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Electroosmosis law via homogenization of electrolyte flow equations in porous media

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Abstract

By the homogenization approach we justify a two-scale model of ion transport in porous media for one-dimensional horizontal steady flows driven by a pressure gradient and an external horizontal electrical field. By up-scaling, the electroosmotic flow equations in horizontal nanoslits separated by thin solid layers are approximated by a homogenized system of macroscale equations in the form of the Poisson equation for induced vertical electrical field and Onsager's reciprocity relations between global fluxes (hydrodynamic and electric) and forces (horizontal pressure gradient and external electrical field). In addition, the two-scale approach provides macroscopic mobility coefficients in the Onsager relations.

Keywords: Porous media; Electroosmosis; Nanomembranes; Nonlocal Poisson–Boltzmann equation; Existence; Homogenization

1. Introduction

The electroosmosis phenomenon first discovered by F.F. Reiss (1808, Moscow University) implies that a difference in the electric potentials applied to the water in a U-tube results in a change of water levels (see Fig. 1) when the tube is filled partially with thin sand. Later G. Kwinke (1859) discovered an inverse phenomenon amounting to the effect that flows through a membrane induce electrical field.

Both these phenomena have their origin in an electrical double layer associated with the interface between minerals and pore fluid [15]. The surfaces of the mineral grains in rocks usually display net electric charges due to the presence of unsatisfied chemical bonds, whereas groundwater is electrolyte in nature. In water-saturated porous rocks an electric potential is therefore usually produced at the contact between the water and solid. As a result the electric charges within the fluid separate into an electrical double layer. The inner or Stern layer consists of ions adsorbed onto the solid surface through electrostatic and Van der Waals' forces, while the outer diffuse or Gouy layer in the water is formed by ions under the influence of ordering electrical and disordering thermal forces.

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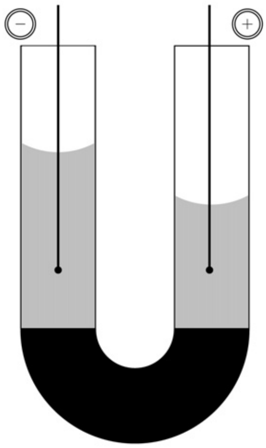

Fig. 1. Electroosmosis.

Charge separation in the double layer is responsible for electrokinetic phenomena. In the presence of an outer electric field, a relative motion between the outer diffuse ions and inner strongly bound ions occur (electrophoresis and electroosmosis). Due to viscosity, the bulk neutral fluid is also involved into motion. On the other hand, a relative motion of cations and anions produced by a pressure gradient (or due to sedimentation) results in a difference of electric potentials and electric current.

Understanding and managing electroosmotic flow is central both to microchip separations of analytes in nano-channels and to the manifold techniques associated with separations analysis [7]. The transport at nano-channels is markedly different from that occur in microchannels. The most notable feature at the nanoscale is dominance of the electrical field transverse to the flow direction, which could significantly affect the electroosmotic flow.

Most advanced models of ion transport [12] are nonlinear systems of partial differential equations consisting of the Navier–Stokes equation for bulk fluid and some generalizations of the Nernst ionic flux equations coupled with the Poisson equation for electrical field. Such systems can be resolved only numerically; this is why many authors perform simulations to study electrokinetics and species transport problems quantitatively.

In this paper we develop an asymptotic approach for the qualitative analysis of the above mentioned electroosmotic flow equations. To this end we consider horizontal flows through a vertical membrane, and we treat this membrane as a number of thin horizontal liquid layers of the same thickness h_l separated by thin solid layers of the same thickness h_s. Driving forces are horizontal pressure gradient and horizontal electrical field. Electroosmotic force manifests itself by way of an induced vertical electrical field. If N is the total number of liquid layers, the total membrane thickness is equal to $L = N(h_l + h_s)$. In our study the total thickness L is fixed and the ratio $\delta = (h_l + h_s)/L$ is a small parameter.

By the electrical double layer theory, the solid/liquid interface is not a mathematical surface but rather a transition layer. The question of boundary conditions is a matter of current research [11]. Commonly, the no-slip boundary conditions for fluid flow are applied at the shear plane where the electric potential is termed as the ζ-potential. The Stern layer is not included in the flow domain and the solid domain is assumed electrically neutral. This is why the Poisson equation for electrical field becomes the Laplace equation inside the solid layers. Since there is no charge concentration at the no-slip planes we set at these planes the condition of continuity of the normal component $\mathbf{D} \cdot \mathbf{n}$ of the induction vector $\mathbf{D} = \varepsilon \mathbf{E}$, assuming that the solid and the liquid dielectric permittivities are different. Thus, we do not specify potential values at the inner solid/liquid interfaces. Instead, we write the no-jump conditions for $\mathbf{D} \cdot \mathbf{n}$.

Our asymptotic analysis is the well-known homogenization procedure based on two-scale asymptotic expansions [2,6,13] to up-scale the micromechanical picture of ion transport near solid surfaces. We derive both microscale and macroscale equations. The first equations serve to identify constant coefficients in the second equations. It turned out that the macroscale equations include a generalized Darcy law for the flows in a porous media with the porosity $\Phi = h_l/(h_l + h_s)$.

Being hydrodynamically isolated, the flows in adjacent horizontal slits interact through the vertical electrical field. Nevertheless, as it follows from the macroscale equations, the macroscale horizontal fluid flux V does not depend on the vertical variable. With J standing for the macroscale horizontal electrical current, the generalized Darcy law which we derive is

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

where p_x is the horizontal pressure gradient and ψ_x is the horizontal gradient of electric potential. System (1) relates fluxes and forces; such systems are known in thermodynamics of irreversible processes as a number of the Onsager reciprocity relations [5]. We calculate the mobilities λ_{ij} and verify that they obey the Onsager symmetry relation $\lambda_{12} = \lambda_{21}$. For flows in a thin capillary, the kinetic coefficient λ_{12} was first evaluated by Boltzmann and Smoluchowski [14]. The full macroscale system consists of Eqs. (1) and a Poisson equation for macroscale electric potential. To derive rigorously governing micro and macro equations we adopt a hypothesis about a small order of magnitude of the solution-ions diffusion coefficients.

Proofs of the mathematical results below are strongly based on a priori estimates independent of δ of the norm $\|\varphi\|_{H^1}$ for solutions of the nonlinear nonlocal Poisson–Boltzmann equation

$$\big(\varepsilon(z)\varphi_z\big)_z = -f(\varphi), \quad 0 < z < L, \tag{2}$$

where $\varepsilon(z)$ is a discontinuous stepwise periodic function with the periodicity cell $a_n < z < a_{n+1}$, $a_{n+1} - a_n = O(\delta)$; given a liquid interval $a_n < z < b_n$ ($b_n < a_{n+1}$), the nonlocal term $f(\varphi)$ defined as follows:

$$f(\varphi)|_{a_n<z<a_{n+1}} = 4\pi \mathbf{1}|_{a_n<z<b_n} \sum_{\pm} c_i^- q_i e^{\frac{q_i}{kT}(\varphi(d_n)-\varphi(z))}, \quad d_n = \frac{a_n + b_n}{2},$$

where $\mathbf{1}(z)|_\omega$ is the characteristic function of the set ω.

The theory that we develop for Eq. (2) reveals that there are three types of electrolytes depending on the sign of the number $E = \sum_{\pm} c_i^- q_i$. Particularly, in the case of the "convex" electrolyte when $E < 0$, any solution of (2) satisfies the alternative property: either $\varphi_z(z) \neq 0$ for any z or there is a unique point d_m such that $\varphi_z(d_m) = 0$ and $(z - d_m)\varphi_z(z) > 0$ for $z \neq d_m$. To study the potential of the convex electrolyte in the alternative case when the property $\varphi_z(z) \neq 0$ does not hold, we pass to a rearrangement function $\varphi'(z')$, which is a shift transformation of the function $\varphi(z)$, such that

$$\varepsilon_l \varphi'_{z'z'} = -f'(\varphi'), \quad 0 < z' < L' = \Phi L, \tag{3}$$

$$f'(\varphi')|_{a'_n<z'<a'_{n+1}} = 4\pi \sum_{\pm} c_i^- q_i e^{\frac{q_i}{kT}(\varphi'(d'_n)-\varphi'(z'))}, \quad d'_n = \frac{a'_n + a'_{n+1}}{2},$$

where $\varepsilon_l = \text{const}$ is the value of $\varepsilon(z)$ on the liquid domain and the points a'_n are chosen in such a way that $a'_{n+1} - a'_n = b_n - a_n$ and $a_0 = a'_0$. It is essential that $\varphi'_{z'}(z') = \varphi_z(z)$ at the corresponding points z' and z, and the function $\varphi'_{z'}(z')$ is continuous everywhere whereas $\varphi_z(z)$ has jumps at the points a_n and b_n. Next, we introduce the local function $w'^{(n)}(z') = \varphi'(z') - \varphi'(d'_n)$ which solves on each interval $a'_n < z' < a'_{n+1}$ the "local" equation

$$\varepsilon_l w_{z'z'} = -4\pi \sum_{\pm} c_i^- q_i e^{-\frac{q_i}{kT} w}, \quad w(d'_n) = 0. \tag{4}$$

Taking into account the fact that the right-hand side of the equation in (4) is a convex function of w, we establish a comparison inequality for any two solutions of (4). We find out that the local function $w'^{(m)}(z')$ is given by an explicit formula at the interval with the center point d_m which enables us to estimate the norm of $w'^{(m)}(z')$ in $H^1(a'_m < z' < a'_{m+1})$. Applying the comparison inequality we verify that there is an extension $W'(z')$ of local solution $w'^{(m)}(z')$ onto the entire interval $0 < z' < L'$ such that $W'(z')$ serves as a majorant for any local function $w'^{(n)}(z')$. On this way, we estimate the norm of $\varphi'(z')$ in $H^1(0, L')$ using the local equality $w'^{(n)}_{z'}(z') = \varphi'_{z'}(z')$.

2. Basic equations

The slow bulk flows of a binary electrolyte solution are governed by the Stokes equation

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \mu \Delta \mathbf{v} + \mathbf{E} \sum_{i=\pm} \frac{q_i \rho_i}{m_i} + \rho \mathbf{g}. \tag{5}$$

Here ρ is the total density, $\mathbf{v}$ is the total velocity, μ is the viscosity, m_i is the ion mass, 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 mass density of the gravitation force. If e is the elementary charge, $q_i = z_i e$ where z_i is the valency of each ionic species. In chemical journals the ratio $c_i = \rho_i / m_i$ is known as concentration.

As for the momentum law for the ion flows, we start from the Nernst equilibrium equation [14]

$$0 = -\frac{\rho_i q_i}{m_i} d\psi - \frac{kT}{m_i} d\rho_i, \qquad \mathbf{E} = -\nabla\psi, \tag{6}$$

where ψ is the potential of $\mathbf{E}$, k is the Boltzmann constant, and T is the temperature. Equality (6) implies that the chemical potentials are constant when all the contact phases are in equilibrium.

When we pass to dynamics, we generalize the force balance law (6) as follows [16]

$$\rho_i \frac{\partial \mathbf{v}_i}{\partial t} = \mu_i \Delta \mathbf{v}_i - \alpha_i \nabla p + \frac{\rho_i q_i}{m_i} \mathbf{E} - \frac{kT}{m_i} \nabla \rho_i + \frac{\gamma_i \rho_i}{m_i} (\mathbf{v} - \mathbf{v}_i) + \rho_i \mathbf{g}, \tag{7}$$

where the drag-force parameter γ_i is given by the Stokes–Einstein–Sutherland formula [10]

$$\gamma_i = \frac{kT}{D_i}. \tag{8}$$

Here $\mathbf{v}_i$ is the ion velocity, μ_i is the viscosity of the ith ion component, and α_i is the volume fraction, $\alpha_1 + \alpha_2 \leqslant 1$. The fifth term in the right-hand side of (7) is the diffusion force, with D_i being 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 reads

$$\operatorname{div} \mathbf{D} = 4\pi \sum_{\pm} \frac{\rho_i q_i}{m_i}, \quad \mathbf{D} = \varepsilon_l \mathbf{E}, \quad \mathbf{E} = -\nabla\psi, \tag{9}$$

where $\mathbf{D}$ is the electric induction vector and ε_l is the dielectric permittivity of the electrolyte. The bulk and ion mass conservation laws are

$$\operatorname{div} \mathbf{v} = 0, \quad \rho = \text{const}, \quad \frac{\partial \rho_i}{\partial t} + \operatorname{div}(\rho_i \mathbf{v}_i) = 0. \tag{10}$$

Inside the solid dielectric, the electrical field obeys the equations

$$\operatorname{div} \mathbf{D} = 0, \quad \mathbf{D} = \varepsilon_s \mathbf{E}, \quad \mathbf{E} = -\nabla\psi, \tag{11}$$

where ε_s is the dielectric permittivity of the solid dielectric.

3. One-dimensional flows

Our study is motivated by the electrolyte flow through a membrane of thickness l (see Fig. 2) 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 ith ion is prescribed.

We study electrolyte steady flows through the 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 the same thickness h_s. The central points d_n of the liquid intervals $a_n < z < b_n$ are the points of reference where the ion inflow densities ρ_i take the prescribed values ρ_i^-.

Let Q_f and Q_s stand for fluid and solid domain

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

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

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

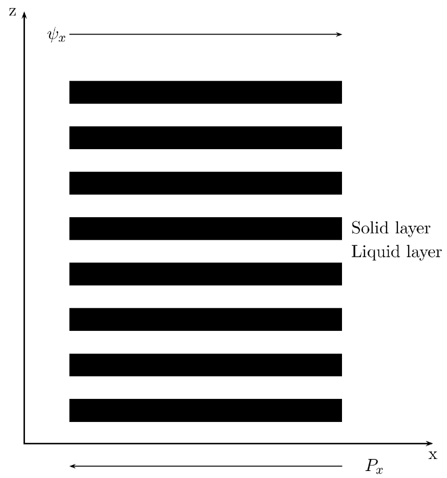

Fig. 2. Flow trough membranes.

We look for steady solutions of the fluid equations (5)–(10) in the domain Ω_f in the form

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

where $\alpha = \text{const}$ and $\beta = \text{const}$. System (5)–(10) reduces to

$$\mu v_{zz} - \alpha - \beta \sum_{\pm} c_i q_i = 0, \quad c_i = \frac{\rho_i}{m_i}, \tag{12}$$

$$-P_z - \varphi_z \sum_{\pm} c_i q_i - \rho g = 0, \tag{13}$$

$$-\beta c_i q_i + \frac{kTc_i}{D_i}(v - v_i) = 0, \tag{14}$$

$$-c_i q_i \varphi_z - kTc_{iz} - gc_i m_i = 0, \tag{15}$$

$$\varepsilon_l \varphi_{zz} = -4\pi \sum_{\pm} c_i q_i. \tag{16}$$

In the solid domain Ω_s the potential φ solves the equation

$$\varepsilon_s \varphi_{zz} = 0. \tag{17}$$

Conditions of continuity of the potential φ and the induction field D are

$$\text{at } z = a_n \text{ and } z = b_n\text{:} \quad [\varphi] = [\varepsilon \varphi_z] = 0, \qquad \text{at } z = d_n\text{:} \quad c_i = c_i^-, \tag{18}$$

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

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

No-slip conditions of the velocities are

$$\text{at } z = a_n \text{ and } z = b_n\text{:} \quad v = 0, \quad \text{where } n = 0, \dots, N. \tag{19}$$

We assume that φ satisfies the external boundary conditions

$$\varphi|_{z=0} = \zeta_0, \qquad \varphi|_{z=L} = \zeta_L. \tag{20}$$

Thus, one-dimensional flows are governed by Eqs. (12)–(17) and conditions (18)–(20). Let us derive some consequence of the above formulation.

In what follows we assume that the dielectric permittivity function

$$\varepsilon = \begin{cases} \varepsilon_l, & z \in \Omega_f, \\ \varepsilon_s, & z \in \Omega_s \end{cases} \tag{21}$$

is extended periodically for every z.

Let us exclude the concentrations c_i. Eq. (15) reduces to

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

Integrating between d_n and $z \in (a_n, b_n)$, we obtain

$$c_i = c_i^- \exp\left[\frac{q_i}{kT}\big(\varphi(d_n) - \varphi(z)\big) + \frac{g m_i}{kT}(d_n - z)\right]. \tag{22}$$

Hence, the potential φ solves in each liquid domain (a_n, b_n) the Poisson–Boltzmann equation [14]

$$\varepsilon_l \varphi_{zz} = -4\pi \sum_{\pm} c_i^- q_i \exp\left[\frac{q_i}{kT}\big(\varphi(d_n) - \varphi(z)\big) + \frac{g m_i}{kT}(d_n - z)\right]. \tag{23}$$

With $[z]_e$ standing for the entire part of a number z, the functions

$$H_a(z) = h\left[\frac{z}{h}\right]_e, \quad H_d(z) = \frac{h_l}{2} + h\left[\frac{z}{h}\right]_e, \quad H_b(z) = h_l + h\left[\frac{z}{h}\right]_e, \quad h \equiv h_l + h_s \tag{24}$$

take the constant values a_n, d_n, and b_n if $a_n < z < a_{n+1}$. Let χ be the characteristic function of the liquid domain Ω_f. Thus to define φ on the whole interval $0 < z < L$, one should solve the equation

$$(\varepsilon \varphi_z)_z = -4\pi \chi(z) \sum_{\pm} c_i^- q_i \exp\left[\frac{q_i}{kT}\big(\varphi\big(H_d(z)\big) - \varphi(z)\big) + \frac{g m_i}{kT}\big(H_d(z) - z\big)\right] \tag{25}$$

jointly with the conditions (18) and (20). Observe that the function $\xi_d = H_d(z) - z$ is periodic, and $\xi_d = h_l/2 - z$ on the interval of periodicity $0 < z < h$.

4. Scaling and identification of a small parameter

We look for an asymptotic solution of problem (12)–(20) assuming that the ratio

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

is a small parameter for some positive entire number N. We argue by the homogenization approach, so the entire interval $\Omega = \{0 < z < L\}$ is fixed and δ varies in $(0, 1)$. In that case

$$h(\delta) = \delta L, \quad h_l = \delta \bar{h}_l, \quad h_s = \delta \bar{h}_s, \quad \bar{h}_l + \bar{h}_s = L, \quad \Phi := \bar{h}_l / L.$$

Here, Φ is porosity, is much more smaller relative to the jump conditions (18) should be modified.

We call $z \in \Omega$ a slow variable and we introduce the fast variable $y = z/(\delta L)$. With δ being small, the periodic functions $\varepsilon(z)$ and $\chi(z)$ oscillate strongly and they can be represented as functions of the fast variable

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

where

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

are periodic functions with the period equal to 1. In what follows the functions

$$\tilde{\xi_a}(y) = -Ly, \quad \tilde{\xi_d}(y) = L(\Phi/2 - y), \quad \tilde{\xi_b}(y) = L(\Phi - y), \quad y \in Y \equiv (0, 1)$$

are extended periodically. One can verify easily that functions $H_a(z)$, $H_d(z)$, and $H_b(z)$ defined in (24) can be represented as

$$H_a(z) = z + \delta\tilde{\xi_a}\left(\frac{z}{\delta L}\right), \qquad H_d(z) = z + \delta\tilde{\xi_d}\left(\frac{z}{\delta L}\right), \qquad H_b(z) = z + \delta\tilde{\xi_b}\left(\frac{z}{\delta L}\right).$$

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

$$\left(\tilde{\varepsilon}\left(\frac{z}{\delta L}\right)\varphi_z\right)_z = -f(\varphi), \tag{26}$$

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

with the boundary conditions (20). It follows from (12) and (16) that the bulk velocity satisfies the equation

$$z \in \Omega_f^\delta:\quad \mu v_{zz} + \frac{\beta\varepsilon_l}{4\pi}\varphi_{zz} = \alpha; \qquad z \in \partial\Omega_f^\delta:\quad v = 0. \tag{27}$$

With c_i given by (22), the ion velocities solve the problems

$$z \in \Omega_f^\delta:\quad -\beta c_i q_i + \frac{kTc_i}{D_i}(v - v_i) = 0. \tag{28}$$

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. $f = \bar{f}f'$. The special scaling notations are accepted for the following variables:

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

The length

$$l_d = \left(\frac{\varepsilon_l kT}{2\bar{c}\bar{q}^2}\right)^{1/2} \tag{29}$$

is known as the Debye length. In terms of dimensionless variables equations (12)–(16) in the fluid domain read

$$\left(\frac{\mu\bar{v}/L^2}{\bar{p}/L}\right)_4 v'_{z'z'} + \frac{\beta'}{\pi}\left(\frac{l_d^2}{L^2}\right)_2\left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1\left(\frac{\bar{q}\bar{\varphi}\bar{c}}{\bar{p}}\right)_3\varphi'_{z'z'} = \alpha', \tag{30}$$

$$-\beta' q_i' D_i'\left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1 + \left(\frac{\bar{v}L}{\bar{D}}\right)_5(v' - v_i') = 0, \tag{31}$$

$$\left(\frac{l_d^2}{L^2}\right)_2\left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1\varphi'_{z'z'} = -\pi\sum_{\pm} c_i' q_i' \exp\left(q_i'\left(\frac{\bar{q}\bar{\varphi}}{kT}\right)_1\left\{\varphi'\left(H_d'(z')\right) - \varphi'(z')\right\} + \left(\frac{g m_i L}{kT}\right)_7\left(H_d'(z') - z'\right)\right). \tag{32}$$

In the solid domain, Eq. (17) reads $(\varepsilon_s)_6\varphi'_{z'z'} = 0$.

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

$$(\cdot)_i = \delta^{n_i},\quad i = 1,\dots,6, \qquad (\cdot)_7 = 0, \tag{33}$$

we obtain a hierarchy of problems to study. In this paper we restrict ourselves to the case when all the powers n_i are equal to zero, i.e. $(\cdot)_i = O(1)$. The meaning of these hypotheses is the following. The relation $(\cdot)_1 = O(1)$ implies that electroosmotic force and thermal force are of the same order. Observe that the relation $(\cdot)_1 = O(1)$ holds, for example, for the symmetric electrolyte (where $z_+ = z_-$ and $c_+^- = c_-^-$) in water at $T = 298$ K, $z = 1$, with the ζ-potential equal to 25 [mV] [7]. When $(\cdot)_1$ is not small, the Debye–Hückel linearization of the Poisson–Boltzmann equation does not work. Under the condition $(\cdot)_1 = O(1)$ the Debye length l_d can be longer compared to electrical double layer, moreover the double layer overlapping could occur. Indeed, it is useful rule of thumb [7] that $l_d = 9.6/(z\sqrt{\bar{c}})$. For the above mentioned electrolyte with the counterion molar concentration $\bar{c} = 0.01$ [mM] we have $l_d = 100$ [nm], whereas the double electric layer is normally only a few nanometers thick [7] and the nanocapillary membrane may have the pore diameter of 15 [nm] [4]. For such cases the hypothesis $(\cdot)_2 = O(1)$ is natural. Hypothesis $(\cdot)_3 = O(1)$ amounts to the effect that the horizontal pressure gradient and the applied horizontal electrical field are of the same order. The relation $(\cdot)_4 = O(1)$ means that viscous response is of the same order as the applied horizontal pressure gradient. The dimensionless quantity $(\cdot)_5$ is the Péclet number *Pe*, thus the hypothesis $Pe = O(1)$ implies that convection and diffusion are of the same order. For water with low electrolyte concentration $\bar{c}$ the hypothesis $(\cdot)_6 = O(1)$, i.e. $\varepsilon_s/\varepsilon_l = O(1)$, is natural. Clearly one can assume that $(\cdot)_7 = 0$ since m_i is negligible.

We close this section by reminding the Debye–Hückel approach to the Poisson–Boltzmann equation (23) in the single layer $z > 0$ with the boundary conditions $\varphi \to 0$ and $\varphi_z \to 0$ as $z \to \infty$ and $\varphi|_{z=0} = \zeta_0$. In the case of symmetric electrolyte, the linearized equation (23), in the SI system of units where 4π is substituted by 1, becomes $l_d^2\varphi_{zz} = -\varphi$, since the nonlocal term $\varphi(d)$ vanishes as $d \to \infty$. Clearly, $\varphi = \zeta_0 e^{-z/l_d}$ is a solution. This explains the notion (29).

5. A priori estimates for solutions of the Poisson–Boltzmann equation

We proceed by returning to the dimensional variables. First, we study how solutions of problem (26)–(28) depend on δ. We call the electrolyte concave, linear or convex if

$$\sum_{\pm} c_i^- q_i > 0, \qquad \sum_{\pm} c_i^- q_i = 0, \qquad \sum_{\pm} c_i^- q_i < 0,$$

respectively. We remind that $q_1 = q_+ > 0$ and $q_2 = q_- < 0$. Denote

$$p_1 = \frac{4\pi q_1 c_1^-}{\varepsilon_l}, \quad p_2 = \frac{4\pi |q_2| c_2^-}{\varepsilon_l}, \quad r_1 = \frac{q_1}{kT}, \quad r_2 = \frac{|q_2|}{kT}. \tag{34}$$

With these notations at hands, Eq. (23) in the fluid domain reads

$$\varphi_{zz} = p_2 e^{r_2(\varphi(z)-\varphi(H_d(z)))} - p_1 e^{-r_1(\varphi(z)-\varphi(H_d(z)))}.$$

We prove that there is a positive constant B_1 such that

$$\int_0^L \varphi_z^2(z)\,dz \leqslant B_1, \qquad \max_{0\leqslant z\leqslant L} \bigl|\varphi(z)\bigr| \leqslant B_1. \tag{35}$$

Here and in what follows, constants B_i do not depend on δ.

Linear electrolyte. First, we consider the case when $p_1 = p_2 = p$. We start from the following assertion: if there is a point $z_0 \in [a_n, a_{n+1}]$, such that $\varphi_z(z_0) = 0$ then $\varphi_z(d_n) = 0$ also. Indeed, assume $z_0 < d_n$. The function $w(z) = \varphi(z) - \varphi(d_n)$ solves the problem

$$w_{zz} = g_1(w), \quad w(d_n) = 0, \quad w_z(z_0) = 0, \tag{36}$$

where

$$g_1(w) = \frac{dg(w)}{dw}, \quad g(w) = \frac{p}{r_1}e^{-r_1 w} + \frac{p}{r_2}e^{r_2 w} - \frac{p}{r_1} - \frac{p}{r_2}.$$

We multiply Eq. (36) by w and integrate between the points z_0 and d_n using the inequality $wg_1(w) \geqslant 0$. As a result we obtain

$$\int_{z_0}^{d_n} \bigl(|w_z|^2 + wg_1(w)\bigr)\,dz = 0 \quad \text{and} \quad \int_{z_0}^{d_n} |w_z|^2\,dz \leqslant 0.$$

Thus, our claim is proved. The case $z_0 > d_n$ can be considered similarly.

Next, we assert that φ_z can vanish only at the points d_n. Indeed, if there is $z_n^* \in [a_n, a_{n+1}]$ such that $\varphi_z(z_n^*) = 0$ then, by the above arguments, $\varphi_z(d_n) = 0$ also. Clearly, $w_z(d_n) = w(d_n) = 0$. It follows from $(36)_1$ that

$$\frac{d}{dz}\bigl(w_z^2 - 2g(w)\bigr) = 0. \tag{37}$$

Integrating between d_n and z we obtain the equality

$$w_z^2 = 2g(w).$$

Hence, the solution w is defined on each interval (a_n, d_n) and (d_n, b_n) uniquely up to the sign by the formula

$$\pm \int_0^w \frac{d\omega}{\sqrt{2g(\omega)}} = z - d_n. \tag{38}$$

By this representation, $w_z \neq 0$ if $z \neq d_n$. The claim is proved. Observe, that by (38), the values of w_z are defined at the points a_n and b_n uniquely up to the sign.

Now we prove that $\varphi_z(d_n) = 0 \Rightarrow \varphi_z^2(d_{n-1}) + \varphi_z^2(d_{n+1}) = 0$. Assuming that $\varphi_z(d_{n+1}) > 0$, we derive from (37) the representation formula for the function $w^{(n+1)}(z)$ on the interval (a_{n+1}, b_{n+1})

$$\int_0^{w^{(n+1)}(z)} \frac{d\omega}{\sqrt{\kappa^2 + 2g(\omega)}} = z - d_{n+1}, \quad \kappa^2 = \bigl(w_z^{(n+1)}(d_{n+1})\bigr)^2. \tag{39}$$

The value of the constant κ should be such that the continuity condition

$$\varepsilon_s w_z^{(n)}(a_{n+1} - 0) = \varepsilon_l w_z^{(n+1)}(a_{n+1} + 0)$$

be true. One can verify that the solution of the boundary-value problem

$$w_{zz} = g_1(w), \quad w_z(a_{n+1} + 0) = \frac{\varepsilon_s}{\varepsilon_l} w_z^n(a_{n+1} - 0), \quad w(d_{n+1}) = 0, \tag{40}$$

on the interval $a_{n+1} < z < d_{n+1}$ is uniquely defined and is given by the representation formula (38), with d_n substituted by d_{n+1}. By uniqueness, $\kappa = 0$.

By the above discussions, the solution φ of the problem (18), (20), (25) is strictly monotone on the whole interval $0 < z < L$ otherwise $\varphi_z(d_n) = 0$ for each n. In the first case

$$\max_{0<z<L} \bigl|\varphi(z)\bigr| \leqslant B_1, \quad B_1 = \max\bigl\{|\zeta_0|, |\zeta_L|\bigr\}. \tag{41}$$

We multiply the equation

$$\bigl(\varepsilon(z)\varphi_z\bigr)_z = -4\pi\chi(z)\sum_{\pm} c_i^- q_i \exp\biggl(\frac{q_i}{kT}\bigl\{\varphi\bigl(H_d(z)\bigr) - \varphi(z)\bigr\}\biggr) \equiv f(\varphi), \tag{42}$$

by the function $\varphi(z) - \varphi_0(z)$,

$$\varphi_0(z) = \frac{\zeta_L - \zeta_0}{L} z + \zeta_0,$$

and, because of the estimate (41), we obtain the inequality

$$\int_0^L \varepsilon(z)\varphi_z^2(z)\,dz \leqslant B_2 + \int_0^L \varepsilon(z)\varphi_z\varphi_{0z}\,dz. \tag{43}$$

Now, to derive the first estimate in (35), it suffices to apply the Young inequality

$$|\varphi_z\varphi_{0z}| \leqslant \frac{\mu}{2}\varphi_z^2 + \frac{1}{2\mu}\varphi_{0z}^2. \tag{44}$$

Let us consider the second case. Clearly, $|f| \leqslant B_3$. We again multiply Eq. (42) by $\varphi - \varphi_0$ to arrive at the inequality

$$\int_0^L \varepsilon(z)\varphi_z^2(z)\,dz \leqslant \int_0^L \bigl(\varepsilon(z)\varphi_z\varphi_{0z} + B_3|\varphi - \varphi_0|\bigr)\,dz. \tag{45}$$

On the other hand,

$$\varphi-\varphi_0=\int_0^z \varphi_z\,dz-\frac{\zeta_L-\zeta_0}{L}z, \qquad \int_0^z |\varphi_z|\,dz\leqslant\int_0^z \frac{1}{2}\varepsilon(z)\varphi_z^2(z)\,dz+\int_0^z \frac{1}{2\varepsilon(z)}\,dz. \tag{46}$$

Now, from (45) and (46), both the estimates (35) follow.

Convex electrolyte. Let us consider "convex" electrolyte with the condition $p_2 > p_1$. On each fluid interval $a_n < z < b_n$, the function w is continuous and

$$w_{zz}=g_1(w), \quad w(d_n)=0, \tag{47}$$

where

$$g_1(w)=\frac{dg(w)}{dw}, \quad g(w)=\frac{p_1}{r_1}e^{-r_1w}+\frac{p_2}{r_2}e^{r_2w}-\frac{p_1}{r_1}-\frac{p_2}{r_2}.$$

Observe, that the function g is convex and $g_1(w)\geqslant p_2-p_1$ for $w\geqslant 0$.

Step 1. We prove the following assertion:

$$\varphi_z(z_0)=0 \quad \text{for some } z_0\in(a_n,b_n) \quad \Rightarrow \quad \varphi_z(d_n)=0.$$

Assume $z_0<d_n$. Given $\lambda>0$, the function $w^\lambda=\lambda w$ solves the boundary-value problem

$$w^\lambda_{zz}=g_1^\lambda\big(w^\lambda\big), \quad w^\lambda(d_n)=0, \quad w_z^\lambda(z_0)=0, \tag{48}$$

where

$$g_1^\lambda(w)=\frac{dg^\lambda(w)}{dw}, \quad g^\lambda(w)=\frac{p_1}{r_1}e^{-r_1w/\lambda}+\frac{p_2}{r_2}e^{r_2w/\lambda}-\frac{p_1}{r_1}-\frac{p_2}{r_2}.$$

We multiply Eq. (48) by w^λ and integrate between the points z_0 and d_n using the inequality $wg_1^\lambda(w)\geqslant(p_2-p_1)w$. As a result we obtain

$$\int_{z_0}^{d_n}\big(\big|w_z^\lambda\big|^2+w^\lambda g_1^\lambda\big(w^\lambda\big)\big)\,dz=0 \quad \text{and} \quad \int_{z_0}^{d_n}|w_z|^2\,dz\leqslant\frac{p_2-p_1}{\lambda}\int_{z_0}^{d_n}|w|\,dz.$$

Thus, $\varphi_z(d_n)=0$ since λ is arbitrary. The case $z_0>d_n$ can be considered similarly.

Step 2. We prove that $\varphi_z(z)\neq 0$ on the whole interval $(0,L)$ otherwise there is d_m such that

$$\varphi_z(d_m)=0, \quad (z-d_m)\varphi_z(z)>0, \quad \forall z. \tag{49}$$

Let (a_m,b_m) be the first interval such that $\varphi_z(z_m)=0$ for some $z_m\in(a_m,b_m)$. Then $\varphi_z(d_m)=0$ and, on the interval $a_m<z<b_m$, the function $w^{(m)}(z)=\varphi(z)-\varphi(d_m)$ solves the problem

$$\frac{d}{dz}\big(w_z^2-2g(w)\big)=0, \qquad w(d_m)=w_z(d_m)=0. \tag{50}$$

Integrating between d_m and $z\in(a_m,b_m)$, we obtain the representation formula

$$\int_0^{w^{(m)}(z)}\frac{d\omega}{\sqrt{2g(\omega)}}=|z-d_m|, \qquad w_z^{(m)}=\sqrt{2g\big(w^{(m)}\big)}\,\mathrm{sign}(z-d_m). \tag{51}$$

Clearly, $\varphi_z(z)<0$ for $z<d_m$ and

$$0<w^{(m)}(a_m)=w^{(m)}(b_m), \qquad 0>w_z^{(m)}(a_m)=-w_z^{(m)}(b_m).$$

It is impossible that $\varphi_z(z_{m+1})=0$ for some $z_{m+1}\in[a_{m+1},b_{m+1}]$. Indeed, if it is the case, we have $\varphi_z(d_{m+1})=0$ and the function $w^{(m+1)}$ on the interval (a_{m+1},b_{m+1}) is given by the same formula (51), with d_m substituted by d_{m+1}.

Hence, $w_z^{(m)}(b_m) > 0$ and $w_z^{(m+1)}(a_{m+1}) < 0$. These inequalities contradict to the no-jump condition $[\varepsilon w_z] = 0$ at the points b_m and a_{m+1}. Hence, $\varphi_z(z) > 0$ on the interval $[a_{m+1}, b_{m+1}]$. By the same reason, $\varphi_z(z) > 0$ for $z > d_m$. If φ is monotone on the whole interval $0 < z < L$, it is clear that $|\varphi(z)| \leqslant \max\{|\zeta_0|, |\zeta_L|\}$ and one can proceed as in the case of the linear electrolyte.

Step 3 *(Exclusion of solid domain).* Let us consider the alternative case (49). We exclude the solid domain by passing to a *rearrangement function* $\varphi'(z')$, $0 < z' < \Phi L = L'$ as follows. We divide the interval $0 < z' < L'$ into N subintervals of the same length $\delta\bar{h}_l$ by the points $a_i' = i\delta\bar{h}_l$, $i = 0, \dots, N$, $a_0' = 0$, $a_N' = L'$. We define

$$\varphi'(z')|_{a_0'<z'<a_1'} = \varphi(z'),$$

$$\varphi'(z')|_{a_i'<z'<a_{i+1}'} = \varphi(z' + a_i - a_i') - \sum_{k=1}^{i}\bigl(\varphi(a_k) - \varphi(b_{k-1})\bigr), \quad \text{if } i \geqslant 1.$$

Denoting $d_i' = a_i' + \delta\bar{h}_l/2$ and taking into account the no-jump conditions (18), we see that the function $\varphi'(z')$ belongs to $C^1[0, L'] \cap W^{2,\infty}(0, L')$ and solves the problem

$$\varphi'_{z'z'} = g_1\bigl(\varphi'(z') - H_d'(z')\bigr), \quad \varphi'(0) = \zeta_0, \quad \varphi'(L') = \zeta_L - \sum_{k=1}^{N}\bigl(\varphi(a_k) - \varphi(b_{k-1})\bigr), \tag{52}$$

where $H_d'(z')$ is a step-wise function such that

$$H_d'(z') = d_i' \quad \text{if } a_i' < z' < a_{i+1}'.$$

Because of the equalities

$$\varphi(a_k) - \varphi(b_{k-1}) = \int_{b_{k-1}}^{a_k} \varphi_z\, d\xi = \frac{\varepsilon_l \delta\bar{h}_s \varphi_z(b_{k-1} - 0)}{\varepsilon_s} = \frac{\varepsilon_l \delta\bar{h}_s \varphi'_{z'}(a_k')}{\varepsilon_s},$$

the boundary condition at $z' = L'$ in (52) writes

$$\varphi'(L') = \zeta_L - \frac{\varepsilon_l(1-\Phi)L}{\varepsilon_s}\sum_{k=1}^{N}\varphi'_{z'}(a_k'). \tag{53}$$

One can verify that correspondence between the functions $\varphi(z)$ and $\varphi'(z')$ is bijective.

The condition (49) means that

$$\varphi'_{z'}(d_m') = 0, \quad (z' - d_m')\varphi_{z'}(z') > 0, \quad \forall z'. \tag{54}$$

Clearly, the function $w'^{(m)}(z') = \varphi'(z') - \varphi'(d_m')$ is given by the formula

$$\int_0^{w'^{(m)}(z')} \frac{d\omega}{\sqrt{2g(\omega)}} = |z' - d_m'|, \qquad w'^{(m)}_{z'} = \sqrt{2g\bigl(w'^{(m)}\bigr)}\,\operatorname{sign}(z' - d_m'), \tag{55}$$

on the interval $|z' - d_m'| < \delta\bar{h}_l/2$.

The integral $\int_0^w g^{-1/2}(\omega)\,d\omega$ is well defined for any $w > 0$. The function $W'(z')$ defined by the formula

$$\int_0^{W'(z')} \frac{d\omega}{\sqrt{2g(\omega)}} = |z' - d_m'|, \quad 0 < z' < L', \tag{56}$$

is an extension of the function $w'^{(m)}(z')$, $|z' - d_m'| < \delta\bar{h}_l/2$, given by (55). Clearly, $W'(z')$ solves equation $w_{z'z'} = g_1(w)$ on the whole interval $0 < z < L'$.

Step 4. We claim that $W'_{z'}(z') \geqslant w'^{(n)}_{z'}(z') \geqslant 0$ for any interval $a'_n < z' < a'_{n+1}$, $n > m$, and $W'_{z'}(z') \leqslant w'^{(n)}_{z'}(z') \leqslant 0$ for any interval $a'_n < z' < a'_{n+1}$, $n < m$. To this end we first prove the following comparison inequalities.

Lemma 5.1. *Let w_1 and w_2 be two solutions of the equation $w_{zz} = g_1(w)$ on the interval $a < z < b$ such that $w_1(a) > w_2(a)$ and $w_{1z}(a) \geqslant w_{2z}(a)$. Then $w_1(z) > w_2(z)$ and $w_{1z}(z) \geqslant w_{2z}(z)$ for any $a < z < b$.*

Proof. Let us denote $w = w_1 - w_2$. Given $z > a$, we integrate the equality $w_{zz} = \int_{w_2(z)}^{w_1(z)} g''(s)\,ds$ over the interval (a, z) to obtain that

$$w_z(z) = w_z(a) + \int_a^z ds \int_{w_2(s)}^{w_1(s)} g''(\xi)\,d\xi, \qquad w(z) = w(a) + \int_a^z w_z(\xi)\,d\xi. \tag{57}$$

By continuity, the inequality $w_1(z) > w_2(z)$ is valid not only for $z = a$ but on some interval $a \leqslant z < z_0$. Due to convexity of the function $g(w)$, the inequality $w_z(z) \geqslant 0$ holds for $a \leqslant z \leqslant z_0$. Hence, $w(z_0) > 0$, $w_z(z_0) \geqslant 0$ and one can extend the interval $a \leqslant z < z_0$. Assume that the maximal interval $a \leqslant z < z_*$ does not coincide with the interval $a \leqslant z < b$. It means that $w(z_*) = 0$ and $w_z(z) \geqslant 0$ for $a \leqslant z \leqslant z_*$. But this claim contradicts the second equality in (57). The lemma is proved. □

Let us compare $W'(z')$ and $w'^{(m+1)}(z')$ on the interval $a'_{m+1} < z' < a'_{m+2}$. Due to (54) and (55) we have $w'^{(m+1)}(a'_{m+1}) < 0$ and $W'(a'_{m+1}) > 0$. The continuity of $\varphi'_{z'}(z')$ implies that $W'_{z'}(a'_{m+1}) = w'^{(m)}_{z'}(a'_{m+1}) = w'^{(m+1)}_{z'}(a'_{m+1})$. By Lemma 5.1, $W'(z') > w'^{(m+1)}(z')$ and $W'_{z'}(z') \geqslant w'^{(m+1)}_{z'}(z')$ for $a'_{m+1} < z' < a'_{m+1}$. The same arguments are applied for the functions $W'_{z'}(z')$ and $w'^{(m+2)}(z')$ on the interval $a'_{m+2} < z' < a'_{m+3}$, etc. Thus,

$$\int_0^{L'} |\varphi'_{z'}|^2\,dz' = \sum_{k=0}^{N-1} \int_{a'_k}^{a'_{k+1}} \left|w'^{(k)}_{z'}\right|^2 dz' \leqslant \int_0^{L'} |W'_{z'}|^2\,dz' \leqslant B \tag{58}$$

and

$$\left|\varphi'(z')\right| = \left|\zeta_0 + \int_0^{z'} \varphi'_{z'}(s)\,ds\right| \leqslant B. \tag{59}$$

It follows from the identity

$$w^{(n)}(z) - w^{(n)}(d_n) = \int_{d_n}^{z} w^{(n)}_z(s)\,ds$$

that $|w^{(n)}(z)| \leqslant B$ for any interval $a_n < z < b_n$. Then one obtains estimates (35) as in the linear electrolyte case. The case of concave electrolyte ($p_2 < p_1$) can be considered similarly.

One can write the Poisson–Boltzmann equation as

$$\big(\varepsilon(z)\varphi_z\big)_z = \varepsilon_l \chi(z) g_1\big(w(z)\big) = \varepsilon_l (p_2 - p_1)\chi(z) + \varepsilon_l \chi(z)\big(g_1\big(w(z)\big) - g_1(0)\big), \tag{60}$$

where $w(z) = \varphi(z) - \varphi(H_d(z))$ and $g_1(0) = p_2 - p_1$. It follows from (35) that

$$\sum_{n=0}^{N-1} \int_{a_n}^{a_{n+1}} w_z^2(z)\,dz \leqslant B, \qquad \max_{0 \leqslant z \leqslant L} \left|w(z)\right| \leqslant B.$$

We prove that there is a constant B independent of δ such that

$$\left|g_1\big(w(z)\big) - g_1(0)\right| \leqslant B\delta. \tag{61}$$

To this end, we pass to the function $\varphi'(z')$ solving the problem (52). By definitions,

$$g_1\big(w(z)\big) - g_1(0) = g_1\big(\varphi'(z') - H'_d(z')\big) - g_1(0).$$

Let z' lies in the interval $a'_n < z' < a'_{n+1}$, then

$$g_1\big(w'(z')\big) - g_1(0) = \int_{d'_n}^{z'} g_{ww}\big(w'(z')\big)\varphi'_{z'}(z')\,dz'. \tag{62}$$

We integrate the identity

$$\varphi'_{z'}(z') - \varphi'_{z'}(z'_1) = \int_{z'_1}^{z'} \varphi'_{z'z'}(x)\,dx$$

over the variable z'_1 to obtain that

$$L'\varphi'_{z'}(z') = \zeta_L - \zeta_0 - \sum_1^N \big(\varphi(a_k) - \varphi(b_{k-1})\big) + \int_0^{L'} dz'_1 \int_{z'_1}^{z'} \varphi'_{z'z'}(x)\,dx.$$

Observe that

$$\left|\sum_1^N \big(\varphi(a_k) - \varphi(b_{k-1})\big)\right| \leqslant \int_0^L |\varphi_z|\,dz.$$

It follows from Eq. (52) that $|\varphi'_{z'z'}|$ is bounded uniformly in δ, hence $|\varphi'_{z'}|$ verifies this property also. Now, estimate (61) results from (62) and from the inequality

$$\left|\int_{d'_n}^{z'} g_{ww}\big(w'(z')\big)\varphi'_{z'}(z')\,dz'\right| \leqslant \delta\bar{h}_l \max_{|\omega|\leqslant 2B_1}\big|g_{ww}(\omega)\big| \max_{0<z'<L'}\big|\varphi'_{z'}(z')\big|/2.$$

6. Existence

Here we consider the question of solvability of problem (25), (18), (20) for any fixed value of δ. We apply the Leray–Schauder fixed point theorem [8] and to this end we define operators A_λ, $0 \leqslant \lambda \leqslant 1$, as follows. Given a Hölder continuous function $v \in C^\alpha(\bar{\Omega})$, $0 < \alpha < 1/2$, we find a function $\varphi(z) \in H^1(\Omega)$, $\varphi = A_\lambda v$, as a unique solution of the linear boundary-value problem

$$\int_\Omega \varepsilon(z)\varphi_z(z)\psi_z(z)\,dz = -\lambda\varepsilon_l \int_\Omega \chi(z) g_1\big(v(z) - v\big(H_d(z)\big)\big)\psi(z)\,dz, \tag{63}$$

for any test function $\psi \in H^1_0(\Omega)$ where $\varphi(0) = \zeta_0$ and $\varphi(L) = \zeta_L$. Clearly, $\varphi \in C^{2+\alpha}[a_n, b_n]$ and $\varphi \in C^{2+\alpha}[b_n, a_{n+1}]$ for any n. Thus, the operators $A_\lambda : C^\alpha(\bar{\Omega}) \to C^\alpha(\bar{\Omega})$ are well defined and a fixed point of A_1 solves the problem (25), (18), (20).

Because of a priori estimates (35) and the continuous embedding of $H^1(\Omega)$ into $C^{1/2}(\bar{\Omega})$ there is a constant M such that $\|\varphi_\lambda\|_{C^{1/2}} \leqslant M$ for any fixed point φ_λ of A_λ. Given a constant $M' > M$, we introduce the ball

$$U = \big\{v \in C^\alpha(\bar{\Omega}):\ \|v\| \leqslant M'\big\}$$

in the Banach space $C^\alpha(\bar{\Omega})$. The restrictions $A_\lambda : U \to C^\alpha(\bar{\Omega})$ enjoy the following properties. By constructions, the boundary of U does not contain fixed points of A_λ, $0 \leqslant \lambda \leqslant 1$. The set $\bigcup_{\lambda\in[0,1]} A_\lambda(U)$ is compact in $C^\alpha(\bar{\Omega})$ because of compact imbedding of $C^{1/2}(\bar{\Omega})$ into $C^\alpha(\bar{\Omega})$ for $0 < \alpha < 1/2$. The family of maps $\{v \to A_\lambda v\}_{\lambda\in[0,1]}$ is equicontinuous on U. The mapping $(\lambda, v) \to A_\lambda v$ is continuous from $[0,1] \times U$ to $C^\alpha(\bar{\Omega})$. The operator A_0 has a unique fixed point in the interior of U, and the mapping $v \to v - A_0(v)$ has an inverse near this fixed point. This means that we have verified all the conditions of the Leray–Schauder theorem. Thus, problem (25), (18), (20) has a solution $\varphi \in H^1(\Omega)$ such that $\varphi \in C^{2+\alpha}[a_n, b_n]$ and $\varphi \in C^{2+\alpha}[b_n, a_{n+1}]$ for any $0 < n < N-1$. The derivation of a priori estimates (35) independent of δ is justified.

7. Two-scale compactness

We consider the passage to limit in problem (26)–(28), as $\delta \to 0$. First, we recall the following convergence result [1,9]

$$\int_\Omega f\left(x, \frac{x}{\delta}\right) dx \to \int_\Omega \int_Y f(x,y)\, dx\, dy, \quad \forall f \in L^1\big(\Omega; C_{\mathrm{per}}(Y)\big),$$

where Ω is an open bounded set in $\mathbb{R}^n$ and Y is the unit cube in $\mathbb{R}^n$. In what follows, we use a special type of convergence in $L^2(\Omega)$. A sequence $u^\delta \subset L^2(\Omega)$ is said two-scale converges [1,9] to a limit $u \in L^2(\Omega \times Y)$ if for any $\psi \in C^\infty(\Omega; C^\infty_{\mathrm{per}}(Y))$ one has

$$\lim_{\delta \to 0} \int_\Omega u^\delta(z) \psi\left(z, \frac{z}{\delta}\right) dz \to \int_\Omega \int_Y u(z,y) \psi(z,y)\, dz\, dy. \tag{64}$$

The two-scale limit has the following property [1,9]. *From each bounded sequence in $L^2(\Omega)$ one can extract a subsequence which two-scale converges to a limit $u \in L^2(\Omega \times Y)$.*

As for derivatives, we will use the following assertion [1,9]. *Let $u^\delta(z)$ and $u^\delta_z(z)$ be bounded sequences in $L^2(\Omega)$. Then there exist functions $u \in L^2(\Omega)$, $w \in L^2(\Omega; H^1_{\mathrm{per}}(Y))$ and a subsequence such that both $u^\delta(z)$ and $u^\delta_z(z)$ two-scale converge to $u(z)$ and $u_z(z) + w_y(z,y)$, respectively.*

Because of the estimates (35), there are a sequence $\varphi^\delta(z)$ and two functions $\varphi^0(z)$ and $\varphi^1(z,y)$ such that $\varphi^0 \in L^2(\Omega)$ and $\varphi^1 \in L^2(\Omega; H^1_{\mathrm{per}}(Y))$ and

$$\int_\Omega \varphi^\delta(z) \psi\left(z, \frac{z}{\delta L}\right) dz \to \int_\Omega \int_Y \varphi^0(z) \psi(z,y)\, dz\, dy,$$

$$\int_\Omega \varphi^\delta_z(z) \psi\left(z, \frac{z}{\delta L}\right) dz \to \int_\Omega \int_Y \big(\varphi^0_z(z) + \varphi^1_y(z,y)/L\big) \psi(z,y)\, dz\, dy,$$

$\forall \psi \in C^\infty(\Omega; C^\infty_{\mathrm{per}}(Y))$ as $\delta \to 0$ [1,9].

We have

$$\int_\Omega \tilde{\varepsilon}\left(\frac{z}{\delta L}\right) \varphi^\delta_z \Psi_z(z)\, dz = -\varepsilon_l \int_\Omega \tilde{\chi}\left(\frac{z}{\delta L}\right) g_1\big(w^\delta\big) \Psi(z)\, dz, \quad \forall \Psi \in H^1_0(\Omega). \tag{65}$$

Taking $\Psi(z) = \delta \psi(\frac{z}{\delta L})$, with $\psi \in H^1_{\mathrm{per}}(Y) \cap C^\infty_0(Y)$, and sending δ to 0, we obtain a microequation in the cell Y

$$\int_\Omega \int_Y \tilde{\varepsilon}(y) \big(\varphi^0_z(z) + \varphi^1_y(z,y)/L\big) \psi_y(y)\, dz\, dy = 0. \tag{66}$$

With the function $\varphi^0(z)$ at hand, we find $\varphi^1(z,y)$ by the method of separation of variables in the form $\varphi^1(z,y) = \varphi^0_z(z) w_1(y)$, where $w_1(y)$ is a periodic solution of the problem

$$\frac{d}{dy}\left(\tilde{\varepsilon}(y)\left(1 + \frac{1}{L}\frac{dw_1}{dy}\right)\right) = 0, \qquad \int_Y w_1(y)\, dy = 0. \tag{67}$$

Clearly, w_1 is defined uniquely and

$$\tilde{\varepsilon}(y)\left(1+\frac{1}{L}\frac{dw_1}{dy}\right)=\varepsilon_h(\Phi)=\text{const},\qquad \varepsilon_h(\Phi)=\left(\int_0^1 1/\tilde{\varepsilon}(y)\,dy\right)^{-1}=\frac{1}{\frac{\Phi}{\varepsilon_l}+\frac{1-\Phi}{\varepsilon_s}}. \tag{68}$$

Taking in (65) $\Psi(z)=\psi(z)$, with $\psi\in H_0^1(\Omega)$, and sending δ to 0, we obtain a macroequation on the interval Ω

$$\int_\Omega\int_Y \tilde{\varepsilon}(y)\big(\varphi_z^0(z)+\varphi_y^1(z,y)/L\big)\psi_z(z)\,dz\,dy=-\varepsilon_l g_1(0)\int_\Omega\int_Y \tilde{\chi}(y)\psi(z)\,dz\,dy. \tag{69}$$

Hence, $\varphi^0(z)$ is a solution of the boundary-value problem

$$\varepsilon_h(\Phi)\varphi_{zz}^0=-4\pi\Phi\sum_\pm c_i^- q_i,\quad \varphi^0(0)=\zeta_0,\quad \varphi^0(L)=\zeta_L. \tag{70}$$

Observe that the representation formula for ε_h is exactly the well-known Maxwell formula for the mixture of two dielectrics [3].

Let us consider the velocity sequence $v^\delta(z)$. Integrating Eq. (27) we obtain the following representation formula for the bulk velocity on the fluid intervals $a_n<z<b_n$:

$$\mu v^\delta(z)=\frac{a_n-z}{b_n-a_n}\int_{a_n}^{b_n}(b_n-\lambda)G(\lambda)\,d\lambda+\int_{a_n}^{z}(z-\lambda)G(\lambda)\,d\lambda,\qquad G=\alpha-\frac{\beta\varepsilon_l}{4\pi}\varphi_{zz}^\delta. \tag{71}$$

Let us extend v^δ by zero onto the solid domain Ω_s^δ, denoting the extension by $\hat{v}^\delta(z)$. It follows from (71) that for any $z\in\Omega$

$$\mu\hat{v}^\delta(z)=\tilde{\chi}\left(\frac{z}{\delta L}\right)\left(\frac{\tilde{\xi}_a(\frac{z}{\delta L})}{\bar{h}_l}\int_{z+\delta\tilde{\xi}_a(\frac{z}{\delta L})}^{z+\delta\tilde{\xi}_b(\frac{z}{\delta L})}\left(z+\delta\tilde{\xi}_b\left(\frac{z}{\delta L}\right)-\lambda\right)G(\lambda)\,d\lambda+\int_{z+\delta\tilde{\xi}_a(\frac{z}{\delta L})}^{z}(z-\lambda)G(\lambda)\,d\lambda\right)\equiv I(G). \tag{72}$$

Particularly, it follows from estimate (61) that

$$I\left(\alpha-\frac{\beta\varepsilon_l}{4\pi}g_1(0)\right)=\left(\alpha-\frac{\beta\varepsilon_l}{4\pi}g_1(0)\right)\frac{\delta^3\bar{h}_l}{2}\tilde{\xi}_a\left(\frac{z}{\delta L}\right)\tilde{\xi}_b\left(\frac{z}{\delta L}\right), \tag{73}$$

$$\big|I\big(g_1\big(w^\delta\big)-g_1(0)\big)\big|\leqslant\delta^4 B. \tag{74}$$

By the above calculations, the sequence $\hat{v}^\delta/\delta^2$ two-scale converges

$$\frac{\hat{v}^\delta}{\delta^2}\xrightarrow{\text{t.s.}}\frac{1}{2\mu}\tilde{\chi}(y)\tilde{\xi}_a(y)\tilde{\xi}_b(y)\left(\alpha+\beta\sum_\pm c_i^- q_i\right)\equiv v^0(y)\quad\text{as }\delta\to 0. \tag{75}$$

Since $Pe=O(1)$ and $v=O(\delta^2)$, we assume that $D_i=\delta^2\tilde{D}_i$. Let $\hat{v}_i$ be the zero extension of v_i onto Ω_s^δ. Then it follows from (28) that

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

Clearly,

$$\text{t.s.}\lim_{\delta\to 0}\frac{\hat{v}_i^\delta}{\delta^2}=v^0(y)-\frac{\beta q_i\tilde{D}_i\tilde{\chi}(y)}{kT}\equiv v_i^0(y). \tag{76}$$

8. A corrector and error estimates

The two-scale limits $\varphi^0(z)$, $v^0(y)$, and $v_i^0(y)$ approximate the functions $\varphi^\delta(z)$, $v^\delta(z)/\delta^2$, and $v_i^\delta(z)/\delta^2$ for small values of δ. Here, we improve the approximations by finding a corrector to the function $\varphi^0(z)$. We argue by the formal expansion series [13] approach. To this end we assume that there is a function $\varphi^2(z,y)$ defined for $0<z<L$ and 1-periodic in y such that

$$\varphi^\delta(z)=\varphi^0(z)+\delta\varphi_z^0(z)w_1(y)+\delta^2\varphi^2(z,y)+o\big(\delta^2\big), \tag{77}$$

where $\varphi^0(z)$ and $w_1(y)$ are defined by (70) and (67), respectively.

We introduce the flux $F^\delta(z)$ as follows

$$F^\delta(z)=\tilde\varepsilon\left(\frac{z}{\delta L}\right)\frac{d}{dz}\varphi^\delta(z),\qquad \frac{d}{dz}F^\delta=\varepsilon_l\tilde\chi\left(\frac{z}{\delta L}\right)g_1\big(w^\delta(z)\big), \tag{78}$$

where $w^\delta(z)\equiv\varphi^\delta(z)-\varphi^\delta(H_d(z))$, and represent it also by the expansion series

$$F^\delta(z)=F^0(z,y)+\delta F^1(z,y)+o(\delta),\quad y=z/(\delta L). \tag{79}$$

Applying the derivative formula

$$\frac{d}{dz}\varphi^2\left(z,\frac{z}{\delta L}\right)=\varphi_z^2\left(z,\frac{z}{\delta L}\right)+\frac{1}{\delta L}\varphi_y^2\left(z,\frac{z}{\delta L}\right),$$

we inset the expansions (77) and (79) into the first equality in (78) arriving at an equality

$$\sum_{-1}^{1}\delta^k(\cdots)_k=o(\delta). \tag{80}$$

We conclude that $(\cdots)_k=0$ for each $k=-1,0,1,\ldots$. These equalities imply that

$$\varphi_y^0(z,y)=0,\qquad F^0(z,y)=\varphi_z^0(z)\tilde\varepsilon(y)\big(1+w_{1y}(y)/L\big), \tag{81}$$

$$F^1(z,y)=\tilde\varepsilon(y)\big(\varphi_{zz}^0(z)w_1(y)+\varphi_y^2(z,y)/L\big). \tag{82}$$

Then we insert the expansions (77) and (79) into the second equality in (78). Similarly, we obtain (paying attention to the powers δ^{-1} and δ^0) the equalities

$$\varphi_z^0(z)\frac{\partial}{\partial y}\big\{\tilde\varepsilon(y)\big(1+w_{1y}(y)/L\big)\big\}=0, \tag{83}$$

$$\varphi_{zz}^0\tilde\varepsilon(y)\big(1+w_{1y}(y)/L\big)+\frac{1}{L}\frac{\partial}{\partial y}\left\{\tilde\varepsilon(y)\left(\varphi_{zz}^0w_1(y)+\frac{1}{L}\varphi_y^2(z,y)\right)\right\}=\varepsilon_l\tilde\chi(y)g_1(0). \tag{84}$$

We find $\varphi^2(z,y)$ by the method of separation of variables assuming that there is a function $w_2(y)$ such that $\varphi^2(z,y)=\varphi_{zz}^0(z)w_2(y)$. Insetting this representation formula into (84), we obtain that $w_2(y)$ should be a periodic solution of the equation

$$\varepsilon_h\varphi_{zz}^0+\frac{1}{L}\varphi_{zz}^0\frac{d}{dy}\left\{\tilde\varepsilon(y)\left(w_1(y)+\frac{1}{L}\frac{d}{dy}w_2(y)\right)\right\}=-4\pi\chi(y)\sum_{\pm}c_i^-q_i. \tag{85}$$

Clearly, this equation has a unique solution satisfying the equality $\int_0^1 w_2\,dy=0$.

Let us introduce a two-scale corrector

$$\varphi^c(z,y)=\varphi^0(z)+\delta\varphi_z^0(z)w_1(y)+\delta^2\varphi_{zz}^0(z)w_2(y).$$

Its crucial property is that

$$\left(\tilde\varepsilon\left(\frac{z}{\delta L}\right)\varphi_z^{c,\delta}\right)_z=\varepsilon_l\tilde\chi\left(\frac{z}{\delta L}\right)g_1(0),\quad \varphi^{c,\delta}\equiv\varphi^c\left(z,\frac{z}{\delta L}\right), \tag{86}$$

this equality can be verified in a straightforward manner.

The difference $h = \varphi - \varphi^{c,\delta}$ solves the problem

$$\int_\Omega \tilde{\varepsilon}\left(\frac{z}{\delta L}\right) h_z(z)\psi_z(z)\,dz = \varepsilon_l \int_\Omega \tilde{\chi}\left(\frac{z}{\delta L}\right)\psi(z)\big(g_1\big(w^\delta\big) - g_1(0)\big)\,dz, \tag{87}$$

$$h(0) = -\delta\varphi_z^0(0)w_1(0) - \delta^2\varphi_{zz}^2(0)w_2(0) \equiv h_0,$$

$$h(L) = -\delta\varphi_z^0(L)w_1(1) - \delta^2\varphi_{zz}^2(L)w_2(1) \equiv h_L$$

for any $\psi \in H_0^1(\Omega)$. Denoting

$$h_0(z) = z(h_L - h_0)/L + h_0,$$

we insert the function $\psi_0 = h - h_0 \in H_0^1(\Omega)$ into (87) to obtain that

$$\int_\Omega \tilde{\varepsilon}\psi_{0z}^2\,dz = -\int_\Omega \tilde{\varepsilon}\psi_{0z}\,dz - \varepsilon_l \int_\Omega \tilde{\chi}\psi_0\big(g_1\big(w^\delta\big) - g_1(0)\big)\,dz.$$

Applying the Young inequality and inequality (61), we conclude that

$$\|\psi_0\|_{H_0^1(\Omega)} \leqslant B\delta \quad \text{and} \quad \big\|\varphi^\delta - \varphi^{c,\delta}\big\|_{H_0^1(\Omega)} \leqslant B\delta. \tag{88}$$

9. Two-scale model

We can summarize the results as follows. There are functions $\varphi^c(z,y)$, $v^0(y)$, and $v_i^0(y)$ of the slow and fast variables such that the expansions

$$\varphi^\delta(z) = \varphi^c\left(z, \frac{z}{\delta L}\right) + O(\delta), \qquad \frac{\hat{v}^\delta}{\delta^2} = v^0\left(\frac{z}{\delta L}\right) + O(\delta), \qquad \frac{\hat{v}_i^\delta}{\delta^2} = v_i^0\left(\frac{z}{\delta L}\right) + O(\delta) \tag{89}$$

hold in $H^1(\Omega)$. (Two latter estimates follow from (74).) Eqs. (67), (70), (85), (75), and (76) serving for determination of these functions constitute a two-scale model.

Being more simple, the two-scale model allows to distinguish between micro and macro variables. The macrovariables are mean values of $\varphi^c(z,y)$, $v^0(y)$, and $v_i^0(y)$ over the fast variable y:

$$\varphi^0(z) = \int_Y \varphi^c(z,y)\,dy, \qquad V = \int_Y v^0(y)\,dy, \qquad V_i = \int_Y v_i^0(y)\,dy. \tag{90}$$

These definitions are natural since, as it follows from the definition of the two-scale convergence, the above mean values are weak limits in L^2 of φ^δ, $\hat{v}^\delta/\delta^2$, and $\hat{v}_i^\delta/\delta^2$ as $\delta \to 0$.

We use macrovariables to formulate macroscopic electroosmotic laws as follows. Integrating equality in (75), we obtain

$$V = -\lambda_{11}\alpha - \lambda_{12}\beta, \tag{91}$$

where the hydrodynamic and electrochemical mobilities are given by the formulas

$$\lambda_{11} = \frac{L^2\Phi^3}{12\mu}, \qquad \lambda_{12} = \frac{L^2\Phi^3}{12\mu}\sum_\pm c_i^- q_i. \tag{92}$$

Let us introduce microscopic and macroscopic electric current

$$j = \sum_\pm c_i q_i v_i^0(y), \qquad J \equiv \int_0^1 j(y)\,dy.$$

One can verify that

$$J = -\lambda_{21}\alpha - \lambda_{22}\beta, \tag{93}$$

where

$$\lambda_{21} = \frac{L^2\Phi^3}{12\mu}\sum_{\pm} c_i^- q_i, \qquad \lambda_{22} = \frac{L^2\Phi^3}{12\mu}\left(\sum_{\pm} c_i^- q_i\right)^2 + \frac{\Phi}{kT}\sum_{\pm} q_i^2\tilde{D}_i c_i^-. \tag{94}$$

We recall that α and β are the derivatives along the horizontal variable x: $\alpha = p_x$ and $\beta = \psi_x$. Hence, we have derived the macroscopic electroosmotic equations

$$V = -\lambda_{11} p_x - \lambda_{12}\psi_x, \qquad J = -\lambda_{21} p_x - \lambda_{22}\psi_x, \tag{95}$$

with the mobilities λ_{ij} satisfying the Onsager condition of symmetry $\lambda_{12} = \lambda_{21}$.

Eqs. (95) deliver a simple explanation of the electroosmosis effect depicted in Fig. 1 and they enable us to calculate the difference of water levels. Indeed, if the total bulk velocity vanishes, the pressure gradient p_x can be obtained due to the following equality

$$p_x = -\frac{\lambda_{12}}{\lambda_{11}}\psi_x. \tag{96}$$

Eqs. (95) also explain why the flow through the membrane (see Fig. 2) induces an electrical field. For neutral electrolytes we have $J = 0$, hence it follows from the second equation in (95) that the pressure gradient p_x gives rise to an electrical field such that

$$\psi_x = -\frac{\lambda_{21}}{\lambda_{22}} p_x. \tag{97}$$

The induced electrical field reduces hydrodynamic permeability. Because of (97), it follows from the first equation in (95) that

$$p_x = -\lambda_{ef}\psi_x, \quad \lambda_{ef} = \lambda_{11} - \lambda_{12}^2/\lambda_{22}. \tag{98}$$

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.

10. Conclusions

We have justified a two-scale one-dimensional model for the horizontal electroosmotic flows in a number of thin horizontal nanoslits, with a horizontal pressure gradient and a horizontal electrical field being driving forces. The model was derived within the framework of homogenization in the up-scaling of the pore-scale description consisting of Stokes equation for bulk fluid flow and the Nernst-like equations for the ion transport coupled with the Poisson–Boltzmann equation for electrical field. After introduction of an additional (fast) variable, application of a formal asymptotic expansion technique led to a macroscopic model wherein effective coefficients appear strongly related to the microscale description. The homogenized model is a generalization both of the Darcy law and the Boltzmann–Smoluchowski equation. According to this model, both the fluid flux and the electric flux depend linearly on the horizontal pressure gradient and the horizontal electrical field, with the effective mobilities obeying the Onsager symmetry condition.

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