International Journal of Heat and Mass Transfer 52 (2009) 4279–4295

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Electroosmotic flow driven by oscillating zeta potentials: Comparison of the Poisson–Boltzmann model, the Debye–Hückel model and the Nernst–Planck model

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ARTICLE INFO

Article history:
Received 17 November 2008
Received in revised form 2 April 2009
Accepted 2 April 2009
Available online 6 June 2009

Keywords:
Electroosmotic flow
Poisson–Boltzmann model
Nernst–Planck model
Debye–Hückel model

ABSTRACT

We consider electroosmotic flows (EOF) generated by temporally varying zeta potential which is usually adopted for pumping or mixing of fluids. In this case the dynamics of ions in the electric double layer (EDL) influences the induced electric field and consequently the EOF significantly. Therefore, the appropriate model should be the Nernst–Planck (NP) model for all zeta potentials or the Debye–Hückel (DH) model for low zeta potentials rather than the Poisson–Boltzmann (PB) model which is based on the equilibrium distribution of ions in the EDL. In the present investigation, we compare the predictions from the DH model and the PB model with the exact ones from the NP model for a range of frequency of zeta potential oscillation. It is found that one may adopt the PB model when the frequency is low and the DH model when the zeta potential is low. However, for either high frequency of zeta potential oscillation or large value of zeta potential, one must adopt the NP model to get accurate predictions of EOF.

1. Introduction

Recently there have been a renewed interest in electroosmotic flow in capillaries due to its relevance to many microfluidic systems based on the lab-on-a-chip concept. In these microfluidic systems the target chemical species are delivered by activating electroosmotic flow. Electroosmotic flow is induced when an electric field is imposed through the electric double layer, where the separation of positive and negative ions occurs because of the zeta potential at the microchannel wall [1]. The electric force acting on these ions is the driving force of the electroosmotic flow. Usually, one of the following three models is adopted in the analysis of electroosmotic flows; the Nernst–Planck (NP) model, the Debye–Hückel (DH) model and the Poisson–Boltzmann (PB) model. In the Nernst–Planck model the conservation equations for the cations and anions are solved coupled with the Navier–Stokes equation to find the electric potential in the electric double layer induced by ionic unbalance near the wall. Though the most rigorous model, it is difficult to solve the NP model numerically due to the strong nonlinear couplings between velocity, cation concentration, anion concentration and the electric potential induced by the ionic unbalance. A commonly accepted approximation to the Nernst–Planck model is the Debye–Hückel model. The DH model can be derived from the NP model when the zeta potential is small. Under many circumstances the ionic distribution in the electric double layer is not disturbed at a fixed zeta potential, and it follows the equilibrium Boltzmann distribution. In these cases the induced electric field is governed by the Poisson–Boltzmann equation and is decoupled from the velocity field, resulting in the Poisson–Boltzmann model which is the most widely employed model in the analysis of electroosmotic flows due to its simplicity. For a fixed zeta potential, the predictions of the PB model agree with those of the NP model at small values of the Debye length, which occur at large zeta potential and high ionic concentrations [2].

However, there have been attempts to vary wall zeta potential directly by imposing external electric field at the microchannel wall to control electroosmotic flows. When an electric field is applied perpendicular to the channel, a radial electric potential gradient is created across the insulating channel wall that allows for direct control of the zeta potential and the resulting electroosmotic flow. The use of ultrathin insulating walls allows significantly small voltages to create extraordinary fields required to have effective field-effect flow control [3–6]. It is also found that application of a AC voltage across the channel wall generates electroosmotic flows, resulting in pumping or mixing of fluids [7–10]. For the analysis of electroosmotic flows generated by the temporally varying zeta potential, as in the above applications, most investigators have adopted the Debye–Hückel model which permits analytic solutions in certain flow configurations [7,8]. However, the DH model is valid only for small values of zeta potential. In the present investigation, we compare the induced potential and velocity fields obtained from the Nernst–Planck model, the Debye–Hückel model and the Poisson–Boltzmann model systematically when the zeta potential varies sinusoidally at various frequencies, and suggest the range of validity of the DH and PB models.

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doi:10.1016/j.ijheatmasstransfer.2009.04.022

Nomenclature

D	diffusivity of ions
e	elementary charge
J^+	cationic current
J^-	anionic current
k_B	Boltzmann constant
L	characteristic length of the system
N	difference between anionic and cationic concentration $(n^- - n^+)$
n_0	bulk ionic concentration
n^+	cationic concentration
n^-	anionic concentration
P	pressure
Re	Reynolds number
Sc	Schmidt number
T	temperature
t	time
U	characteristic velocity of the system
$\mathbf{v}$	velocity vector
v^z	axial velocity
y	normal direction to the wall
z	valence of ions

Greek symbols

α	parameter defined in Eq. (6)
β	parameter defined in Eq. (6)
δ	parameter defined in Eq. (6)
ϵ_0	permittivity of vacuum
ϵ	dielectric constant
ζ_0	reference zeta potential
ζ	zeta potential
κ	Debye length
μ	viscosity
ρ	fluid density
ϕ	external electric potential
ψ	induced electric potential
ω	frequency of zeta potential oscillation

2. Models of electroosmotic flows

For simple electrolytes that dissociate into two equally charged ions of valence z and $-z$, the dimensionless governing equations for electroosmotic flows may be written under the assumption of the Gouy–Chapman model as [2,11].

$$\frac{\partial n^{+*}}{\partial t^*} + \mathbf{v}^* \cdot \nabla n^{+*} = \frac{1}{ScRe}\nabla^{*2} n^{+*} + \frac{\alpha}{ScRe}\nabla^* \cdot (n^{+*}\nabla^*\psi^*) + \frac{\alpha}{ScRe}\nabla^* \cdot (n^{+*}\nabla^*\phi^*) \tag{1}$$

$$\frac{\partial n^{-*}}{\partial t^*} + \mathbf{v}^* \cdot \nabla n^{-*} = \frac{1}{ScRe}\nabla^{*2} n^{-*} - \frac{\alpha}{ScRe}\nabla^* \cdot (n^{-*}\nabla^*\psi^*) - \frac{\alpha}{ScRe}\nabla^* \cdot (n^{-*}\nabla^*\phi^*) \tag{2}$$

$$\nabla^{*2}\psi^* = \frac{\beta}{2}(n^{-*} - n^{+*}) \tag{3}$$

$$\frac{\partial \mathbf{v}^*}{\partial t^*} + \mathbf{v}^* \cdot \nabla \mathbf{v}^* = -\nabla^* P^* + \frac{1}{Re}\nabla^{*2}\mathbf{v}^* + \delta(n^{-*} - n^{+*})\nabla^*\phi^* \tag{4}$$

$$\nabla^* \cdot \mathbf{v}^* = 0 \tag{5}$$

In the above equations the dimensionless variables have been defined as follows:

$$\mathbf{x}^* = \frac{\mathbf{x}}{L}, \quad \psi^* = \frac{\psi}{\zeta_0}, \quad \mathbf{v}^* = \frac{\mathbf{v}}{U}, \quad P^* = \frac{P}{\rho_f U^2}, \quad t^* = \frac{tU}{L},$$

$$\phi^* = \frac{\phi}{\zeta_0}, \quad n^{+*} = \frac{n^+}{n_0}, \quad n^{-*} = \frac{n^-}{n_0}, \quad w = \frac{1}{\kappa} = \sqrt{\frac{8\pi n_0 e^2 z^2}{\varepsilon_0 \varepsilon k_b T}},$$

$$\alpha = \frac{ez\zeta_0}{k_B T}, \quad \beta = \frac{(wL)^2}{\alpha} = \frac{L^2 2n_0 ez}{\varepsilon_0 \varepsilon \zeta_0}, \quad \delta = \frac{zen_0\zeta_0}{\rho_f U^2},$$

$$Re = \frac{\rho_f LU}{\mu}, \quad Sc = \frac{\mu}{\rho_f D} \tag{6}$$

where, n^+ is the number concentration of the cation, n^- is that of the anion, D is the diffusivity of ions, z is the valence, e is the elementary charge, k_B is the Boltzmann constant, T is the absolute temperature, ψ is the local electric potential induced by ions, ϕ is the externally imposed electric potential, $\mathbf{v}$ is the velocity, ρ_f is the fluid density, P is the pressure, μ is the viscosity, ε_0 is the permittivity of the vacuum and ε is the dielectric constant, L is the width of the microchannel, n_0 is the bulk ionic concentration and ζ_0 is the surface electric potential, which is taken to be the same as the zeta potential, at a reference position and κ is the Debye length characterizing the depth of the electric double layer. The electroosmotic flow model composed of Eqs. (1)–(5) is called the Nernst–Planck (NP) model. Eqs. (1) and (2) represent the conservation equations for the cations and anions, both of which induce electric field ψ^* in the electric double layer. Eq. (3) shows that the ionic unbalance in the electric double layer gives rise to the induced potential ψ^*. The ionic unbalance also acts as a body force in the momentum Eq. (4) when there is external potential gradient $\nabla^*\phi^*$. The Nernst–Planck model takes care of the dynamic effects of ions and is the most rigorous model to be considered in the present investigation. From now on, we delete the asterisk indicating dimensionless variables for the sake of brevity.

Next, we show conditions under which the Debye–Hückel model is derived from the NP model. When the values of α is small, which corresponds to a weak zeta potential, we may approximate the dimensionless ionic fluxes as follows:

$$J^\pm \equiv \mathbf{v}n^\pm - \frac{1}{ScRe}\nabla n^\pm - \frac{z^\pm\alpha}{ScRe}n^\pm(\nabla\psi + \nabla\phi) \approx \mathbf{v}n^\pm - \frac{1}{ScRe}\nabla n^\pm - \frac{z^\pm\alpha}{ScRe}(\nabla\psi + \nabla\phi) \tag{7}$$

since the contribution of the last term in the right hand side of the above equation is not significant compared with other terms. Then the last two terms of Eqs. (1) and (2) are approximated as

$$\frac{\alpha}{ScRe}\nabla \cdot (n^\pm\nabla\psi) = \frac{\alpha}{ScRe}\nabla^2\psi; \quad \frac{\alpha}{ScRe}\nabla \cdot (n^\pm\nabla\phi) = \frac{\alpha}{ScRe}\nabla^2\phi \tag{8}$$

Defining a new variable N such that

$$N \equiv n^- - n^+ \tag{9}$$

and exploiting the fact that the external potential ϕ satisfies $\nabla^2\phi = 0$, the set of equations defining the NP model, Eqs. (1)–(4), reduces to the following set of equations called the Debye–Hückel (DH) model:

$$\frac{\partial N}{\partial t} + \mathbf{v} \cdot \nabla N = \frac{1}{ScRe}\nabla^2 N - \frac{\alpha\beta}{ScRe}N \tag{10}$$

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla P + \frac{1}{Re}\nabla^2\mathbf{v} + N\delta\nabla\phi \tag{11}$$