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Streaming-field-induced convective transport and its influence on the electroviscous effects in narrow fluidic confinement beyond the Debye-Hückel limit

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We pinpoint the limitations in traditional electroviscous analysis for narrow fluidic confinements. We show that because of neglecting the convective transport of ions originated out of the established streaming field itself, the traditional approach may result in physically inconsistent flow rate predictions. We show that the larger the value of an ionic Peclet number and narrower the confinement, the more conspicuous are these erroneous predictions, within threshold limits of the nondimensional ζ potential. We come up with an improved mathematical model to overcome such discrepancies.

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Analysis of hydrodynamics within the electrical double layer (EDL) is central to the understanding of the transport of charged colloids and biological macromolecules in narrow fluidic confinements. One important consequence of the establishment of an EDL in pressure-driven flows through microchannels or nanochannels is the development of a so-called streaming potential, by virtue of the convective ionic transport in the mobile part of the EDL toward the downstream end of the conduit under the influence of the driving force. This causes an electrical current, known as the streaming current, to flow in the direction of the imposed fluid motion. However, the resultant accumulation of ions in the downstream section of the channel sets up its own induced electrical field, known as the streaming potential. This field, in turn, generates a current to flow back against the direction of the pressure-driven flow (see Fig. 1 for illustration). This so-called conduction current balances the streaming current at steady state, so that the net electrical current becomes zero, consistent with a pure pressure-driven flow condition. Researchers have utilized the generation of streaming potential to convert hydrostatic pressure differences into useful electrical energy, to characterize interfacial charge of organic thin films, to measure wall charge inversion in the presence of multivalent ions in a nanochannel, to analyze ion transport through nanoporous membranes, to design efficient nanofluidic batteries, to quantify hydrodynamic dispersion in nanochannels, etc., as some of the technologically relevant applications [1].

One important consequence of the EDL-induced counteracting ionic migration mechanism in pure-pressure-driven flows through narrow fluidic confinements is believed to be manifested through an enhanced effective viscous resistance, so as to oppose the very cause to which the forward motion of the ionic charges is due. If the reduced flow rate is compared with the flow rate predicted by conventional fluid dynamics without considering the presence of the EDL, it appears that the liquid would have an enhanced effective viscosity. This is usually referred to as the electroviscous effect [2]. Theoretically, this effect is commonly analyzed with the assumption of an open-circuit channel, where the steady-state streaming potential is determined by equating the streaming current with the conduction current, as mentioned earlier.

In a continuum limit without involving any EDL overlap (thin EDL limits), the physics of electroviscous effects is traditionally addressed with the aid of a Poisson-Boltzmann formulation [3], in conjunction with a "weak surface potential" approximation. This later assumption, although in principle limited by the range of validity of its underlying hypothesis, has proved to be immensely effective in capturing many essential features of electroviscous effects in microchannels and nanochannels, through an effective linearization (commonly known as the Debye-Hückel linearization) of the charge density expression in the Poisson's equation for the electrical potential distribution. These limitations, however, have been successfully overcome by the nonlinear Poisson-Boltzmann models (for example, see Ref. [4]) in which the Debye-Hückel linearization is not presumed *a priori*. Despite this generalization, the electroviscous effects in narrow fluidic confinements beyond the Debye-Hückel linearization still remains to be poorly understood, particularly within the purview of the conventional description of the streaming potential concept. This deficit essentially stems from the fact that *although the convective transport of ions, even in a pure-pressure-driven flow-field, should involve an effective contribution from the induced (streaming) electric field as well, the later effects are routinely neglected in the velocity profiles employed for the traditional electroviscous analysis* (hereafter referred to as *approach 1*), as compared to the convective contributions from the imposed pressure gradient itself. While this routinely omitted contribution may turn out to be negligible in comparison to the ionic conduction for microchannels with low surface potentials, the underlying implications need not be trivially overruled for the more general cases.

Here what is proposed (hereafter referred to as *approach 2*) is believed to be, to the best of our knowledge, the extended theoretical model on electroviscous effects that effectively considers the streaming-field-induced convective transport of the ionic species for the electroviscous effect estimations, without necessarily incurring any low surface potential approximation. Through this modification of the traditional approach, we attempt to address the following im-

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portant question: *what is the role of the induced (streaming) electrical field in the convective transport of ionic charges in pure-pressure-driven flows?* In particular, we show that an omission of the streaming electric field in the calculation of the rate of convective transport of ionic charges may result in significant overpredictions of the streaming potential, especially beyond the low surface potential limits. Nontrivially, we also show that this may result in a serious error in predicting the effective viscosity and the net volumetric flow rate, or may even lead to a physically inconsistent prediction of the sign of the effective viscosity. By postulating an effective generalization of the streaming potential as a unique function of the relative surface potential, relative characteristic EDL thickness and a unique nondimensional combination of the physical properties of the fluid, we emphasize how the present development eliminates the possibilities of such anomalous and physically inconsistent predictions over a wide range of surface potential.

For theoretical analysis, we begin with the standard EDL description, in which the electric potential in the EDL (ψ) is a function of the net charge density distribution, ρ_e, and is expressed through the Poisson equation as $\nabla^2\psi=-\rho_e/\varepsilon$, where $\rho_e=e(z_+n_++z_-n_-)$, $n_\pm$ being the respective ionic number densities. Under nonoverlapped EDL conditions [3], the later ones are expressed through the Boltzmann distribution as $n_\pm=n_0\exp(-ez_\pm\psi/k_BT)$. This, in turn, can be employed to estimate the total ionic current as $I_{ionic}=e\int_0^{2H}(z_+u_+n_+ +z_-u_-n_-)dy$. Here u_+ (u_-) refer to the axial velocities of the cations (anions), expressed as $u_\pm=u+z_\pm eE/f_\pm$. Under the assumption of symmetric electrolyte ($z_+=-z_-=z$) and identical values of cationic and/or anionic friction coefficient of charge $f_\pm$ ($f_+=f_-=f$), the expression for I_{ionic} simplifies to

$$I_{ionic}=ez\int_0^{2H}(n_+-n_-)udy+\frac{z^2e^2E}{f}\int_0^{2H}(n_++n_-)dy. \quad (1)$$

For pure-pressure-driven transport, I_{ionic} becomes identically zero at steady state; the corresponding value of E is known as the streaming field (E_S).

Consistent calculation of the net ionic current necessitates an appropriate substitution of the velocity field in the expression of the velocity field in its convective component, as evident from Eq. (1). Traditionally (approach 1), the ion convection is assumed to be solely due to the pressure-driven velocity field, disregarding this implicitly induced streaming potential. In an effort to illustrate the implications of this assumption, we consider Stokes flow in a parallel-plate narrow confinement of height $2H$, with $y=0$ and $y=2H$ as the location of the two confining boundaries, so that solution of the velocity field for a constant fluid viscosity μ reads $u=u_p=-\frac{1}{2\mu}\frac{dp}{dx}(2Hy-y^2)$, the subscript "$p$" duly emphasizing a pure-pressure-driven nature of the assumed fluid dynamic transport. However, in reality, the induced streaming potential is also likely to introduce an additional convective transport of the fluid medium, opposing the driving convective influences of the imposed pressure gradient. We allow this influence to feature in our present model (approach 2), yielding the following expression for the resultant velocity field to be employed for the pertinent convection current calculations:

$$u=u_p+u_{E_S}=-\frac{1}{2\mu}\frac{dp}{dx}(2Hy-y^2)-\frac{\varepsilon\zeta E_S}{\mu}\left(1-\frac{\psi}{\zeta}\right),$$

where ζ is the potential at the plane of zero shear (also known as the ζ potential) and E_S is the induced streaming potential field. Setting $I_{ionic}=0$ at steady state for pure-pressure-driven transport, one may obtain an expression for the streaming current following approach 2, as

$$E_{S2}=\frac{n_0ez\int_0^{2H}u_P\sinh\left(\frac{ez\psi}{k_BT}\right)dy}{\sigma\int_0^{2H}\cosh\left(\frac{ez\psi}{k_BT}\right)dy+\frac{n_0ez\varepsilon\zeta}{\mu}\int_0^{2H}\left(1-\frac{\psi}{\zeta}\right)\sinh\left(\frac{ez\psi}{k_BT}\right)dy}. \quad (2)$$

The expression for E_{S1} (i.e., following approach 1) appears to be a reduced form of the above, with the second term in the denominator of the expression for E_{S2} being set identically equal to zero. In Eq. (2), σ ($\sigma=n_0e^2z^2/f$) is the electrical conductivity of the fluid (this ionic friction coefficient of charge f can be related to the ionic mobility Λ, Faraday's constant F, and Avogadro number N_A as $f=e^2N_A/F^2\Lambda$), and n_0 is the bulk ionic number density that can be expressed in terms of the Debye layer thickness, λ, as $n_0=\varepsilon k_BT/2\lambda^2e^2z^2$. Since both ζ and ψ are of the same sign, the additional term appearing in the denominator of expression E_{S2} (as compared to expression for E_{S1}) is always positive. Further, noting that the first term in the denominator of Eq. (2) is positive under all circumstances, we may conclude that $|E_{S2}|<|E_{S1}|$ under all conditions. In terms of appropriate definite integrals, dimensionless forms of E_{S1} and E_{S2} can be expressed as (by considering the following nondimensional parameters: $\bar{y}=y/H$, $\kappa=H/\lambda$, $E_0=\frac{-fH^2}{2ze\mu}\frac{dp}{dx}$, $\bar{\psi}=\frac{ez\psi}{4k_BT}$, $\bar{\zeta}=\frac{ez\zeta}{4k_BT}$, $R=\frac{4\varepsilon k_BTf}{\mu e^2z^2}$)

$$\frac{E_{S1}}{E_0}=\frac{I_1}{I_2}\quad\text{and}\quad\frac{E_{S2}}{E_0}=\frac{I_1}{I_2+RI_3},$$

where $I_1=\int_0^2(2\bar{y}-\bar{y}^2)\sinh(4\bar{\psi})d\bar{y}$, $I_2=\int_0^2\cosh(4\bar{\psi})d\bar{y}$, $I_3=\int_0^2\bar{\zeta}(1-\bar{\psi}/\bar{\zeta})\sinh(4\bar{\psi})d\bar{y}$. *Clearly, for $R=0$, E_{S2} and E_{S1} are identical, independent of the details of the EDL potential distribution and the value of $\bar{\zeta}$.* In general, the relative difference between E_{S1} and E_{S2} is solely dictated by the variations in $\bar{\zeta}$, as well as the dimensionless parameters R and κ.

Potential distribution (ψ) within the EDL, which is another important influencing factor dictating the differences between E_{S2} and E_{S1}, is intrinsic to the electrochemical interfacial phenomena and is strongly influenced by the extent of interactions between the EDLs formed at the opposite plates (which in turn is strongly dictated by the parameter κ). In the present study, we investigate an interesting transitional behavior in which the EDLs are not thin enough to be of negligible extent as compared to the characteristic channel dimensions and at the same time are not thick enough to incur any EDL overlap. Such cases can be perceived as in-

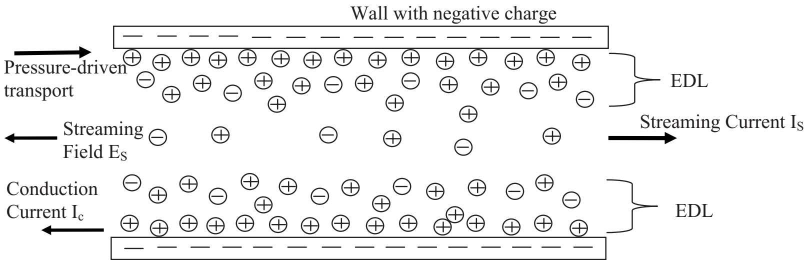

FIG. 1. A schematic diagram depicting the action of streaming field.

termediate limits between thin and thick EDLs, for which the pertinent expression for ψ can be obtained as [3] $\bar{\psi}(\bar{y}) = \{\tanh^{-1}[\tanh(\bar{\zeta})\exp(-\kappa\bar{y})] + \tanh^{-1}[\tanh(\bar{\zeta})\exp(-2\kappa+\kappa\bar{y})]\}$. Based on this potential field, we plot (see the right inset of Fig. 2) the variations in E_{S2}/E_{S1} with $\bar{\zeta}$, as a parametric function of R. For low magnitudes of $\bar{\zeta}$ (a common basis for the celebrated Debye-Hückel linearization approximation), the ratio of E_{S2}/E_{S1} decreases monotonically with increases in $|\bar{\zeta}|$, because of more rapid competitive enhancements in the streaming-field induced convective strength as compared to the conduction currents. On the other hand, for high magnitudes of $\bar{\zeta}$, the ratio monotonically increases with increments in the magnitude of $\bar{\zeta}$. This enhancement is because a rapid increment in the value of I_2 (physically, indicating augmentations in the relative strength of ionic conduction within the EDL) with increments in $|\bar{\zeta}|$ for high values of $|\bar{\zeta}|$, rendering the contribution due to ionic convection RI_3 less significant. Eventually, an asymptotic state $\left(\frac{E_{S2}}{E_{S1}} \to 1\right)$ is reached where the ratio I_3/I_2 almost vanishes [noting that $\frac{E_{S2}}{E_{S1}} = \frac{I_2}{I_2+RI_3}$]. Thus, there occurs an extremum in between, at which the differences between E_{S2} and E_{S1} occur to be the most significant ones. Physically, the strength of convective transport due to the streaming field relative to that due to the externally imposed pressure gradient is the most significant one under these conditions. Importantly, larger values of R amplify the disparities in prediction of E_{S2} and E_{S1} to greater proportions. Physically, greater values of R (effectively, an ionic Peclet number consistent with the established streaming field) are possible for buffers with low viscosity, low electrical conductivity, and poor ionic mobility, so as to ensure a stronger ionic advective strength relative to the diffusive strength. Further, when the value of κ is progressively reduced, differences between E_{S2} and E_{S1} turn out to be more prominent (compare the lines with and without markers in the right inset of Fig. 2). This is because of a greater strength of the ionic convection due to significantly enhanced ionic number densities over a more substantial extent in the transverse direction of the nanochannel, with enhancements in the EDL thickness relative to the channel hydraulic diameter. Thus it can be inferred that for large κ values (>100), typically for a microchannel, the two approaches converge, indicating the modified approach is useful only for sufficiently small channels [$\mathrm{H} \sim O(100\ \mathrm{nm})$].

Based on the expressions for the streaming electric field, one may derive pertinent expressions for quantifying the "electroviscous" influences, by equating the actual flow rate with the flow rate predicted from a traditional pressure-driven transport consideration but with an enhanced effective viscosity, μ_{eff} (to implicitly account for the additional flow resistances because of the streaming effects). Accordingly, the two approaches result in their respective flow rate predictions Q_1 and Q_2, which are related as

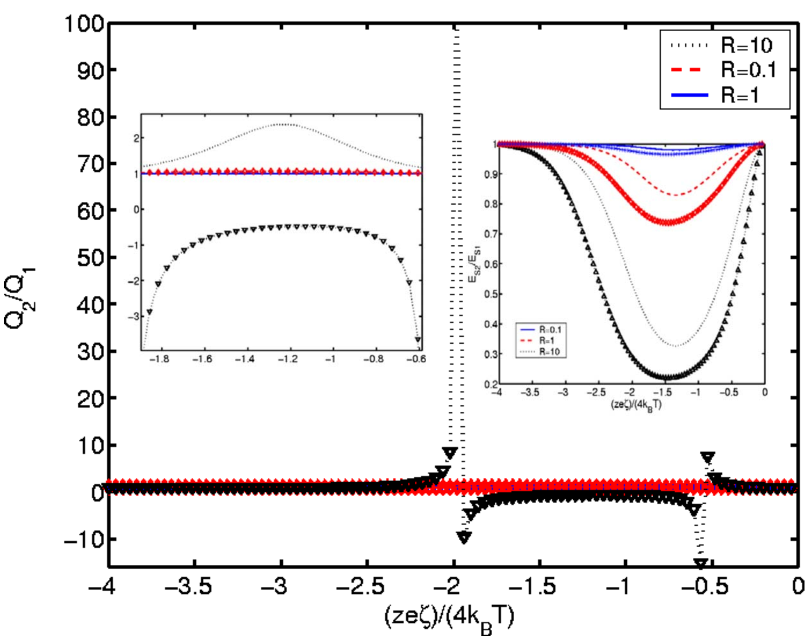

FIG. 2. (Color online) Ratio of the volumetric flow rates predicted from the two approaches (Q_2/Q_1) as a function of the nondimensional ζ potential. In the left inset, a magnified view of the same plot is presented. In the right inset, the ratio of the streaming fields (E_{S2}/E_{S1}), as predicted by the two approaches, is plotted. The lines with markers represent cases with $\kappa=4$, whereas those without markers represent the variations with $\kappa=10$.

$$\frac{Q_2}{Q_1} = \frac{\mu_{eff,1}}{\mu_{eff,2}} = \frac{1 - rE_{S2}/E_{S1}}{1 - r}, \quad \text{where } r = 0.75RI_4\frac{I_1}{I_2}. \quad (3)$$

In Fig. 2, we plot this variation as a function of $\bar{\zeta}$, for the two chosen representative values of κ. For $\kappa=10$, we observe that $Q_2 > Q_1$, irrespective of the value of R, without incurring any reversal in their relative algebraic signs. This is primarily because of the fact that for this case the differences between E_{S2} and E_{S1} are not large enough (their ratio remains close to unity) to create a reversal in the sign of $1-r\frac{E_{S2}}{E_{S1}}$, as compared to that of $1-r$ (note that r is a positive number, for all cases). Physically, the strength of ionic convection due to the induced streaming field is not substantial enough to create any significant changes in the qualitative behavior over this operating regime, although the distinctive quantitative predictions from the two approaches are conspicuous. However, remarkably and rather nonintuitively, it can be observed that the physical behavior tends toward a shift in the notional paradigm as the value of κ is reduced and the value of R is progressively enhanced. Such combinations may give rise to a situation (for example, refer to the characteristics corresponding to $R=10$ and $\kappa=4$ in Fig. 2) in which there are ranges of $\bar{\zeta}$ for which Q_2/Q_1 turns out to be negative. This implies that an "opposing" streaming field itself has completely overcome the effects of the imposed pressure gradient to create a global flow reversal, because of either Q_2 or Q_1 turning out to be negative relative to the other. This "global" flow reversal need not be confused with a physically plausible and admissible "local" flow reversal close to the solid boundaries because of viscous retardation effects, since in the later case a physically consistent proposition of the unidirectional bulk flow in the same sense of the driving field is still maintained. Further, a closer examination reveals that the direction of Q_2 is always in physical accordance with the direction of an externally imposed pressure-driven flow notwithstanding any streaming effects. Thus, the physical inconsistency arises because of an anomalous flow-rate prediction from approach 1. As such, for higher values of R and lower values of κ, the ratio of E_{S2} and E_{S1} may become small enough to create a reversal in sign of $1-r\frac{E_{S2}}{E_{S1}}$, as compared to that of $1-r$. In this case, approach 1 predicts a negative effective viscosity. Physically, such an anomalous prediction originates because of the fact that the approach 1 neglects the additional "forward" advective strength due to the streaming field effects. In doing so, it overestimates the resistance against the "driving" influences. For thicker EDLs and larger values of R, this overestimation may turn out to be strong enough to impose such a high value of the fictitious resistance that a physically inconsistent reverse flow is predicted. Consistent with the trends in E_{S2}/E_{S1}, such erroneous predictions with approach 1 are most prominent for the following combinations: larger values of R, smaller values of κ, and an intermediate range of $\bar{\zeta}$.

To summarize, we have shown that the traditional electroviscous analysis may yield erroneous as well as physically inconsistent flow-rate predictions, as a consequence of neglecting the influences of streaming-potential-induced electro-osmosis in the ionic convection current. Since the charge separation induces its own electric field, which acts upon the ions within the liquid and thereby, via friction on the liquid itself, the consequent alteration in the advective transport enhances the flow resistance. We have further demonstrated that larger the value of an ionic Peclet number and narrower the confinement, more significant is likely to be this effect, within threshold limits of the nondimensional ζ potential. However, since the reported investigations on electroviscous effects have not yet effectively explored the different plausible ranges of these parameters beyond a few restricted limits, the concerned defects in the traditional modeling efforts have not yet been well exposed in the literature.

[1] J. Yang, F. Lu, L. W. Kostiuk, and D. Y. Kyok, J. Micromech. Microeng. **13**, 963 (2003); R. Schweiss, P. B. Welzel, C. Werner, and W. Knoll, Colloids Surf., A **195**, 97 (2001); F. H. J. van der Heyden, D. Stein, K. Besteman, S. G. Lemay, and C. Dekker, Phys. Rev. Lett. **96**, 224502 (2006); S. F. Alkafeef and A. F. Alajmi, J. Colloid Interface Sci. **309**, 253 (2007); H. Daiguji, Y. Oka, T. Adachi, and K. Shirono, Electrochem. Commun. **8**, 1796 (2006); X. Xuan and D. Sinton, Microfluid. Nanofluid. **3**, 723 (2007).

[2] D. Burgreen and F. R. Nakache, J. Phys. Chem. **68**, 1084 (1964); C. L. Rice and R. Whitehead, *ibid.* **69**, 4017 (1965); S. Levine, J. R. Marriott, G. Neale, and N. Epstein, J. Colloid Interface Sci. **52**, 136 (1975); S. Chakraborty, Phys. Rev. Lett. **100**, 097801 (2008).

[3] R. J. Hunter, *Zeta Potential in Colloid Science* (Academic Press, London, 1981).

[4] M. S. Kilic, M. Z. Bazant, and A. Ajdari, Phys. Rev. E **75**, 021502 (2007).