Simulation of Electrokinetic Flow and Analyte Transport in Nano Channels

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ABSTRACT

This paper demonstrates the electrokinetic flow and transport of charged and neutral analytes in nanochannels by solving full system of governing Poisson-Nernst-Planck equations. The issues related to the spatial and time scales are resolved using first-order perturbation approach [1]. When the ζ potential is strong or the background electrolyte is weak, the electric double layer (EDL) may be considerably thick and overlap. In particular if the EDL occupies significant portion of the channel, the velocity profile will be no longer be plug shaped, and the local electrostatic force may potentially expel counterions (to the surface charge). The resulting non-uniform velocity serves as mechanism for charge-based separation and is demonstrated in this paper. In addition, we demonstrate that overlapping EDL in nanochannel arrays for the manipulation of sample of interest.

Keywords: nanofluidics, Poisson-Nernst-Planck model, sample separation, preconcentration, numerical simulation

1   INTRODUCTION

With the increasing focus on building an integrative genomic, proteomic and metabolomic map to investigate human diseases, the life-science community is challenged with the development of analytical tools for separation of proteins obtained from single or few cells. Devices that exploit nanoscale features are very attractive in this aspect, since they consume very little reagent and can work with very little amount of sample. In this regard, electrokinetic flow and analyte transport in nanochannels have received lots of attention [1, 2]. The transport at nano-channels is markedly different from that occur in microchannels. The most notable feature at the nanoscale is the dominance of the electric field transverse to the flow direction, which could significantly affect the EOF and analyte transport. This field arises due to the surface zeta (ζ) potential. In addition, the conductance of nanochannels is regulated by surface charge at low ionic strength, and by the geometry and bulk ionic concentration at high ionic strength. Modifying the surface charges or varying the applied electric field can facilitate charged-based separation. These unique characteristics in nano-channels provide new techniques to separate and preconcentrate analytes of interest, particularly proteins.

The present paper investigates the (geometric) size-dependant nanoscale phenomenon, charge exclusion effect of the electric double layer (EDL) that pushes analytes toward the center of the channel. The analytes once migrate toward the center, will then separate based on charge and valence. In addition, the overlapping EDLs at a nanochannel array can be used to manipulate samples of interest. We demonstrate these mechanisms using the multiphysics simulation (CFD-ACE+ from ESI-CFD, Huntsville, AL [3]). The mathematical model is based on the continuum description of electrokinetic flow and analyte transport. The resulting coupled, non-linear partial differential equations are solved using Finite Volume Method. The model is validated against the data in literature. Special attention is paid to overlapping EDL and its effect on electric potential distribution, flow profile, and ionic concentration, with emphasis on how the predicted results differ from those simulated for typical microfluidic systems with non-overlapping EDLs.

2   NANO ELECTROKINETICS
2.1   Formulation of Continuum Model

The continuum model assumes that the transport coefficients are independent of position and time, and that the macroscopic state variables do not vary appreciably in the system and can be derived from statistical models at molecular level. We will use continuum-based model description since the length scales are larger than 5 nm and the time scale is greater than 1 ns. We assume that the surface charge or the ζ potential is arbitrary. The electric field is described by the Poisson equation as:

$$\varepsilon_0 \varepsilon_r \nabla^2 \phi + F \sum_i z_i c_i = 0 \qquad (1)$$

where ε is the electrical permittivity, F is Faraday constant, z_i is the valence and c_i is the concentration of the ith electrolyte. The continuity equations for each background electrolyte is expressed as:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{J}_i = 0 \quad (2)$$

Here the flux $\mathbf{J}_i$ of ith ion is given by Planck-Nernst-Poisson equation

$$\mathbf{J}_i = -D_i \nabla c_i + \mathbf{u} c_i + \omega_i z_i \mathbf{E} c_i \quad (3)$$

where ω_i is the electrophoretic mobility, D_i is the diffusivity, $\mathbf{u}$ is the velocity vector and $\mathbf{E}$ is the electric field. Here, instead of solving Poisson-Boltzmann equation, we use Poisson-Nernst-Planck equation, which is general enough to describe extreme situations of overlapping EDL. The fluid flow satisfies Navier-Stokes equation for incompressible fluid:

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} = \mu \nabla^2 \mathbf{u} - \nabla p + \mathbf{f}_e \quad (4)$$

$$\nabla \cdot \mathbf{u} = 0$$

where $\mathbf{f}_e$ is the electrostatic body force (Kelvin force), expressed as:

$$\mathbf{f}_e = \mathbf{E} F \sum_i z_i c_i - \frac{1}{2}\mathbf{E}^2 \nabla \varepsilon_0 \varepsilon + \frac{1}{2}\nabla\left[\rho\left(\frac{\partial \varepsilon_0 \varepsilon}{\partial \rho}\right)_T \mathbf{E}^2\right] \quad (5)$$

Here ρ is the fluid density and T is the temperature. The first term on the right side is the Columbic force, and the second and third terms are dielectrophoretic and electrostriction forces. For transport through nanochannels, the second and third terms can be neglected. Only the Coulombic force is considered.

In a fully ionized electrolyte solution electroneutrality assumption ($\mathbf{f}_e=0$) is valid outside the EDL. However, we will not make such assumption for nanochannels since the EDL thickness is comparable to the channel dimension. The distribution of EDL depends not only on the surface charge (ζ potential) and the ionic strength of the buffer solution, but also on the external flow and the electric field. Order of magnitude analysis indicates that the EDL is not dramatically affected by external electric field. Besides, the deformation of EDL due to the external flow will not influence the transverse potential distribution, though significant streaming potential may be generated. Hence, in this study the polarization and retardation of the EDL are neglected, allowing decoupling of the problem into two sub-problems:

(a) Determination of EDL and associated transverse electric field distribution without external flow or electric field, and

(b) Calculation of the response of this system to an external flow or electric field (in tangential direction) and analyte transport.

2.2 Analyte/Sample Transport

To study analyte transport, we assume low concentrations (dilute) that will not alter the background ionic equilibrium. As demonstrated using the perturbation analysis by Bharadwaj and Santiago[4], the zeroth order equations show that background electrolyte ions follow bulk electrolyte dynamics and are not affected by the transport of the relatively low concentration analyte. Following this procedure, the first-order sample/analyte distribution is expressed as:

$$\frac{\partial c_a}{\partial t} + \mathbf{u}^{(0)} \cdot \nabla c_a = D_a \nabla^2 c_a + \omega_a z_a \nabla \cdot (c_a \nabla \phi^{(0)}) \quad (6)$$

where ω_a is the electrophoretic mobility, D_a is the diffusivity and z_i is the valence of the analyte. The superscript (0) denotes the values obtained from system in the absence of the sample. Equation (6) is essentially the combination of equation of (2) and (3) where background flow and electric fields are unaffected by the presence of the sample. The governing equations described above are highly nonlinear. These coupled equations are solved using Finite Volume Method on a structured grid [3]. The conservative equations are integrated on each control volume/grid, leading to a set of algebraic equations that are solved in an iterative manner.

3 RESULT AND DISCUSSION

Model Validation: Electroosmotic Flow in a Channel: The EOF in a straight channel is studied by the current approach. The electrolyte solution is flowed in a channel with different wall zeta potential. An external field is applied to drive the flow. We define characteristic variable as

$$L_c = h, \ U_c = -\frac{\varsigma_d \varepsilon_0 \varepsilon_r}{\mu} E_\infty, \ \varphi_c = \varsigma_d$$

In Figure 1, the dimensionless transverse electric field for both thin and thick double for various zeta potentials is plotted. The averaged flux as a function of EDL thickness or zeta potential ratio is also presented. These results agreed well with high-order compact finite difference methods developed in-house.
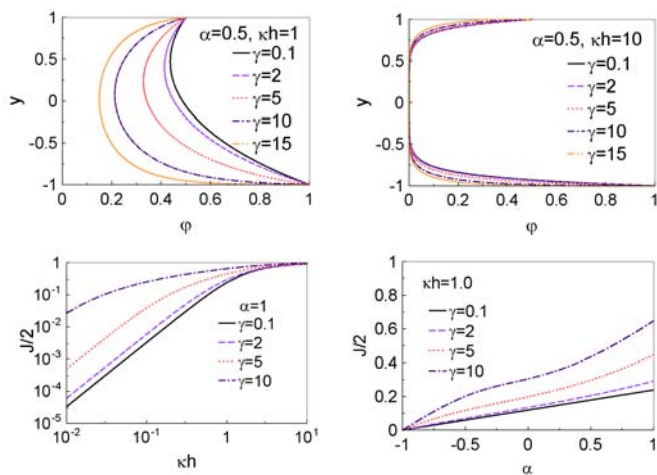
Figure 1: Validation Study for $\alpha=0.5$ for potential and flux for various parameters

Double Layer Around Two Adjacent Spheres: This example is designed to illustrate the overlapping of the EDL in a colloidal suspension, as shown in Figure 2a. The particle diameter is 0.72μm and the gap is 90 nm. The concentration of NaOH buffer used in the simulation is 10μM. The EDL thickness is thus approximately in the range of 100nm. The strong overlapping of the EDLs is illustrated from PNP model based simulations. Figure 2(a)-(c) show concentration of NA^+ and OH^- as well as potential. In Figure 2d, potential for non-overlapping EDL is demonstrated.
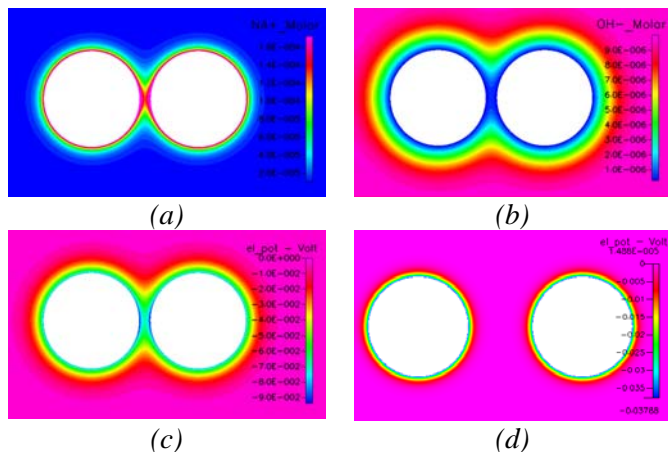

Figure 2: Electric field & ionic concentration contours for (a) overlapping & (b) non-overlapping EDL.

Ionic Transport in Nano Channel: Recently numerical simulation for ion transport driven by either electric or hydrodynamic field is presented by Daiguji et.al.[5]. We simulated the same problem using the present method and the results are compared in Figure

3. Excellent agreement is demonstrated. Figure 3(a) shows the problem definition and the simulation domain. A channel of 30nm width is connected by two 1 by 1 μm reservoirs containing KCl solution of 0.1 mM strength. An external electric potential of 5V is applied across the channels so that a steady state EDL and ionic currents are established. The channel surface charge density is $10^{-4}C/m^2$. The potential distribution and the ionic concentration for both K^+ and Cl^- are solved. The results are graphically indistinguishable with published data Figure 3b,c).
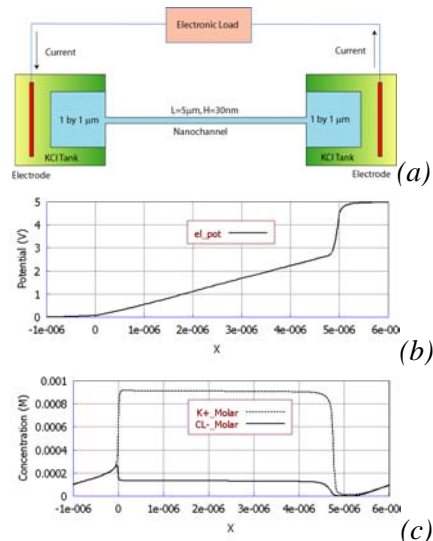

Figure 3: (a) Sketch of a silica nano channel. (b) The electric potential profiles along the axis of the channel and (c) ionic density along the x- axis.

Nanochannel as a Device for Charge-Based Separation: A salient characteristic of the electrokinetics in nanochannel is the predominance of electrostatic effect, in which the EDL serves as screening layer for analytes if their charges are the same of the wall. In addition, when the channel size is comparable to the EDL thickness, both EOF velocity and analyte distribution will be non-uniform. This scenario can be exploited to achieve separation of charged analytes from neutral analytes.

We simulate analyte separation in a nanochannel by considering a system (Figure 4a) that consists of a vertical injection microchannel and a horizontal separation nanochannel. The analyte is injected at the intersection of nanochannel with the microchannel by applying a pulsed electric field. After washing the injection microchannel, we apply an electric field to separate analyte plug. Electric potential contours are shown in Figure 4a. As demonstrated before, the

velocity profile across the nanochannel is highly non-uniform. Potential across the channel exhibits parabolic shape, demonstrating that the EDLs overlap. Due to the charged nature of the channel surface the analyte carrying the same charge is expelled toward the center of the channel, where velocity is maximum, and hence migrates faster.   The neutral analyte on the other hand occupies the entire cross section of the channel. Even though the velocity is highly non-uniform across the channel, it stays plug shaped and axially diffused due to the transverse diffusion.
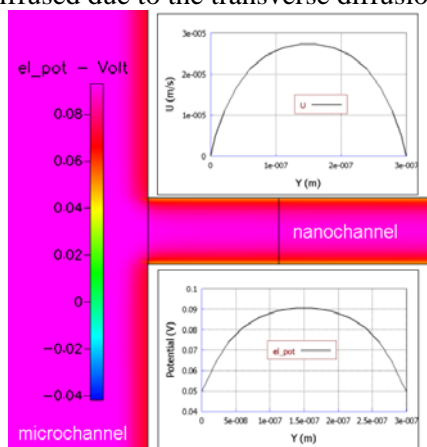

Figure 4a: Contours of potential shown along with velocity and potential across the nanochannel

t=0, negatively charged

t=0, neutral analytes

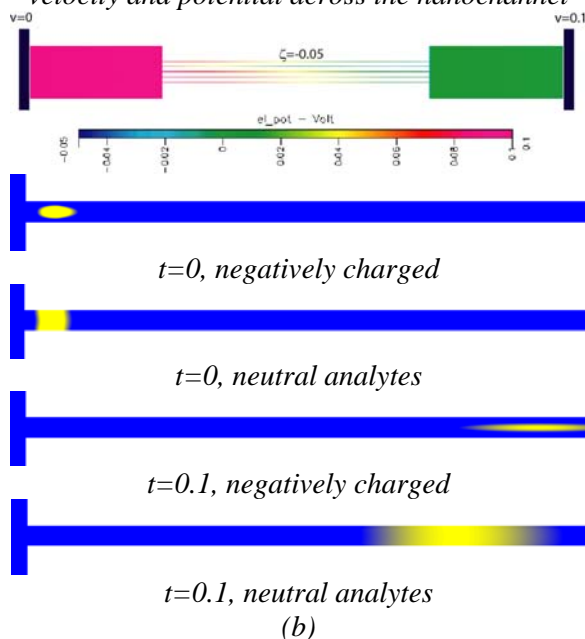*t=0.1, negatively charged*

t=0.1, neutral analytes

(b)

Figure 4b: Separation of charged analytes from a neutral analytes (velocity averaged concentration distribution).

In Figure 4b, the concentration fields of charged and neutral analyte are shown at t=0 and 0.1s.   The separation is observed even within a short period of time.

In Figure 5, we have simulated overlapping EDLs in a nanochannel array. In this, it becomes very clear that at the interface between nanochannel array and the main channel, an analyte of interest can be prevented from migrating through the channel array.   Such a device can be engineering to perform single cell analysis.
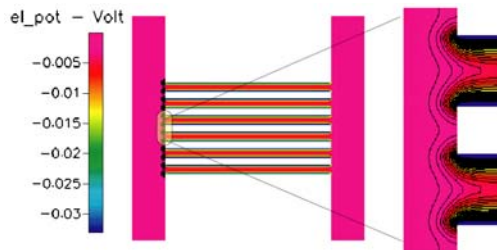

Figure 5: The simulation of the overlapping EDL in a nanochannel array.

In summary we have developed simulated electrokinetic transport in nanochannels using continuum-based models.   The model is capable of predicting a sample separation and preconcentration in nanoscale devices.

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