Influences of streaming potential on cross stream migration of flexible polymer molecules in nanochannel flows

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We execute augmented Brownian dynamics (BD) simulation studies to show that the migration of flexible polyelectrolyte chains through nanochannels may be strongly governed by a complicated interplay between the electroviscous effects, near-wall interaction mechanisms, and diffusophoretic transport due to thermal gradients prevailing in the system. We further illustrate that in presence of mutually opposing pressure-driven and electro-osmotic transport and with an optimal choice of the ratio of the strength of these two flow fields, the electroviscous effects may turn out to be immensely consequential in strengthening the effective confinement of the polyelectrolyte. This, in turn may permit in achieving important biophysical feats that are otherwise obtainable only through significantly reduced nanochannel dimensions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3157258]

I. INTRODUCTION

Emerging miniaturization technologies revolutionizing biology by altering statistical mechanical properties of flexible molecules in confined geometries have triggered intense research investigations in many critical applications, including the prestretching and stabilization of DNA before threading through a nanopore, DNA sequencing on a single molecule level, probing the molecular level interactions of the DNA binding proteins, and encoding information in DNA sequences for patterning materials and nanocrystals. Since DNA extensions in nanochannels are indicative of the numbers of its base pairs, there holds a direct mapping between the genomic order and the measured location along the stretched molecule, thereby allowing site-specific interactions of enzymes and florescent probes to be captured with unprecedented accuracy, provided that the wall-solvent-polyelectrolyte interactions consistent with the appropriate physical scales are sufficiently well resolved. It has been well appreciated that the proximity of bounding walls is likely to induce a number of complicated effects such as steric and solvation interactions, nontrivial electroviscous effects, and strongly coupled diffusophoretic transport in relation to the background flow, which may significantly influence the polyelectrolyte transport characteristics. However, in most of the standard Brownian dynamics (BD) simulation studies, the effects of confining boundaries are represented only through the consideration of wall induced hydrodynamic interactions, in conjunction with a simple wall potential. As a consequence, the standard BD based simulation strategies have not yet turned out to be very successful in capturing the underlying physical consequences pertinent to the transport mechanisms of polyelectrolytes through nanofluidic channels, primarily attributable to their inherent constraints in describing the concerned thermofluidic interactions by explicitely considering all the physical details. At the same time, it also needs to be appreciated that the complexities in describing thermofluidic interactions at physical scales that are substantially larger than those addressed by the molecular simulation strategies enable the molecular dynamics (MD) studies to probe the dynamical characteristics of only reduced and simplified systems, without emphasizing elaborately on many important physicochemical events over multiple spatiotemporal scales. Therefore, there is a strong need of developing a thoughtful simulation strategy, which may act as an optimal compromise between the needs for embedding the underlying complex thermodynamics through standard BD based approaches that are otherwise unable to capture the disparate physical scales directly, and the needs for accessing computationally tractable as well as experimentally relevant physical scales that are truly beyond the reach of computationally expensive MD simulations.

Despite testing the limits of even the most sophisticated computing platforms, a number of significant research studies have recently been reported in literature on MD simulation of polymer transport in nanofluidic channels. Khare et al., in a seminal study, investigated the cross stream migration of flexible polymeric chains in nanochannel flows through comprehensive MD simulations. Interestingly, they obtained two off-center peaks of chain center of mass density profiles in the presence of Poiseuille flows, as attributed to the competing wall-directed migration due to the gradients in chain mobilities (caused by the gradients in the velocity field) and centerline directed migration due to thermal diffusion as well as hydrodynamic interactions (HIs). However, effects of streaming potential, a spontaneous and extremely significant feature of electrolytic transport in nanofluidic channels, were not considered in their study. As such, intensive computational demands of capturing the details of the underlying electrochemical and thermodynamic interactions and the pertinent physical complexities have often threatened to be somewhat prohibitive in nature in offering any physical
insights on the nontrivial interactions between the streaming potential and polyelectrolyte transport in nanofluidic channels, either through BD or MD simulations.

Implications of streaming potentials in narrow fluidic confinements effectively stem from the physical basis that on application of an external forcing mechanism, surplus counterions in the mobile part of the electrical double layer (EDL) get spontaneously and preferentially transported with the liquid motion toward the downstream end. However, the resultant accumulation of ions sets up its own induced electrical field, known as the streaming potential, which, in turn, generates a current to flow back against the direction of the external actuation. This, in equivalence, results in an enhanced effective flow resistance, so as to oppose the very cause (i.e., the externally imposed driving influence) to which the forward motion of the ionic charges is due. The reverse flow established due to streaming potential effects may also interact in an interesting and somewhat nontrivial manner with the transport of flexible molecules (such as polyelectrolytes) in nanofluidic channels, which may give rise to intriguing physical phenomena that have largely been ignored in literature. In the present work, on the other hand, we outline an augmented BD simulation study to elucidate the consequent physicochemical interactions pertinent to cross stream migration of flexible molecules in narrow fluidic confinements, by appealing to the detailed fluid dynamic consequences of the induced streaming potential.

The present model is an augmentation of the standard BD approach in a sense that it invokes special considerations for capturing the nontrivialities associated with the transverse phoretic motion, thermal-gradient induced molecular diffusion, as well as the electroviscous influences on the confinement-induced steric interactions. We embed three distinctive and novel thermophysical features into our BD model, despite constraining ourselves to computationally tractable physical scales without explicitly resolving the solvent details. First, we introduce extended considerations to capture the consequences of electroviscous effects, originating out of the advective back-electromotive transport of ionic species in the diffuse EDL. On confinement-induced HI of flexible molecules. Second, we accommodate additional wall-head interactions in the forms of van der Waals and EDL forces as well as steric and solvation effects, within the framework of the BD simulations. Third, we introduce an upscaling approach for capturing the effect of temperature-gradient induced phoretic transport (also known as the Ludwig–Soret effect) in our BD based formalism, which gets more emphatically manifested under strong viscous dissipation influences that are routinely prevalent in nanofluidic channels.

Addressing the underlying physics behind the above highly interconnected and complicated issues through an integrated approach in the framework of the present augmented BD model, we focus our investigation toward assessing certain nontrivial implications of the streaming potential on the strength of the off-center peaks in the polymer density distribution in nanofluidic channels. In effect we demonstrate that such peak formation may be a complex nonlinear interplay between streaming potential effects, externally imposed pressure gradients and/or electrical fields, near-wall interaction mechanisms, confinement-induced HI, and diffusophoretic transport, which dictates a nontrivial chain center of mass distribution in nanoscale confinements. We subsequently extend these considerations to discover a paradigm of electrohydrodynamically focused augmented confinement strengthening effects for efficient molecular stretching, which are otherwise realizable only through substantially more reduced channel dimensions. This, in essence, establishes a yet unrevealed paradigm of realizing complex biophysical feats, an effect which may not otherwise be realized except for ultrathin channel dimensions that may be virtually impossible to achieve with precise reproducibility, in practice, even by employing the most sophisticated nanofabrication techniques.

The outline of the remaining part of this paper is as follows. In Sec. II we briefly discuss the fundamental fluid dynamic considerations invoked in our model. We then discuss in Sec. III the augmented BD model for studying the polymer transport in presence of the electroviscous flow field. In Sec. IV we discuss the necessary simulation details and postprocessing of the pertinent physical variables. In Sec. V we present the important results. First, we demonstrate the quantitative capabilities of the augmented BD model in capturing the thermophoresis-influenced macromolecular transport in nanochannels without resolving the solvent explicitly, by reproducing the results reported in Khare et al.14 We subsequently present our new results, depicting the relative strength of the different wall effects, alteration of the flow field due to the streaming effects, and the resulting polymer center of mass distribution. Finally in Sec. VI, we summarize significant implications and special biophysical consequences of our findings.

II. FLOW FIELD: ELECTROHYDRODYNAMIC AND THERMAL EFFECTS

We consider a single polymer molecule transported through a slitlike nanochannel of height 2H, length L, and width w (w ≫ H, L). The fluid, in general, may be subjected to a combined electro-osmotic and pressure-driven transport. A complete description of the flow physics involves a coupled solution of the EDL potential distribution (Poisson equation), ionic species conservation equation (Nernst equation), continuity equation, and momentum conservation equation (Navier–Stokes equation). These equations, their appropriate boundary conditions and their solutions are described below.

Poisson equation:

$$\nabla^2 \psi = -\varepsilon \sum N \frac{z_i n_i}{r_i}.$$  

Nernst equation:

$$\nabla \cdot (D_i \nabla n_i) = \nabla \cdot (\mu_{ep}(n_i) E).$$
This equation may be numerically solved by imposing the number density of ions and pressure, respectively. The symbols : the EDL potential, number density of the th ionic species, the net electrical field, the velocity field, and the present the EDL potential, number density of the th ionic species, electrophoretic mobility of the th ionic species, density of the fluid, and dynamic viscosity of the fluid, respectively.

For modeling the EDL transport in an unperturbed state, we assume the electrolyte to be a symmetric (i.e., ) solution of ionic charges. Traditionally for microchannel transport, the steady state ionic concentration distribution in the EDL may be derived from Eq. (2) in a simple analytic form, by neglecting the advection of ions and their finite size effects, and depicting a balance between the Coulombic and entropic interactions. However, such simple forms of the ionic species concentration distribution (the celebrated Boltzmann distribution) may turn out to be somewhat inaccurate for nanochannel transport. This is because of certain oversimplistic approximations in-built with the underlying theoretical description consistent with the Boltzmann distribution, which may not be appropriate for ultrathin confinements. The most important corrective measure that needs to be taken in the context of the present study is to account for the steric interactions and the corresponding entropic contributions to the free energy due to finite sizes of the ionic species. A minimization of the consequent free energy description, in effect, leads to the following modified description of the Boltzmann distribution:

where is the Steric or size factor (being the bulk number density of ions and being an equivalent length scale denoting the average size of the ions). It may be easily observed that when (i.e., size effect of the ions is not important), Eq. (5) reduces to the classical Boltzmann distribution. Equation (5) may be substituted in Eq. (1) to yield the following governing equation for EDL potential distribution:

This equation may be numerically solved by imposing the following boundary conditions at the channel centerline and the channel walls (located at and ):
where $\sigma$ is the electrical conductivity of the fluid. In Eqs. (9) and (10), $\zeta$ is the effective zeta potential, which may be evaluated by referring to the interfacial potential gradient-surface charge density relationship given by Eq. (6c).

It needs to be mentioned here that in addition to the electrokinetic effects described as above, the velocity field is also strongly coupled with the thermal effects prevailing in the flow domain, primarily attributable to the high rates of viscous dissipation in nanoscale confinements (which are, in turn, functions of the rates of deformation in the incipient flow conditions) that may give rise to appreciable temperature rises within the system, in addition to the Joule heating effects originating out of the net ionic currents obtained in presence of externally imposed electrical fields. The corresponding temperature distribution may be obtained by appealing to the energy equation, which may be expressed as

$$
\frac{D}{Dt}(\rho C_P T) = \nabla \cdot (k_{th} \nabla T) + \bar{\tau}_s \cdot \vec{D}_s + \sigma E^2, \quad (11)
$$

where $\sigma$ is the electrical conductivity of the fluid, $k_{th}$ is the thermal conductivity, and $\vec{D}_s$ is the rate of deformation tensor. Under the assumptions of steady and hydrodynamically fully developed background flow, and negligible variations in thermophysical properties within the range of temperature addressed in this work, the governing equation for temperature distribution at steady state simplifies to

$$
\rho C_P \frac{\partial T}{\partial t} = k_{th} \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + \mu \left( \frac{\partial u}{\partial y} \right)^2 + \sigma E^2. \quad (12a)
$$

Equation (12a) is solved numerically using a standard finite volume method, subject to the following boundary conditions:

$$
T|_{x=0,y} = T_{\text{inlet}}, \quad \left( \frac{\partial T}{\partial x} \right)_{x=L_y} = 0,
$$

$$
T|_{x,y=0} = T_W, \quad T|_{x,y=2H} = T_W. \quad (12b)
$$

where $T_m$ is the bulk mean temperature of flow. The temperature distribution, thus obtained, is employed for estimating the spatial variations in the local temperature-dependent thermal noise effects, depicting the effect of collision of the solvent molecules with the beads, consistent with the paradigm of BD simulations (as detailed in Sec. III). It is pertinent to mention in this context that physically, as the bulk temperature increases with increments in the flow strength (noting the considerable dominance of the viscous dissipation effects over axial advection effects in extremely narrow confinements), or equivalently increments in the shear rate (represented by the parameter $\omega$) for identically sized confinements, corresponding to a fixed wall temperature, the same would consequently give rise to enhanced strengths of the resultant theromphoretic effect as well as the effects of thermal noise, thereby influencing the dynamical evolution of the polymeric chain to a significant extent.

### III. AUGMENTED BROWNIAN DYNAMICS FOR POLYMER TRANSPORT

The flexible polymer molecule, dissolved in the viscous solvent, may be represented by an equivalent bead-spring model, with $N_b$ numbers of beads being connected through $N_s=(N_b-1)$ numbers of entropic springs. The dynamics of this chain may be represented by the stochastic differential equation

$$
dr = \left[ u + \frac{D}{k_BT} + \frac{\partial}{\partial \tau} \cdot \vec{D} \right] dt + \sqrt{2} \vec{B} \cdot dw, \quad (13)
$$

$$
\vec{D} = \vec{B} \cdot \vec{B}'. \quad (14)
$$

In Eq. (13), $\vec{r}$ is a vector containing $3N_b$ spatial coordinates of the beads constituting the polymer chain, $\vec{f}$ is a vector of length $3N_b$ denoting the non-Brownian nonhydrodynamic forces acting on each bead and $\vec{u}$ is a vector of length $3N_b$ representing the unperturbed fluid velocity field at the location of the bead. The three components of $d\vec{w}$ may be obtained from a real-valued Gaussian distribution having mean zero and variance $dt$. The movement of each segment of the chain disturbs the unperturbed background velocity field [described by Eq. (9)], which, in turn, affects the motion of the entire polymer, as manifested through mechanisms known as HIs. These interactions may be represented by a $3N_b \times 3N_b$ diffusion tensor, expressed as

$$
\vec{D}_{ij} = k_BT[6\pi\eta R_b]^{-1} \vec{I} \delta_{ij} + \Omega_{ij}], \quad (15)
$$

where $R_b$ is the bead hydrodynamic radius, and $\Omega_{ij}$ is the HI tensor that relates the velocity perturbation at a position $\vec{r}_i$ due to a point force exerted at $\vec{r}_j$. The Brownian forces, which appear in the last term of Eq. (13), are related to these velocity perturbations through the fluctuation-dissipation theorem [Eq. (14)]. When the polymer is in a confinement, the HI tensor is a linear combination of the interaction tensor in an infinite domain and the interaction tensor representing...
the correction that accounts for the constraints imposed by the confining walls. Thus $\Omega_{ij}$ can be expressed as:

$$\Omega_{ij} = \Omega^W(r_i, r_j) + (1 - \delta_{ij})\Omega^{OB}(r_i - r_j),$$

(16)

$$\Omega^{RPY}(r_i - r_j) = \frac{1}{8\pi\mu|r_i - r_j|} \left[ C_1 I + C_2 \frac{(r_i - r_j)(r_i - r_j)}{|r_i - r_j|^3} \right] \text{ if } |r_i - r_j| \geq 2R_b$$

$$= \frac{1}{6\pi\mu R_b} \left[ C'_1 I + C'_2 \frac{(r_i - r_j)(r_i - r_j)}{|r_i - r_j|^3} \right] \text{ if } |r_i - r_j| < 2R_b,$$

(17)

where

$$C_1 = 1 + \frac{2R_b^2}{3|r_i - r_j|^2}, \quad C_2 = 1 - \frac{2R_b^2}{|r_i - r_j|^2},$$

$$C'_1 = 1 - \frac{9|r_i - r_j|}{32R_b}, \quad C'_2 = \frac{3|R_i - r_j|}{32R_b}.$$

(18)

To retain the symmetric positive semidefiniteness of $D$ despite this replacement, $\Omega^W_{ij}$ may be modified as

$$\Omega^W_{ij} = 0.5(\Omega^W_{ij} + \Omega^W_{ji}).$$

(19)

The wall hydrodynamic interaction tensor $\Omega^W$ is such that the velocity perturbation it creates due to a point force $f(x_i)$ located at a point $x_i$ is

$$v^W_w(x_i, x_j) = \Omega^W(x_i, x_j) \cdot f(x_j).$$

(20)

This perturbation may be obtained by solving the following boundary value problem:

$$-\nabla p + \mu\nabla^2 v^W_w + \left( \sum_{N} z\rho_i \right) E = 0, \quad \nabla \cdot v^W_w = 0$$

(21)

subject to

$$v^W_{RPY} + v^W_w = 0 \text{ at the walls.}$$

(22)

The $i$th column of $\Omega^W(x_i, x_j)$ can accordingly be evaluated as

$$\begin{bmatrix} \Omega^W_{1i} & \Omega^W_{2i} & \Omega^W_{3i} \end{bmatrix}^T = \frac{1}{f_i} v^W_w,$$

(23)

where $f_i$ is a point force acting along $x_i$ and located at $x_j$.

The nonhydrodynamic and non-Brownian force $f$ appearing in Eq. (13) is composed of interbead spring force, force arising from the finite rigidity of the chain, bead-bead dispersion-repulsion interaction force captured by standard LJ potential, mutual Columbic electrostatic interaction force between the charged beads, electrophoretic force due to interaction of charged beads with the electric field (applied and induced) present in the system, bead-wall interaction forces, and force due to Ludwig–Soret effect or thermophoresis. We present the details of these interaction forces below, pertinent to the considerations made in the present formalism.

The spring force between the adjacent beads may be modeled using wormlike chain approximation, such that

$$f^s_i = \frac{k_BT}{2b_i^2} \left[ \left( 1 - \frac{|r_i - r_j|}{q_0} \right)^{-2} - 1 + 4 \frac{|r_i - r_j|}{q_0} \right] \frac{|r_i - r_j|}{|r_i - r_j|}.$$

(24)

Here $f^s_i$ represents the spring force exerted on the bead $i$ by the bead $j$, $b_i$ is the Kuhn length of the polymer chain, $q_0$ is the maximum extension of the molecule (expressed as $q_0 = N_{K,S}b_k$, with $N_{K,S}$ being the number of Kuhn segments per spring). The finite rigidity of the chain may be accounted by appealing to the harmonic bending potential between the adjacent beads

$$U^\text{bend}_{ij} = 0.5k_s \{\text{arccos}(\hat{b}_{ij} \cdot \hat{b}_{ij})\}^2,$$

(25)

where $\hat{b}_{ij} = (r_{i+1} - r_i)/|r_{i+1} - r_i|$, and $k_s$ is the constant of rigidity. The bead-bead dispersion-repulsion force may be characterized by standard LJ interaction, expressed as

$$f^{\text{LJ}}_{ij} = 4\varepsilon_{\text{LJ},b} \left[ \left( \frac{12\sigma_{\text{LJ},b}^6}{|r_i - r_j|^13} - \frac{6\sigma_{\text{LJ},b}^6}{|r_i - r_j|^7} \right) \frac{r_i - r_j}{|r_i - r_j|} \right] \text{ for } |r_i - r_j| \leq 2^{1/6}\sigma_{\text{LJ},b}$$

$$= 0 \text{ for } |r_i - r_j| > 2^{1/6}\sigma_{\text{LJ},b},$$

(26)
where \( \varepsilon_{1,1,b} \) and \( \sigma_{1,1,b} \) are LJ parameters corresponding to the beads. The force due to interbead Columbic electrostatic potential for bead \( i \) may be expressed as:\[ f_c = -\sum_j \frac{Q_b^2}{\lambda_D^2} \exp \left( -\frac{|r_i - r_j|}{\lambda_D} \right) \frac{r_i - r_j}{|r_i - r_j|}, \] (27)

where \( Q_b \) is the charge on the bead, \( \lambda_D \) is the Debye Layer thickness, and \( l_B = e^2/4\pi \varepsilon_0 k_B T \) is the Bjerrum length. The characteristic length scales are few nanometers and may be expressed in terms of the bead-bottom wall separation distance \( s_i \) as the zeta potential of the bead surface and \( h_s \) is the separation distance of the bead from the channel bottom wall.

Also in Eq. (29), \( f_{\text{DL}} \) is the van der Waals force of interaction between the particle and the channel walls, expressed as:\[ f_{\text{DL}} = \begin{dcases} 
\frac{32eR_b}{\lambda_D^2} \left( k_B T \right)^2 \frac{\tanh \left( \frac{\zeta_{bs}}{4k_B T} \right) \tanh \left( \frac{\zeta_{bb}}{4k_B T} \right)}{1 + \frac{2R_b}{\lambda_D + 1} \tanh^2 \left( \frac{\zeta_{bb}}{4k_B T} \right)} \left[ \exp \left( -\frac{h_s}{\lambda_D} \right) - \exp \left( -\frac{2H - 2R_b - h_s}{\lambda_D} \right) \right] \\
\frac{1}{6} \left( \lambda + 3h_s \right)^2 \left[ \ln \left( \frac{h_s + 2R_b}{h_s + 2R_b} \right) - A \left( \frac{\lambda}{\lambda + 3h_s} \right) \frac{2R_b^3}{3h_s^3(h_s + 2R_b)^2} \right] - A \left( \frac{\lambda}{\lambda + 3h_s} \right) \frac{2R_b^3}{3h_s^3(h_s + 2R_b)^2} \\
\frac{1}{6} \left( \lambda + 3(2H - 2R_b - h_s) \right)^2 \left[ \ln \left( \frac{2H - h_s}{2H - 2R_b - h_s} \right) - \frac{2R_b}{2H - 2R_b - h_s} \frac{2H - R_b - h_s}{2H - h_s} \right] + A \left( \frac{\lambda}{\lambda + 3(2H - 2R_b - h_s)} \right) \frac{2R_b^3}{3(2H - 2R_b - h_s)^2(2H - h_s)^2} 
\end{dcases} \] (30)

where \( A \) is the Hamaker constant for interaction between the bead and the wall with an intervening liquid medium, \( \lambda \) is the “London characteristic wavelength” (here taken as 100 nm), and \( \tilde{s} \) is a constant (here taken as 11.16). We also account for the bead-wall Steric repulsion, expressed as:\[ f_{\text{steric}} = -\frac{5\varepsilon_0 k_B T}{(\gamma - H)^3} \frac{\gamma_j}{l_0} \] (32)

where \( \gamma_j \) is the transverse coordinate of the bead and \( l_0 \) is the equilibrium bond length. The short-range solvation interactions result from the disruption of the layering of solvent molecules in between the bead surface (facing the wall) and the wall. The characteristic length scales \( (l) \) over which the solvation forces become active is typically of the order of few nanometers and may be expressed in terms of the bead-bottom wall separation distance \( h_s \), as:\[ f_{\text{solv}} = U \left( \frac{l}{\gamma_h} + \frac{1}{\gamma_s} + \frac{1}{\gamma_0} \right) \exp \left( -\frac{h_s}{l} \right) \\
- U \left( \frac{l}{(2H - h_s)^2} + \frac{1}{l} + \frac{1}{2H - h_s} \right) \exp \left( -\frac{2H - h_s}{l} \right), \] (33)

where \( U \) is the solvation interaction energy. Another ultrashort range interaction potential comes into play because of the straining in the chemical bonds between the liquid molecules and the solvation-induced layer structure close to the walls. This potential may be mathematically approximated as:\[ f_{\text{strain}} = -\frac{E_e \gamma_0^2}{2} \left[ \exp \left( -\frac{h_s}{l} \right) - \exp \left( -\frac{2H - h_s}{l} \right) \right], \] (34)

where \( E_e \) is the elastic modulus of the solid phase of the liquid (which may be heterogeneously nucleated to form a solid-like layered structure adhering to the substrate) and \( \gamma_0 \) is
the strain in the first monolayer (typically ranging between 0% and 5%).

Finally, we consider a possible thermophoretic migration of molecules caused by viscous dissipation induced appreciable local temperature gradients prevailing in the nano-fluidic systems. By integrating the Smoluchowski equation, a thermodynamically consistent expression for the resultant thermal (Soret) diffusion coefficient \( D_T \) may be obtained in the following form:

\[
D_T = D_0 \frac{\rho_b}{T} \left[ \alpha_T \phi_b + O(\phi_b^2) \right],
\]

(35)

where \( \rho_b \) is the number density of the polymer beads, \( T \) is the absolute temperature, \( \phi_b \) is the bead volume fraction, \( D_0 = k_B T / 6\pi \eta R_b \), and \( \alpha_T \) is a leading-order virial coefficient.\(^{45}\)

We account for the consequent thermophoretic transport by incorporating an additional forcing term \( 1 / \rho_b (-D_T \nabla T) dt \) in the stochastic equation of motion of the polymer chain. On the basis of identical considerations, \( D_{ij} \) may also be modified to account for thermal gradients prevailing in the system, by multiplying the same with the correction factor \( [1 + \alpha_m \phi + O(\phi^2)] \), where \( \alpha_m \) is a leading-order virial coefficient. It needs to be mentioned in this context that the effects of the thermophoretic forcing term, \( 1 / \rho_b (-D_T \nabla T) dt \), may get significantly enhanced with increments in the effective shear rate (or, equivalently We), by virtue of more prominent viscous dissipation effects in the system. Thus, the polymer dynamics is strongly coupled with the background thermofluidic transport, more prominently for ultrathin confinements characterized with high rates of deformation in the flow.

IV. SIMULATION DETAILS

We integrate the governing equation describing the trajectory of the individual beads [Eq. (13)] using explicit forward Euler scheme. It can be seen that the bead trajectory has a two way dependence on the flow field acting at the bead center. First, there is a direct dependence with the motion being augmented by the unperturbed background flow strength at the particle center. There is also an implicit dependence through the perturbed velocity components \( \vec{v}_{\text{RPY}} \) and \( \vec{v}_{\text{w}} \) which depend on the effective drag force at the particle center. This drag force results from the flow field that is a combination of the unperturbed background flow and the flow resulting from the disturbance induced by the wall hydrodynamic interactions. This disturbed component of the flow field may be calculated through the following set of equations:

\[
- \nabla p + \mu \nabla^2 \vec{v}_{\text{w},\text{bf}} + \rho_b \vec{E} = 0, \quad \nabla \cdot \vec{v}_{\text{w},\text{bf}} = 0
\]

subject to

\[
\vec{v}_{\text{w},\text{bf}} = - \vec{v}_{\text{RPY}} \text{ at the walls},
\]

(36)

where \( \vec{v}_{\text{w},\text{bf}} \) is the wall induced perturbation to the background flow.

For each time step, we assume that for the first iteration \( \vec{v}_{\text{w},\text{bf}} = \vec{0} \), i.e.,

\[
\vec{v}_{\text{bf}} = \vec{u},
\]

(38)

where \( \vec{v}_{\text{bf}} \) denotes the background flow velocity and decides the value of the drag force. This may be used to calculate \( \vec{v}_{\text{RPY}} \) (at the same iteration level) as

\[
\left( \vec{v}_{\text{RPY}} \right)_{y=0,2H} = - \sum_{j=1}^N (1 - \delta_{ij}) \Omega_{ij}^{\text{RPY}} (\vec{r}_i - \vec{r}_j) \cdot \vec{f}_{\text{drag}}
\]

(39)

(with \( y = 0, 2H \) for bottom and top walls).

This \( \vec{v}_{\text{bf}} \) may, in turn, be used to obtain the drag force and hence \( \vec{v}_{\text{RPY}} \) at the same iteration level, through Eq. (39). In this way, inner iterations may be continued (at a given time level) until \( \vec{v}_{\text{bf}} = \vec{u} + \vec{v}_{\text{w},\text{bf}} \) ceases to alter appreciably (with a relative error of less than 0.01% between successive iterations).

The various simulation parameters used in the present study (all these values are referenced with respect to the pertinent LJ scales for typical water molecules: \( \sigma_{\text{LJ}}, \rho = 0.316 \text{ nm}, m = 2.99 \times 10^{-26} \text{ kg}, \text{ and } \epsilon_{\text{LJ}} = 0.65 \text{ kJ/mol} \) are as follows: \( \rho \text{density} = 0.6, T_{\text{wall}} = 1.5, 2H = 18, \sigma_b = 0.6965, \text{ chain mass fraction} = 0.0116, \text{ number of beads in a chain } (N_b) = 20, A = 0.9283, l_b = 1, D_0 = 0.0072, \sigma_T = 0.7538, \sigma_m = 0.7538, E_0 = 500, \tau = 3.159, \epsilon_b = 0.04, \text{ and } k_b = 2.5. \text{ We apply periodic boundary conditions along } x \text{ and } y \text{ directions, with a box dimension of } 13. \text{ The time step size and simulation duration are } 0.0025 \text{ and } 144 \times 10^6 \text{ LJ time units [one LJ time unit corresponds to } \sqrt{(m \sigma_{\text{LJ}}^2 \epsilon_{\text{LJ}})} = 1.66 \times 10^{-12} \text{ s}], \text{ respectively. It is important to mention here that we adjust the simulation parameters to obtain a relaxation time of } 281 \text{ LJ units. We parametrize the effective Weisenberg number } (\text{We}) \text{ as } \text{We} = \gamma_{\text{eff}} A, \text{ where } \gamma_{\text{eff}} \text{ is the effective shear rate expressed as } \gamma_{\text{eff}} = u_{\text{max}} / H \text{ (} u_{\text{max}} \text{ being the maximum velocity of the background Poiseuille flow, or combined Poiseuille and external field electro-osmotic flow) and } \lambda_i \text{ is the chain relaxation time (} \lambda_i \text{ may be obtained by combining the Zimm model for friction force on polymer drags with the center of mass diffusion coefficient; for the assumed } \rho \text{ and } T_{\text{wall}} \text{ values, this results in } \lambda_i = 281 \text{ LJ units).} \text{ We compute one important measurable parameter, namely, the bead center of mass density, as follows. First, the channel height may be divided in } N_{\text{bin}} \text{ number of divisions (or bins) and center of each division } (y_{c,i}) \text{ may be calculated. At each time step, the bin to which the center of mass of the chain belongs may be determined, and the number count of the respective bin } (N_i) \text{ may be increased by one. At the end of simulation, probability of center of mass falling within a designated bin may be evaluated as } \text{p}_i = N_i / \sum_{i=1}^{N_{\text{bin}}} N_i. \text{ Subsequently, the bulk density } (\rho_b) \text{ and the chain center of mass density } (\rho_{\text{CM}}) \text{ may be calculated as}
V. RESULTS AND DISCUSSION

We first demonstrate our results for a special case in which we switch off the externally imposed electrical field and the transverse electrophoretic effects in the generalized model to be zero. In conjunction, we first neglect the streaming potential influences, so as to exactly recover the simulation test bench as provided by Khare et al., consistent with the simulation data mentioned in Sec. IV. Under these conditions, the resultant chain center of mass density profile, as obtained from the present extended BD model, agrees well with the corresponding MD simulation predictions of Khare et al., both for the equilibrium case \( \text{We}=0 \) (see Fig. 1), as well as for the cases with background pressure-driven flow [see Fig. 2(b)]. In Fig. 2(a), we plot the transverse velocity of the beads (in dimensionless form) on account of Soret effects \( v_{\text{Soret}} \) with varying \( \text{We} \). From Fig. 2(a) it is revealed that the transverse thermophoretic transport due to Soret effects (as a consequence of the local temperature gradients due to viscous dissipation effects) get strengthened with increasing \( \text{We} \). On the other hand, higher \( \text{We} \) values (essentially higher flow strengths) imply the formation of more prominent hydrodynamically induced depletion layers adhering to the wall. Chains within this thin layer are stretched to a greater extent out of steric constraints, since only highly elongated molecules fit effectively near the walls. Despite this, the highly stretched chains migrate to the centerline faster than the weakly stretched ones. Further, the chains are severely compressed against the wall at high shear rates as well as due to strong layering of the solvent near the walls, so that their extensional fluctuations get somewhat arrested. Consequently, the chain width in the \( y \)-direction becomes comparable to the bead-wall interaction length scale. The general features of nonmonotonicity in the chain density profiles and multiple peaks [Fig. 2(b)] may be fundamentally attributed to a delicate balance between the Brownian migration away from the centerline on account of hydrodynamic coupling with the spatial variations in the molecular conformational distribution and the transverse diffusophoretic influences along with other confinement-induced wall-specific interactions (including wall-repulsive HI). In addition, for pressure-driven flows, gradients in the deformation rate across fluid layers lead to differential stretching of the polymer chains, resulting in a net gradient in the chain mobility. This effect adds to the relative strength of the wall-attractive influences and may become substantial in locally equilibrating the strong Soret effects that are aggravated by high local tem-

\[
\rho_b = \frac{\sum_{i=1}^{N_{\text{bin}}} \rho_{b,i} c_i p_i}{\sum_{i=1}^{N_{\text{bin}}} c_i p_i},
\]

\[
\rho_{CM} = \frac{p_1}{\rho_b}.
\]

FIG. 1. Chain center of mass density profiles for \( \text{We}=0 \); present BD simulations are compared to reported MD data (Ref. 14). Typical magnitudes of uncertainty are shown for BD simulation results.

FIG. 2. (a) Transverse velocity (made dimensionless with \( u_{av,p} \)) where \( u_{av,p} \) is \( u_{av,p} = \int_0^H u_p dy / \int_0^H dy \) of the beads due to Soret effect for different values of \( \text{We} \) shown for the bottom half of the channel. Sign (+) of the velocities indicates that the beads are pushed toward the centerline due to the Soret effect. (b) Chain center of mass density profiles; present BD simulations are compared to reported MD data (Ref. 14). Typical magnitudes of uncertainty are shown in Fig. 1.
temperature gradients (on account of significant viscous heating in narrower confinements and high We), so as to give rise to multiple off-center peaks in the resultant chain density profiles. These observations agree quantitatively with the results from the previous MD simulations, as evident from Fig. 2(b). This remarkable agreement of the present BD based predictions with the reported benchmark MD solutions essentially provides a validated simulation platform, based on which certain critical propositions exclusively considered in the present study may be comprehensively addressed, as outlined in the subsequent discussions.

Next, we consider in addition the streaming effects corresponding to the pressure-driven background flow (with no externally applied electric field), along with the other considerations made in producing Fig. 2, so that there is a back-electrokinetic transport due to the induced electrical field on account of the advection of ionic species with the pressure-driven flow. Such effects are virtually inevitable for flows in narrow confinements, though not explicitly considered in the previous studies on polymer transport in microchannels or nanochannels. Further, for imparting realistic biophysical perspectives to the present study, we consider the beads to be charged, thereby incurring additional electrophoretic effects as well. Interestingly, such electrophoretic effects may be operative even if there is no externally imposed electrical field, because of the influences of the streaming potential field. Although the induced streaming field may be elusively small in many cases, its implication becomes progressively more significant in nanochannel dynamics where the EDL effect tend to protrude significantly into the bulk. The primary consequence of this in perspective of the present study is that it introduces its own opposing velocity profile. This perturbs the original pressure-driven velocity profile to a significant extent, so that there may be a drastic reduction in the strength of the centerline velocity, leading to a consequent reduction in shear rates over the system length scale [see Fig. 3(a)]. The induced streaming field strengthens with increments in the wall charge density and the EDL thickness (or with decrements in the bulk ionic number density $n_0$). Although in addition, the streaming field induced wall-adjacent local backflow regions result in high shear gradient locations close to the no-slip boundaries [see Fig. 3(a)], such locations are inaccessible due to bead-wall volume exclusions, and are hence inconsequential in dictating the polymer chain density distribution. Importantly, for the transport of an ionic solution in a nanochannel, the value of We as prescribed solely on the consideration of a pressure-driven flow may turn out to be somewhat elusive in revealing the actual state of straining, since it disregards a reduction in $u_{\text{max}}$ as a consequence of the streaming potential induced back-flow effects. For the same We value, lowering of effective shear due to streaming potential implies that the formation of a hydrodynamically induced depletion layer adhering to the walls is relatively less favored. However, a reduced effective shear rate causing an equivalent lowering in the chain mobility ensures a less emphatic push on the chains away from the centerline toward the direction of increasing straining. The later gets dynamically balanced with a reduced strength of the Soret effect as well, thereby effectively pushing the chain toward the centerline. Consequently, the randomness in molecular migration does not get totally outweighed and there is a strong tendency to equilibrate the polymer density distribution in the bulk, leading to very weak off-center peaks [see Fig. 3(b)], unlike the prominent ones that are obtained without the consideration of streaming effects. The nonlinear coupling between the electrically and nonelectrically induced forcing mechanisms, as manifested for such cases, may be more fundamentally appreciated by noting that drifts of molecules normal to the imposed streamlines have a Brownian contribution, which arises from the spatial variations in the HI. Wall effects, in addition, tend to introduce their own gradients in HI, as influenced by the perturbation velocities due to streaming potential effects. It also needs to be noted here that local repulsive interactions between charges separated by less than one Debye length in the con-
tour may increase the effective persistence length of the molecular chains. On the other hand, charges greatly separated in the contour introduce repulsions between back looping segments, implying a greater effective excluded volume. Such additional repulsive wall-chain interactions are more significant at low ionic strengths primarily due to entropic depletion interactions. The underlying consequences are even more dramatic and stimulating as the wall surface charge density is increased further. For such cases, the effects of low ionic strengths and high surface charge densities may combine together in augmenting the streaming field to such an extent that the strengths of the off-center peaks are substantially diminished, resulting in an approximately uniform distribution of polymer center of mass density [see Fig. 3(b)]. Thus, in effect, we may extend and somewhat modify the conclusions of Khare et al. in the sense that the polymer density distribution in a nanochannel Poiseuille flow is not necessarily a sole function of the shear rate gradient characteristics of the original background flow, but is an ultimate consequence of a complicated nonlinear interaction between the established background flow and the induced streaming electro-osmotic backflow. Ionic strength of the solution as well as the nanochannel surface charge density, indeed act as two important parameters in dictating the polymer chain distributions in such cases.

The apparently well-resolved physical picture, portrayed as above, may get dramatically altered altogether, in case the background pressure-driven flow is supplemented with an opposing external electro-osmotic transport. The relative strength of these two flow fields is governed by a parameter $K_{rat}$ defined as $u_{HS}/u_{P,max}$, where $u_{HS}$ is the Helmholtz–Smoluchowski velocity. The pressure gradient and the imposed electric field are so chosen that the resultant effective We remains constant at 223, for different values of $K_{rat}$. On the other hand, appropriate choices of the parameter $K_{rat}$ may ensure that the imposed electrical field, acting in tandem with the induced streaming field, interacts with the imposed pressure gradient in a manner so as to enhance the effective shear rates, which would not have otherwise been possible under the sole influences of the combined pressure-driven and electro-osmotic flows neglecting the streaming potential effects. In this context, Fig. 4(a) demonstrates the proposition that the streaming potential may effectively act as a catalyst toward ensuring that the presence of an applied opposing electric field may effectively enhance the shear rates in the resultant flow structure. Such augmented shear rates may shift the dynamic balance between the wall-directed transport on account of an enhanced chain mobility gradients and a counterbalancing transport due to augmented Soret effects, leading to the formation of steeper off-center peaks while satisfying the overall mass conservation [see Fig. 4(b), in which the density profiles are represented for favorable $K_{rat}$ values; the rationale behind such selection of parameters is discussed later]. The consequent creation of a deeper depletion layer adhering to the channel walls may be dramatic and phenomenal, essentially implying that the polymer chain is effectively focused through a narrower confinement than what is indicated by the physical nanochannel dimensions. These effects are perpetual and cumulative in nature, since effectively narrower channels also give rise to more prominent confinement-induced HI, resulting in greater chain mobility gradients as well as enhanced diffuse-phoretic transport on account of augmented rates of viscous dissipation.

It is important to observe from Fig. 4(a) that larger $K_{rat}$ values imply perpetually enhanced shear rates, by virtue of creating an enhanced counterflow in relation to what could have been achieved with a sole streaming potential effect without the consideration of any imposed opposing electro-osmotic transport. However, such increments in $K_{rat}$ values should not be indiscriminate, by virtue of practical implementation constraints and from energetic efficiency considerations of the system design. In this perspective, the role of streaming potential may be critical and decisive, in a sense that with its enhanced strength in cases of nanochannel flows...
(typically attributed with high surface charge density values and thick EDLs), it may permit a relatively low strength of the applied opposing electrical field in achieving identical rates of shear that would have otherwise necessitated substantially higher values of the external electrical field for cases in which the streaming effects are otherwise inconsequential. Thus, the streaming effects may play a favorable role in such propositions, by augmenting the effective confinement without necessitating the enhancements in $K_{rat}$ beyond a threshold limit. Hence, for a nanoconfined polymer, combined pressure and electro-osmotic transport in an opposing sense, consistent with a judiciously selected value of $K_{rat}$, may be used as an efficient design parameter toward ensuring that the streaming effects may be best utilized in forcing the polymer chain through a much strengthened effective confinement than that suggested by the geometric and other physical constraints. This qualitative consideration may be translated into an effective quantification by noting that the Soret effects, which play pivotal roles toward dictating the locations and strengths of the off-center peaks, are in turn strongly dependent on the cross stream velocity gradients (these are physically interlinked through the viscous dissipation mechanisms, as discussed earlier). In an effort toward exploiting the corresponding effects to the most favorable extent, we may define a parameter named gain factor ($G$), as follows:

$$G = \max(du_{tot}/dy/du_{p}/dy) = \max(du_{tot}/du_{p}), \quad (44)$$

where $du_{tot}/dy$ and $du_{p}/dy$ are the transverse gradients induced by the resultant flow velocity considering all the pertinent influences, and the corresponding gradients obtained from the sole consideration of the Poiseuille flow effects, respectively. Physically, the parameter $G$ signifies amplification in the Soret effects due to the consideration of streaming potential and the externally imposed opposing electric field in reference to the applied pressure gradient. As expected, the value of $G$ perpetually increases with increments in $K_{rat}$ for a given set of $\sigma_{c}$ and $n_{0}$ values (see Fig. 5), following a consensus trend. However, as manifested in Fig. 5, the rate of change in $G$ with enhancements in $K_{rat}$ increases until it attains a critical value, beyond which $G$ increases linearly with $K_{rat}$. This critical value physically signifies the onset of a regime in which the externally imposed electrical field grossly overweights the influence of the induced streaming potential and almost solely decides the trends in the resultant flow structure. Although enhancing the strength of the applied electric field beyond this point would still give rise to a further reduced effective confinement, the same may not be energetically favorable. On the other hand, increments in values of $K_{rat}$ until the critical limit may be energetically effective and efficient, since that exploits the favorable consequences of the spontaneous generation of streaming potential to the best possible extent for which one need not pay any additional expenses.

**VI. CONCLUSIONS**

In this paper we have demonstrated through augmented BD simulations that complex interactions between streaming potential and other confinement-induced electrohydrodynamic interactions in nanochannel flows induce additional dependence of polyelectrolyte chain migration on the ionic concentration of the buffer and the charge density of the substrate. We have invoked special considerations for capturing the consequences of transverse migration, temperature-gradient induced diffusophoretic transport, as well as streaming potential gradients on the dynamics of the polyelectrolyte chain. We have demonstrated that the combined effects of low ionic strengths and high surface charge densities may augment the streaming potential field to such an extent that the strengths of the off-center peaks are substantially diminished, resulting in an approximately uniform distribution of polymer center of mass density. Ionic strength of the solution as well as the nanochannel surface charge density have been identified as two most important parameters toward dictating the polymer chain distributions in such cases. In addition, we have demonstrated that dramatic alterations in the resultant transport phenomena may occur in case the background pressure-driven flow is supplemented with an opposing external electro-osmotic transport. In particular, we have elucidated that with electroviscous effects, the strength of the off-center peaks in the polymer chain density profiles are no longer sole functions of the shear rates imposed by the background pressure-driven flow. Rather, the streaming potential may nontrivially dampen out or amplify the off-center peaks, even if the effective shear based on the external flow regulation mechanisms is kept unaltered. Depending on the nature of the background flow, complex thermophysical interactions, therefore, may either make polymer density uniform across the channel or skew it at certain locations close to channel center. Such skewed distribution signifies a greater degree of confinement of the polymer, and the maximum contribution of the streaming effect toward realizing this may be ensured by a judicious selection of the relative strength of pressure-driven and external field electro-osmotic transport, for a specific combination of bulk ionic concentration and surface charge density.