Electro-Osmosis With Corrected Solution of Poisson-Boltzmann Equation That Satisfies Charge Conservation Principle

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Abstract

We derive the electro-osmotic velocity profile in a micro-channel using a recently corrected charge density distribution within an electrolytic solution. Previous distribution did not take care of charge conservation principle while solving Poisson-Boltzmann equation and needed modification, hence the velocity profile also needs modification that we do here. Helmholtz-Smoluchowskii velocity scale is redefined, which accommodates Debye length parameter in it, unlike old definition.

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Electro-osmosis concerns driving an electrolytic solution through a narrow channel using an externally applied axial electric field, exploiting a possible non-trivial charge density distribution (ρ_e) in the solution. It has a very old history [1, 2] and finds applications in many fields [3–5]. Now, ρ_e appears in the body force term in the fluid momentum equation, which takes a very simple form for a flow with small Reynolds number (typical for a narrow channel) and when the flow is steady and hydrodynamically fully developed. For a rectangular geometry, the momentum equation is given by [6, 7]:

$$0 = \mu \frac{d^2 v}{dx^2} + E_y \rho_e \tag{1}$$

 ρ_e and fluid velocity v vary essentially along the smallest side ('2a') of geometry (x direction); E_y is external electric field, applied in y direction; μ is uniform viscosity. Now, solving Poisson-Boltzmann (PB) equation we obtain ρ_e as spatial function that is needed to solve the above equation. However, the old solution [8, 9] did not take care of charge conservation principle properly. This author attempted to remove that discrepancy in Ref [10, 11], and obtained a velocity profile using it in Ref [7]. However, that formulation for ρ_e still had problem, for it was not satisfying Poisson's equation in general. Finally, the correct expression for ρ_e (scaled) has been developed in Ref [12], and is given by,

$$\rho_e^* = \frac{1}{2\sinh(\kappa)} \left[q_0 \kappa \cosh(\kappa \eta) - \delta \sinh(\kappa \eta) \right]$$
⁽²⁾

Meaning of symbols can be found in Ref [7, 12]. We mention them briefly:

$$\kappa \equiv a/\lambda_D; \quad \eta \equiv x/a; \quad \rho_e^* \equiv \rho_e/\rho_0; \quad \rho_0 \equiv \left(\epsilon \kappa^2 \zeta/a^2\right)$$
(3)

Where, λ_D is Debye length [8]; ϵ is permittivity of liquid; ζ is a suitable scale for electrostatic potential ψ , ($\zeta > 0$).

 δ is the potential difference between walls at $\eta = +1$ and $\eta = -1$. If Q_0 is the net charge present in liquid (in a cross-section, per unit axial length), $\int_{-1}^{+1} \rho_e^* d\eta = Q_0/\rho_0 \equiv q_0$, (using Eq. 3). Now, using Eq. 3 and Eq. 2, we can write Eq. 1 as,

$$\frac{d^2 v}{d\eta^2} = -\left(\frac{a^2 E_y \rho_0}{\mu}\right) \rho_e^*
= -\left(\frac{\epsilon \zeta E_y}{\mu}\right) \kappa^2 \rho_e^*
= -M \kappa^2 \left[q_0 \kappa \cosh(\kappa \eta) - \delta \sinh(\kappa \eta)\right]$$
(4)

Where,
$$M \equiv \left(\frac{\epsilon \zeta E_y}{2\mu \sinh(\kappa)}\right)$$
 (5)

Intergrating Eq. 4 twice w.r.t η we get,

$$v = -M \left[q_0 \kappa \cosh(\kappa \eta) - \delta \sinh(\kappa \eta) \right] + C_1 \eta + C_2 \tag{6}$$

We use no-slip conditions at both walls, i.e. v = 0 at $\eta = \pm 1$. Hence,

$$0 = -M \left[q_0 \kappa \cosh(\kappa) - \delta \sinh(\kappa) \right] + C_1 + C_2 \tag{7}$$

$$0 = -M \left[q_0 \kappa \cosh(\kappa) + \delta \sinh(\kappa) \right] - C_1 + C_2 \tag{8}$$

From Eq. 7 and Eq. 8 we solve for C_1 and C_2 and get,

$$C_1 = -M\delta\sinh(\kappa) \tag{9}$$

$$C_2 = Mq_0\kappa\cosh(\kappa) \tag{10}$$

Using Eq. 9 and Eq. 10 in Eq. 6 and rearranging terms,

$$v = M \left[q_0 \kappa \left(\cosh(\kappa) - \cosh(\kappa\eta) \right) - \delta \left(\eta \sinh(\kappa) - \sinh(\kappa\eta) \right) \right]$$

= $M \left[q_0 \kappa \cosh(\kappa) \left(1 - \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \right) - \delta \sinh(\kappa) \left(\eta - \frac{\sinh(\kappa\eta)}{\sinh(\kappa)} \right) \right]$
= $M \kappa \cosh(\kappa) \left[q_0 \left(1 - \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \right) - \delta \frac{\tanh(\kappa)}{\kappa} \left(\eta - \frac{\sinh(\kappa\eta)}{\sinh(\kappa)} \right) \right]$ (11)

Now, using Eq. 5 we get,

$$M\kappa \cosh(\kappa) = \frac{\epsilon \zeta E_y}{2\mu \sinh(\kappa)} \kappa \cosh(\kappa)$$

= $\lambda_{||} \frac{\epsilon \zeta E_0 \kappa}{2\mu \tanh(\kappa)}$ (12)
Where, $\lambda_{||} \equiv \frac{E_y}{E_0}$, with $E_0 > 0$

Let us define corrected Helmholtz-Smoluchowskii velocity scale $v_{H.S.Corr}$ by,

$$v_{H.S.Corr} \equiv \frac{\epsilon \zeta E_0 \kappa}{2\mu \tanh(\kappa)} \tag{13}$$

It differs from old Helmholtz-Smoluchowskii velocity scale, see Ref [8]. Let $\bar{v} \equiv v/v_{H.S.Corr}$. Finally we arrive at,

$$\bar{v} = \lambda_{||} \left[q_0 \left(1 - \frac{\cosh(\kappa\eta)}{\cosh(\kappa)} \right) - \delta \frac{\tanh(\kappa)}{\kappa} \left(\eta - \frac{\sinh(\kappa\eta)}{\sinh(\kappa)} \right) \right]$$
(14)

When we reverse E_y , velocity field must reverse too. In the above equation, the sign of $\lambda_{||}$ changes when we reverse E_y , and hence \bar{v} changes sign as expected; in old works it was not

possible to capture this reversal of direction in the scaled velocity, because $v_{H,S}$ was not defined properly. This author made an attempt to correct it in Ref [7], however ρ_e was still not correct there. We can control the fluid flow easily using the potential difference.

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