

Ejection Dynamics of Semiflexible Polymers out of a Nanochannel*

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Abstract Using theoretical analysis and three-dimensional Langevin dynamics simulations, we investigate the influence of chain rigidity on the ejection dynamics of polymers from a nanochannel. We find that there exist two distinct dynamical regimes divided by a critical chain length for both flexible and semiflexible chains. At the short chain regime, semiflexible chains eject faster than flexible chains of the same chain length due to the longer occupying length. In contrast, at the long chain regime, semiflexible chains eject slower than flexible ones as the effective entropic driving force decreases. Based on these results, we propose that the nanochannels could be used to separate flexible and semiflexible chains effectively.

Keywords: Ejection dynamics; Semiflexible polymers; Langevin dynamics simulations; Chain separation.

INTRODUCTION

A vast number of biopolymers, such as DNA of *E. Coli*, are constrained in cell spaces which are much smaller than their natural size^[1, 2]. In such confined environments, in order to optimize the competing demands of conformational entropy, excluded volume and bending energy, macromolecules often adopt conformations which are unlikely to appear in free spaces^[3–10]. Confined environments play a key role in a number of biological processes and modern technologies, such as DNA packaging into virus capsids^[11–14], bacterial chromosome segregation^[15–25], polymer translocation through nanopores^[26–47], viruses injecting their DNA into a host cell^[48, 49], and nanofluidic devices^[50, 51].

The ejection of a polymer from confined space is of significant interest, and draws a lot of attention over the past few decades due to its high biological relevance in viral gene transfection. Recent experiments have shown a series of fascinating results of the DNA ejection from viral capsids^[52–57]. Evilevitch *et al.*^[52, 53] showed that the ejection of the viral genome can be controlled effectively by varying the external osmotic pressure. Frutos *et al.*^[54] studied the kinetics of DNA ejection from bacteriophage T5, and suggested that the complete ejection of DNA from bacteriophage is a multistep process perhaps due to nicks in the DNA. Therefore, an activation energy of about $70 k_B T$ must be overcome to allow the complete DNA ejection. Grayson *et al.*^[55] provided insights particularly into the effects of genome length and ionic state of the buffer. It was found that shorter genomes eject with lower speeds but shorter total time, and the presence of divalent magnesium ions

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(replacing sodium) reduces the pressure and increases ejection time. L f *et al.*^[56] found that the ejection rate depends on the temperature of system, the length of DNA, and the presence of binding proteins. The initial ejection rate increases exponentially with the temperature. Longer genome lengths and addition of binding proteins also lead to faster ejection rates.

To grasp the physical nature of polymer ejection, a number of theoretical and numerical simulation works have been carried out through simple models^[58–66]. By using the spherical capsid model^[58–63], the purely entropy-driven ejection of polymers has been investigated. Among these studies, many aspects affecting the ejection dynamics, such as the solvent quality^[58], the electrostatic interactions^[59, 60], the knot effect^[61], the shape anisotropy^[62], and the polymer rigidity^[63], have been studied in detail.

Recently, Milchev *et al.*^[64] have studied the escaping dynamics of a flexible polymer chain out of a cylindrical nanotube by means of Monte Carlo simulations. They found that the ejection time has a nonmonotonic behavior with increasing the chain length, which is in accordance with the experimental data^[67]. Sheng *et al.*^[65] have taken into account the topological structure of polymer chains, and found that the ejection of ring chains is faster compared to linear counterparts due to a larger entropic pulling force. Later, Klushin *et al.*^[66] proposed a new approach to separate ring polymer chains from linear ones. Although much efforts have been spent in understanding the entropy-driven ejection of polymers from cylindrical nanotubes, the effect of chain rigidity on its ejection dynamics has not been clarified yet. Given that a variety of biopolymers, such as DNA, actin and collagen have different degrees of rigidity, an answer to this problem is urgently needed.

The confinement free energy $\mathcal{F}$ of semiflexible polymers is much different from that of flexible ones. The expressions of $\mathcal{F}$ of flexible polymers confined in nanochannels were given in the pioneering works of de Gennes by using the blob model^[68, 69]. For semiflexible polymers, this work was done by using the deflection model, known as the Odijk's theory^[70, 71]. Afterwards, a number of numerical works^[72–74] focused on the discrepancy of $\mathcal{F}$ of flexible and semiflexible polymers.

As to the ejection of semiflexible polymers from nanochannels, the driving force originating from the entropic penalty of confinement should be closely related to the persistence length of chains and the extent of confinements. Therefore, we investigate the effect of chain rigidity on the ejection dynamics of polymers from nanochannels by using three-dimensional (3D) Langevin dynamics simulation. The framework of this paper is organized as follows. In the “model and methods” part, we briefly describe our model and the simulation technique. Further, our results and discussion are presented. Finally, we make a summary.

MODEL AND METHODS

In our numerical simulations, the polymer is modeled as a coarse-grained bead-spring chain with adjacent beads connected to each other by the finite extension nonlinear elastic (FENE) potential

$$U_{\text{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln(1 - r^2/R_0^2) \quad (1)$$

where r is the distance between consecutive beads, k is the spring constant, and R_0 is the maximum allowed separation between connected segments. Excluded volume interactions between segments are modeled by the truncated Lennard-Jones (LJ) potential

$$U(r) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \varepsilon, & r \leq 2^{1/6} \sigma \\ 0, & r > 2^{1/6} \sigma \end{cases} \quad (2)$$

Here σ is the diameter of chain segments, r is the distance between a pair of beads, and ε is the well depth of the potential. The chain rigidity is introduced by employing the bending potential between successive bonds,

$$U_{\text{bend}}(\theta) = \frac{\kappa}{2}(\theta - \theta_0)^2 \quad (3)$$

where κ is the bending constant, θ is the angle between adjacent bond vectors with its equilibrium value θ_0 being set at π in this work.

We consider a 3D geometry as sketched in Fig. 1, where a polymer chain is confined in a nanochannel with one end being sealed. The diameter and height of the channel is denoted by D and h , respectively. The interactions between chain segments and the nanochannel are also modeled by the above repulsive LJ potential.

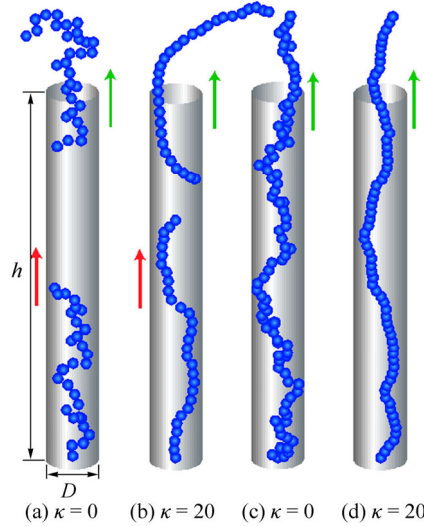


Fig. 1 Schematic illustrations of the ejection process of a short chain with the bending constant (a) $\kappa = 0$ and (b) $\kappa = 20$; a long chain (c) $\kappa = 0$ and (d) $\kappa = 20$ (The diameter and height of the channel are $D = 5$ and $h = 60$, respectively.)

In Langevin dynamics simulation, each chain segment is subjected to conservative, frictional, and random forces, respectively

$$m\ddot{\mathbf{r}}_i = -\nabla(U_{\text{LJ}} + U_{\text{FENE}}) + \mathbf{F}_{\text{ext}} - \xi \mathbf{v}_i + \mathbf{F}_i^{\text{R}} \quad (4)$$

where m , ξ and $\mathbf{v}_i$ are the mass, frictional coefficient and velocity of chain segments, respectively. $\mathbf{F}_i^{\text{R}}$ is the random force which satisfies the fluctuation-dissipation theorem^[67]

$$\begin{aligned} \langle \mathbf{F}_i^{\text{R}}(t) \rangle &= 0 \\ \langle \mathbf{F}_i^{\text{R}}(t) \mathbf{F}_j^{\text{R}}(t') \rangle &= 2dk_{\text{B}}T\xi\delta_{ij}\delta(t-t') \end{aligned} \quad (5)$$

Here d is the space dimensionality, k_{B} is Boltzmann constant, δ_{ij} is the Kronecker delta, $(t - t')$ is the Dirac delta function, and T is the absolute solvent temperature. In our model, the energy, length, and mass scales of the system are determined by the LJ parameters ϵ , σ , and the mass of chain segments m , respectively. Then, the corresponding time scale is given by $t_{\text{LJ}} = (m\sigma^2/\epsilon)^{1/2}$. The dimensionless parameters in the model are chosen to be $T = 1.2$, $\xi = 0.7$, $R_0 = 1.5$, and $\kappa = 30$. The bending constant κ is an adjustable parameter in the simulations ranging from 0 to 20.

The Langevin equation is then integrated in time by the method described by Ermak and Buckholz^[68]. The time step in our simulation is chosen as $\Delta t = 0.005$. Initially, the last segment of the chain is tethered to the bottom of the nanochannel, while the remaining segments are under thermal collisions described by the Langevin thermostat until an equilibrium chain conformation is obtained. Then, the last segment is released and an ejection event begins. The time duration between the release of last segment and its escape from the opening

of the nanochannel is defined as the ejection time. Typically, the data are averaged over 1000 independent ejection events.

RESULTS AND DISCUSSION

Theory

We consider a semiflexible polymer of the persistence length P and the contour length L , which is confined in an infinitely long nanochannel of diameter D . Note that the persistence length P of chains varies with κ ranging from 5 to 20 in a linear way $P = 0.80\kappa + 0.67$ with $P(\kappa = 0) = 1.45$ (data not given here). In the strong confinement limit $D \ll P$, *i.e.*, the classic Odijk regime^[70, 71], the chain can be viewed as a sequence of deflection segments that undulate inside the channel with a typical length $\lambda = P^{1/3}D^{2/3}$. Thus, the mean extension of chain is L/λ times the projection of a deflection segment along the channel axis,

$$R_{\parallel} = \frac{L}{\lambda} \cdot \lambda \cos \theta \approx Nb \left[1 - 2\alpha_0 (D/P)^{2/3} \right] \quad (6)$$

Here L/λ is the number of deflection segments, θ is the average deflection angle, N is the number of chain segments, b is the diameter of chain segments, and $\alpha_0 = 0.1701 \pm 0.0001$ is a dimensionless parameter independent of P and D ^[66]. Then, the confinement free energy $\mathcal{F}$ per unit length is given by^[70, 71]

$$\frac{\mathcal{F}}{R_{\parallel}} = \frac{A_0 k_B T}{P^{1/3} D^{2/3}} \quad (7)$$

The dimensionless constant A_0 is a universal number independent of both macroscopic and microscopic properties of the polymer chain. The value of A_0 is not known exactly at present, but was approximately estimated as 2.3565 ± 0.0004 from computer simulation^[74].

Now, we start to analyze the ejection dynamics of semiflexible polymers from a nanochannel. Intuitively, the ejection process can be divided into two regimes according to the relative length of polymer compared to the height of channel h . As the occupying length of a polymer inside the nanochannel equals to h , *i.e.*, $R_{\parallel} = h$, a critical number of chain segments N_c can be written as

$$N_c = \frac{h}{b[1 - \alpha_0 (D/P)^{2/3}]} \quad (8)$$

Obviously, short chains with $N < N_c$ are initially fully confined inside the nanochannel, while long chains with $N > N_c$ have tails outside the nanochannel.

Ejection of a long chain from a nanochannel

For the ejection of a long chain with $N > N_c$ from a nanochannel, there is an effective pulling force acting on the confined part of the chain. The existence of such a force can be understood by considering the free energy $\mathcal{F}$ of a chain partially confined in a nanochannel with the innermost segment of a distance x from the channel opening,

$$\mathcal{F} = \frac{A_0 k_B T}{P^{1/3} D^{2/3}} x \quad (9)$$

Then, the effective pulling force can be estimated as the derivative of the free energy with respect to x ,

$$f = \frac{\partial \mathcal{F}}{\partial x} \approx \frac{A_0 k_B T}{P^{1/3} D^{2/3}} \quad (10)$$

Let us suppose that the ejection process proceeds in a quasi-equilibrium state. For such a steady-state process, the pulling force f is balanced by the total frictional (drag) force f_{drag} acting on all the segments inside the channel,

$$f = f_{\text{drag}} = n(t) \cdot \xi \frac{dx(t)}{dt} \quad (11)$$

Here $n(t)$ is the real-time number of segments inside the nanochannel, and ξ is the frictional coefficient of a segment. $x(t) \approx n(t)b[1 - \alpha_0(D/P)^{2/3}]$ is the real-time occupying length of a chain inside the nanochannel, and $dx(t)/dt$ is the real-time ejection rate. By integrating the Eq. (11), the ejection time for a long chain is given by

$$\tau_{\text{long}} \approx \frac{\xi h^2 P^{1/3} D^{2/3}}{2A_0 k_B T b [1 - \alpha_0(D/P)^{2/3}]} \quad (12)$$

Ejection of a short chain from a nanochannel

For the ejection of a short chain with $N < N_c$ from a nanochannel, the process consists of two stages. Firstly, the chain needs to diffuse a distance $(h - R_{\parallel})$ to reach the channel opening. During this process, the motion of chain is described by the unbiased one-dimensional (1D) diffusion with no net force acting on the chain. Thus, the time for the chain reaching the channel opening is

$$\tau_{\text{short},1} \approx \frac{(h - R_{\parallel})^2}{2D_{\text{diff}}} \approx \frac{N\xi}{2k_B T} \{h - Nb[1 - \alpha_0(D/P)^{2/3}]\}^2 \quad (13)$$

where $D_{\text{diff}} = k_B T / N\xi$ is the diffusion coefficient of the chain. With a certain number of segment escaping from the nanochannel, the ejection process is driven by a pulling force f , which is the same as the long chain case. By replacing h with $R_{\parallel}$ in Eq. (12), the time spending on this stage is given by

$$\tau_{\text{short},2} \approx \frac{N^2 \xi b P^{1/3} D^{2/3}}{2A_0 k_B T} [1 - \alpha_0(D/P)^{2/3}] \quad (14)$$

Combining Eq. (13) and Eq. (14), we obtain the ejection time of a short chain τ_{short} as

$$\tau_{\text{short}} = \tau_{\text{short},1} + \tau_{\text{short},2} \quad (15)$$

Generally, $\tau_{\text{short},2}$ is negligible compared to $\tau_{\text{short},1}$ for quite short chains as the driven process occurs on a shorter time scale than the diffusive one. Namely, the diffusion of the chain inside the nanochannel dominates the total ejection process, and thus the ejection time τ_{short} is approximately equal to $\tau_{\text{short},1}$.

By setting the partial differential of the ejection time with respect to N at 0, i.e., $\partial \tau_{\text{short}} / \partial N = 0$, we can get two extreme values of N . One is N^*

$$N^* \approx \frac{h}{3b[1 - \alpha_0(D/P)^{2/3}]} \quad (16)$$

at which τ_{short} gets maximal

$$\tau_{\text{max}} \approx \frac{2\xi h^3}{27b k_B T [1 - \alpha_0(D/P)^{2/3}]} \quad (17)$$

The other one is N_c beyond which the ejection enters the long chain regime with the ejection time keeping constant,

$$N_c \approx \frac{h}{b[1 - \alpha_0(D/P)^{2/3}]} \quad (18)$$

which is the same as the Eq. (8).

Numerical Results

Next, we resort to the Langevin dynamics simulations to clarify the effects of chain rigidity on the ejection dynamics, and examine the theory we proposed above.

Figure 2(a) shows the ejection time τ as a function of the chain length N at different bending constants κ . Clearly, the chain rigidity does not alter the general trends of τ with increasing N , *i.e.*, τ has a maximum at the short chain regime while it is nearly independent of N at the long chain regime. Interestingly, we find that for chains of the same N , the chain with a larger rigidity ejects faster at $N < N_c$. This is due to the simple fact that the stiffer the chain becomes, the longer $R_{||}$ is, as implied by Eq. (6). In contrast, the chain with a smaller rigidity ejects faster at $N > N_c$, which is in line with our theoretical analysis (Eq. 12). It is also a natural result of a weaker effective pulling force f with increasing κ . Meanwhile, the chain length where τ gets maximal N^* shifts towards shorter chain lengths, as predicted by Eq. (16). As κ increases, the value of $\tau_{\max}$ decreases with a rapid decay rate, which is in accordance with the prediction of Eq. (17). As predicted by our theory (Eqs. 12, 13, 17 and 18), with an increase in the height of nanochannels, τ , $\tau_{\max}$ and N_c grow accordingly, as illustrated Fig. 2(b).

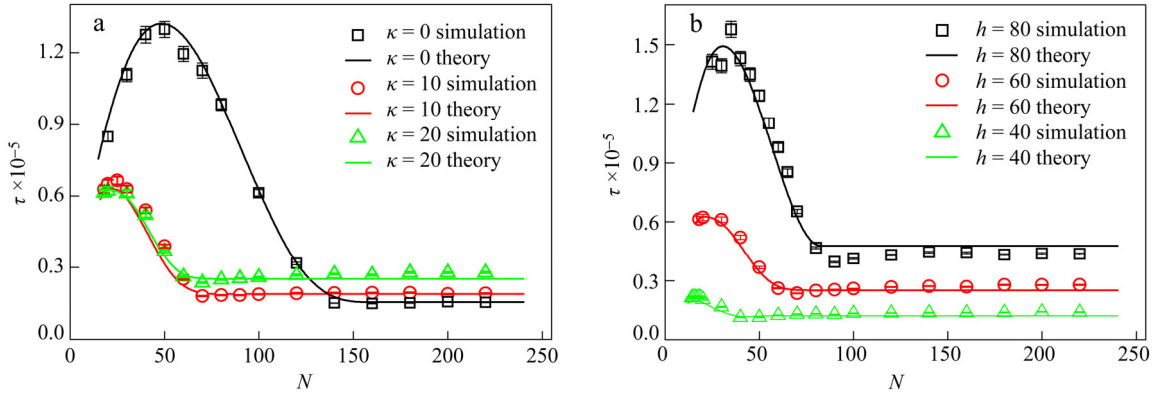


Fig. 2 The ejection time τ as a function of the chain length N at (a) different bending constants $\kappa = 0, 10$ and 20 with $D = 5$ and $h = 60$, and (b) different channel heights $h = 40, 60$ and 80 with $\kappa = 20$ and $D = 5$ (Solid lines are plotted according to Eqs. 12 and 13 with suitable prefactors.)

It has been suggested by previous works^[56, 57] that the maximal ejection time $\tau_{\max}$ of flexible chains scales with the height of nanochannels h as $\tau_{\max} \sim h^\mu$ with $\mu = 3$. This result is reproduced by our simulations with $\mu = 2.95 \pm 0.08$, as shown in Fig. 3. For semiflexible chains, $\mu = 3$ is also suggested by Eq. (17). However, $\mu = 2.84 \pm 0.06$ at the stiffest chain with $\kappa = 20$ we have studied is obtained from the simulations, revealing a nonignorable deviation from the predicted value $\mu = 3$. This deviation stems mainly from the assumption that the ejection of short chains is diffusion-dominated. Specifically, the effective pulling force f for flexible chains is large enough so that this assumption is reasonable. However, it is somewhat reluctant for semiflexible chains as f gets much smaller.

As the chain length exceeds the critical value N_c , the ejection time τ_{long} remains nearly constant. Equation 12 suggests that τ_{long} of semiflexible chains should scale with h as $\tau_{\text{long}} \sim h^\nu$ with $\nu = 2$, which is also valid for flexible chains^[64, 65]. Figure 4 shows that $\nu = 1.88 \pm 0.02$, 1.72 ± 0.01 and 1.61 ± 0.02 for $\kappa = 0, 10$ and 20 , respectively. Obviously, there exist deviations from the theoretical value $\nu = 2$. Furthermore, the deviation gets larger for stiffer chains.

This discrepancy can be explained in terms of the hypothesis about the friction exerted on the segments outside the nanochannel. For flexible chains, the speed of segments inside the nanochannel is much faster compared to that of segments outside the nanochannel. As a result, the ejected segments could not diffuse away from the channel opening. In this case, the hypothesis that segments outside the nanochannel are not affected by friction is valid, leading to the scaling exponent $\nu = 2$ as given in Eq. (12) and the works of Refs. [64] and [65].

However, segments of semiflexible polymers outside the nanochannel would not accumulate around the nanochannel opening due to the high bending energy penalty. Therefore, the above hypothesis is no longer valid. Let us consider another limit, *i.e.*, all the segments of semiflexible polymers outside the nanochannel are affected by friction. Then, Eq. (11) should be rewritten as

$$f_{\text{drag}} = N\xi \frac{dx(t)}{dt} \quad (19)$$

Correspondingly, we can obtain the scaling exponent $\nu = 1$ in this limit. ν obtained from the simulations falls in between 1 and 2, indicating that segments of semiflexible polymers outside the nanochannel are partially affected by friction.

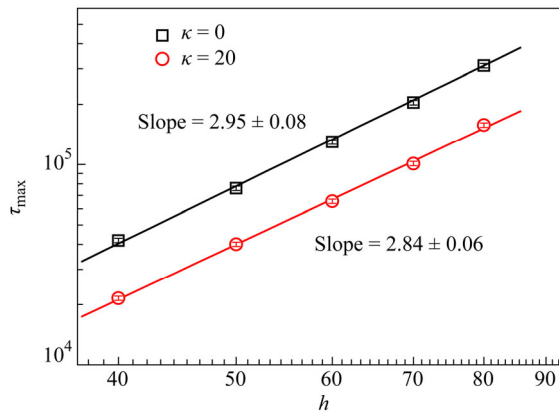


Fig. 3 Plots of the maximal ejection time $\tau_{\max}$ against the height of nanochannels h at two different bending constants $\kappa = 0$ and 20. (Here the diameter of nanochannels is $D = 5$. Solid lines are the linear fittings to the data.)

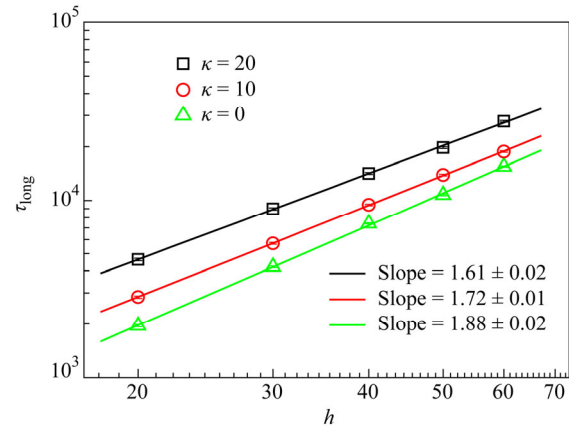


Fig. 4 The ejection time τ_{long} at the long chain regime $N > N_c$ as a function of the height of nanochannels h (Here the diameter of nanochannels is $D = 5$, and the chain length is $N = 200$. Solid lines are the linear fittings to the data.)

As suggested by Eq. (12), τ_{long} should be approximately proportional to $P^{1/3}D^{2/3}$ due to the small constant α_0 . By plotting τ_{long} against $P^{1/3}D^{2/3}$ at different κ , we find that all data points collapse to a single straight line, as shown in Fig. 5. This validates our theory directly.

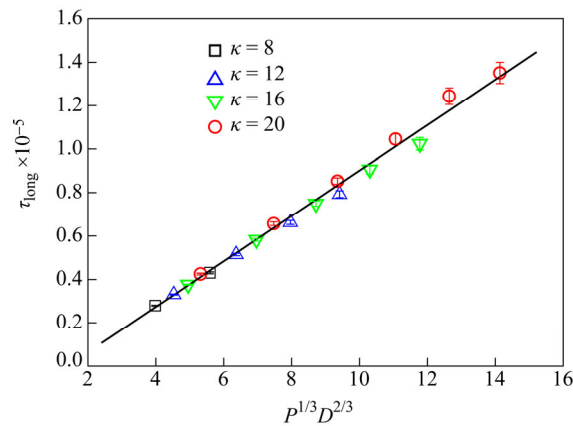


Fig. 5 Plot of τ_{long} against $P^{1/3}D^{2/3}$ (Here the height of nanochannel is $h = 100$, and the chain length is $N = 200$. The solid line is a linear fitting to the data.)

For the sake of a deeper understanding about ejection process, we have recorded the waiting time of each segment $t_{\text{wt}}(s)$ defined as the time duration that the s th segment and the $(s + 1)$ th one eject from the nanochannel sequentially. As shown in Fig. 6(a), $t_{\text{wt}}(s)$ of short chains decreases rapidly at the beginning, indicating that there is a short induction period. After a certain number of segments escaping from the nanochannel, the ejection is driven by a constant force f , and $t_{\text{wt}}(s)$ shows a slow and linear decrease. It indicates that the ejection rate $dx(t)/dt$ should increase linearly with the decreasing $n(t)$ to maintain the balance between f and f_{drag} , as predicted by Eq. (11). The duration of the induction period relies on the chain rigidity. For the flexible chain, the crossover of the waiting time occurs at $s \approx 15$, which is roughly the number of segments $g \approx (D/\sigma)^{3/5} \approx 15$ in a compression blob of size $D = 5$. For semiflexible chains, this crossover emerges at $s \approx 6$ and 7 for $\kappa = 10$ and 20 , respectively. These values match the corresponding typical length of the deflection segments $\lambda = P^{1/3}D^{2/3}$.

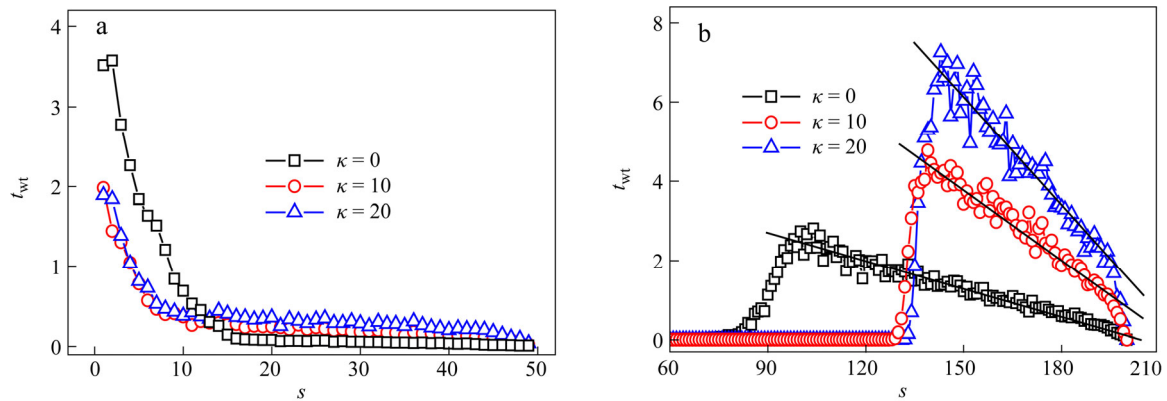


Fig. 6 The waiting time $t_{\text{wt}}(s)$ of (a) short chains of length $N = 50$ and (b) long chains of length $N = 200$ at three different bending constant $\kappa = 0, 10$ and 20 (Here the height of the nanochannel is $h = 60$, and the diameter of the nanochannel is $D = 5$.)

For long chains $N > N_c$, no induction period is observed due to the fact that the whole ejection is a driven process. As expected, $t_{\text{wt}}(s) = 0$ at small s regime and afterwards, there is a sharp increase in $t_{\text{wt}}(s)$ since the initial conformation of the chain is random so that the exact serial number of the segment locating at the channel opening is uncertain. Similar to the case of short chains, a linear decrease in $t_{\text{wt}}(s)$ occurs subsequently as shown in Fig. 6(b). However, unlike the flexible chain, the ejection of the last 5–6 segments accelerates significantly.

Besides, we have checked the effects of chain rigidity on the distributions of the ejection time at both short and long chains regimes. Figure 7(a) shows highly asymmetric distributions with long tails for short chains due to the physical nature of the diffusion-dominated ejection process. By comparison, the distribution of τ for the flexible chain is more asymmetric as the distance that the semiflexible one needs to diffuse is shorter. For long chains $N > N_c$, the ejection is dominated by the effective driving force f so that nearly symmetrical distributions are observed. As f is smaller for a semiflexible chain, the corresponding distribution of τ gets wider, as shown in Fig. 7(b).

In view of the significant difference in the ejection time of flexible chains and semiflexible ones at the short chain regime, nanochannels are very likely to be used to separate chains with different rigidities. Here we define a dimensionless parameter γ as follows to characterize the separation effect

$$\gamma = \ln \frac{\tau(\kappa_i, N)}{\tau(\kappa_j, N)} \quad (20)$$

Obviously, a larger value of $|\gamma|$ means a better separation effect. As shown in Fig. 8, the flexible chains could be separated from semiflexible ones effectively at a certain range of N . Since there is no obvious difference in the ejection time of semiflexible chains with different rigidities as shown in Fig. 2(a), we do not

expect a good separation effect when these chains are mixed together by using of their ejection from a nanochannel.

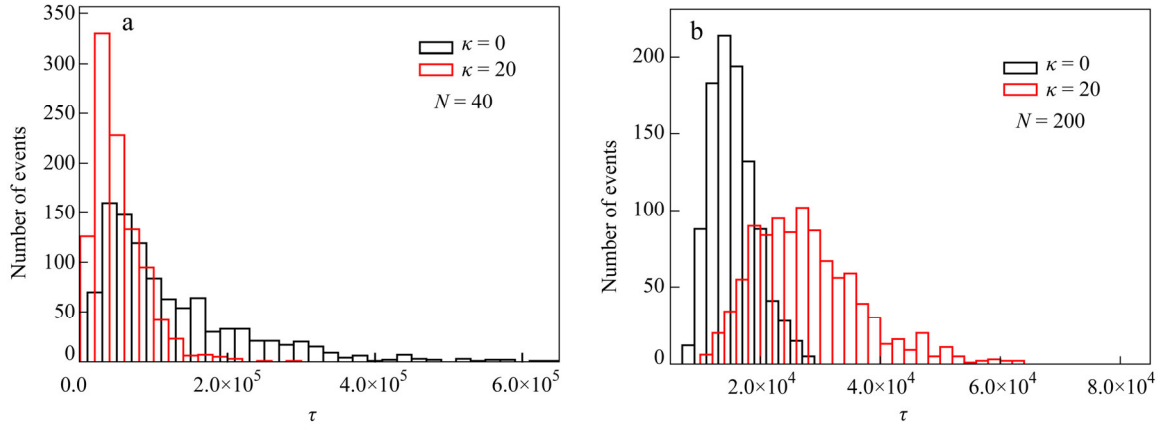


Fig. 7 Distributions of the ejection time of (a) short chains $N = 40$, and (b) long chains $N = 200$ at two different bending constants $\kappa = 0$ and 20 (Here the height of the nanochannel is $h = 60$, and the diameter of the nanochannel is $D = 5$.)

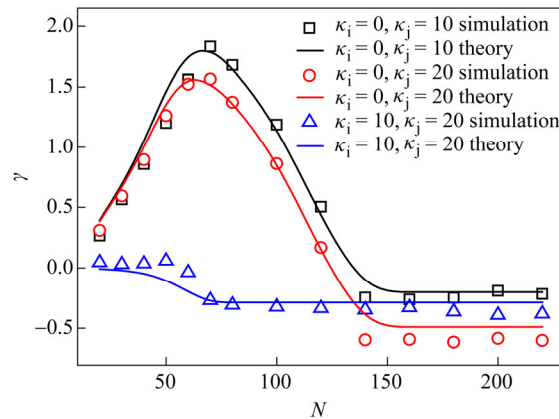


Fig. 8 The ratios of the ejection times of chains with different rigidities γ (Here the height of the nanochannel is $h = 60$, and the diameter of the nanochannel is $D = 5$.)

We have noticed that the equilibrium distribution of semiflexible polymer chains between a macroscopic dilute solution phase and small voids of cylindrical shape was studied recently^[77], which is closely related to potential separation of semiflexible polymer chains from flexible ones by using the gel permeation chromatograph (GPC). It was found that the equilibrium partition coefficient $K = c_i/c_E$ decreases with increasing chain rigidity, suggesting that for the same GPC column, the stiffer chain would elute earlier than the more flexible one of the same chain length^[77]. Here c_i and c_E are the equilibrium polymer concentrations of the interior and the exterior solution phases, respectively. As stated above, the ejection of a semiflexible chain is much slower than that of a flexible one, which means that the flexible chain would be separated first. Obviously, this result is in contrast to that reported by Wang *et al.*^[77]. It may be noted that in our simulations, all the polymer chains are initially confined in nanochannels so that there does not exist a partition process of chains between two different phases. However, GPC separation is relied on the difference in the equilibrium partition coefficient K of polymer chains with different rigidities. Therefore, the idea that separates semiflexible polymer chains from flexible ones based on nanochannel ejection here differs from the microscopic mechanism of GPC separation in nature.

CONCLUSIONS

Using 3D Langevin dynamics simulations, we have investigated the ejection dynamics of semiflexible polymers from a nanochannel. We find that there exist two distinct dynamical regimes regardless of the chain rigidity divided by a critical chain length N_c . At the short chain regime $N < N_c$, the ejection of a semiflexible chain is faster than that of a flexible one in that the former occupies a longer distance inside the nanochannel. In contrast, the ejection of long semiflexible chains gets slower with increasing the chain rigidity as the effective pulling force decreases. A deviation in the power law $\tau_{\max} \simeq h^\nu$ indicates that the proportion of $\tau_{\text{short},2}$ in τ_{short} becomes larger for stiffer chains. Due to the high bending energy penalty, the accumulation of segments around the channel opening is not the right physical picture describing the ejection of semiflexible chains. It leads to a change in the scaling law $\tau_{\text{long}} \sim h^\nu$. Moreover, we predict that $\tau_{\text{long}} \sim P^{1/3} D^{2/3}$, which is subsequently verified by our simulation results directly. By calculating the waiting time, we show that the ejection rate increases linearly with the progress of the ejection process. In comparison to the distribution of τ of flexible chains, the distribution of τ of semiflexible chains is narrower at $N < N_c$; while it becomes wider at $N > N_c$. Based on these results, we propose that nanochannels can be used to separate flexible and semiflexible chains effectively.

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