Electrophoretic mobilities of counterions and a polymer in cylindrical pores

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We have simulated the transport properties of a uniformly charged flexible polymer chain and its counterions confined inside cylindrical nanopores under an external electric field. The hydrodynamic interaction is treated by describing the solvent molecules explicitly with the multiparticle collision dynamics method. The chain consisting of charged monomers and the counterions interact electrostatically with themselves and with the external electric field. We find rich behavior of the counterions around the polymer under confinement in the presence of the external electric field. The mobility of the counterions is heterogeneous depending on their location relative to the polymer. The adsorption isotherm of the counterions on the polymer depends nonlinearly on the electric field. As a result, the effective charge of the polymer exhibits a sigmoidal dependence on the electric field. This in turn leads to a nascent nonlinearity in the chain stretching and electrophoretic mobility of the polymer in terms of their dependence on the electric field. The product of the electric field and the effective polymer charge is found to be the key variable to unify our simulation data for various polymer lengths. Chain extension and the electrophoretic mobility show sigmoidal dependence on the electric field, with crossovers from the linear response regime to the nonlinear regime and then to the saturation regime. The mobility of adsorbed counterions is nonmonotonic with the electric field. For weaker and moderate fields, the adsorbed counterions move with the polymer and at higher fields they move opposite to the polymer's direction. We find that the effective charge and the mobility of the polymer decrease with a decrease in the pore radius. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4895397>]

I. INTRODUCTION

In the past few decades, transport properties of charged macromolecules through micro and nano-meter size channels have received broad interest due to their relevance in biological systems,¹ DNA sequencing technology,^{2–4} and due to challenges in their fundamental understanding.⁵ Nano-scale channels and pores are exploited in various studies such as artificial gels,⁶ microfabricated trap arrays for the separation of long DNA molecules,^{5,7} and translocation of various polyelectrolytes through solid state and protein pores.⁵ The physical behavior of macromolecules in narrow confinements deviates substantially from their bulk behavior, due to interplay of complex surface-polymer interactions,⁸ anisotropic hydrodynamic friction,^{9,10} and electrostatic interactions. Soft macromolecules under confinement exhibit interesting dynamical behavior such as suppression of diffusion,¹¹ cross-streamline migration,^{12,13} polymer-stretching,¹⁴ etc.

Inside the channel, the structural and dynamical properties of polyelectrolyte chains are governed by the interplay of hydrodynamic and electrostatic interactions, degree of confinement, and driving forces such as an electrical potential gradient or a pressure gradient along the channel. There are extensive experimental data reported in the literature^{15–25} related to different measures of the way a charged polymer undergoes translocation. The phenomenology of polyelectrolyte

translocation through a nanopore is quite complex and full of puzzles still to be understood. Even in the bulk, the molar mass independence of the electrophoretic mobility is still not completely understood,^{26–28} despite several theoretical and simulation attempts.^{29–34} The mobility of a polyelectrolyte chain inside a nanopore is strongly coupled to the behavior of the counterions trapped inside the pore, conformational changes due to confinement effects, and the hydrodynamic coupling between the solvent and the ions. Nonlinear effects set in under an externally imposed electric field.

The focus of the present study is to gain an understanding of the structural and transport properties of a polyelectrolyte chain along with the dynamics of counterions by accounting for the hydrodynamic and electrostatic forces present in a nanopore. We have performed coarse-grained molecular dynamics simulation of the polymer and counterions, by taking hydrodynamic interactions into account with the multiparticle collision dynamics method. We have monitored the binding/unbinding equilibria of counterions, average degree of ionization, radius of gyration and the mean square end-to-end distance of the polymer, diffusion coefficient of the center-of-mass of the chain, electrophoretic mobility of the polymer, and mobilities of adsorbed and unadsorbed counterions, all as functions of the strength of the external electric field and pore radius. Vivid details have emerged demonstrating collective nonlinear coupling among the counterions, polymer, electric field, and confinement.

This article is organized as follows: In Sec. II, we discuss the simulation method, and modeling of the

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polyelectrolyte and the explicit solvent by the multiparticle collision dynamics (MPC). All simulation results are presented in Sec. III. The results section is divided into several subsections, describing the binding time, effective charge, chain conformations, chain diffusion, electrophoretic mobility of the polyelectrolyte chain, and the mobility of counterions. Major conclusions are summarized in Sec. IV.

II. MODEL AND SIMULATION METHOD

We consider a single linear polyelectrolyte molecule with its monovalent counterions and solvent molecules, confined inside a uniform cylindrical pore under an externally imposed electric field (Figure 1). The polyelectrolyte chain and the counterions obey the respective Newton's equations along with the "no-slip" boundary condition with the solvent through the bead friction coefficient. The solvent molecules are treated explicitly by the multiparticle collision dynamics. The details of the solved equations and the chosen values of the parameters are as follows.

The polyelectrolyte chain is linear and is comprised of N_m soft spherical monomeric units, each of mass M and charge $-e$, where e is the electronic charge. Monomers are connected with the harmonic spring potential (U_b), given as

$$U_b = \sum_{i=1}^{N_m-1} \frac{k_s}{2} (r_{i,i+1} - l)^2, \quad (1)$$

where l is the equilibrium bond length, r_i is the position of the i th monomer, $r_{i,i+1} = |\mathbf{r}_{i+1} - \mathbf{r}_i|$ is the magnitude of bond vector, and k_s is the spring constant. The counterions are assumed to be identical to the polyelectrolyte monomers, except for the opposite sign of the charge $+e$. Excluded volume interactions among the monomers and counterions are taken into account by using repulsive, truncated, and shifted Lennard-Jones (LJ) potential (U_{LJ}), given as,

$$U_{LJ} = \frac{1}{2} \sum_{i,j} 4\epsilon_{LJ} \left[\left(\frac{\sigma}{r_{i,j}} \right)^{12} - \left(\frac{\sigma}{r_{i,j}} \right)^6 + \frac{1}{4} \right] \times \Theta(2^{1/6}\sigma - r_{i,j}), \quad (2)$$

where σ is the LJ diameter of the monomer, ϵ_{LJ} is the interaction energy and $\Theta(r)$ is the Heaviside step function ($\Theta(r) = 0$ for $r < 0$ and $\Theta(r) = 1$ for $r \geq 0$), N is the total number

FIG. 1. Snapshot of a polyelectrolyte (red beads) with counterions (blue and green beads) in a cylindrical pore of radius $R_p = 5$, for the polymer length $N_m = 50$ and Coulomb interaction strength $\Gamma = 3$. Only a portion of the pore is shown, and the solvent molecules treated by MPC dynamics are suppressed in the visual display.

of units which includes polymer monomers as well as all the counterions in the solution. All charged particles interact with the Coulomb potential U_c ,

$$U_c = \frac{1}{4\pi\epsilon} \sum_{i=1}^N \sum_{j>i}^N \frac{q_i q_j}{r_{i,j}}, \quad (3)$$

where q_i is $+e$ for the counterions and $-e$ for the polymer monomers, and the permittivity of the medium is $\epsilon = \epsilon_0 \epsilon_r$, with ϵ_r being the dielectric constant of the solution.

As the strength of the long ranged Coulomb interaction does not vanish in finite simulation boxes, special techniques involving periodic images need to be implemented in computing the electrostatic interactions.³⁵⁻³⁷ The Lekner summation,³⁶ and MMM2D and MMM1D methods³⁷ have been used to compute interactions between charged particles under confinement in 1D and 2D. We have adopted a slightly different approach to compute the long range forces in the present situation of a cylindrical pore which is periodic only in the x direction. In our simulations, we consider long pores in the periodic direction. Thus, we need only a few periodic images for the force calculation. In this way we can efficiently compute the forces between particles in the primary box and from their various periodic images. Since the pore is very long, we need to consider only a few periodic images of the primary box. Typically, only 20 periodic images are required to be considered from both sides of the pore in order to compute the pair forces within the accuracy of 10^{-4} , for a polymer length of 10. Nevertheless, the present method can be efficiently used only for long periodic channels and electrically neutrals systems. For simplicity of the calculations, dielectric constant of the solvent medium and the pore material is taken to be the same. Further, in electrophoresis, every charged particle is exposed to a constant external field $\vec{E} = E_0 \hat{e}_x$. The interaction potential (U_E) for charged particles with the external field is

$$U_E = \sum_{i=1}^N q_i \vec{E} \cdot \mathbf{r}_i. \quad (4)$$

Hydrodynamic interactions among the polymer beads and counterions are incorporated by the multi-particle collision dynamics. This method is an explicit-solvent based simulation technique, where the solvent is modeled by point particles with positions $\mathbf{r}_i$ and velocities $\mathbf{v}_i$, ($i = 1, \dots, N_s$). Their dynamics proceeds in discrete time increments of the collision time h with alternating streaming and collision steps.^{38,39} In the streaming step, the solvent particles, each of mass m , move ballistically with their respective velocities. Their positions are updated according to

$$\mathbf{r}_i(t+h) = \mathbf{r}_i(t) + h\mathbf{v}_i(t). \quad (5)$$

To define the multiparticle collision environment, the simulation box is partitioned into small cubic cells (MPC cells) of side length a . The solvent particles are sorted into these cells. During the collision, their relative velocities, with respect to the center-of-mass velocity of the cell, are rotated around a randomly oriented axis by an angle γ , i.e.,

$$\mathbf{v}_i(t+h) = \mathbf{v}_i(t) + (\mathcal{R}(\gamma) - \mathcal{I})(\mathbf{v}_i(t) - \mathbf{v}_{cm}(t)), \quad (6)$$

where $\mathcal{R}$ is the rotation matrix, $\mathcal{I}$ is the unit matrix, and $\mathbf{v}_{cm} = \sum_{j=1}^{N_c} \mathbf{v}_j / N_c$ is the center-of-mass velocity of the MPC cell with N_c particles. The details of the rotation matrix $\mathcal{R}$ are fully described in Ref. 40. Momentum and energy of each cell are conserved during the rotation. Conservation of momentum ensures that hydrodynamic behavior will emerge on larger length and time scales.⁴¹

Furthermore the no-slip boundary conditions are imposed at the channel walls. In order to implement the no-slip boundary conditions at the channel wall, we adopt a bounce-back rule. The velocities of the solvent particles are reversed, when they reach the wall, i.e., $v_i^\beta = -v_i^\beta$ where $\beta \in x, y, z$. The discrete nature of the spatial and temporal interaction of the solvent particles with the channel wall leads to finite slip at the boundaries. To suppress the slip at the boundaries, virtual particles are added in MPC cells at the wall.^{39,42} Velocities of the virtual particles are drawn from the Maxwell-Boltzmann distribution with zero mean at the same temperature as the solvent. The interaction of the solute particles with the wall is incorporated differently. We assume that the pore is made of similar particles as polymer monomers. Repulsive truncated Lennard-Jones interaction potential (Eq. (2)) is taken between the channel wall and monomers.

The interaction of the monomers with the solvent particles occurs during the MPC collision step. In this step, velocities of the solute particles are also included according to Eq. (6),^{39,43,44} with modified center-of-mass velocities of the cell, given as

$$\mathbf{v}_{cm}(t) = \frac{1}{mN_c + MN_c^m} \left(\sum_{i=1}^{N_c} m\mathbf{v}_i(t) + \sum_{j=1}^{N_c^m} M\mathbf{V}_j(t) \right). \quad (7)$$

Here, $\mathbf{V}_j$ is the velocity of j th monomer and N_c^m is the number of monomers in a given MPC cell. Thereby, momentum is redistributed between solvent and monomers in the same cell. Monomer velocities are now changed due to collision with the solvent. This gives correlated kick to the monomers. The collision cell length a is the shortest distance over which two monomers interact through the solvent. Thus a is the smallest length scale to resolve the hydrodynamic interaction in this model. Between two successive MPC steps many molecular dynamics steps are performed to update solute positions and velocities.

The equation of motion is scaled in basic MPC simulation units. Length is in units of average bond length of the polymer l and the MPC collision cell dimension is chosen to be the same, i.e., $a = l = 1.0$. Both the thermal energy $k_B T$ and mass of the solvent are taken to be unity. Time is scaled in units of $\tau = \sqrt{ml^2/k_B T}$. The transport coefficients of the MPC solvent depend on the collision time h , the rotation angle γ , and the average number of particles $\langle N_c \rangle$ per cell. For the solvent, we use the collision time $h = 0.1\tau$, rotation angle $\gamma = 130^\circ$, and the average number of fluid particles in a collision cell $\langle N_c \rangle = 10$. These parameters correspond to the solvent viscosity $\eta_s = 8.7\sqrt{mk_B T/l^4}$.^{45,46}

It is to be noted that the MPC method has successfully been used in equilibrium and non-equilibrium studies of various soft-matter systems such as polymers, polyelectrolytes,

colloids, and vesicles.^{33,34,38,39} Previous studies^{33,34} on dynamical properties of short polyelectrolyte chains have also shown that the use of MPC gives good agreement with experimental results.

For the polymer, we set $\epsilon_{LJ} = k_B T$ and the spring constant $k_s/(k_B T/l^2) = 5000$, the LJ diameter of monomers and counterions are taken to be, $\sigma/l = 0.8$ and their masses such that, $M = 10m$. We have taken spring constant $k_s = 5000$, so that even at very high field strength average bond length does not change.

We integrate Newton's equation of motion for the polymer monomers and counterions given by

$$M \frac{d\mathbf{V}_j}{dt} = -\nabla(U_{LJ} + U_b + U_c + U_E). \quad (8)$$

We have used the velocity Verlet algorithm to integrate the above equation with the time step $h_m = 5 \times 10^{-5}$. Furthermore, after every h time unit, monomers and counterions undergo collision with the solvent. During the collision, they exchange their momenta with the solvent so that the velocity $\mathbf{V}'_j(t)$ of the j particle after collision with the solvent is given by

$$\mathbf{V}'_j(t) = \mathbf{V}_j(t) + (\mathcal{R}(\gamma) - \mathcal{I})(\mathbf{V}_j(t) - \mathbf{v}_{cm}(t)). \quad (9)$$

After the collision, we update the position and velocity of the particles using their Newton's equation of motion.

The polymer length is varied from $N_m = 10$ –100, and the pore radius is varied in the range of $5l$ – $20l$. We always take the length of the pore to be twice the contour length of the polymer, i.e., $L_x = 2N_m l$. As will be described below, one of the major results of the present study is the varying extent of counterion adsorption to the polymer and the consequent effects on mobility, diffusion, and polymer conformation, depending on the extent of confinement, chain length, and the electric field. As a result, we have fixed the monomer concentration for all polymer lengths, by appropriately changing the pore length, for a given pore radius.

For simplicity, we assume that the solvent particles do not bear any charge. Thus, under the electric field $\bar{E}$, only the solute particles respond to the field. The electric field $\bar{E}$ is made dimensionless in units of $E = (E_0 l |e|)/k_B T$. The electrostatic interactions are characterized in terms of the Coulomb interaction strength $\Gamma = l_B/l$, where the Bjerrum length l_B defines the length over which the electrostatic interaction energy between two unit charged particles is equal to the thermal energy, $l_B = e^2/(4\pi\epsilon k_B T)$. We choose $\Gamma = 3.0$ in our simulations, which is close to the situation of a typical flexible polyelectrolyte in water at room temperature. Taking one unit length scale as $2.5 \text{ \AA}$ and Bjerrum length as $l_B = 7.5 \text{ \AA}$ which is close to the Bjerrum length of water at room temperature $T = 300 \text{ K}$ and the unit charge as $e = 1.6 \times 10^{-19} \text{ C}$, the range of applied electric field in the present simulations is in the range of 10^5 to 10^7 V/m , which is in the range of electric field applied in the study of various translocation experiments.^{15–25}

III. RESULTS

The size and shape, diffusion, and mobility of the polyelectrolyte chain under confinement and an external electric

field depend crucially on the dynamics of its counterions. The extent of adsorption of counterions on the polymer, which in turn determines the degree of ionization of the polymer, depends on the strength of the electric field and the pore diameter. First, we summarize the results on the counterion adsorption, followed by results on the size and shape of the polyelectrolyte by varying pore radius R_p and polymer length N_m in a salt-free solution. Finally, we present simulation data on the diffusion and electrophoretic mobility of the polymer along with the coupled mobility of the counterions. The release of adsorbed counterions by the electric field is shown to affect the onset of the nonlinear response regime for the polymer mobility.

A. Counterion dynamics and binding time

We have monitored the arrangement and dynamics of the counterions around the polymer under confinement. As in the case of a polyelectrolyte chain in unconfined solutions, there is an equilibrium with a certain number of counterions adsorbing on the polymer on an average. The average number of adsorbed counterions is dictated by the compromise between the electrostatic attraction between the polymer and the counterions, and the translational entropy of unadsorbed counterions. By following our earlier work,⁴⁷ we define a tube-like region (Figure 2(a)) around the backbone of the chain with a cut-off distance r_c as the distance of the closest approach for the counterion to the polymer. We have taken $r_c = 2l_B/(3k_B T)$ as the distance at which the electrostatic interaction energy of the adsorbed counterion equals the thermal energy. As illustrated in Figure 2(a), the counterions within r_c , denoted by the blue circles, are taken to be adsorbed and those outside r_c (such as the green circle in Figure 2(a)) are taken to be unadsorbed.

We have found that an adsorbed counterion undergoes a correlated stochastic motion around the polymer backbone. Once the counterion approaches the distance r_c , it quickly reaches the distance l and forms a temporary dipole bond with a polymer monomer and stays there for a while. As time proceeds, it either moves to a new monomer and follows the motion of that monomer or it goes away from the polymer. Figure 2(b) displays the closest distance of a counterion from the polymer as a function of time. When some counterions leave the polymer, some other counterions adsorb on the polymer. As a result, there is a continuous exchange of counterions around the polymer, although an average number of adsorbed counterions can be determined.

The duration of the time spent by an adsorbed counterion is a stochastic variable. We define the binding time of a counterion as follows. A counterion is called dynamically bound to the polymer, if it reaches a distance less than the bond length l . In computing the binding time, we start counting the time once the counterion has reached a distance less than r_c and we stop counting the time when it has gone a distance larger than r_c . There are two possibilities for the trajectory of the counterion between these two times. In one possibility, the counterion reaches a distance less than l before escaping out of r_c . Such trajectories are taken as binding events. In the other possibility, the counterion escapes out of r_c without ever reach-

FIG. 2. (a) Definition of adsorbed counterions on the polymer backbone. Red circles are polymer monomers, green is a free counterion, and blue circles are adsorbed counterions on the polymer. Black circles represent the cutoff radius r_c for each monomer. (b) Typical trajectory of a counterion near the polymer backbone in a cylindrical pore of radius $R_p = 5$ and $\Gamma = 3$ and polymer length $N_m = 50$. $R_{mc}(t)$ is the closest distance of a counterion from a polymer monomer at the dimensionless time t in units of l . Red and green lines show the first and second cutoff for the counterion binding. t_{b1} , t_{b2} , t_{b3} , and t_{b4} are binding times of the counterion. (c) Probability distribution of binding time t_b of a counterion to a polyelectrolyte for polymer length 10, 20, 40, and 80 in a channel of radius $R_p = 5$. Inset shows the scaled average binding time as a function of polymer length N_m .

ing l due to the thermal fluctuations taking it away from the polymer ($R_c > l$). We do not include such events as adsorbed events. In Figure 2(b), t_{b1} , t_{b2} , t_{b3} , and t_{b4} denote the binding times according to our definition. We have performed nearly 50 independent simulations for a given set of parameters to generate a distribution of the binding time.

The normalized probability distributions of the binding times for various polymer lengths ($N_m = 10, 20, 40$, and 80) are plotted in Figure 2(c) for $\Gamma = 3$, $R_p = 5$, and $E = 0$. The binding time t_b is scaled with the diffusion time $t_d = (\sigma/2)^2/(2D_0)$ of a free monomer in solution. We have taken D_0 as 0.017 in dimensionless units. For polymer lengths $N_m > 20$, the distributions look almost identical. We have also computed the average binding time $\langle t_b \rangle$ as a function of the polymer length. The inset of Figure 2(c) shows the average binding time as a function of N_m . The average binding time increases with the polymer length and reaches nearly a constant value for $N_m > 20$, where the chain end effects are negligible.

B. Effective charge

The effective charge of the polymer is different from its nominal charge due to the adsorption equilibrium between the counterions and the polymer, which in turn depends on the pore radius, chain length, and the electric field. By monitoring the trajectories of the counterions over time durations that are several orders of magnitude longer than the average binding time, we have computed the average number N_a of adsorbed counterions. The effective charge of the polymer is the difference between the total charge $Q_p = N_m(-e)$ and the charge neutralized by the adsorbed counterions, $Q_{eff} = -(N_m - N_a)e$. From the effective charge, we compute the degree of ionization of the polymer as $\alpha = Q_{eff}/Q_p = 1 - N_a/N_m$.

The inset of Figure 3(a) displays the degree of ionization of the polymer, α_0 , in the absence of the electric field, as a function of the polymer length N_m in equilibrium for $R_p = 5$ and $\Gamma = 3$. With increasing value of N_m , the degree of ionization of the polymer decreases and approaches an asymptotic plateau value for very large N_m values, in agreement with previous simulation results.^{33,48} The observed decrease in the degree of ionization and the asymptotic approach towards a constant value as the chain length increases is due to the progressively increasing spatial extension of the chain along the pore axis. After a threshold value of N_m for a given R_p , the chain conformations are essentially the same with the accompanying adsorption isotherms being the same. The asymptotic value of α_0 is determined by the volume of the pore and the Coulomb strength parameter Γ .

In the presence of an electric field, the distribution of counterions around the polymer is significantly modified. On average, the counterions are dragged away from the polymer by the externally imposed electric field resulting in an increase in the degree of ionization. By using the same scheme of Figure 2(a), we have computed the degree of ionization α of the confined polymer under the electric field E as well. Figure 3(a) displays the dependence of the degree of ionization α on the (dimensionless) electric field for various polymer lengths. The dependence of α on E is sigmoidal. Even for a weak electric field, the degree of ionization increases although only by a small amount. However, α reaches a saturation value for very large E values. It is clear that α and hence the effective polymer charge Q_{eff} are E -dependent. The electric field dependence of the degree of ionization depends further on the extent of confinement inside the pore, as shown

FIG. 3. (a) Dependence of the effective degree of ionization α of the polymer on the dimensionless electric field E for $R_p = 5$, $\Gamma = 3$, and various polymer lengths $N_m = 20$ (bullet), 40 (square), 50 (diamond), 80 (triangle up), and 100 (triangle left). Inset shows the effective degree of ionization α_0 , for $E = 0$, as a function of chain length N_m for $R_p = 5$ and $\Gamma = 3$. (b) Degree of ionization α of the polymer as a function of E for various pore radii shown in the legend for polymer length $N_m = 50$. Inset shows degree of ionization α_0 at $E = 0$ vs. pore radius R_p .

in Figure 3(b). In general, as the pore radius R_p decreases, the volume for realizing the translational entropy by the counterions is reduced, resulting in a higher counterion adsorption, namely, a less degree of ionization. As seen in the inset of Figure 3(b), when $E = 0$, the degree of ionization α_0 decreases as the pore radius R_p is reduced due to enhanced counterion adsorption. The dependence of α on E is also sigmoidal for the various pore radii simulated in the present study. Summarizing the above results, the effective polymer charge depends on both the electric field and pore radius, and cannot be taken as a fixed constant value in interpreting the data on electrophoresis experiments.

C. Conformation of polyelectrolyte

Under an external electric field the polymer chain undergoes substantial conformational changes. To characterize the effects of the external field and confinement on the conformational properties of the polyelectrolyte, we have computed the radius of gyration tensor of the polymer providing the

average size of the polymer in different spatial directions, which is defined by

$$G_{\gamma\delta} = \frac{1}{N_m} \left\langle \sum_{i=1}^{N_m} \Delta r_i^\gamma \Delta r_i^\delta \right\rangle, \quad (10)$$

where Δr_i is the position of i th monomer of the chain with respect to the center-of-mass, and $\gamma, \delta \in \{x, y, z\}$. In bulk, all the non-diagonal components are nearly zero in the absence of electric field. All diagonal elements are equal, i.e., $G_{\gamma\gamma} = G_{\gamma\gamma}^0 = R_g^0{}^2/3$, where R_g^0 is the average radius of gyration. Equilibrium conformational properties of a polyelectrolyte strongly depend on the Coulomb interaction strength Γ . In bulk solution, R_g^0 follows the scaling relation, $R_g^0{}^2 \sim N_m^{2\nu} l^2$. For weak Coulomb interaction strength $\Gamma \leq 1$, the polymer chain is stretched due to electrostatic repulsion among the polymer beads. $R_g^0{}^2$ scales with exponent $\nu \sim 1$, displaying the rod-like scaling behavior. However, for $\Gamma \gg 1$, the polymer chain collapses and the radius of gyration follows the scaling relation with the exponent $\nu \sim 0.33$.^{47,49} Using the present MPC dynamics accounting for the solvent molecules, we have recovered these results in the literature which were obtained without any explicit treatment of the solvent.

We have computed the radius of gyration of the polymer as a function of N_m and pore radius R_p , first in the absence of the electric field. Figure 4(a) illustrates the mean square radius of gyration $R_g^0{}^2$ (bottom curve) and the mean square end-to-end distance $R_{ee}^0{}^2$ between the polymer ends (top curve) as a function of N_m . R_g^0 and R_{ee}^0 increase with the polymer length. For $N_m \geq 20$, R_g^0 displays a rod-like behavior in the pore, i.e., $R_g^0{}^2$ and $R_{ee}^0{}^2$ follow the scaling relation $R_g^0{}^2 \sim N_m^{2\nu}$ with the power law exponent, $\nu = 1.0$. The ratio of $R_{ee}^0{}^2/R_g^0{}^2$ lies between 6.2–10, which increases with N_m in the range studied. Although structural properties of a polyelectrolyte inside the pore show the rod-like scaling relation, they acquire conformations quite similar to semi-flexible polymers.

Furthermore, we have investigated the influence of the electric field on polymer conformations inside a pore. Figure 4(b) displays the ratio of the mean square radius of gyration to its equilibrium value $R_g^2/R_g^0{}^2$ for various chain lengths N_m with increasing field strength for $R_p = 5$ and $\Gamma = 3$. Since the degree of ionization increases with E , the chain expands due to enhanced intra-chain electrostatic repulsion in addition to the stretching effects arising from the electric field. In order to account for the charge regularization due to the electric field, we have identified the variable EQ_{eff} as the key variable dictating the structure of the polyelectrolyte. Indeed, $R_g^2/R_g^0{}^2$ displays a universal behavior with the effective force $E|Q_{eff}|$ for all values of N_m studied. In the weak field strength, the polymer is weakly perturbed. In this narrow regime of weak E , the radius of gyration shows a linear dependence on E . In the high field limit, the counterions are stripped off the polymer backbone resulting in a strong intra-chain electrostatic repulsion. This leads to an extended chain conformation aligned along the electric field. Similarly the end-to-end distance of the polymer increases with E and displays a universal sigmoidal dependence on $E|Q_{eff}|$ as shown in Figure 4(c).

FIG. 4. (a) Mean square radius of gyration $R_g^0{}^2$ (square) and mean square end to end distance $R_{ee}^0{}^2$ (bullet) as a function of polymer length N_m in a channel at radius $R_p = 5$, $\Gamma = 3$, and $E = 0$. Dashed black line shows the N_m^2 dependence of the plot. (b) Normalized mean square radius of gyration $R_g^2/R_g^0{}^2$ of the polymer as a function of effective force $E|Q_{eff}|$ for various polymer lengths. (c) Normalized mean square end to end distance $R_{ee}^2/R_{ee}^0{}^2$ of the polymer as a function of effective force $E|Q_{eff}|$ for various polymer lengths.

We have also explored the effect of confinement on the structure of the polymer by varying the pore radius R_p . The inset of Figure 5(a) shows $R_g^0{}^2$ as a function of R_p for a given polymer length $N_m = 50$ for $E = 0$. Interestingly, for $E = 0$, we observe a non-monotonic dependence of R_g^0 on R_p .

FIG. 5. (a) Normalized mean square radius of gyration $R_g^2/R_g^0^2$ of the polymer as a function of external electric field $E|Q_{eff}|$ for various pore radii at polymer length $N_m = 50$. Inset shows equilibrium mean square radius of gyration $R_g^0^2$ as a function of pore radius R_p . (b) Normalized mean square radius of gyration longitudinal to pore axis $R_{gL}^2/R_{gL}^0^2$ of polymer vs $E|Q_{eff}|$. Inset shows the mean square radius of gyration transverse to the pore axis $R_{gt}^2/R_{gt}^0^2$. Legends show the pore radius for the corresponding plots.

For larger pore radii that are larger or comparable to R_g , there is an increase in the effective concentration of counterions as R_p is decreased. An increase in the counterion concentration in the pore results in the adsorption of more counterions on the polymer backbone, which in turn leads to less intra-chain electrostatic repulsion. Therefore R_g decreases with an increase in R_p for larger values of pore radii. On the other hand, when the pore radius is smaller than the radius of gyration of the polymer, the confinement causes more and more elongation of the polymer as the pore radius is increased. Although, the number of adsorbed counterions is increasing, the polymer-wall interaction dominates and leads to an increase in the size of the polymer length with R_p for smaller values of pore radii.

The role of pore radii on the dependence of the ratio of the longitudinal components of the radius of gyration in the presence and absence of the electric field on E is given in Figure 5(b). The relative change in R_{gL}^2 increases with increasing R_p . For $R_p > R_g^0$, $R_{gL}^2/R_{gL}^0^2$ is almost independent of R_p . In the radial direction, the polymer is compressed with the

field and the compression increases with E due to chain alignment along the pore axis. Inset of Figure 5(b) shows $R_{gt}^2/R_{gt}^0^2$, which decreases with increasing E for all pore radii R_p under a strong field. Relative change in the transverse conformation $R_{gt}^2/R_{gt}^0^2$ increases with an increase in R_p .

D. Diffusion coefficient of polyelectrolyte

As a prelude to the investigation of the electrophoretic mobility of the polyelectrolyte and counterions, we have computed the diffusion coefficient of the polymer chain in the pore. The additional motivation for this calculation is the validation of MPC dynamics method for treating the hydrodynamic interactions correctly. The diffusivity of the chain is computed from the mean square displacement of the center-of-mass of the polyelectrolyte in the long time limit,

$$\langle R_{cm}^2(t) \rangle = (4D_t + 2D_l)t, \quad (11)$$

where D_t and D_l are the diffusion coefficients in the transverse and longitudinal directions to the pore axis, respectively. In the long time limit, diffusivity in transverse direction is zero. We have computed the diffusivity along the longitudinal direction D_l from the mean square displacement of the center-of-mass of the polymer along the pore axis. Figure 6(a) plots D_l/D_0 as a function of the chain length N_m at $R_p = 5$ and $\Gamma = 3$. Diffusivity of the polymer decreases with the polymer length. Although approximate analytical formulas are known in the literature^{50–53} for a rod-like polymer in isotropic dilute solutions, analogous expressions are unknown for confined rods inside a pore with partial screening of hydrodynamic interactions and restricted rod orientation. However, we find that $D_l \sim N_m^{-1}$ as shown by the best fit (solid line) of the data in Figure 6.

E. Electrophoretic mobility of the polymer

We have computed the electrophoretic mobility μ_p of the chain according to

$$\mu_p = V_{cm}/E, \quad (12)$$

FIG. 6. Diffusion coefficient D_l/D_0 of the polyelectrolyte chain as a function of polymer length N_m for $R_p = 5$ and $\Gamma = 3$. Solid line shows the linear dependence of D_l/D_0 on N_m^{-1} .

where V_{cm} is the average velocity of the center of mass of the chain under the electric field E . This result is only a net average value as the electric field acts on all charged monomers and counterions and there is a rich collective dynamics of monomers and counterions mediated by solvent molecules. When the electric field is weak enough, the electrophoretic mobility is independent of E and thus the chain mobility is in the linear response regime. Now the velocity of the chain is directly proportional to E . Under these linear response conditions, we label μ_p as μ_p^0 .

Before embarking on the nonlinear response regime at higher electric fields, we have computed the electrophoretic mobility of the polyelectrolyte in the linear response regime for various polymer lengths (Figure 7(a)) and pore radii (Figure 7(b)). The inset of Figure 7(a) displays the relative mobility μ_p^0/μ_0 of the polyelectrolyte as a function of the chain length N_m for pore radius $R_p = 5$. Here μ_0 is the mobility of a free monomer in an infinitely dilute solution. μ_0 is given by the Einstein relation, $\mu_0 = qD_0/k_B T$, and is 0.014

FIG. 7. (a) Scaled electrophoretic mobility μ_p/μ_0 of the polyelectrolyte chain as a function of $E|Q_{eff}|$ for various polymer lengths 20, 40, 50, 80, and 100 for $R_p = 5$ and $\Gamma = 3$. Inset shows the electrophoretic mobility μ_p^0/μ_0 in linear response regime as function N_m for the same parameters. (b) Electrophoretic mobility of the polyelectrolyte chain as a function of $E|Q_{eff}|$ for various pore radii $R_p = 5$ (bullet), 8 (square), 10 (diamond), 12 (triangle up), and 15 (triangle left) for the polymer length $N_m = 50$. Inset shows the electrophoretic mobility μ_p^0/μ_0 in linear response regime as function R_p^{-1} .

in the dimensionless units used in the present paper. As seen from the inset, the mobility of the chain is smaller by a factor of about 5 in comparison with a monomer. Also, the mobility of the polyelectrolyte decreases slowly with the polymer length N_m and approaches a constant value for longer chains. This result of chain length independence for the mobility for long chains is consistent with the behavior of degree of ionization discussed above (inset of Figure 3(a)) and other theoretical^{31,54} and simulation results^{32–34} for bulk. Thus, in the linear response regime, the electrophoretic mobility of the polyelectrolyte is independent of chain length even when the chain is confined inside a pore.

When the dimensionless electric field is higher than about one, the mobility of the polyelectrolyte is not in the linear response regime and it becomes strongly dependent on the strength of the electric field. This is clearly shown in Figure 7(a), where the relative mobility μ_p/μ_p^0 is plotted against the effective force $E|Q_{eff}|$. In view of the charge regularization of the polymer arising from the electric field itself, we have identified the variable $E|Q_{eff}|$ as the key variable for depicting the behavior of the mobility. Figure 7(a) shows a universal behavior for all values of N_m . For $E|Q_{eff}| < 1$, we observe the linear response behavior. For $E|Q_{eff}| > 1$, the mobility increases roughly exponentially until it saturates for very high values of $E|Q_{eff}|$. The occurrence of the nonlinear regime is consistent with previous simulation studies.^{48,55} The sigmoidal nature of the dependence of the mobility on the electric field is reflective of the dependence of the effective degree of ionization on the electric field. An increase in the effective charge of the polymer at higher electric fields would lead to higher mobility. Since the effective charge is E -dependent, it is obvious to expect a nonlinear dependence of the mobility on E . However, we emphasize that the net result of the mobility of the chain is the culmination of E -dependent charge regularization, conformational change, hydrodynamic and electrostatic coupling between the counterions and the polymer, and the nonlinear effects on the chain drift. In order to fully resolve the different contributions to the net mobility, a theoretical model with all of these contributing factors is required and is beyond the scope of current activities in polyelectrolyte research. The effect of pore radius is shown in Figure 7(b). The relative change in the mobility with the electric field is qualitatively the same for all pore radii investigated. Due to the narrow range of pore radii in the present study, we did not attempt at getting any power law dependence of the mobility on the pore radius.

F. Mobility of counterions

The mobility of the counterion exhibits a rich behavior depending on whether it is adsorbed on the polymer, or it is in the proximity of the polymer, or it is far away from the polymer. When the counterions are far away from the polymer, they move freely with nearly the bulk mobility. When a counterion and the polymer approach each other in the opposite directions, the counterion accelerates towards the polymer. While the counterion is adsorbed on the polymer, it can slide past one monomer at a time along the polymer in the opposite direction to that of the motion of the polymer. When

FIG. 8. (a) Universal curve for the mobility of adsorbed counterions as a function of the effective force $E|Q_{eff}|$ for various polymer lengths. (b) Electrophoretic mobility of adsorbed counter ions on polyelectrolyte as a function of effective force $E|Q_{eff}|$ for various pore radii $R_p = 5$ (bullet), 8 (square), 10 (diamond), 12 (triangle up), and 15 (triangle left) for the polymer length $N_m = 50$.

the counterion ultimately escapes from the polymer in the opposite direction of the polymer motion, it gets decelerated by the electrostatic pull. Finally, when the counterion has escaped completely from the polymer, it attains the free solution mobility. Quantitative details of these behaviors are given in Figures 8 and 9.

First, we consider the behavior of an adsorbed counterion, as shown in Figure 8, where the relative mobility of the adsorbed counterion μ_a/μ_p^0 is plotted against $E|Q_{eff}|$. If the electric field is weak, the mobility of the counterion is close to that of the polymer and it moves in the same direction as the polymer, although its ultimate destination is in the opposite direction. As the value of $E|Q_{eff}|$ is increased further, the mobility of the adsorbed counterion increases along with that of the polymer as the counterion has not desorbed from the polymer. However, at very high values of the electric field, the counterions come off the initial locations of adsorption and slide along the polymer in the opposite direction to the motion of the polymer. When the counterion is adsorbed and if the electric field is high, the net mobility of the counterion begins to decrease but still moving in the same direction as the polymer. The relative mobility of the adsorbed counterion

FIG. 9. Average local mobility $\mu_c/|\mu_0|$ of any counter-ion with respect to the center-of-mass of the polymer for various chain lengths $N_m = 20$ (blue), 50 (black), 80 (green), and 100 (red) for $R_p = 5$ and at electric field $E = 0.1$.

depends universally on $E|Q_{eff}|$ for different chain lengths as seen in Figure 8(a) for $R_p = 5$ and $\Gamma = 3$. Such a universal behavior on $E|Q_{eff}|$ is seen in other properties of the polymer as well (Figures 4(b) and 7(a)). Therefore, we conclude that the mobility of the adsorbed counterions is essentially determined by the polymer properties.

In order to elucidate the non-uniform mobility of counterions inside a pore in the vicinity of the polyelectrolyte chain, we have computed the mobility of counterions as a function of the relative distance of the counterion from the center-of-mass of the polymer along the direction of electric field. The mobility ratio $\mu_c/|\mu_0|$ of a counterion as a function of the relative distance from the center-of-mass of the polyelectrolyte chain is shown in Figure 9. Here R_c is the position of the counterion, R_{cm} is the position of the center-of-mass of the polymer, and L_x is the pore length. When the counterion is far away from the polymer, its mobility is close to the bulk mobility of free ions. However, when the counterion is adsorbed on the polymer due to electrostatic attractions, it is moving in the same direction as the polymer, as seen in Figure 8(a). In between these two cases, when the counterion is approaching the polymer chain, its drift velocity increases dramatically. This is due to the strong attractive force between the polymer chain and the counterion. Note that here the external field and the electrostatic attractive force on the counterion act in the same direction, causing an enhancement of the drift velocity. The substantial increase in the local mobility of the counterion and the range of distance over which such a boost occurs depend on the chain length as is evident from Figure 9. Longer chains in the pore are more aligned and more polarized along the pore axis with the electric field and hence exert large attractive force on the counterion, which is reflected in the relative mobility of counterion near the polymer chain.

Once the counterions have reached very close to the polymer, they get adsorbed on the chain by making temporary dipole bonds. In this region, the electrostatic attraction between the polymer and the counterion dominates over external field. Therefore, the counterion velocity is approximately that of the velocity of the polymer. In fact, the direction of

mobility of the counterion is now opposite to that in the region far away from the polymer as discussed above. The adsorbed counterions also slide on the polymer backbone in a direction opposite to the polymer's motion, which causes them to ultimately separate from the polymer. After the separation process, the counterion mobility decreases first to change the direction and then increases slowly to attain its bulk value. In the latter stage, the counterion decelerates due to the competition between the external electrical force and the electrostatic attraction from the polymer, as seen in Figure 9. Due to the inevitable intervention of such nonlocal and nonlinear counterion mobility around the polymer, interpretation of pore currents in experiments involving single-molecule electrophoresis through nanopores can be a challenge.

IV. SUMMARY

We have simulated a single flexible polyelectrolyte chain confined inside a nanopore in the presence of an external electric field, by fully accounting for the hydrodynamic and electrostatic interactions. The solvent dynamics is treated by the multiparticle collision dynamics method and the dynamics of the polyelectrolyte and its counterions are treated by their Newton's equations. The effects of confinement inside the pore and the externally imposed electric field on the conformational and transport properties of the chain and counterions are systematically investigated.

One of the key findings is the rich dynamics of the counterions around the polyelectrolyte under the external electric field. As the counterions (taken to be positively charged) stream towards the negative electrode, they encounter the polyelectrolyte which is essentially stretched along the pore axis. In the far side proximity of the polymer (from the negative electrode), the counterions accelerate towards the polymer due to the combination of electrostatic attraction between the counterions and the polymer and the preferred direction of mobility towards the electrode. Once the counterions get captured by the polymer, they move with the chain towards the opposite (positive) electrode, while sliding along the chain backbone towards the negative electrode. Eventually, the counterion gets freed and tries to move towards the negative electrode. In the near side proximity of the polymer (from the negative electrode), the counterions are decelerated due to the antagonistic combination of electrostatic attraction between the counterions and the polymer (which tries to pull the counterions back) and the preferred direction of motion towards the negative electrode.

On average, the number of adsorbed counterions on the polyelectrolyte is a sensitive quantity depending on the strength of the external electric field and the pore radius. As the strength of the electric field increases, the number of adsorbed counterions decreases resulting in an increase in the effective charge of the polymer. The effective degree of ionization α of the polymer exhibits a sigmoidal shape against the electric field. At low electric fields (E), α is independent of E . After a threshold value of E , α increases rapidly until it reaches a plateau value at very high E values. This behavior in turn contributes to more chain expansion and higher electrophoretic mobility of the polymer with nonlinear depen-

dencies on E for values of E higher than the threshold. The degree of ionization of the polymer also depends on the extent of chain confinement inside the pore. As the pore radius decreases, the degree of ionization decreases as the adsorption equilibrium is shifted towards more adsorption for lower volumes.

The radius of gyration and the diffusion coefficient of the chain under confinement follow the expected rod-like scaling behavior in the absence of E , although the chain is strictly not a rod. The radius of gyration shows a nonmonotonic dependence on the pore radius due to the competing effects from enhanced counterion adsorption and enhanced polymer-pore interaction as the pore radius is decreased. In the presence of E , the radius of gyration exhibits a sigmoidal behavior with E , reflecting the sigmoidal shape of α and the confinement effect. The contribution from the charge regularization due to the electric field is taken into account in constructing the product of E and the effective charge Q_{eff} as the key variable in describing the structural and transport properties of the chain. We observe universal curves for the radius of gyration and the mean square end-to-end distance of the chain when plotted against $E|Q_{\text{eff}}|$ for various chain lengths. As intuitively expected, the change in the chain extension by the electric field is progressively smaller as the pore radius is decreased.

The electrophoretic mobility μ_p of the chain shows a universal behavior with $E|Q_{\text{eff}}|$ for various chain lengths. At lower values of E , μ_p is independent of E , as expected in the linear response regime. For E higher than a threshold value, μ_p depends on E almost exponentially until it reaches a plateau value for very high E values. This sigmoidal behavior is reflective of that of the counterion adsorption and is further modified by effects from the confinement, nonlinear drift from the electric field, and hydrodynamic coupling among the counterions and polymer. The mobility of the counterions is not uniform and depends on its relative location from the polymer. For low and moderate strengths of the electric field, the mobility of adsorbed counterions tracks with that of the polymer and in fact they move in the direction of the polymer towards the "wrong" electrode. However, for higher E values, the counterions come off the polymer, consistent with the higher degree of ionization, and move towards their "correct" electrode.

Studies of specificity of the counterion, presence of additional electrolyte ions, and ionic currents are of immediate interest, which are not addressed here. One of the key assumptions in the present model is the lack of dielectric heterogeneity between the inside and outside of the pore, which requires to be lifted in future simulations. Accounting of the image charges arising from the dielectric mismatch at the pore wall is likely to affect the quantitative details of the forces near the wall.

Our simulation results with such vivid details offer opportunities to interpret the various perplexing experimental results on single-molecule electrophoresis through protein pores and solid-state nanopores.^{5,17,19,21,22,24,56} Furthermore, the present work demands formulations of adequate theoretical models to account for the cooperative nonlinear effects arising from counterion adsorption, chain stretching under confinement, and hydrodynamic forces in the presence of

externally imposed electric fields, in describing the transport properties of polyelectrolytes in nanoscopic environments. In order to facilitate comparisons between future theories and the present simulation results, we have provided all of our data in tabular form as the supplementary material.⁵⁷

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