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Numerical Modeling of Ion-Size Effect on Electroosmotic Flow in Nanochannels

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Abstract.

When fluids are confined in a structure at nanoscale, such as in a nanochannel, the electric double layers (EDLs) from opposite walls may have strong interactions. This phenomena results in EDL overlap, which leads to significant changes in the electric field and the fluid properties. Electroosmotic flow (EOF) describes the motion of electrolyte due to the existence of an EDL. Ions in electrolyte have finite sizes which become comparable to EDL thickness in nanochannels and thus cannot be neglected during the formulation. Ion size have been shown to influence the extent of EDL overlapping in channel [S. Das and S. Chakraborty, *Physical Review E*, vol. 84, p. 012501, 2011]. The electrokinetic effects for a system that are not less than 10nm are examined, where van der Waals forces cease to be significant compared to the electrostatic forces. Thus, it is appropriate to apply continuum equations in modeling. For systems below 10nm the continuum approach is not applicable but the understanding based on continuum modeling are still beneficial as a quantitative reference. In this paper, the electroosmotic flow in nanochannels is investigated by using the asymmetric ion size model proposed by [Y. Han, S. Huang, and T. Yan, *Journal of Physics: Condensed Matter,* vol. 26, p. 284103, 2014]. The effect of size of ions on the flow behavior in nanochannels is examined. The average electroosmotic mobility is obtained for both the cases of symmetric and asymmetric ion sizes for different nanochannel widths.

Keywords: Electric double layer, electroosmotic flow, steric effect, Navier-Stokes equation.

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1 Introduction

Nanofluidic flow is generally referred to transport of fluids that are confined to the systems with at least one characteristic dimension below 100 nm [1, 2]. When fluids is confined in a structure at nanoscale, such as in a nanochannel, the EDLs from opposite walls may have strong interactions. This phenomena results in EDL overlap, which leads to significant changes in the electric field and the fluid properties. Electroosmotic flow (EOF) describes the motion of electrolyte due to the existence of an electric double layer (EDL). The EOF has been studied extensively in microchannels. The basic researches on the EOF were carried out by Burgreen and Nakache [3] and Rice and Whitehead [4] for slit and cylindrical capillaries, assuming low zeta potentials. In microchannels, the EDL thickness is small compared to channel width, but coming down to nanoscale the EDL thickness becomes comparable to the nanochannel width. This leads to EDL overlap and consequently many phenomena such as ion enrichment and depletion [5], pressure driven flows [6]. There is a need to better understand electrokinetic effects, particularly with the presence of the EDL overlap. These phenomena helps in various applications and investigation in nanofluidics [7, 8].

Over last few decades, several analytical and numerical models have been developed to investigate the overlapping EDLs [9] , ionic size, viscosity and surface charge density of the channel walls and the channel size. Qiao [10] studied that the electroosmotic mobility in nanochannels increases with the surface charge density of the channel walls. Pennathur and Santiago [11] studied the EOF and ion transport in nanochannels theoretically and proved that in nanochannels the EOF velocity profile is non-uniform when EDL thickness is comparable to nanochannel width and EOF velocity decreases in the presence of overlapped EDLs. Das et al. [12] explored streaming potential and electroviscous effects in a nanocapillary with thick overlapping EDLs. Haywood et al. [13] investigated the EOF in nanofluidic channels. They show that for very much smaller nanochannels, the EDL extends into the nanochannels, and due to confinement within the channels, the average electroosmotic mobilities decrease. Peng and Li [14] studied EOF in single PDMS nanochannels. They show that the EOF velocity in smaller nanochannels with overlapped EDL is proportional to the applied electric field.

Steric effects on electrokinetic flow has also been investigated by many researchers. Bazant et al. [15] investigated the steric effects on ac electro-osmosis. Garai and Chakraborty [16] investigated steric effects in narrow fluidic channels with finite aspect ratio. Bandopadhyay and Chakraborty [17] investigated the ion size effect on electroosmosis in ion-selective channels and ionic size dependent electroviscous effects in ion-selective nanopores [18]. These studies show that ion size cannot be neglected in nanochannels. We will examine electrokinetic effects for a system that are not less than 10nm, where van der Waals forces cease to be significant compared to the electrostatic forces. Thus, it is appropriate to apply continuum equations in modelling. In this chapter the electroosmotic flow in nanochannels is investigated by using the asymmetric ion size model propsed by Han et al. [19]. The average electroosmotic mobility is obtained for both the cases of symmetric and asymmetric ion sizes for different nanochannel widths.

2 Mathematical Formulation

The geometry of the problem domain is described in the Fig. 1. The model geometry is divided into three regions: the entrance, the middle region and the exit region. Our centre of attention is the middle region which has nanoscale dimensions. We consider a 1: 1 symmetric electrolyte, that is transported axially (x-direction) along a rectangular nanochannel with transverse directions as y and z. The velocity in the nanochannel is governed by the continuity equation and Navier-Stokes equations.

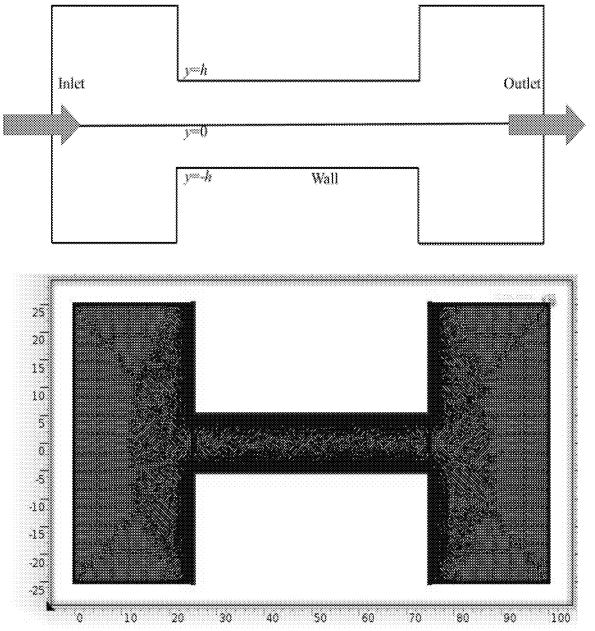

Fig. 1. Schematic of (a) the problem domain and (b) refined mesh in COMSOL 4.3a.

Neglecting the inertial terms due to low Reynolds number in narrow channels, the unidirectional steady-state fluid flow governed by the x-component is given by

$$-\nabla p + \mu \nabla^2 \mathbf{u} + \mathbf{F} = 0 \tag{2.1}$$

$$-\frac{dp}{dx} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u_x}{\partial y}\right) + \rho_e E_x = 0 \tag{2.2}$$

where p is the pressure, μ is the dynamic viscosity of the fluid, $\mathbf{u}$ and $\mathbf{F}$ representing the velocity and body force vectors, respectively. In this problem, the body force acts in the x-direction and $F_x = \rho_e E_x$ with $E_x = -d\psi/dx$ denoting the electric field.

The potential Φ is the combination of external electric potential ψ and EDL potential ϕ, $\Phi = \phi + \psi$.

To take steric effects into consideration, for a 1:1 electrolyte, the dimensionless modified Poisson-Boltzmann equation is considered.

$$\tilde{\nabla}^2\phi^* = -\frac{1}{\gamma}\frac{\exp\left(-\phi^*\right)-\exp\left(\phi^*\right)\left[\dfrac{\xi\exp\left(\phi^*\right)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}-1}}{\exp\left(-\phi^*\right)+\left(\xi+\eta\right)\left[\dfrac{\xi\exp\left(\phi^*\right)+\eta}{\xi+\eta}\right]^{\frac{1}{\xi}}} \tag{2.3}$$

where $\phi^* = \dfrac{ze\phi}{k_B T}$ is the dimensionless electrostatic potential, γ is the compressibility (also known as steric factor), $\eta = \dfrac{2}{\gamma} - 1 - \xi$ is the porosity, $\tilde{\nabla} = \kappa^{-1}\nabla$, where $\kappa^{-1} = \lambda_D = \left(2e^2 z_i^2 n_b / \varepsilon k_B T\right)^{-\frac{1}{2}}$ is the Debye length and the asymmetric ion size parameter ξ is the volume ratio of an anion to a cation, i.e. $\xi = \dfrac{V_-}{V_+} = \dfrac{a_-^3}{a_+^3}$, where a_+ and a_- represent the radii of cation and anion, respectively. It is assumed that the size of anion is less than or equal to that of cation $\left(\xi \le 1\right)$.

When $\xi = 1$, the ions have same size and the expression becomes the Kornyshev's equation [20]: $\tilde{\nabla}^2\phi^* = \dfrac{\sinh\left(\phi^*\right)}{1+2\gamma\sinh^2\left(\phi^*\right)}$. (2.4)

The boundary conditions for the modified Poisson- Boltzmann equations are

$$\phi^*_{y^*=\pm\kappa h} = V^*, \left(\frac{d\phi^*}{dy^*}\right)_{y^*=0} = 0 \tag{2.5}$$

where V^* is the dimensionless potential at walls of the nanochannel .

The governing equations are non-dimensionalized using the following dimensionless variables $y^* = \kappa y, x^* = \kappa x, u^* = u \Big/ \left(\dfrac{\kappa\varepsilon_r\varepsilon_0 {k_B}^2 T^2}{\mu z^2 e^2}\right)$, $E^* = \left(\dfrac{ze\kappa}{k_B T}\right)E$ and $p^* = p \Big/ \left(\dfrac{\mu u^*}{\kappa}\right)$.

The boundary conditions for flow field is no slip condition at the walls and zero pressure at inlet and outlet of the problem domain. These dimensionless equations are solved using COMSOL Multiphysics 4.3a. The solutions are obtained till they become mesh independent. The meshed domain is shown in Fig. 1(b). The boundary near the walls of the nanochannel are meshed to be very fine since the EDL formed near boundary is more important objective of our study.

Based on the profile of the electroosmotic flow (EOF) velocity, one can obtain the average velocity in the nanochannel by integrating the velocity in the y direction:

$$u_{av} = \frac{1}{2\kappa h}\int_{-\kappa h}^{\kappa h} u_{EOF}(y)dy \tag{2.6}$$

Also, the average electroosmotic mobility can be calculated as

$$\mu_{eo} = \frac{1}{2\kappa h\overline{E}}\int_{-\kappa h}^{\kappa h} u_{EOF}(y)dy \tag{2.7}$$

where, $\overline{E}$ is the dimensionless external electric field applied at the outlet of the nanochannel. The dimensionless potential at the nanochannel wall $V^* = -6$ is used in this simulation. The external applied electric field is 25 V/cm.

3 Results and Discussion

The average velocity is plotted for different values of steric factor with respect to nanochannel widths in Fig. 2. It is observed that increase in ion size parameter leads to reduction in average velocity. Also as the nanochannel width decreases the avg. velocity decreases. This is in agreement with the previous investigations. Due to the increase in steric effects, the body force in the nanochannel decreases in the momentum equation which leads to decrease in average EOF velocity. With increase in steric factor the average velocity decreases as compared with the case of no steric factor. Also at small nanochannel width the velocity is very low due to strong EDL overlap, but as κh increases the velocity increases. The increase in steric factor increases the EDL overlapping in nanochannels [21, 22].

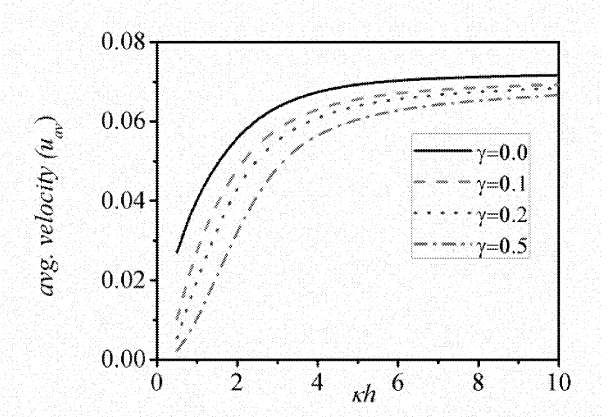

Fig. 2. The average velocity derived using Eq. (2.6), for electric field 25 V/m.

The average electroosmotic mobility is plotted for different values for steric factor with respect to nanochannel width in Fig. 3. The average electroosmotic mobility show maxima at small nanochannel widths due to steric effects. With increase in steric factor, the maxima reduces and shifts towards increasing nanochannel width. At smaller κh the nanochannel overlap increases. This shows that the degree of overlap depends on nanochannel dimension and Debye length. In the results of Haywood et al. [13] the average electroosmotic mobility shows maxima at small values of κh even in the absence of steric factor numerically and experimentally.

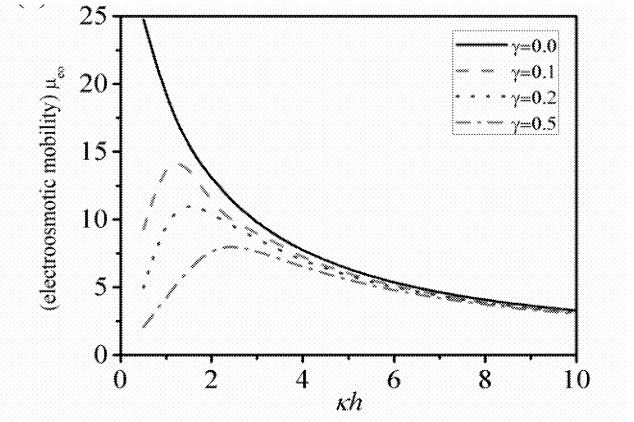

Fig. 3. Electroosmotic mobility defined as in Eq. (2.7) with respect to width of the nanochannel for different steric factors.

Since the assumption of asymmetry parameter assumes anions to be bigger than cations, the negative potential at the nanochannel wall will give a constant electroosmotic mobility. When ξ decreases (asymmetry of ion size increases), the size of the anions (coions) are smaller and cations being bulky limit the ions attracted to the nanochannel wall. Thus to investigate the asymmetry ion size effect positive potential at the nanochannel wall is considered. The average electroosmotic mobility shows a maxima around κh =2 when the asymmetry parameter is fixed at 0.5 and γ=0.5 as shown in Fig. 4. But this phenomena does not occur at small steric factor values. This is due to restriction of movement of ion in the nanochannel due to considerable size of ions. The EDL is overlapped at small κh values. And this overlapping increases with increase in steric factor.

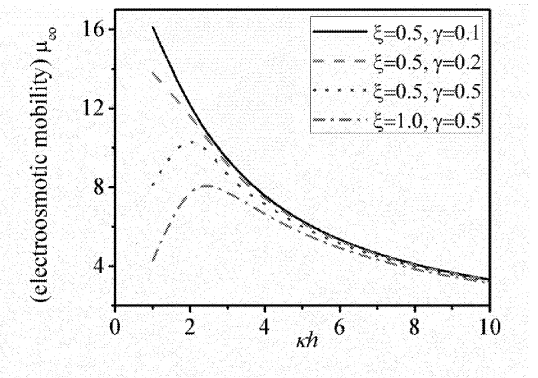

Fig. 4. The electroosmotic mobility variation with respect to nanochannel width for different steric factors at a fixed asymmetry of the ions for electric field 25 V/m.

4 Conclusion

We have modeled the electroosmotic flow in a nanochannel considering the size effects of ions in the electrolyte. In the case of symmetric ion size, the average electroosmotic mobility shows maxima at κh =2. This is due to increased EDL overlap. With increase in steric factor, the EDL overlap increases and the maxima decreases. In the case of asymmetry ion sizes, the nanochannel wall condition is changed due to the assumption of the asymmetry parameter where anion is bigger than cation. The walls are positively charged. The trend of the average velocity and average electroosmotic mobility show a similar trend as in the case of symmetric ion size case. But the symmetric ions show smaller average electroosmotic mobility. The more the ions are asymmetric the higher is the electroosmotic mobility.

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