Numerical Issues in Simulating Electroosmotic Micro/Nano Flow

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Summary

Electroosmosis is a promising means to manipulate fluid motion and associated mass transports in micro- and nanofluidic devices. There are several numerical difficulties in simulating electroosmotic flow, which are mainly associated with the resolution to extremely thin electric double layer forming on a charged surface. This paper introduces a numerical model for electroosmotic flow in a micro- and nanochannel. The non-equilibrium transports of ionic species are represented by by the Nernst-Planck equation. The raised numerical issues are addressed, which encompass handling of boundary conditions, associated treatment of electric potential, and evasion of nonlinearity due to electric body force. Exemplary simulation results are presented.

1. Introduction

A micro- and nanochannel is an essential element in transporting various bio and chemical species as well as buffer fluids in microfluidic devices. As the hydraulic diameter of the channel decreases, the conventional pressurization has encountered critical technical difficulties in driving flow. Recently, electroosmosis has been considered as the promising alternative [1]. The electroosmotic flow (EOF) denotes the electrically-driven motion of fluid parcels having net charge. In a channel filled with a neutral electrolyte solution, the fluid region with net charge is confined to the very limited region, called the Debye layer or electric double layer (EDL), forming on the liquid-solid interface [2]. The thickness of EDL, depending on the ion concentration of electrolyte solution, is typically of an order of ten nanometers or smaller.

The height of a conventional microchannel is several to hundred micrometers. The evolution of net charge in the EDL does not give significant influences on electric and chemical balance in the bulk fluid outside the EDL. As a result, the main body of fluid shows a plug-like flow pattern and the velocity can be linearly controlled by the intensity of applied electric field. In this case, the presence of extremely thin EDL could easily be modeled by the slip boundary condition.

Remarkable advance in modern micro-fabrication technique realizes a fluidic device in which the hydraulic diameter of flow channel is hundreds or several tens of nanometers. Analytical treatment of a picoliter sample tends to be practical. As the channel is miniaturized to have a height of submicron, simplifications based on the assumption of extremely thin EDL is no longer valid. The resolution to EDL has emerged as an essential issue since EDL gives a direct impact on the structures of EOF [4]. Recently, there have been atomistic computations examining EOF in a nanochannel (see, e.g., [4]). However, the channel dimension considered was still O(10 nm) and the channel of height O(100 nm) is computationally challenging. A different approach using the continuum-based model has also been made to describe the detailed structure of EDL [5-7]. Most of these studies are based on the Boltzmann equilibrium for induced electric field. Various numerical attempts have been made to perform a full scale simulation of non-equilibrium EOF. But, a successful numerical model without defects is still under question.

In this study, a numerical model is introduced, which is designed for simulating the non-equilibrium EOF in a micro- and nanochannel. In the course of model description, several numerical issues are discussed. The numerical difficulties in simulating the EOF with resolution to EDL are presented and the practical modeling methods to avoid these hurdles are briefly touched on.

2. Model

The Gouy-Chapman continuum model is the basis of for the present numerical model for simulating EOF. The governing equations are the Navier-Stokes equations for an incompressible fluid under an electric field

$$\rho \frac{\partial \vec{u}}{\partial t} + \rho \vec{u} \cdot \nabla \vec{u} = -\nabla p - \rho_e \vec{E} + \nabla \cdot (\eta \nabla \vec{u}) , \tag{1}$$

$$\nabla \cdot \vec{u} = 0 , \tag{2}$$

where $\vec{u}$ is the velocity vector, t the time, p the pressure, ρ the density, and η the dynamic viscosity. In the electric body force term, ρ_e is net change density and $\vec{E}$ is the electric field given by

$$\vec{E} = \nabla\Phi\,, \tag{3}$$

where Φ is the electric potential The equation governing the distribution of electric potential is

$$\nabla\cdot(\varepsilon\nabla\Phi) = -\rho_e\,, \tag{4}$$

in which ε is the electric permittivity.

The first issue raised is how to handle electric potential which has two components of different origin, i.e., the electric potential formed by an externally applied electric field ϕ and the intrinsic electric potential induced by formation of EDL ψ. The magnitude of ψ is several tens mV only near the charged wall, thus, it is negligible in macroscopic flow situations. However, in a microflow, this amount of induced potential could be a viable means to drive EOF. The problem is that the use of a single quantity Φ poses some difficulties in treating boundary conditions.

In general, the channel surfaces for EOF are fabricated to be insulated for external electric field and the induced charge at the wall is represented by the zeta potential ζ. As seen by the numerical model by Lin et al. [7], the employment of a single potential Φ leads to an unnatural combination of boundary conditions. A practical approach to resolve this is to decompose Φ into two parts [3, 5-6]

$$\Phi = \phi + \psi\,. \tag{5}$$

The Eq. (5) is now modified to be

$$\nabla\cdot(\varepsilon\nabla\phi) = 0\,, \tag{6}$$

$$\nabla\cdot(\varepsilon\nabla\psi) = -\rho_e\,, \tag{7}$$

and the reasonable boundary conditions can be applied at the wall

$$\nabla\phi\cdot\vec{n} = 0\,, \tag{8}$$

$$\psi = \zeta\,, \tag{9}$$

in which $\vec{n}$ is the unit normal vector to wall.

The second issue is how to evaluate net charge density, which is closely related to the solution to Eq. (7). Theoretically, the net charge density is determined by the concentration of ionic components dissolved in the solution, i.e.,

$$\rho_e = e\sum c_i z_i\,, \tag{10}$$

where e is the unit charge of a proton. c_i and z_i are respectively the concentration (number density) and valence of i-th ionic component.

A conventional approach is to assume that the concentration of anion and that of cation follow the Boltzmann distribution,

$$\rho_e = -2ezc_0\sinh(ez\psi/k_BT)\,, \tag{11}$$

in which c_0 is the number density of ionic component in electrolyte solution, k_B is the Boltzmann constant, and T is the absolute temperature. Then, Eq. (7) is reduced to the well-known Poisson-Boltzmann equation.

The third issue is on the natural and consistent boundary conditions for the electric field. The most popular boundary condition in EOF is that the zeta potential is used for the induced electric potential at the charged wall, i.e.,

$$\psi = \zeta \,, \tag{12}$$

When the Poisson-Boltzmann equation is employed, this boundary condition is plausible. By the way, when the Nernst-Planck equation is employed, it is difficult to find a proper boundary condition for mass transfer of ionic component at the charged wall, which is consistent with Eq. (12). A remedy suggested was that the concentration of ionic species was inversely calculated from the Boltzmann distribution, i.e.,

$$c_i = c_0 \exp(-ez_i\zeta / kT) \quad \text{on the charged wall.} \tag{13}$$

However, this idea is contradictory since employment of the Nernst-Planck equation is for simulating non-equilibrium phenomena.

An alternative choice, which is adopted in this study, is to use the surface charge density, σ, instead of the zeta potential, for specifying boundary condition for intrinsic electric potential,

$$\varepsilon \nabla \psi \cdot \vec{n} = \sigma \quad \text{on the charged wall.} \tag{14}$$

Note that the surface charge density is more physically meaningful than the zeta potential which is artificially defined as the electric potential at the Stern plane. An additional advantage is that a consistent boundary condition for mass transfer of ionic species can be derived using Eq. (14). Without unsteady and advection terms, the balance in mass transfer should be achieved between the diffusive flux and the electrophoretic flux. This leads to a new condition,

$$\nabla c_i \cdot\cdot \vec{n} + c_i \frac{ez_i}{kT}\frac{\sigma}{\varepsilon} = 0 \quad \text{on the charged wall.} \tag{15}$$

Equations (14) and (15) constitute a new set of consistent boundary conditions for intrinsically induced electric field and the ionic concentration.

In view of numerical simulation, there is an additional issue associated with dealing with the electric body force in Eq. (1),

$$-\rho_e \vec{E} = \varepsilon \nabla^2 \psi (\nabla \phi + \nabla \psi) \,. \tag{16}$$

As shown in Eq. (16), the electric body force term is nonlinear. Considering that the electric potential due to external electric field is given, the nonlinearity in the electric body force is mainly due to the gradient of intrinsic electric potential. Moreover since the fluid with net charge is concentrated in the EDL, the nonlinear term becomes conspicuous only in the EDL. As deduced from Eq. (1), normal to the wall in the EDL, the only mechanism to balance this locally intensive force is pressure gradient. Thus, the numerical model should be designed to take this flow characteristic into consideration for efficient and reliable computation.

In many macroscopic CFD methods, the pressure gradient normal to the wall has often been considered to be zero. However, this treatment results in a force unbalance in the EDL and the difficulties in numerical convergence. A different approach is to consider the pressure boundary condition driven from the Navier-Stokes equations. Even in this case, the locally intensive electric body force may lead to a huge pressure gradient at the wall. The serious consequence is that a large number of iteration is necessary for acquiring the converged solution to the Poisson equation.

In order to avoid the numerical stiffness, a strategic decomposition of pressure is made as

$$p = p^* + p_{ES}\,, \quad \text{where } \nabla p_{ES} = \varepsilon \nabla^2 \psi \nabla \phi \tag{17}$$

where p^* is the reduced pressure and p_{ES} is the pressure due to the electrostatic body force in the EDL. Here, it is worth adopting an assumption that the electric field due to intrinsic electric potential does not affect EOF. This is reasonable since the potential gradient normal to wall does not create fluid motion across the wall. The implication is that, normal to the charged wall, the electric body due to intrinsic electric potential gradient is balanced by an electrostatic pressure gradient. This is similar to the conventional handling of the gravitational body force associated with hydrostatic pressure distribution. As a consequence, the electric body force is simply expressed as

$$\nabla p + \rho_e \vec{E} = \nabla p^* + \varepsilon \nabla^2 \psi \nabla \phi\,. \tag{18}$$

Now, the above-stated numerical troubles disappear and the standard methods applied for macroscopic flow could be applicable to EOF in a micro- and nanochannel.

In order to get the numerical solution to the governing equations with the prescribed boundary conditions, a finite volume numerical model is developed. The model is based on the fractional time step method. Spatial descretization is implemented on the collocated grid network.

3. Examples of Simulation Results

In the preceding section, four issues encountered in developing a numerical model to simulate EOF are introduced and the methods to resolve the raised issues are discussed. In this section, two simple examples of numerical simulations are presented to illustrate the usefulness and applicability of the numerical model.

The first successful application of the present numerical model was the simulation of formation of EDLs in a nano-scale channel [3]. Fig. 1 shows the transient evolution of ionic concentration in the channel. In most of studies examining electrokinetic phenomena, the Boltzmann equilibrium is assumed to be established near the charged wall. This computation was the first to show that the significant overlap of electric double layers is established in a long nanopore. The mechanisms and time scales for the transient transport process were discussed. This example ascertains the capability of the present model in simulating the EOF affected by time-dependent transports of ionic species which do not obey the Boltzmann equilibrium.

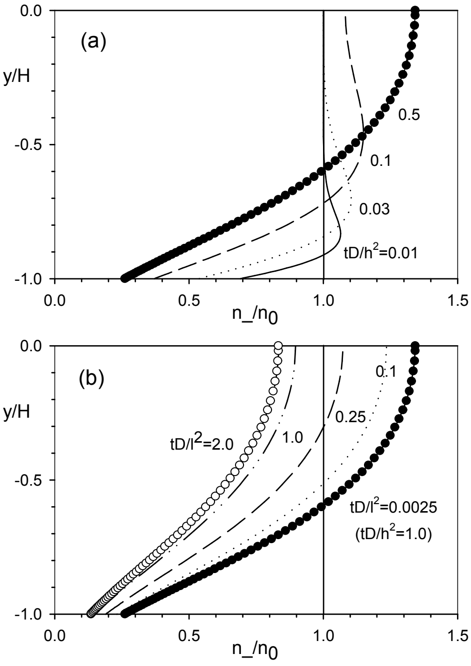

Figure 1 Temporal evolution of the concentation of anions along the cross-section at the middle of the channel. (a) Early-time behavior; (b) long-term behavior. The symbols ○ and ●denote respectively the numerical solution for the infinite channel and the Boltzmann distribution.

Another example, the EOF in a micro flow passage having a nanopore contraction, is selected to reveal a wide applicability of the present numerical model. The hydraulic diameter of the nanopore is several times of the Debye length and that of the micropore is much larger. A key notion here is that the nanopore establishes an overlapped EDLs as shown in Fig. 1. In the core of the microchannel, the fluid is electrically neutral and there is no net charge. However, in the core of the nanochannel, the fluid has net charge since the two EDLs are overlapped. These establish a difference of natural potential near the entrance and exit of the nanopore, which may play a role to trap charged proteins. Numerical computation was conducted to explore this idea.

In order to exemplify the effects of nanopore, the variations of intrinsic electric potential and externally-driven electric potential are plotted in Fig. 2 as well as the total electric potential. It is clearly visible that there is a local maximum of electric potential near the nanopore exit. Consider negatively charged proteins moving toward positive charge in the channel (i.e., toward the region of higher electric potential). The proteins experience a abrupt change in the gradient of electric potential at the exit of nanopore. A proper utilization of this phenomenon is a conceptual basis for the electrophoretic trap that can be used a s a new mechanism for separation of nanomaterials.

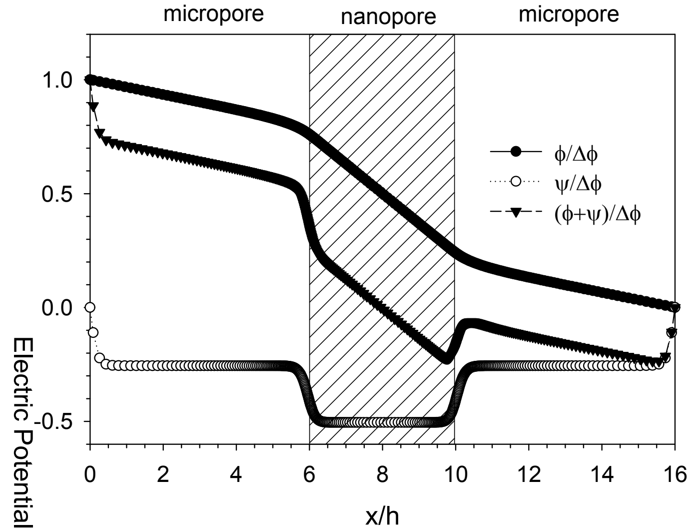

Figure 2 Distribution of electric potential in a micropore having a nanopore contraction.

4. Concluding Remarks

The presence of extremely thin EDL poses formidable barriers to the full scale numerical simulation. In this paper, a numerical model is designed for simulating EOF in a micro- and nanochannel, which is capable of simulating nonequilibrium transports of participating ionic species. Several numerical hurdles are overcome by incorporating the following techniques: (i) the decomposition of electric potential into externally-driven and intrinsically-induced components; (ii) employment of surface charge density for the consistent boundary conditions for intrinsic electric potential and mass transfer of ionic species; (iii) employment of the Nernst-Planck equation; and (iv) the simplification of nonlinear electric body by introducing electrostatic component of pressure which is balanced by the electric body force due to the gradient of intrinsic electric potential. Two illustrative examples verify the applicability of the present model.

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