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Electrokinetic flow-induced currents in silica nanofluidic channels

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ABSTRACT

Electrokinetic flow-induced currents inside slit-shaped silica nanochannels are investigated. The unusual features observed experimentally in silica nanochannels are described successfully using a new theoretical framework. First, a simple and reliable physicochemical boundary condition at the interface between the channel surface and the solution is suggested. It accounts for the surface conduction effect through the Stern layer and the dependence of the surface charge on the salt concentration and pH, which were commonly neglected in previous studies. Second, the proposed boundary condition is then incorporated into the traditional Poisson–Boltzmann and Nernst–Planck models to complete the self-consistent model. Model predictions are validated by comparison with experimental data. It is found that the direct numerical predictions of the concentration polarization and the induced potential or pressure field are possible, and these allow us to describe the dependence of currents on the solution properties in the nanofluidic channel more accurately than the models proposed in previous studies.

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1. Introduction

Ever since the discovery of the electrokinetic effect, many theoretical and experimental attempts have been made to explain the physical mechanism [1] and to widen its engineering applications. These include capillary electrophoresis [2], drug delivery and screening [3], electric power generation [4], liquid pumps [5], and electronics cooling [6]. These applications are realized mostly using channels with various cross-sectional shapes whose dimension is on the order of micrometers or less. Basic understanding and the analysis of electrokinetic fluid flow inside the channel are of great importance in designing electrokinetic devices.

Electrokinetic flow in a micro-sized channel can be readily analyzed using the Poisson–Boltzmann and Stokes equations (hereafter we call this approach the PB model). This approach was first introduced by Burgreen and Nakache [7,8] and Osterle's group [9,10]. They independently derived analytic expressions for electrokinetic parameters such as streaming current, streaming potential, and energy conversion efficiency. In their model, the ion distribution in the electric double layer (EDL) is obtained by solving the Boltzmann equation. The Boltzmann equation is based on the assumptions of constant electrochemical potential everywhere and nonoverlapping EDLs [1]. Thus it is applicable for the ionic concentration in the channel whose critical dimension is much greater than the thickness of EDLs.

In the case of nanochannels whose characteristic dimension is comparable to the EDL thickness, the PB model fails to describe the interesting features observed experimentally in recent studies [11,12]. For example, the concentration polarization effect caused by selective ion transport through the charged nanochannel becomes significant as the degree of EDL overlap becomes large. This phenomenon cannot be explained by using the PB model because it is limited to the nonoverlapping EDLs. Nonetheless, many investigators [5,13–19] used the PB model in modeling the electrokinetic flow in nanochannels, maybe due to its simplicity and easy of use.

The overlapping behavior of EDLs can be precisely described by using the Nernst–Planck model (hereafter we call this approach the NP model). In this model, the characteristics for the electrokinetic flow are obtained by numerically solving the Poisson equation, the Nernst–Planck equation, and the Navier–Stokes equation, simultaneously [20–24]. Although the computational cost for the numerical calculation of full governing equations is extremely high compared to that for the simple PB model, the advantages of the NP model can overshadow this weakness. For example, the NP model can describe the nonlinear electrokinetic behaviors such as the concentration polarization effect [11,12], the limiting-current behavior [25], and the transient characteristics [26,27], which cannot be generally predicted by the PB model. Nevertheless, research on a direct comparison between the NP model and the PB model or between the NP model and the experimental data has been insufficiently carried out so far [28].

The zeta potential or surface charge density is an intrinsic property of a surface and it is used as an electrostatic potential boundary condition for the PB and NP models. As noted by Kirby

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and Hasselbrink [29], zeta potential varies significantly depending on the solution pH and concentration. This is also true for the surface charge density. Nevertheless, many studies are based on the constant zeta potential [20,24] or constant surface charge density [13,21–23,25,26] at surfaces when modeling electrokinetic flow under the conditions of varying concentration. For example, the model of Stein et al. [13] was made to fit to experimental data and showed good model predictions. However, their boundary condition is physically incorrect because they neglected the dependence of the surface charge density on concentration. As alternatives, the basic Stern layer capacitance model [4,14,30] and the site-dissociation–site-binding model [31–37] were introduced. In these models, the surface charge density varies, depending on the solution pH and concentration. A common feature of these models is that the physicochemical parameters such as equilibrium constants and Stern layer capacitance are unknowns, although they are usually determined to be within ranges of reported values [14], and obtained by fitting the model to the experimental data case by case, which is a very tedious process. Therefore, it will be meaningful to propose a boundary condition for the electric potential which is both physically reasonable and simple to use.

The purpose of the present study is to propose a better modeling method that accurately describes the electrokinetic flow and ion transport in nanofluidic channels. The proposed model will be validated by comparing the results based on the model with recently measured streaming and electrical currents in fused silica nanochannels [4,14]. The main objectives of this study are as follows: (a) to propose a wall boundary condition for the electric potential and surface charge density that can be applied to a silica surface easily and self-consistently and (b) to investigate the fundamental transport characteristics and mechanism of the electrokinetic flow inside the nanochannel using the PB and NP models.

2. Theoretical formulation and numerical method

2.1. Governing equations

The governing equations for the velocity field and electric potential inside the channel are the Navier–Stokes and Poisson's equations, respectively,

$$\rho\left(\frac{\partial \vec{u}}{\partial t} + \vec{u}\cdot\nabla\vec{u}\right) = -\nabla p + \mu\nabla^2\vec{u} + \rho_e\vec{E}, \tag{1}$$

$$\nabla^2\phi = -\frac{1}{\varepsilon_0\varepsilon_r}\sum_i n_i z_i e, \tag{2}$$

where ρ is the fluid density, $\vec{u}$ the fluid velocity vector, p the local pressure, μ the fluid dynamic viscosity, $\rho_e = \sum_i n_i z_i e$ the volume charge density, $\vec{E}$ the externally applied electric field, ϕ the local electric potential, ε_0 the permittivity of the vacuum, ε_r the relative permittivity, n_i the ion concentration (number of ions per unit volume), z_i the valence of ion i, and e the elementary charge, respectively. Here ε_r is assumed to be uniform throughout the channel. The second term on the left-hand side of Eq. (1) is negligible for the general electrokinetic flow applications without loss of accuracy because the Reynolds number is very small on the order of 10^{-2} or less. Thus one can utilize the following Stokes equation for steady and laminar flow conditions:

$$-\nabla p + \mu\nabla^2\vec{u} + \rho_e\vec{E} = 0. \tag{3}$$

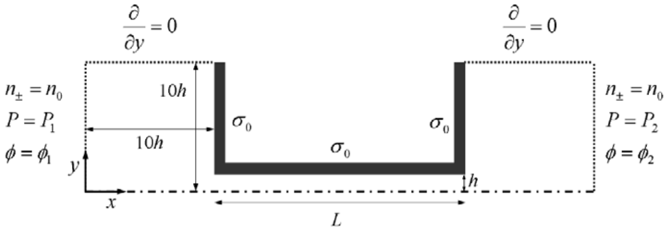

Fig. 1. Schematic of the nanochannel connected with reservoir in both sides of directions and boundary conditions for the reservoir and the wall of the nanochannel.

A current exists in the channel due to the motion of ions, which is induced by the applied electric field, concentration gradient, or pressure gradient. For the dilute electrolyte, the current density is the summation of contributions from diffusion, electromigration, and advection of ions. The current density from ion i can be written as

$$\vec{i}_i = -D_i z_i e\nabla n_i - b_i z_i e n_i\nabla\phi + z_i e n_i\vec{u}, \tag{4}$$

where $\vec{i}$ is the current density, D the diffusivity, and b the ion mobility, respectively. Equation (4) is called the Nernst–Planck equation. Due to ion conservation at steady state, the gradient of Eq. (4) should be equal to zero: that is,

$$\nabla\cdot(D_i\nabla n_i + b_i n_i\nabla\phi) = \vec{u}\cdot\nabla n_i. \tag{5}$$

Equations (2), (3), and (5) compose a set of differential equations with unknowns n_i, $\vec{u}$, and ϕ.

The Boltzmann equation is valid for the assumptions of constant electrochemical potential, no convective transport of ions, and nonoverlapping EDLs in the channel flow. With these assumptions, Eq. (5) can be simplified as

$$n_i = n_0\exp\left(-\frac{z_i e\phi}{kT}\right), \tag{6}$$

where n_0 represents the concentration of bulk solution, k the Boltzmann constant, and T the absolute temperature, respectively. Introducing Eq. (6) into Eq. (2), one can derive the following the Poisson–Boltzmann equation:

$$\nabla^2\phi = -\frac{1}{\varepsilon_0\varepsilon_r}\sum_i z_i e n_0\exp\left(-\frac{z_i e\phi}{kT}\right). \tag{7}$$

We can precisely calculate the concentration and local electric potential distributions using Eqs. (6) and (7), respectively.

The PB and NP models are different from each other; the former uses Eq. (6) to obtain information about the ionic concentration, but the latter uses Eq. (5). The PB model is simple but results in approximate solutions due to its inherent assumptions. That is, it can give poor predictions for the electrokinetic flow in a nanochannel where the EDLs from each wall begin to overlap. On the other hand, the NP model yields exact solutions, but requires full numerical simulation whose computational cost is much higher than that of the PB model.

2.2. Electrokinetic flow and currents inside the nanochannel

We consider the electrokinetic flow in the slit-shaped channel of submicrometer height. Fig. 1 is the schematic view of the nanochannel. In this study, we ignore the z directional variations of the velocity, ion concentration, and potential for the convenience of calculation. Thus, we consider the two-dimensional problem.

2.2.1. The PB model

We can derive an analytic expression for the velocity distribution in the nanochannel using the PB model [5]. Substituting Eq. (2) into Eq. (3) and integrating twice with respect to y, the velocity profile is given by

$$u = \frac{h^2}{2\mu}\frac{\Delta p}{L}(y^{*2} - 1) + \frac{\varepsilon_0\varepsilon_r\zeta}{\mu}\frac{\Delta\psi}{L}\left(\frac{\phi^*}{\zeta^*} - 1\right), \tag{8}$$

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