

**Long charged macromolecule in an entropic trap with rough surfaces**Yevgeni Sh. Mamasakhlisov,<sup>1,2</sup> Shura Hayryan,<sup>1</sup> and Chin-Kun Hu<sup>1,\*</sup><sup>1</sup>*Institute of Physics, Academia Sinica, Nankang 11529, Taipei, Taiwan*<sup>2</sup>*Department of Molecular Physics, Yerevan State University, 1 Alex Manougian Street, Yerevan 375025, Armenia*

(Received 6 June 2011; revised manuscript received 27 January 2012; published 2 November 2012)

The kinetics of the flux of a charged macromolecular solution through an environment of changing geometry with wide and constricted regions is investigated analytically. A model device consisting of alternating deep and shallow slits known as an “entropic trap” is used to represent the environment. The flux is supported by the external electrostatic field. The “wormlike chain” model is used for the macromolecule (dsDNA in the present study). The chain entropy in both the deep and the shallow slits, the work by the electric field, and the energy of the elastic bending of the chain are taken into account accurately. Based on the calculated free energy, the kinetics and the scaling behavior of the chain escaping from the entropic trap are studied. We find that the escape process occurs in two kinetic stages with different time scales and discuss the possible influence of the surface roughness. The scope of the accuracy of the proposed model is discussed.

DOI: [10.1103/PhysRevE.86.051904](https://doi.org/10.1103/PhysRevE.86.051904)

PACS number(s): 87.15.hj, 87.15.ad

**I. INTRODUCTION**

The study of the dynamics, kinetics, and thermodynamics of a macromolecule in a confined geometry by theoretical and experimental methods has attracted much attention in recent decades [1]. The wide interest in the topic is due to its significant importance both for the understanding of many fundamental biological processes and for numerous applications in modern nanotechnological devices. Transportation of the molecules through narrow constrictions is commonly observed in translocation of DNA and RNA through nanopores in nuclear and cellular membranes [2,3], in the process of DNA and proteins sieving [4–7], and in DNA sequencing [8–10]. Of considerable technological importance is the behavior of DNA in nanochannels [11]. Microfabricated entropic trap arrays have been demonstrated to be useful for efficient separating of large (5–200 kbp) DNA molecules [5–7]. The entropy-driven separation of DNA molecules has been investigated extensively [12–16]. Further development of the technique for optimal separation, selectivity, and resolution requires a deeper understanding of the mechanism of entropic trapping and the kinetics of the escape of the macromolecule from the trap. Live biological objects like proteins and membrane channels possess irregular, rough surfaces in microscopic scale and/or nanoscale. Here we study the kinetics and scaling behavior of macromolecules escaping from the entropic trap and discuss the possible influence of surface roughness.

The schematic diagram of the device which mimics the environment of changing geometry is shown in Fig. 1. The idea of the scheme is borrowed from Refs. [5–7]. Entropic barriers can be made in a microfluidic channel by alternating two different (deep and shallow) regions. DNA molecules migrating under an external driving force (electric field of strength  $E_s$  in this case) are retarded at the entropic barriers. It has been shown that the local deformation of DNA molecules at the interface between the deep and the shallow regions is critical for the escape kinetics. The activation energy of this deformation is independent of the length of the chain.

Relatively short, rodlike DNA has been studied theoretically in Ref. [12]. However, the model of the rodlike chain does not include the free energy of elastic extension of dsDNA, the conformational degrees of freedom, and the work of the electric field on the long chain transfer. These factors become non-negligible in the case of the long chains. It should be mentioned that the predictions of the theory developed in Ref. [12] deviate from the experimental data as the DNA length increases to several persistence lengths,  $l_p$ . Here we take into account accurately the conformational degrees of freedom, which allows us in principle to address the intermediate and long chain lengths and to improve the agreement with the experimental data. However, we focus only on the long chain limit because in this case the conformational degrees of freedom play the most important role.

The escape of relatively long DNAs from the entropic trap has been investigated recently in Refs. [17,18], exploiting Brownian dynamics simulations. Here we present an analytical model describing the chain escape from the entropic trap with heterogeneous walls. We take into account the free energy of entropic stretching in a confined environment, the contribution of the electric field work, and the entropy loss in the narrow slit. Our basic goal is to investigate the dynamics of dsDNA repartitioning inside the entropic trap device, described, e.g., in Ref. [7] and, more specifically, the process of escaping of the long polyelectrolyte chain from the entropic trap with fractal walls. We find that the escape process occurs in two kinetic stages with different time scales and discuss the possible influence of the surface roughness.

**II. FREE ENERGY OF THE WORMLIKE CHAIN (WLC) IN THE SLIT**

We assume that the height of the shallow slit  $H_s$  satisfies the condition  $H_s \ll a$ , where  $a$  is the Kuhn length of the chain, and the height of the deep slit  $H_d \sim R_g$ , where  $R_g$  is the mean-square radius of gyration of the polymeric chain in a relaxed configuration. The total change of the free energy, caused by transfer of the subchain of length  $\lambda$  to the confined environment

\*Email address: [huck@phys.sinica.edu.tw](mailto:huck@phys.sinica.edu.tw)

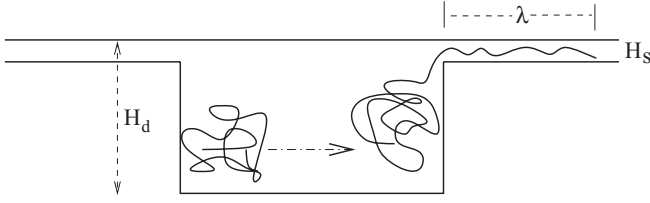


FIG. 1. A macromolecule approaches the right wall and starts to be sucked into the slit. Since  $a \gg H_s$ , the fluctuations in the plane of the page are restricted and the part  $\lambda$ , which has entered the slit, looks stretched. The chain cannot make turns in that plane.

(Fig. 1), consists of three parts discussed in following three subsections.

### A. Free energy change caused by loss of entropy

Using the results from Refs. [19,20], one can estimate the entropy loss caused by transfer of the subchain of length  $\lambda$  from the deep to the shallow slit by

$$\Delta S \simeq -(k_B \lambda / a)(a / H_s)^{2/3}, \quad (1)$$

where  $a$  is the Kuhn's segment of the chain. In the case  $H_s \ll a$ , the corresponding free energy change is

$$\Delta F \equiv -T \Delta S \simeq \frac{k_B T \lambda}{a} \left( \frac{a}{H_s} \right)^{2/3}. \quad (2)$$

Odijk's scaling [19] has been initially obtained for the chain confined in the tube, but in Ref. [20] its validity has been justified for the chain confined in the slit. According to Ref. [20], the more accurate estimation of the entropy loss  $\Delta S$  requires one to use the crossover expression

$$\Delta S \simeq -\frac{k_B \lambda}{a} \frac{(a / H_s)^2}{[C_1(a / H_s)^2 + C_2(a / H_s) + 1]^{2/3}}. \quad (3)$$

Here  $C_1$  and  $C_2$  are some constants.

The next two parts to be calculated in the next two subsections are (i) the free energy change caused by the chain stretching under the electric field and (ii) the free energy change due to the work of the electric field on the chain transfer from the deep slit into the shallow one as a whole. These terms can be calculated separately (and we do so for the convenience) since the physical work in the potential (electrostatic in this case) field depends only on the initial and final states of the system. Thus, although the chain transfer and stretching are not independent processes, one can separate the total free energy into two terms. Below we discuss the limits of accuracy of our approach.

The free energy change in Eq. (2) and the free energy change (i), mentioned in the previous paragraph are not completely decoupled. However, if the Kuhn segment length  $a$  satisfies the condition  $H_s \ll a$ , the transverse conformational fluctuations are substantially suppressed and have no effect on the longitudinal ones. Thus, in case of  $H_s \ll a$ , the free energy terms due to confinement, stretching, and chain transfer can be included through the additive scheme. In this case, the conformational behavior of the chain is expected to be two-dimensional. If  $H_s \leq a$ , the effective two-dimensional behavior is supposed to be described not by the original

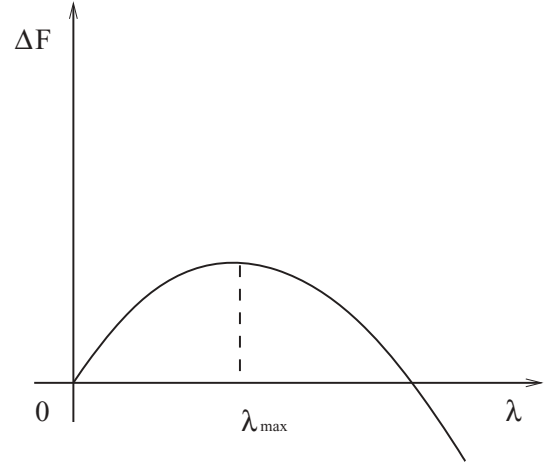


FIG. 2. Dependence of the free energy change  $\Delta F$  on the segment length  $\lambda$ .

persistence length  $l_p$ , but by some effective persistence length (see, e.g., Ref. [21]).

### B. The free energy change due to WLC stretching

If  $\lambda \sim l_p$  with  $l_p = a/2$  being the persistence length, then the free energy of stretching is negligible. Thus, the dependence of the free energy change on  $\lambda$  exhibits the well-known behavior [5] shown in Fig. 2 with a maximum at  $\lambda_{\max}$ . Under typical experimental conditions, the free energy barrier  $\Delta F_{\text{act}}$  is comparable to the thermal energy  $k_B T$  [7] ( $\Delta F_{\text{act}} \sim k_B T$ ). According to Ref. [22], the corresponding activation time  $\tau_{\text{act}}$  for crossing the barrier is  $\tau_{\text{act}} \simeq \tau_0 \exp(\beta \Delta F_{\text{act}})$ , where  $\tau_0 \sim 1/L$  and  $L$  is the total contour length of the chain.

On the scale of  $\lambda_{\max}$ , the WLC behaves as a rigid rod and the free energy is defined mainly by Eq. (2) and  $\Delta F \sim T \lambda - E_s \lambda^2$  [5]. The initial stage of the chain escape from the entropic trap has been investigated, e.g., in Refs. [5,7]. To describe stretching of the long chain ( $\lambda \gg l_p$ ), one needs to estimate the contribution of the entropic elasticity into the free energy. Following Refs. [23,24] we estimate the free energy of the WLC at a given value of the extending external force  $f = q l_p E_s$ , where  $q$  is the effective linear charge density. A similar approach has been developed initially for the end forces. However, as it is shown in Ref. [25], the end force  $f$  transfers along the chain and acts on each segment. That is why the polymer chain can be presented as being located in the effective stretching potential field, tending to orient each segment of the chain. Thus, the stretching of a chain by its end can be equated to the action on it by an external orienting field. As  $f$  is the parameter under control, the chain end-to-end distance  $x$  becomes a physically observable quantity, conjugated to the force  $f$ :

$$x = \frac{\partial \ln Z_\lambda}{\partial (\beta f)}, \quad (4)$$

where  $Z_\lambda$  is the partition function of a WLC of length  $\lambda$ . To calculate the free energy of a WLC at a given value of  $f$ , we define the Legendre transform

$$\Gamma(x/\lambda) = -(\beta/\lambda) \mathcal{F}_{\text{WLC}}[\lambda, f_\lambda(x)] - \beta f x / \lambda, \quad (5)$$

where

$$\mathcal{F}_{\text{WLC}}[\lambda, f_\lambda(x)] = -k_B T \ln Z_\lambda[f_\lambda(x)]. \quad (6)$$

The term  $f_\lambda(x)$  has been defined implicitly in Eq. (4) and corresponds to the force-extension expression derived in Ref. [26] for a WLC in two dimensions. From the Legendre transform, the elastic free energy change of the WLC of length  $\lambda$  and at the given value of  $f = ql_p E$  can be written as

$$\begin{aligned} \Delta G_{\text{el.}}(\lambda, f) &= \int_0^x dx' f_\lambda(x') - fx \\ &= -\frac{k_B T \lambda}{16l_p} \left(\frac{x_0}{\lambda}\right)^2 \left[ \frac{1}{(1-x_0/\lambda)^2} + 3 \right]. \end{aligned} \quad (7)$$

Here  $x_0$  is the mean end-to-end distance of a WLC in a two-dimensional space and is defined by  $f = f_\lambda(x_0)$ , where  $f_\lambda(x)$  is the elastic force of the WLC of length  $\lambda$  [26]:

$$f_\lambda(x) = (k_B T / l_p) [3x/8\lambda - 1/16 + (1/16)(1-x/\lambda)^{-2}], \quad (8)$$

which implies direct proportionality of the end-to-end distance at a given value of  $f$  to the length of subchain,  $x_0 \sim \lambda$ . Thus, the elastic contribution (7) into the free energy from WLC stretching is directly proportional to the length of subchain  $\lambda$  and is written as

$$\Delta G_{\text{el.}}(\lambda, f) = \lambda k_B T g(E, q, l_p), \quad (9)$$

where

$$g(E, q, l_p) = -\frac{1}{16l_p} \left(\frac{x_0}{\lambda}\right)^2 \left[ \frac{1}{(1-x_0/\lambda)^2} + 3 \right].$$

### C. Free energy change due to the work of the electric field

We calculate this term separately for the shallow and the deep regions. For the shallow slit we have

$$\mathcal{E}_s = -qE_s \int_0^\lambda dt x(t), \quad (10)$$

where  $x(t)$  is the mean-square displacement of the segment ( $t; t+dt$ ) along the  $x$  axis inside the shallow slit. Here we assume that  $x(t)$  is not perturbed by chain stretching. To estimate  $\mathcal{E}_s$ , let us consider two limiting cases:  $\lambda \sim l_p$  and  $\lambda \gg l_p$ . When  $\lambda \sim l_p$  one can approximate the chain as a rigid rod, and the free energy  $\mathcal{E}_s$  reads

$$\mathcal{E}_s \simeq -qE_s \int_0^\lambda dt t = -qE_s \lambda^2 / 2. \quad (11)$$

It has been shown in Ref. [20] that, when  $H_s \ll a$ , the polymer segments are forced toward the near-wall regions and thus the WLC in a shallow slit behaves as a two-dimensional polymer in the case of flat walls and as a  $d_s$ -dimensional polymer in the case of rough walls, where  $2 \leq d_s < 3$  is the fractal dimension of the rough surface.

Calculation of the free energy  $\mathcal{E}_s$  requires understanding the typical conformations formed in the process of the chain escape from the shallow slit. The hairpin can cross the activation barrier with probability higher than that of the linear subchain [22]. At the same time, the DNA, confined in a shallow slit with  $H_s < l_p$ , must contain thermally activated hairpins with some typical distance  $g$  (the so-called global persistence length) between them [27].

In a shallow channel with a square cross section,  $g \gg l_p$  [27]. However, for the nanoslit of a rectangular cross section,  $W_s \times H_s$ , where  $W_s \gg H_s$ , the global persistence length is of the same order as the regular persistence length  $l_p$ ,  $g \sim l_p$  [27]. Hence, for  $\lambda \gg l_p$  the typical chain conformation is supposed to be a single stretched subchain of length  $\lambda$ . In this case the reasonable estimate of the mean-square dimension  $x(t)$  is

$$x(t) \simeq a(t/a)^{\nu_2}, \quad (12)$$

where  $\nu_2 = \nu(d)|_{d=2} = \frac{3}{4}$  for the flat surface. For the rough surface, the  $\nu_2$  value depends on the relationship between the excluded volume of the chain and the roughness of the surface [28]. Using Eqs. (10) and (12) we obtain the following for the free energy of a long chain in the shallow slit:

$$\mathcal{E}_s \simeq -\frac{qE_s a^{1-\nu_2}}{1+\nu_2} \lambda^{1+\nu_2}. \quad (13)$$

The free energy decrease caused by the work of the electric field inside the deep slit can be written as

$$\mathcal{E}_d = \mathcal{E}'_d(\lambda) + \mathcal{E}''_d(L, \lambda), \quad (14)$$

where  $\mathcal{E}'_d(\lambda)$  is the free energy loss caused by the transfer of the subchain of length  $\lambda$  from the deep slit and  $\mathcal{E}''_d(L, \lambda)$  is that for the subchain of length  $L - \lambda$ . The first term is calculated in a manner similar to that of Eq. (13):

$$\mathcal{E}'_d(\lambda) \simeq -\frac{qE_d a^{1-\nu_3}}{1+\nu_3} \lambda^{1+\nu_3}, \quad (15)$$

where  $\nu_3 = \nu(d)|_{d=3} = \frac{3}{5}$ . Removing the subchain of length  $\lambda$  from the deep slit means moving by distance  $a(\lambda/a)^{\nu_3}$  the remaining part of the molecule of length  $L - \lambda$  as a whole. Since the force applied to the subchain of length  $L - \lambda$  is equal to  $E_d q(L - \lambda)$ , the free energy decrease reads

$$\mathcal{E}''_d(L, \lambda) \simeq -E_d q(L - \lambda) a(\lambda/a)^{\nu_3} x. \quad (16)$$

Thus, the total free energy decrease in the whole system  $\mathcal{E}(\lambda) = \mathcal{E}_s + \mathcal{E}_d$  caused by the work of electric field is

$$\begin{aligned} \mathcal{E}(\lambda) &\simeq -qa\lambda \left[ \frac{E_s}{1+\nu_2} (\lambda/a)^{\nu_2} - \frac{E_d}{1+\nu_3^{-1}} (\lambda/a)^{\nu_3} \right] \\ &\quad - E_d qaL (\lambda/a)^{\nu_3}. \end{aligned} \quad (17)$$

From Eqs. (2), (9), and (17), the free energy for  $\lambda \gg l_p$  is

$$V(\lambda) \simeq k_B T \lambda (\Delta\Omega + g) + \mathcal{E}(\lambda), \quad (18)$$

where  $\Delta\Omega = \frac{1}{a} (\frac{a}{H_s})^{2/3}$ . Thus, the free energy of stretching just adds some additional term to the entropic barrier  $\Delta\Omega$  and does not change qualitatively the system kinetics.

## III. ESCAPE FROM THE ENTROPIC TRAP

### A. Stochastic equation for dynamics of the chain

Following the approach of Refs. [17,18], one can consider the escape process from the deep slit into the shallow one as occurring in three stages with different characteristic time scales: (1) the approach time  $t_{\text{app}}$ , required for the molecule to reach the gate into the constriction; (2) the activation time  $t_{\text{act}}$ , required to reach the transition state (the point of the free energy maximum); and (3) the escape

time  $t_{\text{esc}}$ , which is the time required to completely exit from the deep slit into the shallow one after the molecule has been activated. Here we focus mainly on the chain escape process, and that is why we consider  $t_{\text{esc}}$  instead of  $t_{\text{cross}}$  [17,18], the time required to exit the shallow slit.

The walls of the slit screen off the hydrodynamic interactions at scales larger than that of the slit depth [29]. Thus, in the shallow slit the total screening of hydrodynamic interactions takes place and the WLC segments undergo a Rouse-like friction [30]. The electric force acts not only on the DNA but also on the counterions. This force induces a flow in the opposite direction, which cancels the hydrodynamic interactions between the monomers, and the polymeric coil becomes freely drained in the wide slit too [31]. Thus the hydrodynamic friction scales as  $L$  and the stochastic equation for the dynamics of the chain to escape from the entropic trap is

$$\gamma \partial_t \lambda = -\partial_\lambda V(\lambda) + \sqrt{2D} \xi(t), \quad (19)$$

where  $V(\lambda)$  is the free energy defined by Eq. (18),  $\gamma = L\eta$  is the coefficient of friction, and  $\eta$  is the solvent viscosity per unit length. It can be estimated as  $\eta = \frac{\zeta}{a}$ , where  $\zeta$  is the viscosity of the Kuhn segment. The diffusion coefficient  $D$  is defined by the equation  $D = \gamma k_B T$  and  $\xi(t)$  is the white noise.

To analyze the escape dynamics we consider two limiting cases: (i)  $a \ll \lambda \ll L$  and (ii)  $L - \lambda \ll L$ , for the early and the late stages of the escape process, respectively.

### B. Early and late stages of escape

For  $a \ll \lambda \ll L$  we have  $V(\lambda) \simeq \mathcal{E} \simeq -E_d q a L (\lambda/a)^{\nu_3}$ . Then for the early stage the dynamic Eq. (19) can be transformed into

$$\partial_t \lambda = (\nu_3 E_d q a^{1-\nu_3} / \eta) \lambda^{\nu_3-1} + (2T/\eta L)^{1/2} \xi(t). \quad (20)$$

If the chain is sufficiently long then one can neglect fluctuations, and the mean value of the chain length  $m = \langle \lambda \rangle$  satisfies the equation

$$\dot{m}(t) \simeq \chi_1 m(t)^{\nu_3-1}, \quad (21)$$

where  $\chi_1 = \nu_3 E_d q a^{1-\nu_3} / \eta$ . By solving this equation one obtains estimates for the time and the velocity of the first stage of escape:

$$t_1 \sim (L/2)^{2-\nu_3}, \quad V_1 = L/2t_1 \sim L^{\nu_3-1}. \quad (22)$$

For the late stage of escape ( $L - \lambda \ll L$ ), we have the following dynamic equation:

$$\partial_t \lambda = (E_s q a^{1-\nu_2} / \eta L) \lambda^{\nu_2} + (2T/\eta L)^{1/2} \xi(t). \quad (23)$$

By neglecting fluctuations we obtain

$$\dot{m}(t) \simeq \chi_2 m(t)^{\nu_2}, \quad (24)$$

where  $\chi_2 = E_s q a^{1-\nu_2} / \eta L$ . Using a procedure similar to that for the early stage, one obtains the time  $t_2$  and the mean velocity  $V_2$  for the late stage of escape:

$$t_2 \sim L^{2-\nu_2}, \quad V_2 = L/2t_2 \sim L^{\nu_2-1}. \quad (25)$$

## IV. CONCLUSIONS AND DISCUSSION

In summary, the chain escaping from the deep slit into the shallow one occurs in two kinetic stages. The first, early stage is governed mainly by work, performed by the electric field inside the deep slit,  $E_d$ . The characteristic time of escape is scaled with the chain length as  $\sim L^{2-\nu_3}$ . Thus, the first stage of escape is defined by conformational statistics in three-dimensional space and  $t_1$  increases with the length of the chain. The second stage is governed by the electric field inside the shallow slit  $E_s$  and scales with the molecular weight of the chain, according to the two-dimensional conformational statistics, as  $\sim L^{2-\nu_2}$ .

With  $E_d \ll E_s$  [7] and  $\nu_2 > \nu_3$ , we see that the escape of the first half of the chain is the limiting factor which slows down substantially the escape of macromolecules from the entropic trap. The total characteristic time of escape increases nonlinearly with the length of the chain, while the mean velocity is decreased. In the thermodynamic limit  $L \rightarrow \infty$ , the total escape time is defined mainly by three-dimensional statistics as  $t_{\text{esc}} \sim L^{2-\nu_3}$ .

Thus, we have obtained analytically the nonlinear  $\sim L^\alpha$  ( $\alpha > 1$ ) scaling dependence for the time of escape from the entropic trap. This nonlinear result differs from the linear dependence, obtained analytically for the crossing time  $t_{\text{cross}} \sim L$  by Sebastian and Paul [22], which is substantially one-dimensional, and it can be reproduced in the framework of our theory in the case of the one-dimensional slit,  $\nu_1 = \nu(d)|_{d=1} = 1$ . Thus, we conclude that the chain escape from the entropic trap is not one-dimensional and conformational statistics is an important point of this process.

To determine the limits of validity of the proposed theory, let us go back to Eq. (19). The length of the chain inside the shallow slit  $\lambda$  is considered as a reaction coordinate of the chain transfer. At the same time,  $-\partial_\lambda V(\lambda)$  is acting as the thermodynamic force, produced by the free energy gradient. The polymer chain needs enough time to explore the available conformational space to consider the free energy as an effective potential for the thermodynamic force. Thus, this approach can be valid only in the case of sufficiently slow dynamics and, consequently, for weak electric fields.

The most interesting case for applications is when the free energy barrier is comparable with the energy of thermal fluctuations,  $\Delta F_{\text{act}} \simeq k_B T$ . From Eq. (1) and the paragraph below Eq. (11), the free energy barrier is written as

$$\Delta F_{\text{act}} = \frac{1}{2qE_s} \left( \frac{k_B T}{a} \right)^2 \left( \frac{a}{H_s} \right)^{4/3}. \quad (26)$$

Thus, the electric field inside the shallow slit must satisfy the equation

$$\frac{a^2 q E_s}{k_B T} \simeq \left( \frac{a}{H_s} \right)^{4/3}. \quad (27)$$

At the same time, the total characteristic time of escape  $t_{\text{esc}}$  must be comparable or larger than the longest relaxation time of the polymer chain (the Rouse relaxation time [32]) to be sufficient for exploration of the conformational space:

$$\tau_R \simeq \frac{\zeta a^2}{k_B T} \left( \frac{L}{a} \right)^{1+2\nu}, \quad (28)$$

where  $\nu$  is the Flory exponent. In the most interesting case of the long chain,

$$t_{\text{esc}} \sim \frac{\zeta}{E_d q a^{2-\nu_3}} L^{2-\nu_3}. \quad (29)$$

Since  $\nu_2 > \nu_3$ , the limiting stage of relaxation will be the second stage of escape and we need to use  $\nu = \nu_2$  in Eq. (28). By comparing the Rouse relaxation time (28) and the characteristic time of escape (29), we obtain that the electric field inside the deep slit must satisfy the equation

$$\frac{a^2 q E_d}{k_B T} \leq \left(\frac{a}{L}\right)^{2\nu_2 + \nu_3 - 1}. \quad (30)$$

Using the values  $\nu_2 = 0.75$  and  $\nu_3 = 0.6$  we obtain the following from Eqs. (27) and (30):

$$\frac{E_d}{E_s} \leq \left(\frac{a}{L}\right)^{1.1} \left(\frac{H_s}{a}\right)^{1.3}. \quad (31)$$

The typical conditions described in Ref. [7] correspond to  $E_d/E_s \sim 10^{-2}$  and  $a \leq H_s$ . In this case the Kuhn length  $a = 2\ell$ , where  $\ell$  is the renormalized persistence length [21], which accounts for the geometric coupling between the normal and transverse fluctuations in the shallow slit.

Taking the Kuhn length value equal to  $a = 300$  bp, we can see that under the experimental conditions used in Ref. [7] our approach should be valid for chains up to tens of kilobase pairs as these lengths have been addressed in Ref. [7].

The proposed analytical approach describes an escape kinetics in terms of Flory exponents  $\nu(d)$ . It allows one to address the influence of the roughness of the surface on the chain escape from the entropic trap. As it was shown, e.g., in Ref. [28], the roughness of the surface affects the mean size  $R$  of the chain. The  $\nu_2$  value depends on the relationship between the excluded volume of the chain and the roughness of the surface [28]. In a two-dimensional case it can reduce the Flory exponent  $\nu_2$  down to  $\nu_2 = 0.5$  and even make  $R$  independent of the molecular weight, i.e.,  $\nu_2 = 0$ . In this case the escape of the second part of the chain becomes limiting. If  $\nu_2 = 0.5$  then  $t_2 \gg t_1$  for the long chain. Thus, the roughness of the narrow constriction can substantially slow down the chain escape from the entropic trap and thereby complicate the separation of macromolecules by molecular weight. To clarify this issue we propose to investigate experimentally the chain escape from the deep slit to the shallow slit with the different roughness of the surface.

#### ACKNOWLEDGMENTS

S.H. and C.-K.H. were supported by the National Science Council in Taiwan under Grant Nos. NSC 100-2811-M-001-014, NSC 100-2923-M-001-003-MY3, and NCTS (North). Y.M. was supported by the Volkswagenstiftung Grant "Equilibrium and non-equilibrium behavior of single- and double-stranded biological molecules".

- 
- [1] See, e.g., A. E. Allahverdyan, Z. S. Gevorkian, C. K. Hu, and T. M. Nieuwenhuizen, *Phys. Rev. Lett.* **96**, 098302 (2006); *Phys. Rev. E* **79**, 031903 (2009); C.-H. Lin, Y.-C. Tsai, and C.-K. Hu, *ibid.* **75**, 031903 (2007).
- [2] A. L. Lehninger, D. L. Nelson, and M. M. Cox, *Principles of Biochemistry* (Worth, New York, 1993).
- [3] A. Meller, *J. Phys.: Condens. Matter* **15**, R581 (2003).
- [4] J. Fu *et al.*, *Nat. Nanotech.* **2**, 121 (2007).
- [5] J. Han, S. W. Turner, and H. G. Craighead, *Phys. Rev. Lett.* **83**, 1688 (1999).
- [6] J. Han and H. G. Craighead, *Science* **288**, 1026 (2000).
- [7] J. Han and H. G. Craighead, *Anal. Chem.* **74**, 394 (2002).
- [8] H. Bayley *et al.*, in *Single Molecules and Nanotechnology*, edited by R. Rigler and H. Vogel (Springer, Heidelberg, 2008).
- [9] G. Maggla *et al.*, *Proc. Natl. Acad. Sci. USA* **105**, 19720 (2008).
- [10] A. Aksimentiev *et al.*, *Biophys. J.* **87**, 2086 (2004).
- [11] J. D. Cross, E. A. Strychalski, and H. G. Craighead, *J. Appl. Phys.* **102**, 024701 (2007).
- [12] J. Fu, J. Yoo, and J. Han, *Phys. Rev. Lett.* **97**, 018103 (2006).
- [13] M. Streek *et al.*, *J. Biotechnol.* **112**, 79 (2004).
- [14] E. Moendarbary, T. Y. Ng, H. Pan, and K. Y. Lam, *Microfluid. Nanofluid.* **8**, 243 (2010).
- [15] R. B. Schoch, J. Han, and P. Renaud, *Rev. Mod. Phys.* **80**, 839 (2008).
- [16] N. Douville, D. Huh, and S. Takayama, *Anal. Bioanal. Chem.* **391**, 2395 (2008).
- [17] A. S. Panwar and S. Kumar, *Macromolecules* **39**, 1279 (2006).
- [18] Y. M. Lee and Y. L. Joo, *J. Chem. Phys.* **127**, 124902 (2007).
- [19] T. Odijk, *Macromolecules (Washington, DC, US)* **16**, 1340 (1983); **19**, 2313 (1986).
- [20] J. Z. Y. Chen and D. E. Sullivan, *Macromolecules (Washington, DC, US)* **39**, 7769 (2006).
- [21] T. Odijk, *J. Chem. Phys.* **125**, 204904 (2006).
- [22] K. L. Sebastian and A. K. R. Paul, *Phys. Rev. E* **62**, 927 (2000).
- [23] S. Blumberg *et al.*, *Biophys. J.* **88**, 1692 (2005).
- [24] Y. Sh. Mamasakhlisov, B. A. Todd, A. V. Badasyan, A. V. Mkrtchyan, V. F. Morozov, and V. A. Parsegian, *Phys. Rev. E* **80**, 031915 (2009).
- [25] A. Yu. Grosberg and A. R. Khokhlov, in *Statistical Physics of Macromolecules* (AIP Press, New York, 1994).
- [26] A. Prasad, Y. Hori, and J. Kondev, *Phys. Rev. E* **72**, 041918 (2005).
- [27] T. Odijk, *Phys. Rev. E* **77**, 060901 (2008).
- [28] S. F. Edwards and Y. Chen, *J. Phys. A* **21**, 2963 (1988).
- [29] O. B. Bakajin, T. A. J. Duke, C. F. Chou, S. S. Chan, R. H. Austin, and E. C. Cox, *Phys. Rev. Lett.* **80**, 2737 (1998).
- [30] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
- [31] D. Long, J.-L. Viovy, and A. Ajdari, *Biopolymers* **39**, 755 (1996).
- [32] P. G. De Gennes, *Macromolecules (Washington, DC, US)* **9**, 587 (1976).