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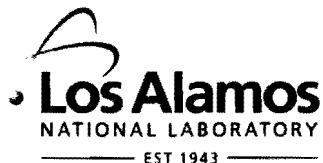
08-7673

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*Intended for:* Publication in Journal of Computational Physics



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# Modeling electrokinetic flows in microchannels using coupled lattice Boltzmann methods

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**Abstract:** We present a numerical framework to solve the dynamic model for electrokinetic flows in microchannels using coupled lattice Boltzmann methods. The governing equation for each transport process is solved by a lattice Boltzmann model and the entire process is simulated through an iteration procedure. After validation, the present method is used to study the applicability of the Poisson-Boltzmann model for electrokinetic flows in microchannels. Our results show that for homogeneously charged long channels, the Poisson-Boltzmann model is applicable for a wide range of electric double layer thickness. For the electric potential distribution, the Poisson-Boltzmann model can provide good predictions until the electric double layers fully overlap, meaning that the thickness of the double layer equals the channel width. For the electroosmotic velocity, the Poisson-Boltzmann model is valid even when the thickness of the double layer is ten times of the channel width. For heterogeneously charged microchannels, a higher zeta potential and an enhanced velocity field may cause the Poisson-Boltzmann model to fail to provide accurate predictions. The ionic diffusion coefficients have little effect on the steady flows for either homogeneously or heterogeneously charged channels. However the ionic valence of solvent has remarkable influences on both the electric potential distribution and the flow velocity even in homogeneously charged microchannels. Both theoretical analyses and numerical results indicate that the valence and the concentration of the counter-ions dominate the Debye length, the electrical potential distribution, and the ions transport. The present results may improve the understanding of the electrokinetic transport characteristics in microchannels.

**Keywords:** Electrokinetic flows; lattice Boltzmann method; multiphysical transport; microfluidics and nanofluidics

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## 1. Introduction

Multiphysical transport has attracted a lot of attention in recent years due to its increasingly important applications in biomedical, environmental, and energy engineering [1; 2; 3; 4; 5]. Electrokinetic flow, which includes fluid flow, electrostatic interaction, species diffusion, and sometimes energy transfer, is one of the most typical multiphysical transport phenomena because of the ubiquitousness of the electrolyte solution in nature and engineering applications [6; 7]. Although numerous theories and models for large-scale electrokinetic flows have been developed for almost one century [6; 8], only in recent decades has the electrokinetic transport shown awakening importance in biophysical applications, especially at micro- and nanoscale. For instance, a better understanding of nanoscale electrokinetic flows will help understand the mass and information transport in ion channels in cell [9; 10]; accurate predictions of micro electroosmotic flow in Lab-on-a-chip devices may shed light on optimal designs of biological-chemical-medical Microsystems, such as those for DNA or protein diagnostics [2; 11; 12; 13]. Electrokinetic flow is also an important non-mechanical actuating technique for microfluidics[12], and has been widely applied for pumping[14; 15; 16], mixing [17; 18; 19], and separating [11].

The Poisson-Boltzmann (PB) model is the most popular method for analyses and predictions of electrokinetic flows in microchannels, which is composed of a Navier-Stokes equation for fluid flow and a PB equation for electric potential distribution [6; 20]. The Boltzmann distribution assumption of ions in electric double layer (EDL) leads to the decoupling between the fluid flow and the ion distribution, which makes the predictions much easier. Many algorithms and analyses based on the PB model have been proposed for the understanding of electrokinetic fluid mechanics and optimization of electrokinetic microdevices [21; 22; 23; 24]. However the Boltzmann distribution is restricted by its preconditions, such as the dilute solution, negligible ionic advection etc.. A more general model is the dynamic model which utilizes the Nernst-Planck equation for ions transport instead of the hypothesized distribution [25]. In the dynamic model, each transport process is governed by the corresponding basic dynamic equation. Because the transport processes are influenced by each other, the governing equations are coupled together. Such coupled partial differential equations pose a great challenge to the numerical solution.

However there are still several efforts that have been made to numerically solve the coupled governing equations in the dynamic model based on the traditional PDE solvers, such as the finite difference method (FDM) [26; 27], the finite volume method (FVM) [28; 29] and the finite element method (FEM) [30]. Recently Lu et al. [31] presented a hybrid framework of finite element and boundary element methods to solve the Poisson-Nernst-Planck equation for electrodiffusion. Hlushkou et al. [32] proposed a coupled lattice-Boltzmann and finite-difference method to solve the dynamic model for electroosmosis in microchannels, in which the lattice Boltzmann method (LBM) was used to model fluid flow and other governing equations were solved by the FDM. This is a good attempt to take advantage of the flexibility and efficiency of the LBM. However the boundary condition might be inconsistent between these two methods on the same set of grid [33]. He and Li [34] provided a multiple LBM process for the electrochemical systems, but they used a local neutrality law to constrain the electric potential distribution which could be inaccurate for charged colloids [35].

The objectives of this contribution are to: 1) present a coupled LB algorithm and framework to solve the governing equations in the dynamic model for the multiphysical transport in

electrokinetic flows in microchannels; 2) simulate the electroosmotic flows in microchannels and to compare the results with those from the PB model to clarify the factors and conditions under which the PB model will fail. The paper is organized as follows. Section 2 introduces the governing equations and the boundary conditions of the dynamic model. In Section 3, we present our evolution equations for all the transport processes and the coupling framework. In Section 4, after validating the accuracy and efficiency of the code, we investigate the applicability of the PB model in homogeneously and heterogeneously charged microchannels by comparing the results from the dynamic model and the PB model. In addition, some results that have never been studied by the PB model will also be presented.

## 2. Mathematical models

### 2.1 Governing equations

Since our scale of interest is much larger than the atomistic scale, the macroscopic hydrodynamic and electrodynamic equations are still valid. For a multi-component Newtonian electrolyte flowing in a microchannel with no mass source, the governing equations for laminar flow are

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (1)$$

and

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \mathbf{u} \cdot \nabla(\rho \mathbf{u}) = \nabla \cdot [\nu \nabla(\rho \mathbf{u})] + \mathbf{F}, \quad (2)$$

where  $\rho$  represents the density of the fluid,  $t$  the time,  $\mathbf{u}$  the velocity vector,  $\nu$  the kinetic viscosity, and  $\mathbf{F}$  the body force.

For the  $i$ -th ion species in the solute, the mass conservation equation describing transport and reaction can be written in the general form [36]:

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \mathbf{J}_i + \lambda_i C_i = R_i, \quad (3)$$

where  $C_i$  denotes the ionic concentration,  $\mathbf{J}_i$  the species flux,  $\lambda_i$  a radioactive decay constant, and  $R_i$  the rate at which the  $i$ -th species is produced or consumed by chemical reactions. The flux  $\mathbf{J}_i$ , in general, consists of contributions from advection, diffusion and dispersion in addition to an electrochemical migration term. Neglecting dispersion, the flux has the form[36]

$$\mathbf{J}_i = -\frac{ez_i D_i}{kT} C_i \nabla \Psi - D_i (\nabla C_i + C_i \nabla \ln \gamma_i) + C_i \mathbf{u}, \quad (4)$$

where the first term on the right refers to electrochemical migration, the second term to aqueous diffusion, and the last term to advective transport. This is the famous Nernst-Planck equation [25]. Here  $z_i$ ,  $D_i$  and  $\gamma_i$  denote the ion algebraic valence, the diffusivity and the activity coefficient of the  $i$ -th species, respectively; and  $e$ ,  $k$ , and  $T$  denote the absolute charge of electron, the Boltzmann constant and the absolute temperature, respectively. The quantity  $\Psi$  represents the local electrical potential caused by the ionic distribution which is governed by the Poisson equation

$$\nabla \cdot (\epsilon \epsilon_0 \nabla \Psi) = -\rho_e = -\sum_i ez_i C_i, \quad (5)$$

where  $\varepsilon_r$  is the local dimensionless fluid dielectric constant,  $\varepsilon_0$  the permittivity of a vacuum, and  $\rho_e$  the net charge density.

Equations (1)-(5) nearly fully describe the hydrodynamic and electrochemical transport processes in electrokinetic flows. For isothermal incompressible uniform fluids with no polarization, radiation or chemical reactions, these equations can be further simplified as

$$\nabla \cdot \mathbf{u} = 0, \quad (6)$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = \nu \nabla^2 \mathbf{u} + \frac{\mathbf{F}}{\rho}, \quad (7)$$

$$\frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i = D_i \nabla^2 C_i + \frac{e \varepsilon_r D_i}{kT} \nabla \cdot (C_i \nabla \Psi), \quad (8)$$

and

$$\nabla^2 \Psi = -\frac{\rho_e}{\varepsilon_r \varepsilon_0}, \quad (9)$$

where  $\mathbf{F}$  can be any kind of body force. In this contribution we only consider the electric force. The general form of electrical force in electrokinetic fluids can be expressed as [23]:

$$\mathbf{F} = \mathbf{F}_{ext} + \rho_e (\mathbf{E}_{int} + \boldsymbol{\xi} \times \mathbf{B}_{int}) + \mathbf{F}_V, \quad (10)$$

where  $\mathbf{F}_{ext}$  represents the external body forces. For only an electrical field,  $\mathbf{F}_{ext} = -\rho_e \nabla \Psi_{ext}$ , where  $\Psi_{ext}$  is the external electrical potential field.  $\mathbf{E}_{int}$  and  $\mathbf{B}_{int}$  are internally smoothed electrical and magnetic fields due to the motion of the charged particles inside the fluid.  $\mathbf{F}_V$  is a single equivalent force density due to the intermolecular attraction, which can be neglected in uniform fluids. Since the velocity of the electrokinetic flows in microchannels is very low, the electromagnetic susceptibility is negligible.

When the ionic convection is negligible and the electric potential is continuously derivable, Eq.(8) has a simple steady solution for dilute electrolyte solutions:

$$C_i = C_{i,\infty} e^{-\frac{e \varepsilon_r \Psi}{kT}}. \quad (11)$$

Substituting Eq. (11) into Eq. (9) yields the famous nonlinear PB equation [37]:

$$\nabla^2 \Psi = -\frac{1}{\varepsilon_r \varepsilon_0} \sum_i e \varepsilon_r C_{i,\infty} \exp\left(-\frac{e \varepsilon_r}{kT} \Psi\right). \quad (12)$$

The PB model leads to the decoupling of the electric potential distribution from the fluid flow, which makes the solution much easier than the dynamic model. The PB model has been numerically solved by numerous methods successfully [16; 21; 22; 23; 24; 26; 33; 38; 39; 40].

## 2.2 Boundary conditions

We assume a longitudinal spatial periodicity for the finite domain under consideration because the length of a microfluidic channel is usually extremely large compared to the width. The periodic boundary conditions include the continuities between inlet and outlet:

$$C_{i,inlet} = C_{i,outlet}, \quad (13)$$

$$\mathbf{u}_{inlet} = \mathbf{u}_{outlet}, \quad (14)$$

and the constant gradient of the external electrical field:

$$\mathbf{E} = -\nabla\Psi_{ext}. \quad (15)$$

At the liquid-solid interface  $\Omega$ , the non-slip velocity and the zero normal flux conditions are applied.:

$$\mathbf{u}_\Omega = 0, \quad (16)$$

$$(\mathbf{v} \cdot \mathbf{J}_i)_\Omega = 0, \quad (17)$$

where  $\mathbf{v}$  is the outer normal to  $\Omega$ . In case of chemical reaction occurring at the interface, the normal flux is related to the reaction rate. For a straight microchannel, substituting Eq. (4) into Eq. (17) leads to:

$$\frac{\partial C_i}{C_i} = -\frac{ez_i}{kT} \partial\Psi. \quad (18)$$

Integrate both sides and compare with the PB model, this boundary condition is then further simplified as:

$$C_{i,\Omega} = C_{i,\infty} e^{-\frac{ez_i\zeta}{kT}}, \quad (19)$$

where  $C_{i,\infty}$  denotes the  $i$ -th ionic concentration at the middle of the channel, and  $\zeta$  the zeta potential. Thus the boundary condition for Eq. (8) becomes a simple Dirichlet type, which has been frequently employed in the previous work [26; 27; 28; 29].

In turn, the electrical potential at the interface can be imposed through either the surface charge density ( $\sigma$ ) or the zeta potential ( $\zeta$ ). The former leads to the Neumann-type and the latter to the Dirichlet-type boundary conditions, respectively. A recent study using the lattice Boltzmann method has proved that these two types of boundary conditions are consistent, but the latter one has a better computational efficiency [39]. Therefore we use the Dirichlet boundary condition for the electric potential equation (Eq. 9):

$$\psi_\Omega = \zeta. \quad (20)$$

### 3. Numerical methods

We propose to solve the governing equations by coupled multiple lattice Boltzmann methods. The LBM is a relatively new numerical method for simulating complex flow and transport phenomena[41; 42]. Unlike conventional computational methods based on macroscopic continuum equations, the LBM uses the mesoscopic Boltzmann equation to determine macroscopic transport dynamics, and makes the governing equations solved by tracking distribution functions of species packets on lattices [43]. The LBM is flexible, broadly applicable, and straightforwardly adaptable for parallel computing. Due to the ease of incorporating complex boundary conditions, it has been successfully applied to multiphase and multicomponent transport [44; 45], multiphysical-chemical transport through porous media [40; 46; 47], and solid particle suspensions [48; 49; 50].

In the rest of this section we introduce the LB evolution equations, the boundary treatments, and the flow scheme of our numerical framework.

#### 3.1 Evolution equations

##### 3.1.1 Evolution equation for hydrodynamics

The evolution equation for laminar flow driven by an external force has the form [41; 51]

$$f_\alpha(\mathbf{r} + \mathbf{e}_\alpha \delta_t, t + \delta_t) - f_\alpha(\mathbf{r}, t) = -\frac{1}{\tau_\nu} [f_\alpha(\mathbf{r}, t) - f_\alpha^{eq}(\mathbf{r}, t)] + \delta_t F_\alpha, \quad (21)$$

where  $\mathbf{r}$  denotes the position vector,  $\mathbf{e}_\alpha$  the discrete velocities,  $\delta_t$  the time step, and  $\tau_\nu$  the dimensionless relaxation time which is a function of fluid viscosity,

$$\tau_\nu = \frac{3\nu}{c\delta_x} + 0.5, \quad (22)$$

For the commonly used two-dimensional nice-speed (D2Q9) model shown in Fig. 1, the discrete velocities are,

$$\mathbf{e}_\alpha = \begin{cases} (0, 0) & \alpha = 0 \\ (\cos \theta_\alpha, \sin \theta_\alpha) c, \quad \theta_\alpha = (\alpha - 1)\pi/2 & \alpha = 1-4, \\ \sqrt{2}(\cos \theta_\alpha, \sin \theta_\alpha) c, \quad \theta_\alpha = (\alpha - 5)\pi/2 + \pi/4 & \alpha = 5-8 \end{cases} \quad (23)$$

where  $c$  is the lattice speed defined as  $\delta_x/\delta_t$ ,  $\delta_x$  the lattice constant (grid size). The density equilibrium distribution  $f_\alpha^{eq}$  can thus be expressed as

$$f_\alpha^{eq} = \omega_\alpha \rho \left[ 1 + 3 \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c^2} + 9 \frac{(\mathbf{e}_\alpha \cdot \mathbf{u})^2}{2c^4} - \frac{3\mathbf{u}^2}{2c^2} \right], \quad (24)$$

with

$$\omega_\alpha = \begin{cases} 4/9 & \alpha = 0 \\ 1/9 & \alpha = 1-4 \\ 1/36 & \alpha = 5-8 \end{cases} \quad (25)$$

For the electrokinetic flow in a long microchannel driven by an external electric field, the external force in the discrete Lattice Boltzmann equation is [52]

$$F_\alpha = \frac{3\rho_e \mathbf{E} \cdot (\mathbf{e}_\alpha - \mathbf{u})}{\rho c^2} f_\alpha^{eq}. \quad (26)$$

After evolution, the macroscopic density and velocity can be calculated using

$$\rho = \sum_\alpha f_\alpha, \quad (27)$$

$$\rho \mathbf{u} = \sum_\alpha \mathbf{e}_\alpha f_\alpha. \quad (28)$$

### 3.1.2 Evolution equations for ion transport

Inspired by the process of lattice Boltzmann model solving the Navier-Stokes equation, people have proposed several models for solving the advection-diffusion equations [23; 52; 53; 54]. We use the following evolution equation to solve the ion transport governing equation for each  $i$ -th ion species, Eq. (8) [23; 39; 54]:

$$\begin{aligned} g_\alpha(\mathbf{r} + \mathbf{e}_\alpha \delta_{i,D_i}, t + \delta_{i,D_i}) - g_\alpha(\mathbf{r}, t) = & -\frac{1}{\tau_{D_i}} [g_\alpha(\mathbf{r}, t) - g_\alpha^{eq}(\mathbf{r}, t)] \\ & + \omega_\alpha \delta_{i,D_i} (1 - \frac{0.5}{\tau_{D_i}}) \frac{e z_i D_i}{kT} \nabla \cdot (C_i \nabla \Psi), \end{aligned} \quad (29)$$

where  $\tau_{D_i}$  is the dimensionless relaxation time for the  $i$ -th ion transport and is related to  $D_i$  in the form

$$\tau_{D_i} = \frac{3D_i}{2c_{D_i}\delta_x} + 0.5, \quad (30)$$

with  $c_{D_i}$  representing the  $i$ -th ionic diffusion lattice speed. The value of  $c_{D_i}$  in Eqs. (29) and (30) is independent of the  $c$  in Eqs. (22) - (24) and can be assigned any positive value as long as the value of  $\tau_{D_i}$  is within (0.5, 2) [39; 54]. Different values of  $c_{D_i}$  lead to different time steps for each ion transport evolution since

$$\delta_{i,D_i} = \delta_x/c_{D_i}. \quad (31)$$

For a D2Q9 lattice system, the equilibrium distribution is [52; 54]

$$g_\alpha^{eq} = \begin{cases} -\frac{2C_i}{3} \frac{\mathbf{u}^2}{c_{D_i}^2} & \alpha = 0 \\ \frac{C_i}{9} \left[ \frac{3}{2} + \frac{3}{2} \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c_{D_i}^2} + \frac{9}{2} \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c_{D_i}^2} - \frac{3}{2} \frac{\mathbf{u}^2}{c_{D_i}^2} \right] & \alpha = 1-4 \\ \frac{C_i}{36} \left[ 3 + 6 \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c_{D_i}^2} + \frac{9}{2} \frac{\mathbf{e}_\alpha \cdot \mathbf{u}}{c_{D_i}^2} - \frac{3}{2} \frac{\mathbf{u}^2}{c_{D_i}^2} \right] & \alpha = 5-8 \end{cases}, \quad (32)$$

The final ionic concentration for the  $i$ -th ion can be calculated after evolution by

$$C_i = \sum_\alpha g_\alpha + \frac{\delta_{i,D_i}}{2} \frac{e z_i D_i}{kT} \nabla \cdot (C_i \nabla \Psi). \quad (33)$$

### 3.1.3 Evolution equation for electrodynamics

In order to solve the static electrodynamics equation, Eq. (9), using LBM, we rewrite it by adding a time-dependent term [39]:

$$\frac{\partial \Psi}{\partial t} = \nabla^2 \Psi + \frac{\rho_e}{\epsilon_r \epsilon_0}. \quad (34)$$

The evolution equation for the electrical potential on the two-dimensional discrete lattices can then be written as [23; 39; 54]

$$h_\alpha(\mathbf{r} + \Delta\mathbf{r}, t + \delta_{t,\psi}) - h_\alpha(\mathbf{r}, t) = -\frac{1}{\tau_\psi} [h_\alpha(\mathbf{r}, t) - h_\alpha^{eq}(\mathbf{r}, t)] + \omega_\alpha \delta_{t,\psi} (1 - \frac{0.5}{\tau_\psi}) \frac{\rho_e}{\epsilon_r \epsilon_0}, \quad (35)$$

where the dimensionless relaxation time is calculated by

$$\tau_\psi = \frac{3}{2c_\psi \delta_x} + 0.5, \quad (36)$$

where  $c_\psi$  is the electrostatic lattice speed, which, similar as  $c_{D_i}$ , can be any positive value only ensuring the relaxation time  $\tau_\psi$  within (0.5, 2) [39]. The time step in Eq. (35) is

$$\delta_{t,\psi} = \frac{\delta_x}{c_\psi}. \quad (37)$$

The equilibrium distribution of the electric potential evolution function  $h$  is [23; 39]

$$h_\alpha^{eq} = \begin{cases} 0 & \alpha = 0 \\ \frac{\Psi}{6} & \alpha = 1-4 \\ \frac{\Psi}{12} & \alpha = 5-8 \end{cases} \quad (38)$$

The steady solution of the evolution equation (35) has been proved consistent with the macroscopic Poisson equation, Eq. (9). The macroscopic electrical potential can be calculated using [39]

$$\Psi = \sum_\alpha (h_\alpha + 0.5\delta_{\alpha,\Psi} \omega_\alpha \frac{\rho_e}{\epsilon_r \epsilon_0}). \quad (39)$$

### 3.2 Boundary condition implementations

Boundary treatments are very critical to any numerical methods. Since we are solving several governing equations on the same set of lattices, i.e.,  $\delta_x$  for all evolution equations is the same, the consistency of the boundary implementations is essential. Although the “bounce-back” model is popular and easy to use, it has only first-order accuracy. In this contribution, we introduce second-order accurate models for all transport processes at the boundaries.

#### 3.2.1 Non-slip model for hydrodynamics

For still walls, the unknown density distribution functions at the wall are determined from the local equilibrium distribution function with a “counter slip” velocity [55; 56]. Take the upper wall as an example. The populations  $f_1$ ,  $f_2$ ,  $f_3$ ,  $f_5$  and  $f_6$  are known from the previous evolution step, but  $f_4$ ,  $f_7$ , and  $f_8$  need to be determined from the boundary condition. The “counter slip” velocity is defined by

$$u' = 6 \frac{-(f_1 - f_3 + f_5 - f_6)}{\rho'} c, \quad (40)$$

where

$$\rho' = 6(f_2 + f_5 + f_6). \quad (41)$$

Thus the unknown density distributions are calculated from the equilibrium distribution function

$$f_4 = \frac{1}{9} \rho' \left[ 1 + 3 \frac{u'}{c} + 9 \frac{(u')^2}{2c^2} - \frac{3(u')^2}{2c^2} \right], \quad (42a)$$

$$f_7 = \frac{1}{36} \rho' \left[ 1 + 3 \frac{u'}{c} + 9 \frac{(u')^2}{2c^2} - \frac{3(u')^2}{2c^2} \right], \quad (42b)$$

$$f_8 = \frac{1}{36} \rho' \left[ 1 + 3 \frac{u'}{c} + 9 \frac{(u')^2}{2c^2} - \frac{3(u')^2}{2c^2} \right]. \quad (42c)$$

#### 3.2.2 Dirichlet boundary treatment for ions

Several boundary treatment methods have been proposed to deal with the Dirichlet type boundary conditions for advection-diffusion equations. Here we follow D’Orazio’s approach [57; 58] which is of second-order accuracy and consistent with the non-slip model for fluid flow. In this approach, the unknown populations are assumed to be from an equilibrium distribution at a concentration  $C_{i,0}$  which is determined by the given constraints. Again for the upper wall, the unknown  $g_4$ ,  $g_7$ , and  $g_8$  can be obtained from the equilibrium distribution of  $C_{i,0}$  which is:

$$C_{i,0} = 3C_{i,\Omega} - 3S_g - 1.5\delta_{i,D_i} \sum_{\alpha} \omega_{\alpha} \frac{e\epsilon_i D_i}{kT} \nabla \cdot (C_i \nabla \Psi), \quad (43)$$

where  $S_g$  is the sum of known populations coming from the internal nodes and nearest wall nodes

$$S_g = g_0 + g_1 + g_2 + g_3 + g_5 + g_6, \quad (44)$$

Thus the unknown distributions are

$$g_4 = C_{i,0} / 6, \quad (45a)$$

$$g_7 = C_{i,0} / 12, \quad (45b)$$

$$g_8 = C_{i,0} / 12. \quad (45c)$$

### 3.2.3 Dirichlet boundary treatment for electric potential

The Dirichlet boundary of electric potential can be treated similarly as that for ions [57; 58]. Still for the upper wall, the  $h_4$ ,  $h_7$ , and  $h_8$  can be obtained from the equilibrium distribution of  $\Psi_0$ :

$$\Psi_0 = 3\Psi_{\Omega} - 3S_h - 1.5\delta_{i,\Psi} \sum_{\alpha} \omega_{\alpha} \frac{\rho_e}{\epsilon_r \epsilon_0}, \quad (46)$$

where  $S_h$  is the sum of known populations coming from the internal nodes and nearest wall nodes

$$S_h = h_0 + h_1 + h_2 + h_3 + h_5 + h_6, \quad (47)$$

Thus the unknown distributions are

$$h_4 = \Psi_0 / 6, \quad (48a)$$

$$h_7 = \Psi_0 / 12, \quad (48b)$$

$$h_8 = \Psi_0 / 12. \quad (48c)$$

## 3.3 Flow scheme of the numerical framework

Since the governing equations, Eqs. (6)-(10), are coupled together, we implement an iterative scheme as shown in Fig. 2. In each iteration procedure, the electric potential distribution is first obtained through the evolutions of electric potential to the steady state based on the evolution equation (35), in which the charge density is calculated from the ion distributions of the last iteration based on Eq. (5) (or from the initial state for the first iteration). Then, the ionic concentration for each species is calculated by the evolution equation (29) for  $N_{C_i}$  steps. The time step,  $\delta_{t,D_i}$ , may differ for different ions, but the total time step within one iteration has to be the same value for all ions, i.e.,  $t_{total} = N_{C_i} \cdot \delta_{t,D_i}$ . The last step in the iteration is to solve the

evolution equation (21) to obtain the velocity field. The evolution number,  $N_v$ , has to ensure the total time step in the iteration to be  $t_{total}$ , i.e.,  $N_v = t_{total} / \delta_t$ .

Thus the coupled governing equations are solved by the iterative multiple lattice evolutions models. This scheme is able to simulate time-dependent process with a very low Reynolds number. In this contribution, we only apply it to steady flows.

To judge if the simulation reaches steady state or not, we define the total divergence rates for electric potential convergence and velocity convergence as

$$\delta_\Psi^{dr} = \sqrt{\sum_r \left( \frac{\Psi^n(\mathbf{r}) - \Psi^{n-1}(\mathbf{r})}{\Psi^n(\mathbf{r})} \right)^2}, \quad (49)$$

$$\delta_v^{dr} = \sqrt{\sum_r \left( \frac{\mathbf{v}^n(\mathbf{r}) - \mathbf{v}^{n-1}(\mathbf{r})}{\mathbf{v}^n(\mathbf{r})} \right)^2}, \quad (50)$$

where  $\mathbf{r}$  denotes the location vector, and the superscript “n” represents the n-th iteration. The simulation stops and the results are regarded as steady state once the divergence rate is less than a given error tolerance (typically  $10^{-6}$ ).

The current method preserves the advantages of the LBM and is suitable for complex flows and parallel computing [46; 47]. Although only 2D problems are considered in this paper, the algorithm can be easily extended to 3D.

#### 4. Results and discussion

In this section, we simulate the electrokinetic flows in homogeneously and heterogeneously charged microchannels using our coupled lattice Boltzmann codes, and compare the results with the PB model, to validate our codes and to investigate the conditions under which the PB model will fail.

##### 4.1 Accuracy and efficiency

###### 4.1.1 Benchmark

To validate the present algorithm and code, we first simulate the electroosmotic flow in a homogeneously charged microchannel, as shown in Fig. 3, with a width  $H$  of one micron. A  $100 \times 10$  uniform grid is used. A 1:1 electrolyte solution is considered and the bulk ionic concentration  $C_\infty = 10^{-5}$  M. The zeta potential for both walls is  $\zeta = -5$  mV. The other properties and physical parameters are: the fluid density  $\rho = 999.9$  kg/m<sup>3</sup>, the dielectric constant  $\epsilon, \epsilon_0 = 6.95 \times 10^{-10}$  C<sup>2</sup>/J m, the dynamic viscosity  $\mu = 0.889$  mPa s, the temperature  $T = 273$  K, the diffusion coefficients for both ions  $D_1 = D_2 = 1 \times 10^{-8}$  m<sup>2</sup>/s and  $E = 1 \times 10^3$  V/m.

Since the x direction is periodic, there is no y-directional flow across the channel. Therefore the electric potential distribution resulted from the coupled dynamic equations, Eqs. (6)-(9), should be consistent with those from the PB model for thin EDL. Fig. 4 compares the electric potential and velocity profiles across the channel respectively between the present simulations and the classical PB model. The ionic concentration is high enough for this case to result in no interaction between the double layers of both walls. No chemical reactions are considered at the interfaces and the boundary conditions for the present dynamic equations are consistent with those for the PB model. The governing equations in the PB model were solved by the LPBM [23;

59]. The good agreements between the present dynamic model and the PB model validate the present algorithm and the codes.

#### 4.1.2 Unphysical parameters

There are two unphysical parameters, the lattice speed ( $c$ ) and evolution number per iteration ( $N$ ). In the present algorithm they can influence the stability, the accuracy and the efficiency of simulations.

Since the physical characteristic times for fluid flow and species diffusions differ significantly, it is hard to find a common lattice speed to ensure that the dimensionless relaxation time ( $\tau$ ) for each evolution equation is within (0.5, 2). We use different lattice speeds for different evolution equations. Because all the boundary condition treatments employed are of second-order accuracy, the accuracy will not change with the value of the lattice speed [55]. As reported before, a larger lattice speed leads to a lower convergence speed [39], but a better stability. One has to balance between the stability and the convergence speed. For the present coupling algorithm, it is better to advance each iteration in a moderate level, i.e. not too drastic, to avoid numerical fluctuation or even divergence, especially for the ion transport.

The evolution number per iteration is the other unphysical parameter that needs to be optimized and balanced between accuracy and efficiency. To ensure the same total time step for each iteration, the evolution number has to satisfy

$$N_{C_1} \cdot \delta_{t,D_1} = N_{C_2} \cdot \delta_{t,D_2} = N_v \cdot \delta_t, \quad (51)$$

where  $N_v$  is usually much greater than  $N_{C_1}$  and  $N_{C_2}$ .

Fig. 5 shows the maximum x-velocity for different evolution numbers per iterative step after finite iterative steps (500), and CPU time per iterative step, where  $C_\infty = 10^{-5}$  M,  $\zeta = -50$  mV,  $E = 5 \times 10^6$  V/m and the other parameters are same as those in 4.1.1. The code was run on the Saguaro cluster at LANL, which has  $64 \times 2$  AMD Opteron CPUs at 2.4 GHz. The results indicate that the simulated velocity becomes independent of  $N_{C_1}$  and stable when  $N_{C_1} \geq 100$ , but the CPU time increases sharply when  $N_{C_1} \geq 2000$ . Another calculation for 2:2 electrolyte solute shows that the simulated results becomes unstable again after  $N_{C_1} \geq 2000$ . Therefore for this case,  $N_{C_1}$  should be an integer within [100, 1000] for good accuracy and satisfactory efficiency. In all the following simulations of this work, we use  $N_{C_1} = 1000$ .

#### 4.2 Effects of the EDL thickness

The applicability of the PB model has been often questioned when the EDL is thick relatively to the channel width. Discrepancies have been reported between results of the PB model and the dynamic model and the breakdown of the PB model was always ascribed to the EDL overlap and interactions [26; 27; 28; 29; 60]. However, after a careful review of the previous work, we find that the inconsistent boundary conditions for different models may be the main reason for such deviations in these reports [60]. Our new algorithm and codes enable us to examine the effects of the EDL thickness on the applicability of the PB model.

Still for a long straight microchannel as shown in Fig. 3, we change the bulk ionic concentration  $C_\infty$  to vary the EDL thickness, namely the Debye length, defined as  $\lambda = \sqrt{\epsilon_0 \epsilon_r kT / (2e^2 z^2 C_\infty)}$  for

1:1 electrolyte solution [6], and keep the other parameters the same as those in 4.1.1. Based on this definition, the EDL thickness for the case in Fig. 4 is 0.18 of the channel width, i.e.  $\lambda=0.18H$ .

Fig. 6 compares the results for different EDL thickness from the dynamic model and from the PB model. For the EDL thickness ( $\lambda$ ) much smaller than the channel width ( $H$ ), the ions distribution and flow velocities from both models are in excellent agreement, as shown in Fig. 4 and Fig. 6(a). When  $\lambda$  is comparable to  $H$ , like in Fig. 6(b), the ion distribution from the PB model begins to deviate from that from the dynamic model, though the deviation is very small (<1%). This deviation increases with the increase of the EDL thickness. However the velocity profiles from both models are still in good agreement even when  $\lambda$  is about  $10H$  as shown in Fig. 6(d). Quite different from the previous studies that the deviation appeared as soon as the EDLs overlapped, the present results show that the PB model is applicable for a wide range of EDL thickness. For ions distribution predictions, the PB model is accurate for  $\lambda$  no greater than  $H$ ; while for flow modeling, the PB model is still applicable even for  $\lambda$  as large as  $10H$ .

#### 4.3 Effects of heterogeneously charged surface

Heterogeneously charged surfaces are usually used to change the flow field or change the wetting property of interfaces, which have many important applications in microfluidics, such as micromixing enhancement [17; 18; 19], biomacromolecules separation, and microchip switch [13; 61; 62].

For the homogeneously charged long channel, there is no difference for the predicted electric potential distributions between the PB model and the dynamic (PNP and NS) model since the electric potential distribution is fully developed everywhere. However for the heterogeneously charged channel, the electric potential distribution is not developed, especially near the interface of different charged surfaces, which may lead to the predicted electric potential distributions of the PB model deviating from the dynamic model. Similar studies can be found in the “entry flow”[26] and in the step charged channels[27]. In this section, we are focusing on how the heterogeneous surface charge influences the electric potential distribution in the channel and whether these effects invalidate the PB model.

Fig. 7(a) shows a symmetrical arrangement of surface charge in a heterogeneously charged microchannel. Each wall is charged with uniform charge density, but with a boundary electric potential of  $\zeta$  for one half and  $-\zeta$  for the other half. The channel is also periodic in x direction. Fig. 7(b) shows a typical velocity vector field with four vertices in this domain.

##### 4.3.1 Zeta potential effects

We first consider the effect of zeta potentials on the electric potential distribution. To avoid the effects from the velocity field, we set the external electric field strength to a low value:  $E=1\times10^3$  V/m. To exclude the effect from different diffusion coefficients, we set them to the same value for both ions:  $D_1=D_2=2\times10^{-9}$  m<sup>2</sup>/s. The channel width is 1  $\mu\text{m}$  and 100×100 grids are used. We vary the zeta potential  $\zeta$  from -5mV to -100 mV and keep the other parameters the same as those in 4.1.1.

When the absolute value of the zeta potential is small, such as 50 mV or lower, the electric potential distribution resulted from the PB model agrees well with that from the dynamic model.

Fig. 8(a) shows the electric potential profiles at the A-A section when  $\zeta = -50$  mV, where the two curves are almost the same. As the zeta potential increases, the result from the PB model begins to differ from that from the dynamic model. Fig. 8(b) illustrates the electric potential profiles for  $\zeta = -100$  mV. For a high zeta potential, the electric potential profile predicted from the dynamic model is not as developed as that from the PB model. This result indicates that it is necessary to replace the PB model with the present dynamic (PNP and NS) model for heterogeneously charged surfaces with high zeta potentials.

#### 4.3.2 Velocity field effects

Since the streamlines are not parallel to the surfaces any more for heterogeneously charged channels, the convection of ions will change the ions distribution and may consequently influence the electric potential distribution. Similar cases can be found even in homogeneously charged channels with blocks, where the velocity field is changed by the geometry. For heterogeneously charged channels, the advection strength can be easily controlled by varying the external electric field strength ( $E$ ). Fig. 9 shows the electric potential distributions at the A-A and the C-C sections for different ionic advection strength controlled by the electric field strength ( $E$ ). The zeta potential is  $\zeta = -50$  mV and the external electric field strength vary from  $1 \times 10^3$  to  $2 \times 10^7$  V/m. The other parameters are the same as those in 4.3.1.

When the electric field strength is small, such as  $E = 1 \times 10^3$  V/m, the ions advection is weak and negligible so that the electric potential distribution from the dynamic model almost overlaps that from the PB model. As the driving force increases, the ions advection becomes stronger and the predicted electric potential distribution deviates more from the PB predictions. When  $E = 1 \times 10^6$  V/m which can be actually easily realized in experiments, the maximum relative error between the two models for the electric potential is as large as 172%. This result indicates that the present dynamic model will better predict and interpret results for the applications of heterogeneously charged channels, such as micromixing enhancements by electrokinetic flows.

Besides the external electric field strength, the velocity field can be also influenced by many other factors. For examples, the ionic advection in the heterogeneously charged channel is also related to the ionic concentration ( $C_{i,\infty}$ ), the fluid viscosity ( $\nu$ ), and the zeta potential ( $\zeta$ ). In engineering applications, the flow may also be driven by other forces, such as pressure gradient ( $\Delta p$ ). The channel may not be a smooth straight one if there are blocks or roughness and cavitations inside. Each of these factors may lead to considerable contribution of ionic advection to the ion redistribution. For such cases, the present model will provide more accurate predictions.

#### 4.3.3 Diffusion coefficient effect

Since the electric potential distribution in a heterogeneously charged microchannel is not fully developed, it is interesting to find out whether the ionic diffusion coefficients and their differences have any influence on the electric potential distributions. For the same microchannel as above, we change the diffusion coefficient values and their ratios from 1:1 to 1:100. Fig 10 shows the electric potential profiles at the A-A section for different ionic diffusion coefficients, where  $\zeta = -50$  mV,  $E = 1 \times 10^3$  V/m and the other parameters are same as those in 4.3.1. The results indicate that the effect from the ionic diffusion coefficients is negligible for the electroosmotic

flows in long microchannels. The reason may be that the characteristic time of ionic diffusion is much smaller than those of fluid flow and ions advection.

#### 4.4 Effects of ionic valence

Although the multi-valence ions have been reported to influence nanoscale electrokinetic transport greatly [63; 64], the effects of ionic valence on the electroosmotic flows in microchannels have never been investigated to the best of the authors' knowledge. The reason is that the net charge term ( $\rho_e$ ) is hard to be linearized if the absolute value of valence ratio,  $|z_1 : z_2|$ , is not 1:1. However it is not a problem for the present algorithm because there is no need for linearization at all.

Consider a homogeneously charged microchannel as shown in Fig. 3. The bulk solvent concentration  $C_\infty = 1 \times 10^{-5}$  M, the external electric field strength  $E = 5 \times 10^6$  V/m, the zeta potential  $\zeta = -50$  mV and the other parameters are the same as those in 4.1.1. Fig. 11 compares the electric potential and velocity distributions for different ionic valence ratios. Four cases are considered:  $|z_1 : z_2| = 1:1, 1:2, 2:1$  and  $2:2$  respectively.  $z_1$  denotes the valence of the positive ions and  $z_2$  that of the negative ones. For the 1:1 valence ratio, the results from a double bulk solvent concentration ( $2C_\infty$ ) are also plotted in the same figures. The results show: (1) the ionic valence does influence the electric potential distribution and the velocity profile in electroosmotic flows. Among the different valence ratios, the 1:1 case leads to the smallest averaged electric potential (absolute value) and velocity across the channel when the other conditions are the same. The electric potential profiles and velocity distributions for the 2:1 and 2:2 valence ratios are close; while those results for the 1:2 valence at a bulk ionic concentration of  $C_\infty$  and the 1:1 valence ratio at  $2C_\infty$  are close. (2) The corresponding Debye length varies with the valence ratio as well. Fig. 11(a) indicates that the EDLs for 1:1 and 1:2 valence ratios are thicker than those for 2:1 and 2:2 ones. The valence number of positive ions seems to dominate the Debye length in the present negatively charged walls.

Our results apparently contradicts a popular definition of the Debye length [65]

$$\lambda = \sqrt{\epsilon_0 \epsilon_r kT / e \sum_i z_i^2 C_{i,\infty}}, \quad (52)$$

which will lead to the same Debye length between 1:2 and 2:1 valence ratios.

To understand these results, let us revisit the original PB equation, Eq. 12, for two-species/ions solutions:

$$\nabla^2 \Psi = -\frac{\rho_{e,\infty}}{\epsilon_r \epsilon_0} \left[ \exp\left(-\frac{e}{kT} z_1 \Psi\right) - \exp\left(-\frac{e}{kT} z_2 \Psi\right) \right], \quad (53)$$

where  $\rho_{e,\infty} = ez_1 C_{1,\infty} = -ez_2 C_{2,\infty}$  denotes the bulk charge density,  $z_1$  is positive and  $z_2$  negative,  $C_{1,\infty}$  and  $C_{2,\infty}$  are the species bulk ionic concentrations for positive and negative ions respectively. For  $|z_1 : z_2| = N:N$ ,  $C_{1,\infty} = C_{2,\infty} = C_\infty$ . When  $|z_1 : z_2| = 1:2$ ,  $C_{1,\infty} = 2C_\infty$  and  $C_{2,\infty} = C_\infty$ . If  $|z_1 : z_2| = 2:1$ ,  $C_{1,\infty} = C_\infty$  and  $C_{2,\infty} = 2C_\infty$ .

Eq. (53) indicates that if the electric potential,  $\Psi$ , is negative, the first term in the square bracket of the right hand side is much greater than the second term, i.e., the valence of positive ions dominates the potential distribution; otherwise the valence of negative ions controls the Debye

length. Such an analysis agrees well with our numerical results that the valence and the concentration of the counter-ions dominate the Debye length. A greater valence of the counter-ions leads to a smaller Debye length. Therefore the definition in Eq. (52) is only valid for 1:1 electrolyte solutions.

## 5. Conclusions

In this contribution, we developed a coupled multiple lattice Boltzmann method framework to solve the dynamic model for electrokinetic flows in microchannels. The governing equation for each transport is solved by a lattice Boltzmann method and the whole transport process is simulated through an iteration procedure. We solve all the governing equations on the same set of lattices with consistent boundary condition treatments. The present algorithm and codes have been validated by comparisons with the results from the lattice PB method for homogeneously charged channels when the ionic advection is negligible.

Using the present method, the applicability of the PB model for electrokinetic flows in microchannels is studied. For homogeneously charged long channels, the PB model can provide good predictions for electric potential distributions until the electric double layers fully overlap which occurs when the thickness of the EDL equals to the channel width. The electroosmotic velocity prediction from the PB model is even good when the thickness of the EDL is ten times of the channel width. For heterogeneously charged microchannels, a high zeta potential will make the PB prediction breakdown since the electric potential distribution is not fully developed. Because the streamlines are not parallel to the surfaces any more, an enhanced velocity field may cause the PB model to fail. However the ionic diffusion coefficients do not have noticeable effects on the steady flows for either homogeneously or heterogeneously charged channels. For the first time, the effects of ionic valence of solvent have been studied on the electric potential and flow velocity distributions in homogeneously charged microchannels. It is found that the valence and the concentration of the counter-ions dominate the Debye length, the electrical potential distribution and ions transport. The present results may improve the understanding of the electrokinetic transport characteristics in microchannels.

## Acknowledgements

This work is supported by LANL's LDRD Project 20080727PRD2, through the J. R. Oppenheimer Fellowship awarded to Dr. Wang M. The authors would like to thank Dr. Wang JK and Prof. Chen SY for helpful discussions.

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## Figure Legends

Fig. 1 Direction system for D2Q9 model

Fig. 2 Flow chart of the coupled lattice Boltzmann method

Fig. 3 The homogeneously charged microchannel

Fig. 4 Comparisons of electric potential and x-velocity distributions between the present simulation and the PB model

Fig. 5 Effects of evolution step number per iterative step on computational accuracy and efficiency

Fig. 6 Comparisons of net charge density and x-velocity profiles for different EDL thicknesses

Fig. 7 Schematic of surface charge arrangement of a microchannel and its velocity field driven only by an external electric field.

Fig. 8 Electric potential profiles at the A-A section for different zeta potentials

Fig. 9 Velocity field effects on the electric potential distributions controlled by the external electric field strength for heterogeneously charged microchannels.

Fig. 10 Electric potential profiles for different ionic diffusion coefficient ratios at the A-A section

Fig. 11 Electric potential and velocity distributions in homogeneously charged channels for different ionic valence ratios.

**Fig. 1**, Wang and Kang, Submitted to *Biophysical Journal*

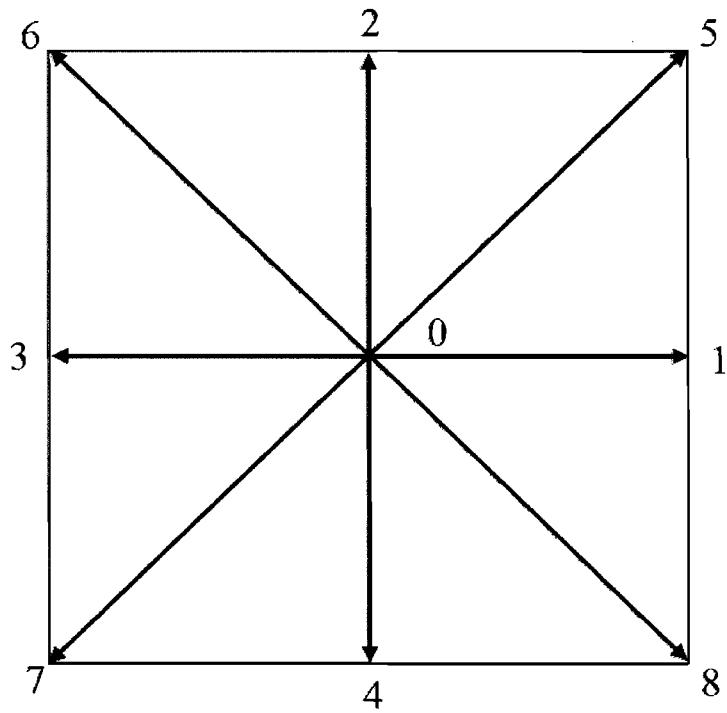


Fig. 1 Direction system for D2Q9 model

**Fig. 2**, Wang and Kang, Submitted to *Biophysical Journal*

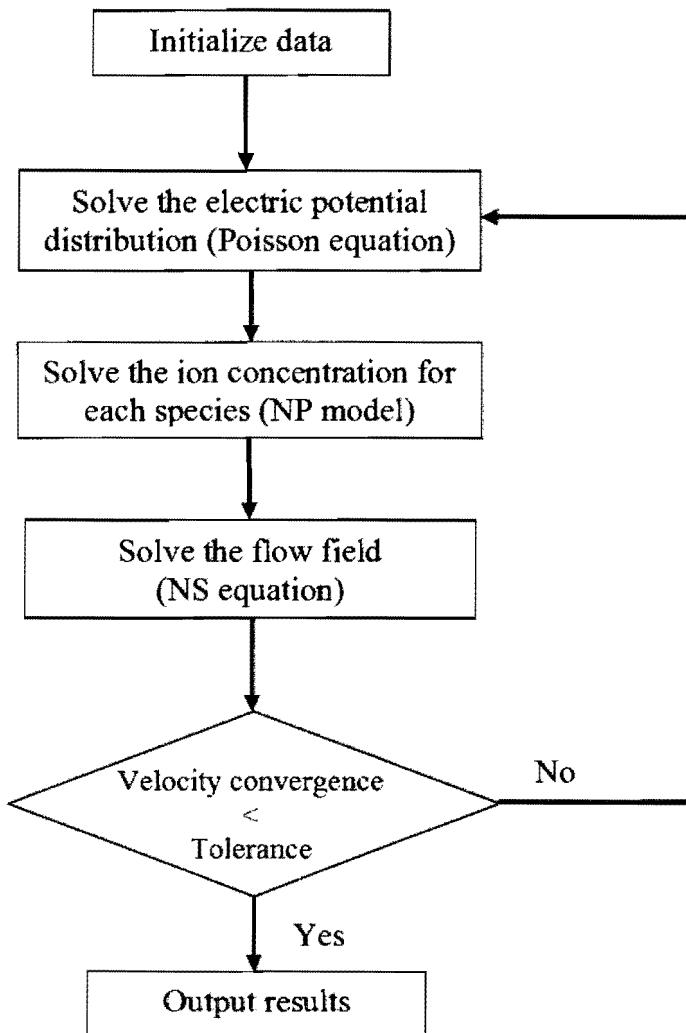


Fig. 2 Flow chart of the coupled lattice Boltzmann method

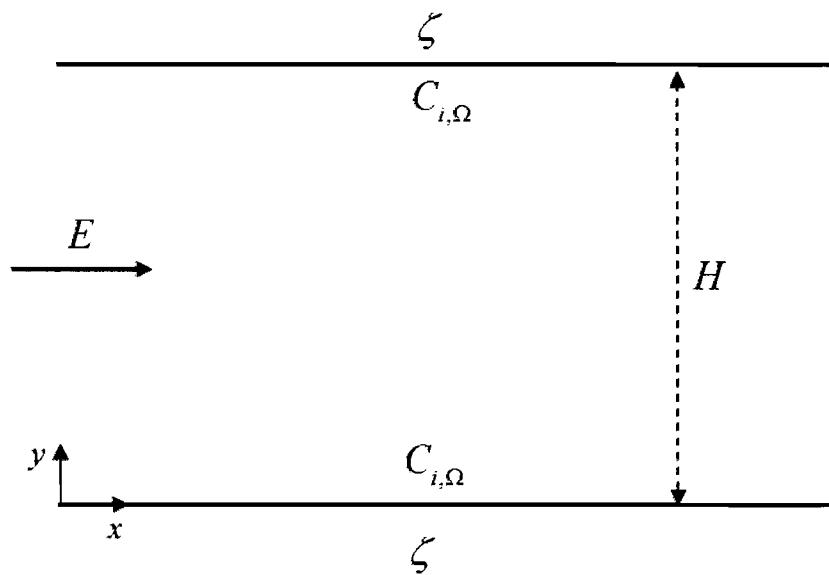
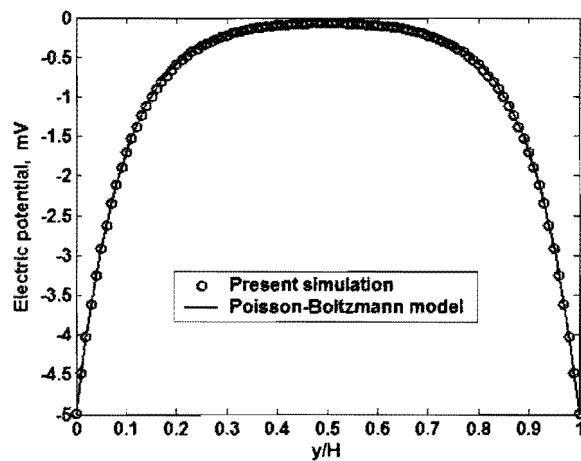
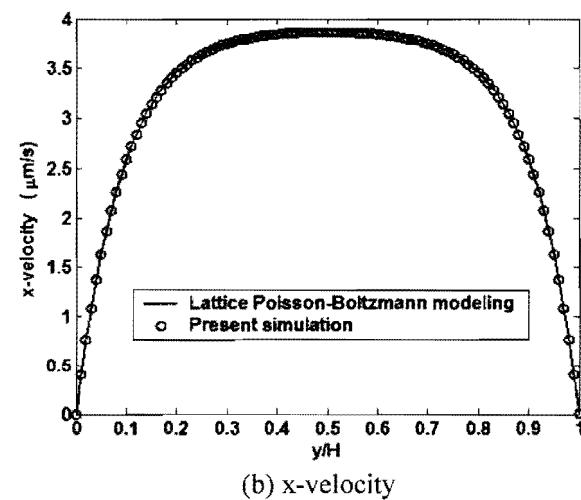
**Fig. 3**, Wang and Kang, Submitted to *Biophysical Journal*

Fig. 3 The homogeneously charged microchannel

**Fig. 4**, Wang and Kang, Submitted to *Biophysical Journal*



(a) Electric potential



(b) x-velocity

Fig. 4 Comparisons of electric potential and x-velocity distributions between the present simulation and the PB model

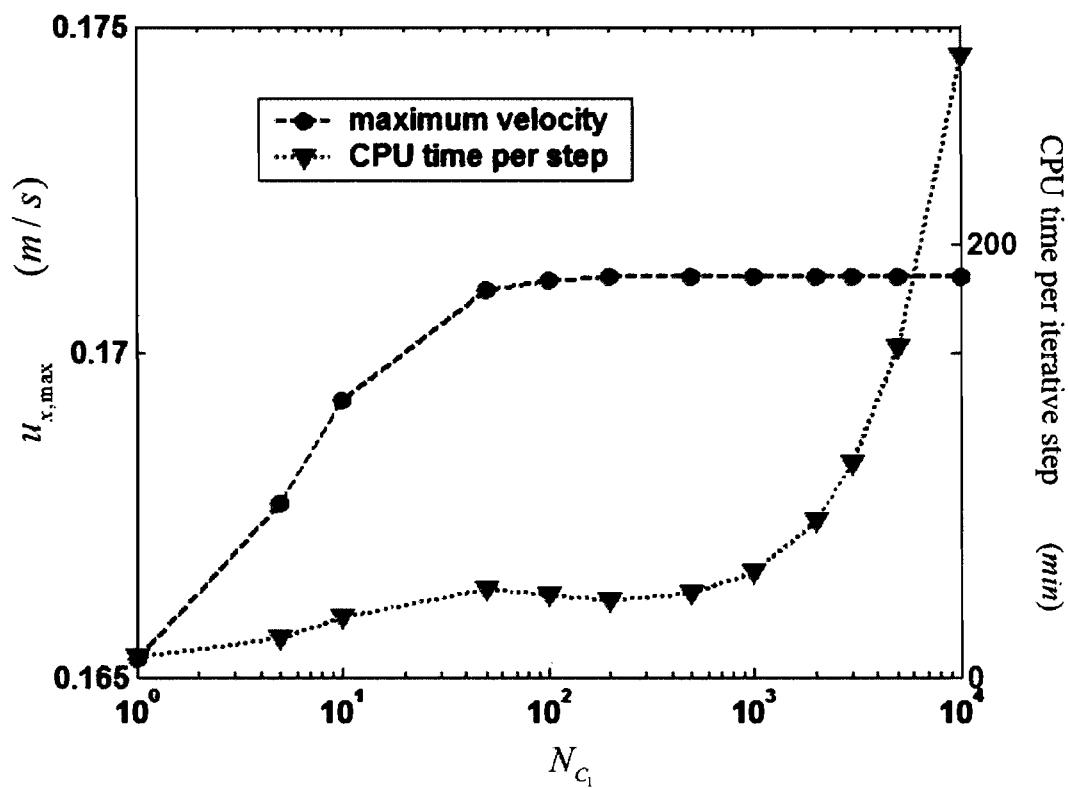
Fig. 5, Wang and Kang, Submitted to *Biophysical Journal*

Fig. 5 Effects of evolution step number per iterative step on computational accuracy and efficiency

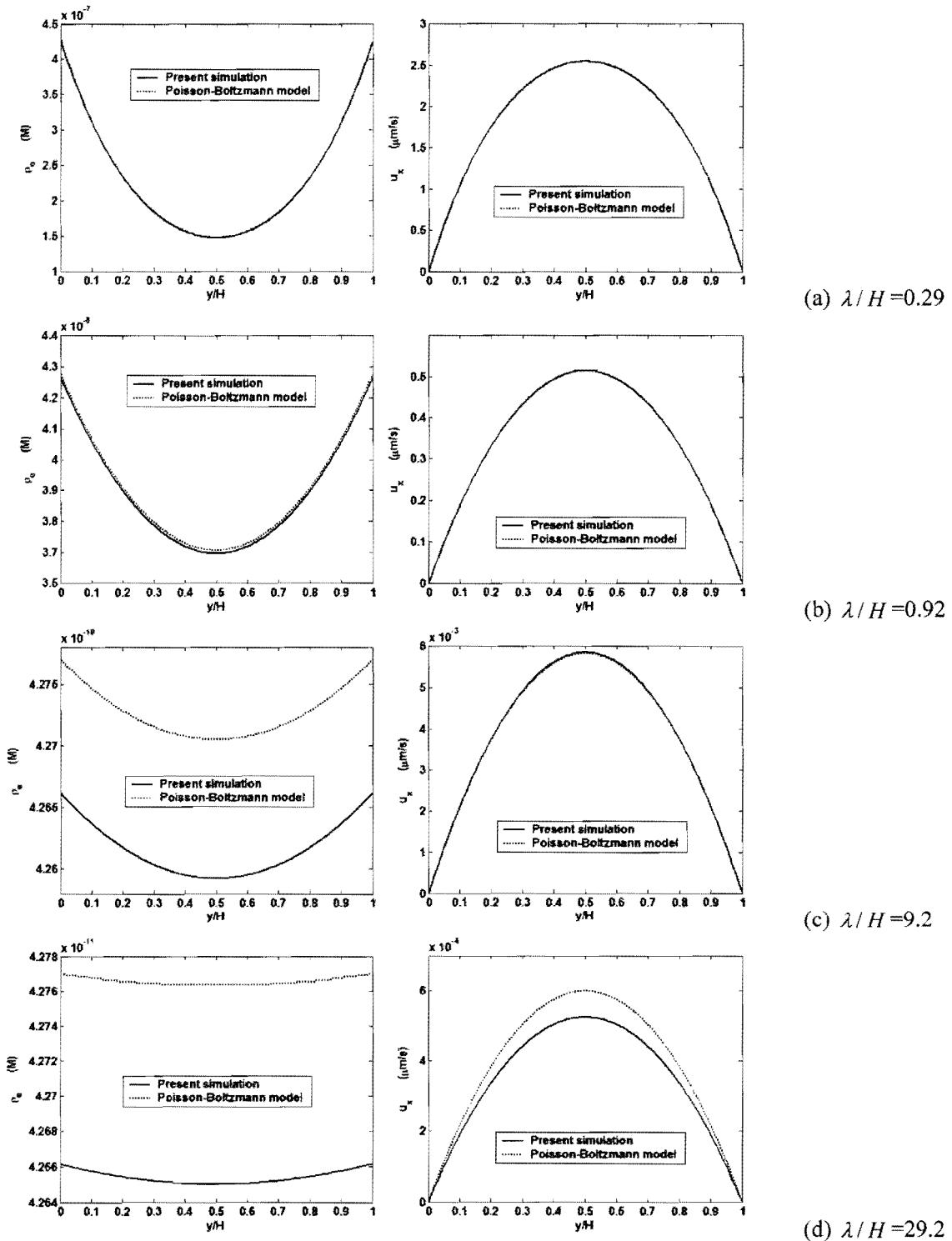
Fig. 6, Wang and Kang, Submitted to *Biophysical Journal*

Fig. 6 Comparisons of net charge density and x-velocity profiles for different EDL thicknesses

**Fig. 7**, Wang and Kang, Submitted to *Biophysical Journal*

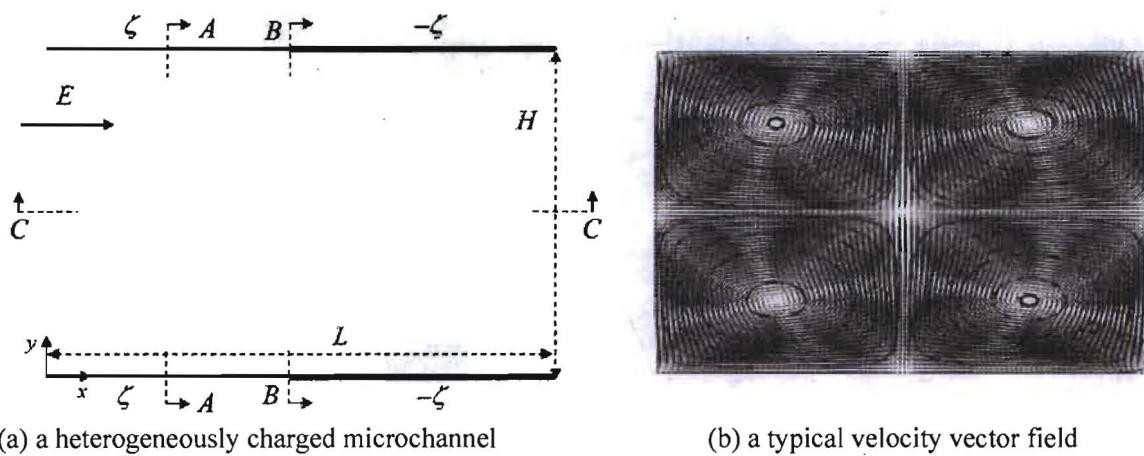


Fig. 7 Schematic of surface charge arrangement of a microchannel and its velocity field driven only by an external electric field.

**Fig. 8**, Wang and Kang, Submitted to *Biophysical Journal*

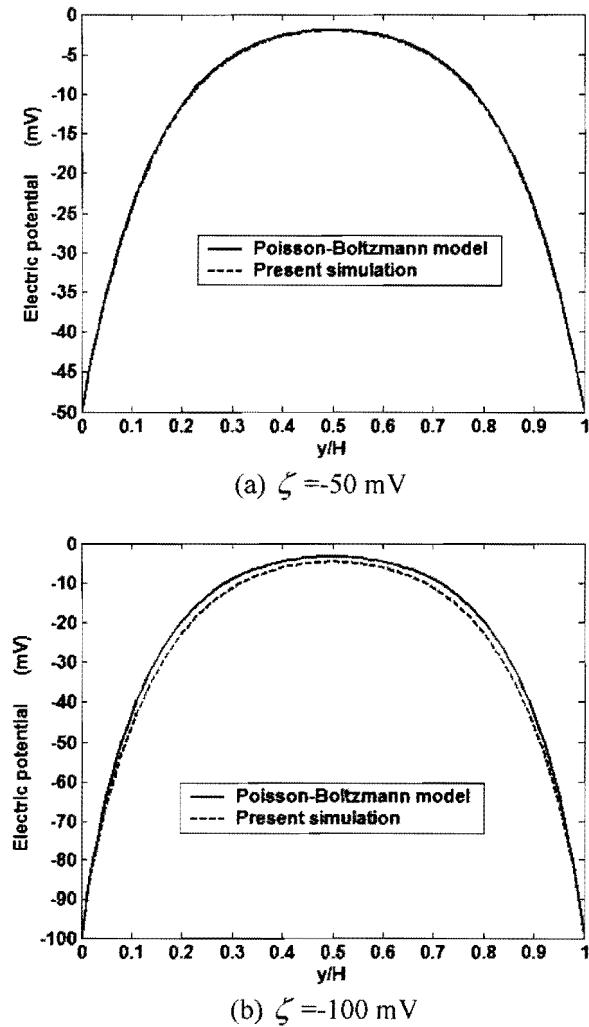
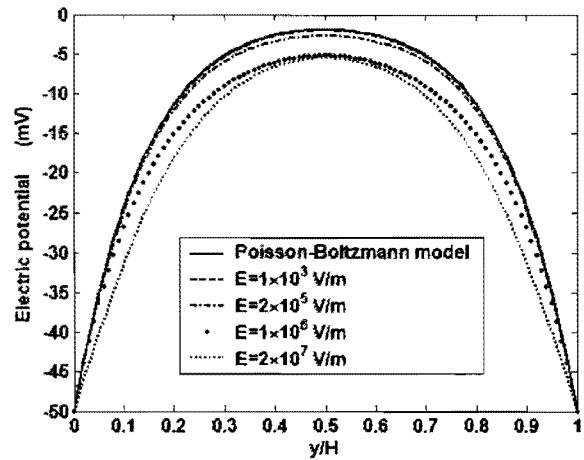
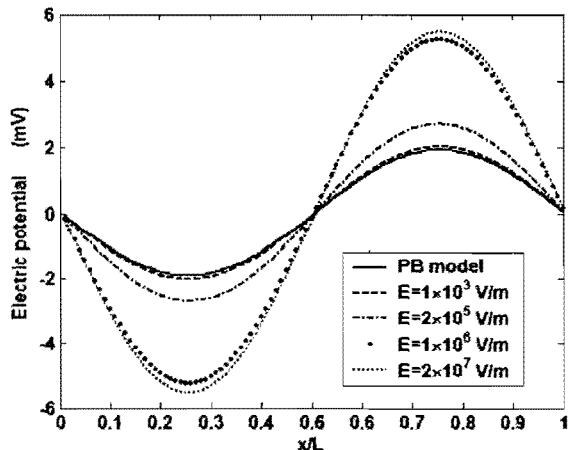


Fig. 8 Electric potential profiles at the A-A section for different zeta potentials

**Fig. 9**, Wang and Kang, Submitted to *Biophysical Journal*

(a) electric potential profiles at A-A section



(b) electric potential distributions at C-C section

Fig. 9 Velocity field effects on the electric potential distributions controlled by the external electric field strength for heterogeneously charged microchannels.

**Fig. 10**, Wang and Kang, Submitted to *Biophysical Journal*

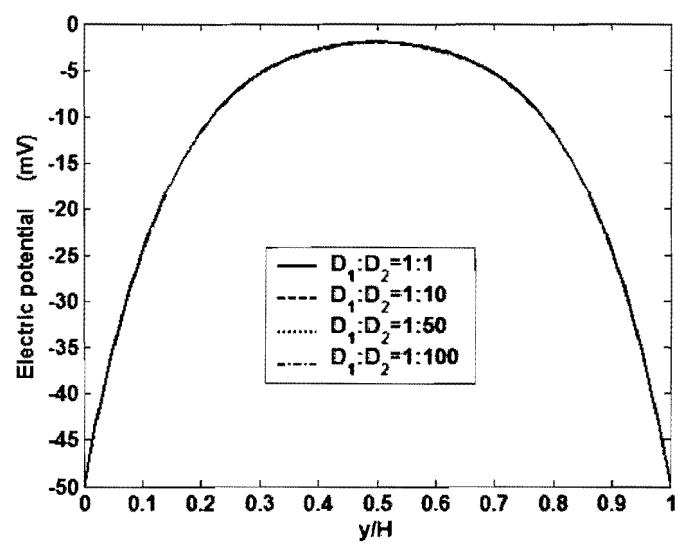


Fig. 10 Electric potential profiles for different ionic diffusion coefficient ratios at the A-A section

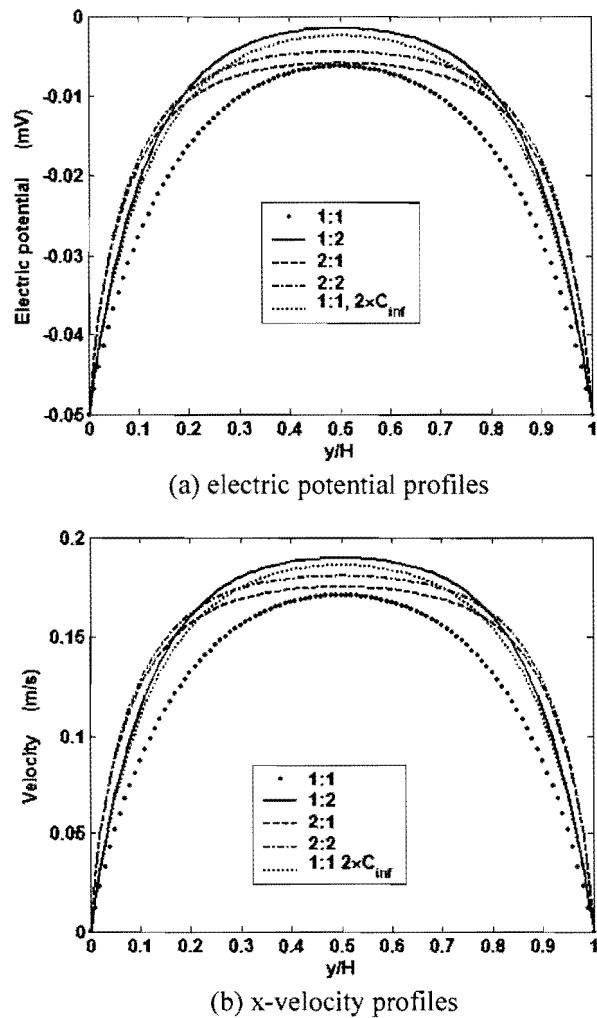
Fig. 11, Wang and Kang, Submitted to *Biophysical Journal*

Fig. 11 Electric potential and velocity distributions in homogeneously charged channels for different ionic valence ratios.