of solid mineral particles and a pore-filling fluid [2]. Because of chemically non-balanced bonds, the particle surface is not electrically neutral, while the usual water is an electrolyte. Therefore, there arises an electric potential on the interface, and the charges become separated, thus, forming an electrical double layer. The inner layer (Stern layer) consists of ions retained by electrostatic forces and van der Waals forces. The outer layer (Gouy layer) is formed by ions trapped by electric forces and "disorder" thermal forces.

The electrokinetic phenomena are caused by the presence of this electrical double layer. An external electric field initiates relative motion of strongly connected ions of the inner layer and mobile ions of the outer layer (electrophoresis and electroosmosis). The neutral bulk fluid is also set into motion because of its viscosity. Simultaneously, an electric potential may arise owing to the relative motion of cations and anions under the action of a pressure gradient.

It is necessary to study the electroosmosis phenomenon to solve problems of separation of constituents in nanochannels [3]. In contrast to microchannel flows, the transverse electric field is extremely important for flows in nanochannels.

Ion-transport models are based on the Navier–Stokes equations for a bulk fluid, Poisson's equation for the electric field potential, and various generalizations of the Nernst law for the ion distribution [4]. Being extremely complicated, such systems can be resolved only numerically; hence, most activities involve quantification of electrical phenomena.

An asymptotic approach for a theoretical analysis of electroosmosis equations is developed in the present paper. For this purpose, we study horizontal flows through a vertical membrane, which is treated as a system of N thin flat horizontal fluid layers of identical thickness h_f separated by solid layers of identical thickness h_s. The flows

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[1] Lavrent'ev Institute of Hydrodynamics, Siberian Division, Russian Academy of Sciences, Novosibirsk 630090; shelukhin@hydro.nsc.ru. [2] Blaise Pascal University, Clermont-Ferrand, France 631177. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 49, No. 4, pp. 162–173, July–August, 2008. Original article submitted July 16, 2007; revision submitted October 11, 2007.

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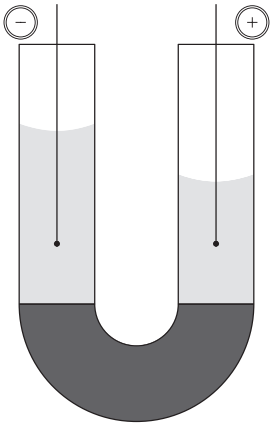

Fig. 1. Schematic of electroosmosis.

are caused by a horizontal pressure gradient and by an applied external horizontal electric field; the electroosmosis forces are caused by an induced vertical electric field. The membrane thickness $L = N(h_f + h_s)$ (N is the number of fluid layers) is assumed to be fixed, and the ratio $\delta = (h_f + h_s)/L$ is assumed to be a small parameter.

Within the theory of the electrical double layer, the particle–fluid interface is not purely mathematical; instead, it is a certain transitional layer, and the issue of the boundary conditions has not been adequately studied yet [5]. The potential of the surface near the particle, where the fluid velocity equals zero, is called the ζ-potential. The Stern layer is motionless and is related to the solid particle, which is assumed to be electrically neutral. Therefore, Poisson's equation transforms to the Laplace equation in the solid layer. If there is no concentration of free charges on the surface of the ζ-potential, where the no-slip condition for velocity is satisfied, then the condition of continuity of the normal component $\boldsymbol{D} \cdot \boldsymbol{n}$ of the induction vector $\boldsymbol{D} = \varepsilon \boldsymbol{E}$ is satisfied on this surface under the assumption that the dielectric permittivity of the solid layer differs from that of the fluid layer. Hence, the condition of continuity of $\boldsymbol{D} \cdot \boldsymbol{n}$ rather than the value of the potential is imposed on the interface between the solid and fluid layers.

The asymptotic approach considered is a method of homogenization [6, 7] based on two-scale asymptotic expansions for equations that describe the ion transport near the solid particles. Homogenization yields micro- and macroequations, and the microequations serve to determine constants for macroequations including the generalized Darcy law for a medium with a porosity $\Phi = h_f/(h_f + h_s)$.

The horizontal isolated fluid layers interact due to the vertical component of the electric field. The macroscopic horizontal flow V, however, is independent of the vertical variable.

The macroscopic electric current J and the flow V satisfy the generalized Darcy law

$$V = -\lambda_{11} p_x - \lambda_{12} \psi_x, \qquad J = -\lambda_{21} p_x - \lambda_{22} \psi_x, \tag{1}$$

where p_x is the horizontal pressure gradient and ψ_x is the horizontal gradient of the electric potential. In thermodynamics of irreversible processes, system (1) relating flows and forces is called the Onsager reciprocal relations [8]. It is possible to calculate the mobility coefficients λ_{ij} and to prove the Onsager relation of symmetry $\lambda_{12} = \lambda_{21}$. For flows in thin capillaries, the kinetic coefficient λ_{12} was first estimated by Boltzmann and Smoluchowski [1]. The full macroscopic system consists of the Darcy law (1) and Poisson's equation for the macroscopic electric potential. The asymptotic analysis is performed in the present paper for a small (as compared with δ) coefficient of ion diffusion.

1. Governing Equations. A real aqueous solution consists of a solvent (water) and ions of various salts (species or components) dissolved in the solvent. A solution may contain several cation and anion species, depending on the valency of this or that ion. In the present paper, 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 [9]

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla p + \mu \Delta \boldsymbol{v} + \boldsymbol{E} \sum_{i=\pm} \frac{q_i \rho_i}{m_i} + \rho \boldsymbol{g}. \tag{2}$$

Here ρ is the density of the medium, $\boldsymbol{v}$ is the velocity of the mixture, μ is the viscosity, m_i is the molecular weight of the ion, p is the pressure, ρ_+ and ρ_- are the mass densities of positive and negative ions, $q_i = z_i e$ is the ion charge, $\boldsymbol{E}$ is the electric field, $\boldsymbol{g}$ is the acceleration due to gravity, 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 [1]

$$0 = -\frac{\rho_i q_i}{m_i}\,d\psi - \frac{kT}{m_i}\,d\rho_i, \qquad \boldsymbol{E} = -\nabla\psi, \tag{3}$$

where ψ is the potential of the field $\boldsymbol{E}$, k is the Boltzmann constant, and T is the temperature. Equality (3) means that the contacting phases, being in equilibrium, have identical chemical potentials. In the dynamic case, Eq. (3) is generalized to the force-balance equation as follows [9]:

$$\rho_i\,\frac{\partial \boldsymbol{v}_i}{\partial t} = \mu_i \Delta \boldsymbol{v}_i - \alpha_i \nabla p + \frac{\rho_i q_i}{m_i}\,\boldsymbol{E} - \frac{kT}{m_i}\nabla\rho_i + \frac{\gamma_i \rho_i}{m_i}\,(\boldsymbol{v} - \boldsymbol{v}_i) + \rho_i \boldsymbol{g}. \tag{4}$$

Here the resistance coefficient γ_i is defined by the Stokes–Einstein–Sutherland [10]

$$\gamma_i = kT/D_i, \tag{5}$$

$\boldsymbol{v}_i$ and μ_i are the velocity and viscosity of the fluid component consisting of ions of the ith type, α_i is the bulk concentration ($\alpha_1 + \alpha_2 \le 1$), the fifth term in the right side of equality (4) is a diffusion term, and D_i is the diffusion coefficient. Because of the low phase concentrations α_1 and α_2, the ion viscosity μ_i and also the terms $\alpha_i \nabla p$ can be neglected.

Poisson's equation of charge conservation has the form

$$\operatorname{div}\boldsymbol{D} = 4\pi \sum_{\pm} \frac{\rho_i q_i}{m_i}, \qquad \boldsymbol{D} = \varepsilon_f \boldsymbol{E}, \qquad \boldsymbol{E} = -\nabla\psi, \tag{6}$$

where $\boldsymbol{D}$ 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:

$$\operatorname{div}\boldsymbol{v} = 0, \qquad \rho = \text{const}, \qquad \frac{\partial \rho_i}{\partial t} + \operatorname{div}(\rho_i \boldsymbol{v}_i) = 0. \tag{7}$$

The charges are not concentrated inside the solid dielectric; hence, the following equations are satisfied in the solid phase:

$$\operatorname{div}\boldsymbol{D} = 0, \qquad \boldsymbol{D} = \varepsilon_s \boldsymbol{E}, \qquad \boldsymbol{E} = -\nabla\psi$$

(ε_s is the dielectric permittivity of the dielectric material).

2. One-Dimensional Equations. This research was motivated by the problem of an electrolyte flow through a membrane of finite thickness l (Fig. 2) where the input pressure (on the left) p_- is greater than the output pressure p_+. In this case, the flow is mainly determined by the pressure gradient $(p_+ - p_-)/l \equiv -\alpha$. The flow may also be induced by the gradient of the potential of the external electric field $E = -(\psi^+ - \psi^-)/l \equiv -\beta$.

Let ρ_i^- be the ion density defined at the output. As a model problem, we consider a steady flow of the electrolyte in an infinite horizontal layer of thickness L consisting of N horizontal slits $a_n < z < b_n$ of identical thickness h_f separated by layers $b_n < z < a_{n+1}$ of a solid dielectric of identical thickness h_s (z is the vertical coordinate). At the central point d_n of the fluid domain $a_n < z < b_n$, the ion densities ρ_i acquire prescribed values ρ_i^-, which corresponds to imposing input concentrations in the case of a finite-thickness membrane.

Let Q_f and Q_s be the fluid and solid domains, respectively:

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

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

$$a_n = n(h_f + h_s), \qquad b_n = a_n + h_f, \qquad d_n = a_n + h_f/2.$$

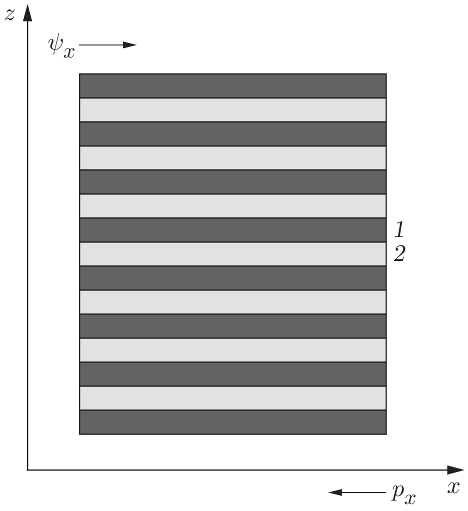

Fig. 2. Flow through the membrane: 1) solid layer; 2) fluid layer.

In the fluid domain Ω_f, the solution of Eqs. (2)–(7) is sought in the form

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

($\alpha = \mathrm{const}$; $\beta = \mathrm{const}$). In this case, system (2)–(7) becomes

$$\mu v_{zz} - \alpha - \beta \sum_{\pm} c_i q_i = 0, \qquad c_i = \frac{\rho_i}{m_i}; \tag{8}$$

$$-P_z - \varphi_z \sum_{\pm} c_i q_i - \rho g = 0; \tag{9}$$

$$-\beta c_i q_i + \frac{kTc_i}{D_i}\,(v - v_i) = 0; \tag{10}$$

$$-c_i q_i \varphi_z - kTc_{iz} - gc_i m_i = 0; \tag{11}$$

$$\varepsilon_l \varphi_{zz} = -4\pi \sum_{\pm} c_i q_i. \tag{12}$$

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

$$\varepsilon_s \varphi_{zz} = 0. \tag{13}$$

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

$$[\varphi] = [\varepsilon \varphi_z] = 0 \quad \text{for} \quad z = a_n \quad \text{and} \quad z = b_n, \qquad c_i = c_i^- \quad \text{for} \quad z = d_n, \tag{14}$$

where $n = 1, \ldots, N-1$; the expression $[\varphi]\Big|_{z=z_0}$ indicates a jump of the discontinuous function φ at the discontinuity point z_0:

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

The no-slip conditions can be written as

$$v = 0 \quad \text{for} \quad z = a_n \quad \text{and} \quad z = b_n \quad (n = 0, \ldots, N). \tag{15}$$

The external values of the potential φ are assumed to be given:

$$\varphi\Big|_{z=0} = \zeta_0, \qquad \varphi\Big|_{z=L} = \zeta_L. \tag{16}$$

Thus, one-dimensional flows are described by Eqs. (8)–(13) with the boundary conditions (14)–(16). Let us give some consequences of these equations.

We introduce a discontinuous function of dielectric permittivity

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

which is assumed to be periodically extended for all values of z.

To eliminate the concentrations c_i, we write Eq. (11) in the form

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

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

$$c_i = c_i^- \exp\Big\{\frac{q_i}{kT}\,[\varphi(d_n) - \varphi(z)] + \frac{gm_i}{kT}\,(d_n - z)\Big\}. \tag{17}$$

Thus, the potential φ on the interval (a_n, b_n) is the solution of the Poisson–Boltzmann equation [1]

$$\varepsilon_f \varphi_{zz} = -4\pi \sum_{\pm} c_i^- q_i \exp\Big\{\frac{q_i}{kT}\,[\varphi(d_n) - \varphi(z)] + \frac{gm_i}{kT}\,(d_n - z)\Big\}. \tag{18}$$

We introduce a 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

$$H_a(z) = h\Big[\frac{z}{h}\Big]_e, \quad H_d(z) = \frac{h_f}{2} + h\Big[\frac{z}{h}\Big]_e, \quad H_b(z) = h_f + h\Big[\frac{z}{h}\Big]_e, \quad h \equiv h_f + h_s \tag{19}$$

take constant values a_n, d_n, and b_n. To determine φ over the entire interval $0 < z < L$, we have to solve the equation

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

with the boundary conditions (14) and (16) (χ is the characteristic function of the fluid domain Ω_f).

3. Transition to Dimensionless Quantities and Comparison of Parameters. We introduce a periodic function $\xi_d = H_d(z) - z$, which acquires the value $\xi_d = h_f/2 - z$ on the periodicity interval $0 < z < h$. We seek for an asymptotic solution of problem (8)–(16), assuming that the parameter

$$h/L = 1/N = \delta$$

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

$$h(\delta) = \delta L, \quad h_f = \delta\bar h_f, \quad h_s = \delta\bar h_s, \quad \bar h_f + \bar h_s = L, \quad \Phi = \bar h_f/L$$

(Φ is the porosity).

In addition to the slow variable $z \in \Omega$, we introduce a fast variable $y = z/(\delta L)$. For small values of δ, the periodic functions $\varepsilon(z)$ and $\chi(z)$ rapidly oscillate and admit presentations in the form of functions of the fast variable

$$\varepsilon(z) = \tilde\varepsilon\Big(\frac{z}{\delta L}\Big), \qquad \chi(z) = \tilde\chi\Big(\frac{z}{\delta L}\Big),$$

where

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

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 assumed to be extended periodically for all values $y \in \mathbb{R}$. The functions $H_a(z)$, $H_d(z)$, and $H_b(z)$ introduced in (19) can be written as

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

In the notation used, the function $\varphi(z)$ on the interval $0 < z < L$ is the solution of the problem

$$\Big(\tilde{\varepsilon}\Big(\frac{z}{\delta L}\Big)\varphi_z\Big)_z = f(\varphi) \tag{20}$$

with the boundary conditions (16), where

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

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 Eqs. (8) and (12) that the bulk velocity satisfies the equation

$$z \in \Omega_f^\delta\colon \quad \mu v_{zz} + (4\pi)^{-1}\beta\varepsilon_f\varphi_{zz} = \alpha, \qquad z \in \partial\Omega_f^\delta\colon \quad v = 0. \tag{21}$$

If the values of c_i are set by formulas (17), then the ion velocity is found as the solution of the problem

$$z \in \Omega_f^\delta\colon \quad -\beta c_i q_i + (kTc_i/D_i)(v - v_i) = 0. \tag{22}$$

Using the symbol $\bar{f}$ for the characteristic value of the dimensional quantity f and the symbol f' for the dimensionless value of this quantity, we pass to the dimensionless variables $f = \bar{f}f'$. We use the following notations:

$$z = Lz', \quad x = Lx', \quad c_i = \bar{c}c_i', \quad q_i = \bar{q}q_i', \quad v = \bar{v}v', \quad v_i = \bar{v}v_i', \quad D_i = \bar{D}D_i',$$

$$\alpha = \bar{p}\alpha'/L \equiv \bar{p}p'_{x'}/L, \quad \beta = \bar{\varphi}\beta'/L \equiv \bar{\varphi}\psi'_{x'}/L, \quad H_d(z) = LH_d'(z').$$

The quantity

$$l_d = \{\varepsilon_f kT/(2\bar{c}\bar{q}^2)\}^{1/2} \tag{23}$$

has the dimension of length and is known as the Debye length. In dimensionless variables, Eqs. (8)–(12) in the fluid domain take the form

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

$$-\beta' q_i' D_i'\Big(\frac{\bar{q}\bar{\varphi}}{kT}\Big)_1 + \Big(\frac{\bar{v}L}{\bar{D}}\Big)_5(v' - v_i') = 0,$$

$$\Big(\frac{l_d^2}{L^2}\Big)_2\Big(\frac{\bar{q}\bar{\varphi}}{kT}\Big)_1\varphi'_{z'z'} = -2\pi\sum_{\pm} c_i' q_i' \exp\Big\{q_i'\Big(\frac{\bar{q}\bar{\varphi}}{kT}\Big)_1\Big[\varphi'(H_d'(z')) - \varphi'(z')\Big] + \Big(\frac{gm_iL}{kT}\Big)_7(H_d'(z') - z')\Big\}.$$

In the solid domain, Eq. (13) is equivalent to the equation $(\varepsilon_s)_6\varphi'_{z'z'} = 0$.

Assuming that the dimensionless parameters $(\,\cdot\,)_i$ obey the constraints

$$(\,\cdot\,)_i = \delta^{n_i}, \quad i = 1, \ldots, 6, \qquad (\,\cdot\,)_7 = 0,$$

we come to a hierarchy of the problems. In this study, we consider only the case where all powers of 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 quantities of the same order. Note that the relation $(\,\cdot\,)_1 = O(1)$ is valid, for instance, for an aqueous solution of a symmetric electrolyte (i.e., for $z_+ = z_-$, $c_+^- = c_-^-$) at $T = 298$ K, $z = 1$, and the value of the ζ-potential equal to 25 mV [3]. If 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 $l_d = 9.6/(z\sqrt{\bar{c}})$ [3]. 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 [3], and the pore size in nanocapillary membranes is 15 nm [11]. 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 $\mathrm{Pe} = O(1)$ means that convection and diffusion are quantities of the same order. If the electrolyte concentration $\bar{c}$

in water is small, then the hypothesis $(\,\cdot\,)_6 = O(1)$, which is equivalent to the equality $\varepsilon_s/\varepsilon_f = O(1)$, 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 (18) for the half-plane $z > 0$ with the boundary conditions $\varphi \to 0$ and $\varphi_z \to 0$ as $z \to \infty$ and with the condition $\varphi = \zeta_0$ at $z = 0$ implies the following. For a symmetric electrolyte, the linearized equation (18) in the SI system of units (where 4π has to be replaced by unity) acquires the form $l_d^2\varphi_{zz} = -\varphi$, because the nonlocal term $\varphi(d)$ disappears as $d \to \infty$. In this case, the solution is given by the formula $\varphi(z) = \zeta_0\,\mathrm{e}^{-z/l_d}$, which implies that the Debye length is determined by Eq. (23).

4. Asymptotic Analysis of the Poisson–Boltzmann Equation. We pass back to dimensional variables. Using the method of two-scale expansions [6, 7], we seek for the solution of Eq. (20) in the form of a series

$$\varphi(z) = \sum_0^\infty \delta^k \varphi^k(z, y)\Big|_{y=z/(\delta L)}, \tag{24}$$

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

$$F(z) = \tilde\varepsilon\Big(\frac{z}{\delta L}\Big)\frac{d}{dz}\,\varphi(z), \qquad \frac{d}{dz}\,F = f(\varphi) \tag{25}$$

and present it as a series

$$F(z) = \sum_0^\infty \delta^k F^k(z, y)\Big|_{y=z/(\delta L)} \tag{26}$$

[$F^k(z, y)$ are functions periodic in the y directions for all $z \in \Omega$].

Using the formula

$$\frac{d}{dz}\,\varphi^k\Big(z, \frac{z}{\delta L}\Big) = \varphi^k_z\Big(z, \frac{z}{\delta L}\Big) + \frac{1}{\delta L}\,\varphi^k_y\Big(z, \frac{z}{\delta L}\Big)$$

and substituting series (24) and (26) into the first equality of (25), 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

$$\varphi^0_y(z, y) = 0, \qquad F^0(z, y) = \tilde\varepsilon(y)(\varphi^0_z(z, y) + \varphi^1_y(z, y)/L); \tag{27}$$

$$F^1(z, y) = \tilde\varepsilon(y)(\varphi^1_z(z, y) + \varphi^2_y(z, y)/L). \tag{28}$$

Substituting series (24) and (26) into the second equality of (25) and retaining only the powers δ^{-1} and δ^0, we obtain

$$\frac{\partial}{\partial y}\,\{\tilde\varepsilon(y)[\varphi^0_z(z, y) + L^{-1}\varphi^1_y(z, y)]\} = 0; \tag{29}$$

$$\frac{\partial}{\partial z}\,\{\tilde\varepsilon(y)[\varphi^0_z(z, y) + L^{-1}\varphi^1_y(z, y)]\} + L^{-1}\,\frac{\partial}{\partial y}\,\{\tilde\varepsilon(y)[\varphi^1_z(z, y) + L^{-1}\varphi^2_y(z, y)]\} = -4\pi\chi(y)\sum_\pm c_i^- q_i. \tag{30}$$

Equations (29) and (30) 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 (27) that the function $\varphi^0(z, y)$ is independent of the variable y. For a given function $\varphi^0(z)$, Eq. (29) 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 $\varphi^1(z, y) = \varphi^0_z(z)w_1(y)$. Substituting this presentation into Eq. (29), we obtain $w_1(y)$, which is a periodic solution of the problem

$$\frac{d}{dy}\Big(\tilde\varepsilon(y)\Big(1 + \frac{1}{L}\,\frac{dw_1}{dy}\Big)\Big) = 0, \qquad \int_0^1 w_1(y)\,dy = 0. \tag{31}$$

Obviously, w_1 is found uniquely, and

$$\tilde{\varepsilon}(y)\Big(1 + \frac{1}{L}\,\frac{dw_1}{dy}\Big) = \varepsilon_h(\Phi) = \text{const}, \qquad \varepsilon_h(\Phi) = \Big(\int\limits_0^1 \frac{dy}{\tilde{\varepsilon}(y)}\Big)^{-1} = \frac{1}{\Phi/\varepsilon_f + (1-\Phi)/\varepsilon_s}. \tag{32}$$

Integrating equality (30) with respect to y, we obtain an equation for $\varphi^0(z)$:

$$\varepsilon_h(\Phi)\varphi^0_{zz} = -4\pi\Phi \sum_{\pm} c_i^- q_i, \qquad \varphi^0(0) = \zeta_0, \quad \varphi^0(L) = \zeta_L. \tag{33}$$

For known functions $\varphi^0(z)$ and $\varphi^1(z,y) = \varphi^0_z(z)w_1(y)$, Eq. (30) 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 $\varphi^2(z,y) = \varphi^0_{zz}(z)w_2(y)$. Substituting this presentation into Eq. (30), we obtain $w_2(y)$, which is a periodic solution of the equation

$$\varepsilon_h\varphi^0_{zz} + L^{-1}\varphi^0_{zz}\,\frac{d}{dy}\Big\{\tilde{\varepsilon}(y)\Big[w_1(y) + L^{-1}\frac{d}{dy}w_2(y)\Big]\Big\} = -4\pi\chi(y)\sum_{\pm} c_i^- q_i. \tag{34}$$

For $\int\limits_0^1 w_2\,dy = 0$, Eq. (34) 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 [12].

5. Asymptotic Analysis of Velocity. Integrating Eq. (21), we obtain the following formula for velocity in each fluid domain $a_n < z < b_n$:

$$\mu v(z) = \frac{1}{b_n - a_n}\int\limits_{a_n}^{z} dr \int\limits_{a_n}^{b_n} ds \int\limits_{s}^{r} G(\lambda)\,d\lambda, \qquad G = \alpha - \frac{\beta\varepsilon_f}{4\pi}\,\varphi_{zz}. \tag{35}$$

We extent the function v by zero to the solid domain Ω^δ_s, using $\hat{v}(z)$ to denote this extension. It follows from Eq. (35) that

$$\mu\hat{v}(z) = \frac{\tilde{\chi}(z/(\delta L))}{\delta\bar{h}_l}\int\limits_{z+\delta\tilde{\xi_a}(z/(\delta L))}^{z} dr \int\limits_{z+\delta\tilde{\xi_a}(z/(\delta L))}^{z+\delta\tilde{\xi_b}(z/(\delta L))} ds \int\limits_{s}^{r} G(\lambda)\,d\lambda, \qquad G = \alpha - \frac{\beta\varepsilon_f}{4\pi}\,\varphi_{zz} \tag{36}$$

for all $z \in \Omega$. Taking into account that the function $\varphi(z)$ is presented as series (24), we seek for $\hat{v}(z)$ in the form

$$\hat{v}(z) = \sum_{2}^{\infty} \delta^k v^{k-2}(z,y)\Big|_{y=z/(\delta L)}, \tag{37}$$

where the functions $v^k(z,y)$ for $0 < y < \Phi$ are periodic with respect to y and $v^k(z,y) = 0$. After simple calculations, we have

$$\int\limits_{z+\delta\tilde{\xi_a}(z/(\delta L))}^{z} dr \int\limits_{z+\delta\tilde{\xi_a}(z/(\delta L))}^{z+\delta\tilde{\xi_b}(z/(\delta L))} ds \int\limits_{s}^{r} \alpha\,d\lambda = \frac{\delta^3\alpha\bar{h}_l}{2}\,\tilde{\xi}_a\Big(\frac{z}{\delta L}\Big)\tilde{\xi}_b\Big(\frac{z}{\delta L}\Big).$$

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

$$\varphi(\lambda) = \varphi^0(z) + \delta\varphi^0_z(z)w_1(y) + \delta^2\varphi^0_{zz}(z)w_2(y) + \ldots, \qquad z = \lambda, \quad y = \lambda/(\delta L);$$

$$\varphi''(\lambda) = \Big\{\frac{\varphi^0_z(z)w_1''(y)}{\delta L^2} + \varphi^0_{zz}\Big(1 + \frac{2w_1'(y)}{L} + \frac{w_2''(y)}{L^2}\Big)\Big\}\Big|_{z=\lambda,\ y=\lambda/(\delta L)} + \delta(\,\cdot\,). \tag{38}$$

By virtue of the term $\tilde{\chi}$ in the right side of Eq. (36), we can assume that $z \in (H_a(z), H_b(z))$. Then, the variables r and s also vary within this interval. As λ is between r and s and, hence,

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

the derivatives $w_1''(\lambda)$ and $w_2''(\lambda)$ in Eq. (38) are meaningful. In addition, it follows from Eqs. (30) and (32) that the functions $w_1(y)$ and $w_2(y)$ for $0 < y < \Phi$ satisfy the equalities

$$w_1''(y) = 0, \qquad \varphi^0_{zz}\varepsilon_f\Big(1 + \frac{2}{L}\,w_1'(y) + \frac{1}{L^2}\,w_2''(y)\Big) = -4\pi\sum_{\pm} c_i^- q_i.$$

Thus, we obtain

$$\varphi''(\lambda) = -\frac{4\pi}{\varepsilon_f}\sum_{\pm} c_i^- q_i + \delta(\,\cdot\,). \tag{39}$$

Substituting Eqs. (37) and (39) into Eq. (36) and considering only the power δ^2, we can show that the function $v^0(z,y)$ does not depend on the variable z and has the form

$$\mu v^0(y) = \frac{1}{2}\,\tilde{\chi}(y)\tilde{\xi_a}(y)\tilde{\xi_b}(y)\Big(\alpha + \beta\sum_{\pm} c_i^- q_i\Big). \tag{40}$$

Integrating equality (40) over the periodicity cell, we obtain a macroscopic equation for velocity

$$V \equiv \int\limits_0^1 v^0(y)\,dy = -\lambda_{11}\alpha - \lambda_{12}\beta, \tag{41}$$

where the hydrodynamic and electrochemical mobilities are defined by the formulas

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

6. Asymptotic Analysis of Ion Velocity. As $\mathrm{Pe} = O(1)$ and $v = O(\delta^2)$, we assume that the diffusion coefficients of the ion components are small: $D_i = \delta^2\tilde{D}_i$. Denoting the zero extension of the function v_i to the solid domain Ω_s^δ by $\hat{v}_i$, we use Eq. (22) to obtain

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

Presenting $\hat{v}_i$ in the form

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

we obtain

$$v_i^0(z,y) = v^0(y) - \beta q_i\tilde{D}_i\chi(y)/(kT). \tag{42}$$

We introduce the total electric current

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

As it follows from Eq. (42) that

$$j^0(z,y) = \sum_{\pm} c_i^- q_i v_i^0(y), \tag{43}$$

the macroscopic electric current is

$$J \equiv \int\limits_0^1 j^0(y)dy = -\lambda_{21}\alpha - \lambda_{22}\beta, \tag{44}$$

where

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

7. Macroscopic Electroosmotic Mobilities. The macroscopic laws of electroosmosis

$$V = -\lambda_{11} p_x - \lambda_{12} \psi_x, \qquad J = -\lambda_{21} p_x - \lambda_{22} \psi_x \tag{45}$$

satisfy an 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 (see Fig. 1) and allow the difference in the water levels in the tubes to be calculated. Indeed, the total velocity in the equilibrium state equals zero, and the pressure difference can be calculated by the equality

$$p_x = -(\lambda_{12}/\lambda_{11}) \psi_x.$$

Equations (45) also allow us to understand why the filtration flow through the membrane (see Fig. 2) induces an electric field. In a neutral electrolyte, we have $J = 0$; therefore, the second equation of (45) implies that the pressure gradient p_x induces an electric field such that

$$\psi_x = -(\lambda_{21}/\lambda_{22}) p_x. \tag{46}$$

The induced electric field reduces hydrodynamic permittivity. With allowance for (46), the first equation of system (45) implies that

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

Though the ζ-potentials ζ_0 and ζ_L determine the macroscopic electric field, the mobilities λ_{ij} are independent of these potentials. The results obtained can be formulated as follows. On the entire interval $0 < z < L$, the electroosmotic flows are described by global variables, including the macroscopic flow V, macroscopic electric current J, and macroscopic potential φ^0. The local variables defined on the periodicity cell $0 < y < 1$ include the microscopic flow $v^0(y)$, microscopic velocities of ions $v_+^0(y)$ and $v_-^0(y)$, and microscopic potentials $w_1(y)$ and $w_2(y)$. The macroequations are Eqs. (45) and (33), whereas Eqs. (31), (34), (40), and (42) form a system of microequations. The global and local variables are related by equalities (41), (43), and (44). An important role of microequations in calculating the macroscopic coefficients λ_{ij} should also be noted.

By virtue of the asymptotic expansions

$$\hat{v}(z) = \delta^2 v^0(y)\Big|_{y=z/(\delta L)} + o(\delta^2), \qquad \hat{v}_i(z) = \delta^2 v_i^0(y)\Big|_{y=z/(\delta L)} + o(\delta^2),$$

$$\varphi(z) = \varphi^0(z) + \delta \varphi_z^0(z) w_1(y)\Big|_{y=z/(\delta L)} + \delta^2 \varphi_{zz}^0(z) w_2(y)\Big|_{y=z/(\delta L)} + o(\delta^2)$$

[$\hat{v}(z)$, $\hat{v}_i(z)$, and $\varphi(z)$ are the solutions of Eqs. (8)–(13); the sign hat means to zero extension to the solid domain), the two-scale model considered is an effective approximate model for exact nonlinear equations (8)–(13).

Conclusions. A two-scale one-dimensional model is proposed 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.

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