Ratchet rectification effect on the translocation of a flexible polyelectrolyte chain

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We report a three dimensional Langevin dynamics simulation of a uniformly charged flexible polyelectrolyte chain, translocating through an asymmetric narrow channel with periodically varying cross sections under the influence of a periodic external electric field. When reflection symmetry of the channel is broken, a rectification effect is observed with a favored direction for the chain translocation. For a given volume of the channel unit and polymer length, the rectification occurs below a threshold frequency of the external periodic driving force. We have also observed that the extent of the rectification varies non-monotonically with increasing molecular weight and the strength of geometric asymmetry of the channel. Observed non-monotonicity of the rectification performance has been interpreted in terms of a competition between two effects arising from the channel asymmetry and change in conformational entropy. An analytical model is presented with predictions consistent with the simulation results. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4961505>]

I. INTRODUCTION

Directed transport of a Brownian particle in a ratchet potential is of considerable interest in the contexts of molecular motors and separation science.^{1–6} A typical Brownian ratchet system possessing a spatial or dynamical symmetry breaking of the potential, combined with an unbiased external input signal, results in a directed stationary transport. Several variants⁵ of Brownian ratchet have been proposed to explain this transport mechanism under different nonequilibrium situations. Typical examples of Brownian ratchet include the transport of particles under the action of unbiased forces of chemical,^{7,8} optical,^{9,10} or mechanical¹¹ origin. In general, Brownian ratchets have been studied with an *ad hoc* physical periodic barrier imposed externally. However, Brownian particles can experience a periodic entropic potential when they are constrained to move in a confined space with periodic boundaries as the boundary effects are manifested as an entropic barrier in the effective free energy expression.^{12–15} Zwanzig¹³ first treated the problem of diffusion of particles through a narrow tube of varying cross sections to explore how the stochastic dynamics experiences a position-dependent entropic potential arising due to the channel asymmetry. In recent times, the concept of entropic barrier and its interplay with the stochasticity of the system have been investigated for model Brownian systems related to ratchet transport^{16–18} in a periodic channel and other noise induced phenomena.^{14–22}

On the other hand, for a soft Brownian particle like flexible macromolecules in a confined space, the particle confronts considerable conformational fluctuations.²³ Thus, when such a macromolecule has been confined in a narrow channel with uneven boundaries, the position dependent changes in its conformational degrees of freedom contribute

significantly to the entropic potential. The influence of this conformational entropy of the chain along with geometric constraints plays a crucial role to control the dynamics of a polymer during translocation processes^{24–37} through narrow pores. The present study deals with the dynamics of a polyelectrolyte (PE) chain in a narrow channel where both the geometric unevenness and the conformation entropic effect contribute to the overall free energy of the system significantly. We consider a system with a PE confined in a narrow channel with varying cross sections as shown in Fig. 1. The difference in local cross sectional area between the position with maximum width (W_m) and the bottleneck position (W) creates an entropic barrier ($\Delta F_c \sim \ln\left(\frac{W_m}{W}\right)$) originating from the geometric constraints.^{13–15} Now, if the width of the bottleneck positions is scaled down to the bead size of the chain, polymer will translocate as a single file across the bottleneck to translocate from one chamber to another. If the width at maximum cross sectional area (W_m) is several times of that at bottleneck position, the chain suffers a strong conformational entropy loss to move from the bulk to the bottleneck. Also, to initiate the translocation process to the next chamber, the polymer chain has to find either of its ends projected towards the face of the bottleneck, which also costs an additional conformational penalty.²⁴ Consequently, the change in conformation entropy contributes significantly to increase the overall free energy barrier (ΔF_c) during the chain translocation. Therefore, to address the issue of how an externally imposed oscillatory signal in time couples to the various conformations of the polymer chain and the entropic gradient due to the channel asymmetry would be of potential interest in view of its implications in macromolecular transport.

In this context, there have recently been several experimental^{38–40} and numerical^{41–48} studies on polymer ratchet devices. A large majority of these studies consists

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FIG. 1. Schematic two dimensional representation of the model periodic channel system under study with different structure parameters.

of an external periodic potential field and does not have any geometric restrictions on the system. For example, Bader *et al.*^{38,39} have experimentally designed a micron-scale ratchet device to control the transport of DNA oligomers. A flashing ratchet type potential has been generated by applying a voltage difference to interdigitated electrodes. A periodic switching between the charged state and a discharged state ensures the flashing saw tooth potential. They have shown that the device could be useful as a pump for separation of small charged macromolecules. Similarly, Hammond and co-workers⁴⁰ have designed an interdigitated electrode array device to create an experimental flashing ratchet setup and studied the directed transport of oligonucleotides. They have shown that the DNA size, applied electric field frequency, and periodic length scales associated with electrode spacing influence the extent of directed transport significantly.

Langevin dynamics simulation studies^{41,42} have also been performed to study the directed transport of a flexible polymer in the presence of an external asymmetric time dependent saw tooth potential (flashing ratchet type). Downton *et al.*⁴² observed that an optimum ratio of the periodic length (L) of ratchet potential to the chain length (N) makes the rectification effect most efficient. For both a high and a low value of periodic length comparative to that of chain size, drift velocity decreases. They have also observed that the internal degrees of freedom of the polymer plays a constructive role in terms of the rectification performance as the polymer velocity decreases more slowly with increasing N than a flashing ratchet of single particle with comparable drag coefficient. Polson and co-workers⁴³ have extended the study with a similar model system and examined how the period length L of the ratchet potential and chain conformation (chain size N) affects the average speed of the chain. They have explored two distinct dynamical regimes with different transport mechanisms. In the limit of low $\frac{N}{L}$, the velocity decreases with increasing N , and the diffusion of center-of-mass dominates the directed motion. In contrast, with high $\frac{N}{L}$ ratio, the velocity is weakly sensitive to variation in N , and the coupling of internal modes to the cycling of the ratchet potential controls the motion. They also showed that hydrodynamic effect increases in the ratcheting performance for both the regimes. In a molecular dynamics simulation study with a polymer in a flashing ratchet potential, Kenward

and Slater⁴⁴ have shown how the shape anisotropy induced by the flashing ratchet potential during its on-time influences the ratchet transport of the polymer. During the off-time the polymer relaxes from an asymmetric shape to a spherical shape. This shape anisotropy relaxation leads to a time-dependent diffusion coefficient which affects the rectification performance.

In a different context, Zhang and co-workers⁴⁵ have reported a purely hydrodynamic polymer ratchet where a semiflexible polymer has been placed inside a uniform narrow channel subjected to an external oscillating Poiseuille flow. They have introduced a feedback control using a time dependent transverse force to the chain. This creates a polymer hydrodynamic ratchet system and the rectification ability has been found to be a maximum for an optimum amount of transverse forcing. Binding protein-assisted ratchet rectification during polymer translocation has been reported recently in several issues.^{37,49,50} The binding proteins, called chaperones, are present on the trans-side and bind with the translocating chain which generates a ratcheting driving force and enhances the translocation speed. One of the most promising practical uses of the polymer ratchet like device lies on the fact that the ratchet transport mechanism can be applied to develop novel techniques for the separation of bio-macromolecules like DNA electrophoresis.^{51,52}

In the absence of any external *ad hoc* periodic potential, Slater *et al.*⁴⁶ first demonstrated an entropic ratchet device for a PE system and showed that the structural asymmetry can induce a directional transport for polymeric system and the degree of polymerization enhances the rectification performance. In this paper, they have demonstrated that a biased random walker migrating through an asymmetric 2D channel can perform ratchet transport where the required periodic potential can be generated only due to steric interactions. Further, they have extended the study for PEs in an asymmetric channel subjected to a zero-mean, time-symmetric, fluctuating external field. The simulation has been performed using a bond-fluctuation algorithm on a square lattice. The channel irregularity appears with a periodically varying pore radius which results for a periodic appearance of bulk regions and bottlenecks along channel axis. They have found that the polyelectrolytes move towards the direction of longer funnel. They further introduced a small bias in the external force in opposite direction to the direction of longer funnel and created a bidirectional motion of PEs of different sizes.

In a follow up study, Teissier and Slater have performed Monte Carlo simulations to investigate the implication of the idea of steric polymer ratchet for a slightly different electrophoretic micro-channel device similar to that for the size separation of large DNA fragments.⁴⁷ The major finding of this study lies on the fact that the ratchet rectification effect on the macromolecules has been found in the presence of a symmetric channel subjected to a time asymmetric unbiased external force. In such a situation, the strength of asymmetry of a time-asymmetric unbiased force influences the ratcheting ability non-monotonically and a proper tuning of system parameters can yield a bidirectional transport for different

molecular sizes. Also, they observe a resonant activation like enhancement in chain velocity at an optimum driving frequency. Recently, Wang and co-workers⁴⁸ have studied the role of hydrodynamic interactions in an entropic polymer ratchet system using explicit solvent molecular dynamics simulation technique. They found complex responses from the associated ratchet device to the structural asymmetry, frequency of the external electric field, and the nature of charge distribution on the PE. The study shows how the competition between three different contributing factors, the entropy force, solvent dissipative force, and conformation inversion resistance control the direction of the net motion of the PE. In short, Refs. 46–48 show that the broken reflection symmetry of a confined channel provides a space dependent asymmetric entropic potential on the confined macromolecules and in the presence of other essential ratcheting ingredients an entropic polymer ratchet device can be realized. In a different geometric setup, the broken spatial reflection symmetry of geometric obstacles in a micro-fabricated sieve has been found to be useful for separation of macromolecules and PEs of different sizes.^{53,54}

As addressed earlier, the primary objective of the present paper is to examine whether we can design an entropic polymer ratchet where both the channel asymmetry and conformational entropy variation during translocation events influence the dynamics significantly and how the molecular weight of the PE and structural asymmetry influence the rectification performance. In the present paper, we perform a Langevin dynamics simulation of a uniformly charged flexible PE confined in a periodic narrow channel as shown in Fig. 1, under the influence of a periodic external electric field (AC drive). We take the width of the bottleneck positions comparable to twice of the bead size to ensure a single file translocation from one chamber to the other. We have found that a proper tuning of the driving frequency and structural asymmetry of the channel results in a directed transport of the PE. We have also observed that both the structural asymmetry effect and conformational entropy cost influence the rectification performance in a nontrivial manner. Consequently, the velocity of the PE varies non-monotonically with both the molecular weight and the extent of structural asymmetry of the channel.

The paper is organized as follows: In Sec. II, we describe the model to study the dynamics of a flexible polyelectrolyte chain subjected to an external alternating electric force in a three-dimensional periodic channel. In Sec. III, we present our numerical simulation results and discuss them systematically. In Sec. IV, we present an analytical treatment to describe the creation of such polymeric entropic ratchet qualitatively. The paper is concluded in Sec. V.

II. SIMULATION MODEL

We study the dynamics of a charged polymer confined in a narrow channel as shown in Fig. 1 under an applied alternating electric field ($f(t)$) along the longitudinal axis of the channel using Langevin dynamics simulation. We express the physical boundaries of the wall using following equations:

$$\begin{aligned} B_u(x) &= \frac{u_0}{l_j}(\bar{x} - nl) + c \quad \text{for } nl \leq \bar{x} < (nl + l_i) \\ &= \frac{u_0}{l_j}(l - (\bar{x} - nl)) + c \quad \text{for } (nl + l_i) \leq \bar{x} < (n+1)l, \\ B_l(x) &= -B_u(x), \quad W(x) = B_u(x) - B_l(x), \\ W(x) &= 2\sqrt{z^2 + y^2}, \end{aligned} \quad (1)$$

where $\bar{x} = |x|$, $i = 1$, $j = 2$ for $x \geq 0$ ($i = 2$, $j = 1$ for $x < 0$) and n is an integer number including zero. B_l , B_u correspond to the lower and the upper wall boundary functions and x , y , and z represent the position coordinates. The geometrical parameters for the channels are u_0 , l , l_i , and c . $W (= 2c)$ is the width of the bottleneck position. l is the periodic chamber length along the channel axis and $l_1 + l_2 = l$ (Fig. 1). u_0 controls broadening of the cross sectional area for different positions. $W(x)$ determines the local diameter of the channel at x . The width with maximum cross sectional area is defined as $W_m = 2(u_0 + c)$. This particular choice of the periodic shape of the channel is inspired by the shape of the channel used to study the different stochastic phenomena for a single Brownian particle associated with a periodic entropic barrier, which in turn mimics the classical setup for the periodic saw-tooth like ratchet potential.¹⁶ The confinement boundaries are acting as reflecting walls. Therefore, the channel wall has been considered as an inert physical boundary. Both the monomer and the wall are incompressible. Monomers confront the wall elastically. No energy and/or momentum have been transferred between them during such collisions. The slope of the boundary wall at the point of impact determines the direction of the reflected monomer.

We have modeled the excluded volume interactions using a truncated Lennard-Jones potential between two beads, given as follows:

$$U_{LJ}(r_{ij}) = \begin{cases} 4\epsilon_{LJ} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon_{LJ} & \text{for } r_{ij} \leq 2^{\frac{1}{6}}\sigma \\ 0 & \text{for } r_{ij} > 2^{\frac{1}{6}}\sigma \end{cases} \quad (2)$$

Here, r_{ij} is the distance between i th and j th beads. The depth of the pair-wise interaction potential is expressed by $\epsilon_{LJ} = \frac{1}{6}k_B T$ for (≈ 0.1 kcal/mol) with $T = 300$ K and $\sigma (= 3.4 \text{ \AA})$ is the diameter of a component bead. k_B is the Boltzmann constant and T denotes the absolute temperature of the system. The LJ potential is truncated at its minimum, i.e., at a distance of $2^{\frac{1}{6}}\sigma$. We express the electrostatic interactions (ESIs) between a pair of charged beads in terms of a truncated Debye-Hückel potential,

$$U_{DH}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} e^{-\kappa r_{ij}} \quad \text{for } r_{ij} \leq r_c, \quad (3)$$

where q_i and q_j are the corresponding charges on i th and j th bead, separated by a distance r_{ij} in a medium of dielectric constant $\epsilon = 80$. Debye length κ^{-1} governs the range of the ESI. We take the value of $\kappa^{-1} = 0.3$ nm corresponding to a typical experimental system with 1M KCl solution. r_c is the cutoff distance at which the ESIs are truncated. We use $r_c > 3\kappa^{-1}$ for all of the numerical simulations. We model the bonds between two successive polymer beads using the

following harmonic potential:

$$U_{har} = K_0(r_b - r_0)^2, \quad (4)$$

where r_b and r_0 are the instantaneous and equilibrium bond lengths between two connected polymer beads, respectively. K_0 is the coupling constant chosen such that U_{har} will be large relative to the thermal energy ($k_B T$) in the system. We fix the average temperature in the simulation to be 300 K, such that $k_B T = 0.59$ kcal/mol. The strength of the harmonic potential (K_0) is taken large enough so that the instantaneous bond length varies from r_0 by less than 10% throughout the simulation.

In Langevin dynamics, the above potentials are used to compute forces on each of the polymer beads. The equation of motion for i th bead of the chain thus takes a form

$$m_i \frac{d^2 r_i}{dt^2} = -\zeta_i \frac{dr_i}{dt} - \nabla_{r_i} (U_{har,i} + U_{DH,i} + U_{LJ,i}) + F_{r,i} + \hat{e}_x F_{ext,i}, \quad (5)$$

where m_i is mass of the bead and has been taken the same ($m \approx 100 Da$) for all beads, ζ_i is the friction coefficient of the i th monomer and again assumed to be the same ($=\zeta$) for all beads. $F_{r,i} \sim \sqrt{6k_B T \zeta}$ is the random thermal force acting on i th monomer at the given temperature T . We introduce the random force as a zero-mean white Gaussian noise obeying the fluctuation-dissipation relation as $\langle F_{r,i}(t) F_{r,j}(t') \rangle = 6k_B T \zeta \delta_{ij} \delta(t - t')$. r_i is the position vector of the i th bead and t is the time. $\hat{e}_x$ is a unit vector along x -direction and the force due to applied oscillating electric field is denoted by $F_{ext,i} = f(t) = f_0 \sin(2\pi \Omega_0 t)$ for all i .

For convenience, we make use of the dimensionless description of the Langevin dynamics. All physical parameters are specified in dimensionless LJ units of length, mass, and energy. The LJ unit of length is specified so that the diameter of a monomer bead is $\sigma = 1$ unit. Consequently, the Debye length (κ^{-1}) becomes 0.88 units and we set $r_c = 3.0$ units to truncate the Debye-Hückel potential. The LJ unit of mass is set to be the mass of the bead ($m = 1$). The unit of energy (ϵ_s) is given by the thermal energy of the system $\epsilon_s = k_B T$. These units of length, energy, and mass determine the LJ unit of time to be $\sqrt{\sigma^2 m / \epsilon_s}$ and the charge to be $\sqrt{4\pi \epsilon_0 \epsilon_s \sigma}$. This makes the depth of the Lennard-Jones potential well $\epsilon_{LJ} = \frac{1}{6}$ units and charge on a bead to be 12.8 units. We use the simulation time step of 10^{-4} (~ 1 fs) units. The equilibrium bond length has been taken as $r_0 = 1$ unit. We take $K_0 = 1500$ units (≈ 10 kcal/(mol $\text{\AA}^2$)) to prevent unrealistic bond extensions ($< 10\%$). We also set the unit chamber length $l = 12$ units, $W \approx 2$ units, and $W_m = (5 + W)$ units. We choose a value of $\zeta = 1$ for all i in all our simulations.

We start our numerical simulation (at time $t = t_0$) with an equilibrium configuration of the polyelectrolyte chain. To obtain this equilibrated structure, we begin with a straight chain aligned to the channel longitudinal axis at time $t = -\infty$ and allow us to equilibrate the system by solving the governing Langevin equation [Eq. (5)] along with the periodic driving force for sufficiently long time ($t = 0$). The polymer chain configuration obtained at $t = 0$ is taken to define initial positions (r_i) and velocities (v_i) of the monomer beads. An improved Euler algorithm is used to solve the Langevin

equation of motion. The equation of motion is then integrated in time until 5 complete cycles of the periodic driving force. We repeat this simulation for 200 different trajectories. We define the velocity of the centre of mass of the PE chain along the channel axis as $\langle v \rangle_{CM} = \lim_{t \rightarrow \infty} \frac{\langle x \rangle_{CM}(t)}{(t - t_0)}$, where $\langle x \rangle_{CM}$ is the mean position of the centre of mass of the chain along channel axis (x -direction) averaged over 1000 (5×200) driving cycles. We also define an asymmetry parameter (Δ) for the channel shape as

$$\Delta = \frac{l_2 - l_1}{2}. \quad (6)$$

For a symmetric channel $\Delta = 0$. Therefore, for the schematic channel as shown in Fig. 1 $\Delta < 0$ which implies that the unit chamber of the periodic channel has a longer funnel towards negative direction of the x coordinate.

III. SIMULATION RESULTS AND DISCUSSION

A. Structural asymmetry induces ratchet transport

We begin our numerical simulation study with the variation of $\langle v \rangle_{CM}$ with asymmetry parameter of the channel Δ , as shown in Fig. 2(a). We study this variation with three

FIG. 2. (a) Variation of average velocity of the center of mass of the chain ($\langle v \rangle_{CM}$) with the asymmetry parameter (Δ) of the channel for different widths of the bottleneck (W). For all cases $f_0 = -0.5$, $\Omega_0 = 0.001$, and $N = 60$. (b) Variation of average velocity of the center of mass of the chain ($\langle v \rangle_{CM}$) with the asymmetry parameter (Δ) of the channel for different chain lengths (N). For all cases $f_0 = -0.5$, $\Omega_0 = 0.001$, and $W = 1.9$.

different widths of the bottleneck $W = 2.3$ (blue line and starred points), 1.9 (red line and triangular points), and 1.7 (black line and circular points) for $f_0 = -0.5$, $\Omega_0 = 0.001$, and $N = 60$. Variations show that for a symmetric channel $\Delta \rightarrow 0$, no directed transport is observed ($\langle v \rangle_{CM} \sim 0$). On the other hand, with the introduction of a spatial asymmetry ($\Delta \neq 0$), a directed motion of the PE along the direction of the longer funnel has been observed ($\langle v \rangle_{CM} \neq 0$). This directed transport supports the existence of a favorable polymeric ratchet device due to the spatial asymmetry towards longer funnel. Periodic variation of cross-sectional area $W(x)$ inside the channel creates an effective entropic potential ($\frac{F_c}{k_B T} \sim -\ln W(x)$) which also varies periodically along channel axis.^{12–15,21} For a symmetric channel $\Delta = 0$ the entropic potential is symmetric and an introduction of spatial asymmetry ($\Delta \neq 0$) keeping the volume of the unit chamber intact makes this potential asymmetric. For such asymmetric channel, the steepness of the effective free energy barrier becomes lower towards the longer funnel direction (towards negative of x direction in Fig. 1) compared to that of the other side. Now, in the presence of a periodic external force, the PE chain experiences a stochastic ratchet effect along the direction with less steeper entropic barrier. Consequently, the PE chain performs a directed motion. The sign of $\langle v \rangle_{CM}$ shows the direction of the velocity. A negative $\langle v \rangle_{CM}$ means that the PE chain is moving towards negative x direction. For example, for $\Delta \leq 0$, the PE transports towards negative direction and consequently $\langle v \rangle_{CM}$ becomes negative. The figure also shows that the magnitude of $\langle v \rangle_{CM}$ decreases with decreasing W . To explain this observation, we recall the effect of the increasing confinement barrier height (ΔF_c) on rectification efficiency in Brownian ratchet devices.¹⁶ In a typical Brownian ratchet device, in the limit of strong barrier height ($\frac{\Delta F_c}{k_B T} \gg 1$), an increase in ΔF_c reduces the rectification ability as the associated barrier crossing rates decrease very sharply in this limit with increasing ΔF_c . On the contrary, in the weak barrier height limit $\frac{\Delta F_c}{k_B T} \ll 1$, thermal noise suppresses the rectification efficiency. Therefore, for a given temperature, the ratcheting performance has a maximum for an optimum barrier height. In the present study, the width of the bottleneck ($W \sim 2r_0$) is much smaller than the width at channel bulk (W_m). This creates a strong confinement entropic barrier as $\ln(\frac{W_m}{W}) > 1$. On top of that the conformational entropy loss for the PE to move from bulk to bottleneck position is also higher in case of a bottleneck with narrower width. So, one can expect that the PE inside the channel experiences a strong free energy barrier ($\frac{\Delta F_c}{k_B T} \gg 1$) during translocation from one chamber to the other. Any further lowering in the width increases the associated free energy barrier. Consequently, $\langle v \rangle_{CM}$ decreases for a narrower bottleneck.

B. High structural asymmetry can suppress rectification ability

Fig. 2(a) also shows a non-monotonic behavior of $\langle v \rangle_{CM}$ with an increasing structural asymmetry ($|\Delta|$). Initially, the rectification is enhanced with an increase in $|\Delta|$, followed by a decrease in $\langle v \rangle_{CM}$ with further increase in $|\Delta|$ resulting in a turnover. This turnover cannot be observed for the case of a Brownian ratchet with single particle as the velocity grows

monotonically with increasing structural asymmetry for the latter. Thus, the observed turnover in $\langle v \rangle_{CM}$ is an additional feature arising out of the degree of polymerization. To cross check this observation, we have studied the variation of $\langle v \rangle_{CM}$ with the structural asymmetry parameter (Δ) in Fig. 2(b) for different values of the chain size ($N = 5$ (pink line and pentagonal points), 10 (green line and squared point), 30 (blue line and circular points), and 60 (red line and triangular points)). The other parameters are taken as $f_0 = -0.5$, $\Omega_0 = 0.001$, and $W = 1.9$. The results show that the depth of the turnover is decreasing with a decrease in chain length N and the position of the turnover has been shifted towards a higher structural asymmetry region. For a short PE chain like $N = 5$, the turnover is shallower whereas the depth of the turnover increases for high N . Thus, the observed turnover can be realized as a consequence of longer chain length.

The origin of this non-monotonicity lies on the fact that high structural asymmetry leads to a strong conformational penalty for the chain capture at the bottleneck positions which leads to a decrease in translocation rate to either direction. This effect competes with the ratcheting gain due to the structural asymmetry, reducing the magnitude of $\langle v \rangle_{CM}$ in high asymmetry limit. The situation can be realized physically as follows. With the present confinement, the polymer can be translocated from one compartment to the other primarily as a single file. Thus, for a translocation from one compartment to another, it is necessary for either of the chain ends to locate the narrow window at the bottleneck position. Now, consider a situation when the asymmetry of the channel is very highly negative. In this case during the negative half of the driving cycle, the steep chamber wall present almost perpendicular to the force direction reflects chain beads to the anti-parallel direction of the forcing. Consequently, a large portion of the polymer chain has been coiled close to the wall. Now, due to the stochastic movement of the monomers, the conformational entropy loss associated with the change of state, from coiled to stretched, during the translocation through bottleneck is very high. Thus, a large portion of the polymer chain has been trapped for a while in a compartment which reduces the translocation rate to either direction of the channel axis. Consequently, the rectification ability reduces for high structural asymmetry. Also, for a given structural asymmetry an increase in chain length enhances this conformational penalty and hence decreases the rectification performance to a preferred direction.

C. Existence of a threshold driving frequency

Next, we study the variation of average velocity ($\langle v \rangle_{CM}$) with the frequency of the external periodic driving force (Ω_0) for different widths of the bottleneck $W = 1.7$ (black line and circular points), 1.9 (blue line and triangular points), and 2.3 (red line and starred points)) as shown in Fig. 3(a). For all cases, other parameters have been chosen as $f_0 = -0.5$, $N = 60$, and $\Delta = -5.0$. The results show that the directed motion is observed only below a threshold driving frequency which is a hallmark of ratchet rectification effect. In principle, under a constant biased DC forcing with a strength in the order of f_0 , the PE chain has a characteristic time scale

FIG. 3. (a) Variation of average velocity of the center of mass of the chain ($\langle v \rangle_{CM}$) with the frequency of the external periodic driving (Ω_0) for different widths of the bottleneck (W). For all cases $f_0 = -0.5$, $N = 60$, and $\Delta = -5.0$. (b) Variation of mean position of the center of mass of the chain ($\langle x \rangle_{CM}$) with the number of the cycle of the external periodic driving (n_c) for different frequency of the external periodic driving (Ω_0). For all cases $f_0 = -0.5$, $W = 1.9$, $N = 60$, and $\Delta = -5.0$.

(say τ_c) to translocate from one chamber to another. Now, if the time scale associated with the driving frequency ($\sim \frac{1}{\Omega_0}$) of $f(t)$ is too low comparative to τ_c ($\tau_c \gg \frac{1}{\Omega_0}$), $f(t)$ remains uncoupled with the chain dynamics and fails to lift the thermodynamic equilibrium condition for the system. Consequently, the ratchet rectification effect vanishes in this limit. Only when $\Omega_0 \sim \frac{1}{\tau_c}$ or lower, $f(t)$ couples with the chain dynamics efficiently which makes the ratchet effect feasible. The figure also depicts that with an increase in width of the bottleneck position (W), the threshold appears at a higher driving frequency. An increase in W makes τ_c shorter which causes a better coupling between $f(t)$ and system dynamics. Consequently, the threshold frequency shifts towards high frequency region. Fig. 3(b) shows the variation of mean position of the center of mass of the chain ($\langle x \rangle_{CM}$) with the number of the cycle of the external periodic driving force (n_c) for different driving frequencies (Ω_0) with the same parameter set as used in Fig. 3(a) except that $W = 1.9$. Results also support the existence of a threshold driving frequency to obtain a directed transport as the PE moves towards negative direction when the driving frequency is 2.5×10^{-3} or lower.

D. Rectification efficiency varies non-monotonically with chain size

Finally, we study the variation of average velocity ($\langle v \rangle_{CM}$) with the chain size N for three different W (1.7 black line and circular points, 1.9 blue line and triangular points, and 2.5 red line and starred points) as shown in Fig. 4(a). For all three cases the other parameters have been chosen as $f_0 = -0.5$, $\Omega_0 = 0.001$, and $\Delta = -5.0$. The variation shows that when the polyelectrolyte chain length is not too high ($N < 15$), $\langle v \rangle_{CM}$ increases with an increasing N . In the limit of high N (> 25), $\langle v \rangle_{CM}$ decreases with a further increase in N . This gives another turnover in $\langle v \rangle_{CM}$ variation which shows a most efficient rectification at an optimal chain length. The observed turnover can be explained qualitatively as follows. The ratchet rectification effect arises here due to the difference in translocation rate between two opposite directions caused due to the difference in the steepness of the associated barrier height. On the other hand, conformational entropy of the PE always increases with an increase in N . Therefore, an increase in N enhances the overall free energy barrier. In low N limit the structural asymmetry effect dominates over the chain conformation entropy effect. As the external forcing ($f(t)$) is acting on every monomer of the chain, a polymer chain with higher N drives the system out of equilibrium

FIG. 4. (a) Variation of average velocity of the center of mass of the chain ($\langle v \rangle_{CM}$) with chain length (N) for different widths of the bottleneck (W). For all cases $f_0 = -0.5$, $\Omega_0 = 0.001$, and $\Delta = -5.0$. (b) Variation of average velocity of the center of mass of the chain ($\langle v \rangle_{CM}$) with chain length (N) for different structural asymmetry parameters (Δ). For all cases $f_0 = -0.5$, $\Omega_0 = 0.001$, and $W = 1.9$.

more strongly and hence utilizes the geometry induced ratchet effect more efficiently. Consequently, the numerical value of the velocity is increasing with increase in chain size in this limit. The behavior of this limit is well consistent with the previous studies.^{21,46} On the contrary, in the high N limit, the conformational entropy loss during the translocation through the bottleneck dominates over the geometric ratcheting gain. As the associated free energy barrier is very high, the translocation rate towards either direction decreases rapidly with increasing N . Thus, the difference between right-left translocation rates also decreases. Also, the external driving frequency (Ω_0) is no longer low enough to interact with the translocation rate to drive the system out of equilibrium for high N . Therefore, $\langle v \rangle_{CM}$ decreases with increasing N in this limit. The competition between aforesaid effects results in a maximum velocity at an intermediate chain length. Thus, for a given channel asymmetry, a PE with an optimum chain size performs best ratchet transport.

Fig. 4(a) also shows that the position of this turnover shifted towards higher N and the magnitude of the $\langle v \rangle_{CM}$ increases with an increase in W . An increase in W leads to faster translocation rates that shifts the turnover position towards higher molecular weight region. In Fig. 4(b), we present the variation of $\langle v \rangle_{CM}$ with the chain length N for four different Δ values. The system parameters have been chosen as $f_0 = -0.5$, $\Omega_0 = 0.001$, and $W = 1.9$. The turnover has been observed for all structural asymmetries ($\Delta = -2$ to -5). Also, the structural asymmetry induced non-monotonicity in ratchet velocity as found in Fig. 2 can be identified independently for moderate to high value of N .

E. Few general remarks

We leave this section after mentioning a few pertinent points. First, the choice of the shape of the channel and relative magnitudes of the associated length scales are very crucial to observe the ratchet rectification effect. For example, the relative values of W and W_m have been taken in the present context such that $\frac{W_m}{W} > 1$. In this limit we have observed that an increase in bottleneck width (W) enhances the rectification performance. In contrast, in the limit of $\frac{W_m}{W} \rightarrow 1$, the ratchet rectification effect will not be feasible at all (not shown here). In this limit, the associated free energy barrier vanishes, $\frac{\Delta F_c}{k_B T} \sim \ln\left(\frac{W_m}{W}\right) \sim 0$ and thermal noise randomizes the dynamics of the PE. In this situation, the polymer experiences a cylindrical channel confinement with uniform cross sectional area ($\sim \frac{\pi}{4}(W + W_m)^2$) and hence no directed flow will be traced irrespective of the Δ value. The periodic variation of the cross sectional area creates spatial roughness on the surface of the channel^{55,56} and the overall diffusion process will be slowed down. Second, in the present study, we report a directed transport phenomena caused by the channel asymmetry in the presence of a symmetric unbiased driving force. However, rectification can also be feasible with the introduction of an asymmetric periodic driving in a symmetric channel ($\Delta = 0$). In principle, these two asymmetric effects of different origin can also be tuned to observe a current inversion phenomenon.¹⁶ Finally, if the size of the PE is too long, the occupancy of the chain in multiple chambers may

generate a more complicated free energy landscape during translocation, which in the presence of the increasing frictional force may affect the ratcheting ability in a non-trivial manner. This could be an interesting issue of interest and beyond the scope of the present article.

IV. ENTROPIC POLYMER RATCHET: AN ANALYTICAL APPROACH

An analytical derivation of the chain velocity inside the channel under an external AC driving force is very complicated. In this section, we provide an approximate description for the present system and derive the stationary flux for the polyelectrolyte chain inside the channel. We first describe the effect of the confinement at equilibrium using blob theory⁵⁷ and calculate an approximate free energy of confinement for different positions of the chain along the channel axis.^{58–60} We assume that one of the chain ends is always anchored to the channel axis and we define a chain propagation coordinate (X_P) in terms of a unidirectional propagation of this chain end. This provides a confinement free energy ($F_c(X_P)$) landscape in equilibrium as a function of the chain propagation coordinate (X_P). Next, we describe the chain propagation dynamics over the confinement free energy barrier ($F_c(X_P)$) with an approximate Fokker-Planck description²⁴ in terms of the chain propagation coordinate (X_P). Finally, we incorporate the effect of the external periodic forcing under adiabatic conditions^{16,56} and calculate the stationary flux of the PE. Although the analytical model and its solution which we discuss in this section do not capture the complete details of the non-equilibrium dynamics of the PE under consideration, the model provides a qualitative understanding about the creation of a polymeric entropic ratchet and the relative role of different factors which determine its rectification ability.

When a polymer chain is confined in a narrow space, the concept of blob theory has frequently been used to study the confinement effect in equilibrium.^{57–60} If the confinement length scales are higher than the bulk radius of gyration, the polymer does not feel any confinement. On the contrary, in the limit of confinement length scales smaller than the polymer size, the chain experiences a strong confinement effect. We begin with a flexible polymer of size N in a cone shaped channel circularly truncated at P as shown in Fig. 5(a). The polymer chain end resides at distance d_0 from the cone truncation point (P) and has spread over a length L along the axis of the conical confinement. θ is the opening angle of the confinement. W is the width of the cone at truncation point. For a flexible polymer inside a cone, the blob size is proportional to the local diameter of the channel ($W(x)$). From the geometrical consideration, we have $W(x) = W + 2(d_0 + x) \tan \theta$. If b_0 is the monomer diameter, the number of monomers ($g(x)$) inside a blob at x in Fig. 5(a) can be written as^{57,58}

$$g(x) \sim \left(\frac{W(x)}{b_0} \right)^{\frac{1}{\nu}}, \quad (7)$$

where ν is the Flory exponent. In the limit of de Gennes' confinement, the chain size can be expressed as^{59,60}

FIG. 5. (a) Model description of a polymer inside a cone shaped channel with different parameters. (b) Variation of free energy of confinement ($\frac{F_c}{k_B T}$) with d_0 for $\theta = \pi/10$ (blue line), $\pi/8$ (red line), and $\pi/5$ (black line). Parameter set has been chosen as $c_0 = 1$, $c_1 = 0.4$, $W = 2.0$, $N = 100$, $b_0 = 1$, and $\nu = 0.5$.

$$N = \frac{c_0}{b_0^{\frac{1}{\nu}} \tan \theta} \left[(W + 2(d_0 + L) \tan \theta)^{\frac{1}{\nu}} - (W + 2d_0 \tan \theta)^{\frac{1}{\nu}} \right], \quad (8)$$

where c_0 is a proportionality constant. The confinement free energy F_c experienced by the polymer at d_0 can be evaluated as

$$\frac{F_c}{k_B T} = \frac{c_1}{2 \tan \theta} \times [\ln(W + 2(d_0 + L) \tan \theta) - \ln(W + 2d_0 \tan \theta)], \quad (9)$$

where c_1 is a proportionality constant. Eq. (9) captures the effect of structural geometry (θ and W) and the chain size N (related to L) at a distance d_0 . In Fig. 5(b), we show that the free energy of confinement F_c felt by the chain as a function of its distance from truncation point (d_0) for three different opening angles (θ). The results show that once the chain approaches towards a narrow truncation point from the bulk, the confinement free energy increases rapidly. Also, a lower opening angle (θ) creates stronger confinement effect as F_c increases with decreasing θ .

We extend this method to calculate the confinement free energy F_c for polymer in a periodic channel as shown in Fig. 6. Now the opening angles are defined as $\theta_1 = \tan^{-1} \frac{W_m - W}{2l_1}$ and $\theta_2 = \tan^{-1} \frac{W_m - W}{2l_2}$. W_m is the width of the channel where the cross sectional area is maximum. W is the width at bottleneck

FIG. 6. Schematic 2D representation of a periodic channel with different structural parameters and with $\Delta > 0$.

positions. $l (= l_1 + l_2)$ defines the period length of the unit chamber along the channel axis. When l_1 and l_2 are of same length, the channel is symmetric. We define a parameter Δ , as $\Delta = l_1 - \frac{l}{2}$ to describe the channel asymmetry ($\Delta \neq 0$). The numerical values of W , W_m , and N have been chosen such that the flexible polymer experiences a strong confinement effect. Now, we assume that one end of the polymer is always anchored to the channel axis. The rest of the chain is anywhere behind this chain front. As the anchored chain end moves forward along the channel axis, we define the position of this chain end as a chain propagation coordinate (X_p). For a given position of the chain front (X_p), we can calculate the number of monomer in different sub-chambers (as shown in Fig. 6) using blob theory for an arbitrary value of c_1 . Followed by the calculation of individual confinement free energies for these sub-chains, one can calculate the total free energy of confinement (F_c) as a function of the chain propagation coordinate (X_p).

Let us explain the calculation of F_c with a specific example. As shown in Fig. 6, one end of a flexible chain of length N is at X_p and the entire chain has been spread over three sub-chambers I, II, and III with N_I , N_{II} , and N_{III} number of chain beads in each sub-chamber, respectively. The total number of monomer $N = N_I + N_{II} + N_{III}$. In sub-chamber I, we assume that a chain of length N_I is confined in a truncated conical channel with opening angle θ_1 at distance $(l - X_p)$ and it has a span of $L_I = (X_p - l_2)$ along channel axis. We can calculate the value of N_I and hence the confinement free energy for this sub-chain for arbitrarily fixed values of c_0 and c_1 as

$$N_I = \frac{c_0}{b_0^{\frac{1}{\nu}} \tan \theta_1} \times \left[(W + 2l_1 \tan \theta_1)^{\frac{1}{\nu}} - (W + 2(l - X_p) \tan \theta_1)^{\frac{1}{\nu}} \right],$$

$$\frac{F_I}{k_B T} = \frac{c_1}{2 \tan \theta_1} \times [\ln(W + 2l_1 \tan \theta_1) - \ln(W + 2(l - X_p) \tan \theta_1)]. \quad (10)$$

Similarly, in sub-chamber II, size of the sub-chain is N_{II} , l_2 is the span of the sub-chain, and the opening angle is θ_2 . The expression for N_{II} and the confinement free energy for sub-chain II follow as

$$N_{II} = \frac{c_0}{b_0^{\frac{1}{\nu}} \tan \theta_2} \left[(W + 2l_2 \tan \theta_2)^{\frac{1}{\nu}} - W^{\frac{1}{\nu}} \right],$$

$$\frac{F_{II}}{k_B T} = \frac{c_1}{2 \tan \theta_2} [\ln(W + 2l_2 \tan \theta_2) - \ln W]. \quad (11)$$

Finally, in sub-chamber III, a sub-chain of length N_{III} has been confined in a truncated conical channel with opening angle θ_1 with a sub-chain span L_{III} . The expression for N_{III} and the confinement free energy are given by the following equations:

$$N_{III} = \frac{c_0}{b_0^{\frac{1}{\nu}} \tan \theta_1} \left[(W + 2L_{III} \tan \theta_1)^{\frac{1}{\nu}} - W^{\frac{1}{\nu}} \right],$$

$$\frac{F_{III}}{k_B T} = \frac{c_1}{2 \tan \theta_1} [\ln(W + 2L_{III} \tan \theta_1) - \ln W]. \quad (12)$$

Thus, the total free energy of confinement $F_c(X_P)$ can be given as

$$\frac{F_c(X_P)}{k_B T} = \frac{F_I}{k_B T} + \frac{F_{II}}{k_B T} + \frac{F_{III}}{k_B T}. \quad (13)$$

Fig. 7(a) depicts the variation of free energy of confinement F_c with chain propagation coordinate X_P for three different values of l_1 . The result shows that the positions of the barrier maximum change with a change in l_1 . Also, during the uphill and the downhill chain propagation across the free energy maximum, the chain experiences a pathway effect in terms of the nontrivially varying steepness of free energy barrier along the propagation axis. In Fig. 7(b), we show the variation of confinement free energy F_c with the propagation coordinate for three different values of N . The figure shows that an increase in chain N increases the confinement barrier height.

For a periodic channel the confinement free energy F_c is also periodic

$$F_c(X_P) = F_c(X_P + l). \quad (14)$$

Let us consider that the chain is also subjected to a weak external periodic driving force $A(t)$, such that

$$A(t) = A_0 \quad \text{for } n\tau \leq t < (n\tau + \tau_1)$$

$$= -\epsilon A_0 \quad \text{for } (n\tau + \tau_1) \leq t < (n+1)\tau, \quad (15)$$

where τ is the time period for $A(t)$ and A_0 is the strength of the external force field. $\tau_1 = \frac{\epsilon\tau}{1+\epsilon}$, where $\epsilon (\geq 1)$ is a constant parameter which controls the symmetry of the external force field. For the present purpose, we consider $\epsilon = 1$, which provides a time symmetric external driving force. In the presence of $A(t)$, we can approximately describe the chain propagation over the periodic confinement free energy F_c by the following Fokker-Planck like equation:

$$\frac{\partial}{\partial t} P(X_P, t) = \frac{\partial}{\partial X_P} \left[\frac{1}{N\zeta} \left(\frac{\partial F(X_P)}{\partial X_P} - A(t) \right) P(X_P, t) \right. \\ \left. + \frac{k_B T}{N\zeta} \frac{\partial}{\partial X_P} P(X_P, t) \right], \quad (16)$$

where $P(X_P, t)$ is the probability of finding the chain propagation end at X_P at time t and ζ is the frictional

FIG. 7. (a) Variation of free energy of confinement ($\frac{F_c}{k_B T}$) with chain propagation coordinate X_P for $l_1 = 10$ (blue line), 30 (black line), and 50 (red line). Parameter set chosen: $c_0 = 0.25$, $c_1 = 0.4$, $W = 1.75$, $N = 200$, $l = 60$, $\zeta = 1$, and $\nu = 0.5$. (b) Variation of free energy of confinement ($\frac{F_c}{k_B T}$) with chain propagation coordinate X_P for $N = 200$ (blue line), 100 (black line), and 50 (red line). Parameter set chosen: $c_0 = 0.25$, $c_1 = 0.4$, $W = 2.0$, $l_1 = 50$, $l = 60$, $\zeta = 1$, and $\nu = 0.5$.

coefficient of monomer. k_B and T are the Boltzmann constant and the absolute temperature of the system, respectively. If $A(t)$ is a weakly varying function with time t , the time period (τ) of $A(t)$ becomes extremely high compared to any other time scale present in the system. In this adiabatic limit, there exists a quasi-steady state. Under such quasi-equilibrium conditions, one can express the stationary flux of the chain propagation along the forward direction (+ve) of the channel axis J_{av}^+ as

$$J_{av}^+ = \frac{\epsilon}{1+\epsilon} J_+(A_0) + \frac{1}{1+\epsilon} J_+(-\epsilon A_0), \quad (17)$$

where

$$J_+(A) = \frac{e^{-\psi(L)} - e^{-\psi(0)}}{I_1 \left[e^{-\psi(L)} \left(\int_0^L e^{\psi(y)} dy - I_2 \right) + I_2 e^{-\psi(0)} \right]},$$

$$I_2 = \frac{\int_0^L e^{-\psi(y)} dy \int_0^y e^{\psi(x)} dx}{\int_0^L e^{-\psi(y)} dy}, \quad (18)$$

$$I_1 = \frac{N\zeta}{k_B T} \int_0^L e^{-\psi(y)} dy,$$

$$\psi(y) = \int^y \frac{F'(x) - A}{k_B T}.$$

FIG. 8. (a) Variation of net flux (J_{net}) with channel asymmetry parameter Δ . Parameter set chosen: $c_0=0.25$, $c_1=0.4$, $W=1.75$, $N=150$, $l=60$, $\zeta=1$, $k_B T=1$, and $\nu=0.5$. (b) Variation of net flux (J_{net}) with chain length (N). Parameter set chosen: $c_0=0.25$, $c_1=0.4$, $W=1.75$, $\Delta=25$, $l=60$, $\zeta=1$, $k_B T=1$, and $\nu=0.5$.

Similarly, the stationary flux (J_{av}^-) of the chain propagation X_P along the backward direction ($-ve$) of the channel axis can be expressed as

$$J_{av}^- = \frac{\epsilon}{1+\epsilon} J_+(-A_0) + \frac{1}{1+\epsilon} J_+(\epsilon A_0). \quad (19)$$

Therefore, the net stationary current for the chain can be obtained as

$$J_{net} = J_{av}^+ - J_{av}^-. \quad (20)$$

Eqs. (17)-(20) are the central results of this section. Using these equations, we show the variation of J_{net} with channel asymmetry (Δ) parameter for $N=150$ in Fig. 8(a). The result shows that an introduction of channel asymmetry leads to a non-zero J_{net} in the direction of longer funnel. Also, for a highly asymmetric shape of the chamber, the non-monotonicity in J_{net} values has been noticed. This indicates the usefulness of the prescription described above to analyze a polymeric entropic ratchet device. In Fig. 8(b), we have studied the variation of J_{net} with the chain length N for high N limit. The result shows that the current decreases with an increase in N . We cannot explore the current variation in low N limit using this model because of the limitation in using blob theory in this limit. The variation of current with polymer size in low N limit can qualitatively be calculated in the spirit of Reguera *et al.*²¹ If the width of bottleneck positions is wider

than the Flory radius of the chain, the situation can be described as an entropic ratchet device for a Brownian particle with finite size. In this regime the rectification performance increases with an increase in polymer size.²¹

Before we leave this section, we mention few important points. The values of c_0 and c_1 have been chosen arbitrarily. c_0 controls the mean occupation number inside a unit chamber and c_1 scales the absolute value of the free energy barrier. These parameters have been chosen arbitrarily considering the fact that the associated free energy barrier height (ΔF_c) remains in the order of $k_B T$. In the limit of $\frac{\Delta F_c}{k_B T} \gg 1$ or $\ll 1$ the rectification efficiency vanishes drastically.¹⁶ In principle, the values of c_0 and c_1 may depend on channel parameter like θ and l . The nature of this dependency has to be verified experimentally. For simplicity we are considering them as constant parameters in the present manuscript. Second, we have considered a weak external driving force, so that the effect of such external forcing affects the equilibrium translocation dynamics within a linear response regime.¹⁶ If the strength of the external driving force is not weak, one has to employ the tension-propagation method⁶¹ to understand the effect under such non-equilibrium situations.^{62,63}

V. CONCLUSION

In conclusion, we have studied the stochastic dynamics of a uniformly charged flexible polyelectrolyte chain confined in a three dimensional narrow channel with periodically varying cross sectional area. The polyelectrolyte chain is acted upon by an AC driving force along the direction of the channel axis. We observe a directed transport for the PE when spatial reflection symmetry of the channel is broken and the PE is driven below a threshold driving frequency. We have also observed two different non-monotonic variations of rectification performance, one with increasing structural asymmetry of the channel and the other with increasing chain length. A competition between the gain, caused by geometric asymmetry effect and the loss due to the conformation entropy change is responsible for both turnovers. We believe that the ratchet effect observed here and its non-monotonic rectification ability in terms of both the molecular weight of the PE and the extent of structural asymmetry would be very useful for macromolecular transports at single molecular level.

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