Barrier crossing of a semiflexible ring polymer

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Motivated by the dynamics of a membrane in response to an external force, we study the thermally activated crossing of a semiflexible ring polymer over a potential barrier. For the bistable potential of Kramers type smoothly varying over a long length scale, we calculate the crossing rate using the multidimensional Kramers’ rate theory and the functional integral method. We find that, due to its conformational fluctuation, the rate for a flexible ring is much larger than that for a stiff ring. For a sufficiently long chain length or a sufficiently weak bending modulus, the ring undergoes a compact-stretch transition. The stretched conformation of the chain results in a decrease of the activation energy and so the further increase of the rate. This result implies that the soft matter conformational flexibility and adaptability facilitate the barrier crossing.

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I. INTRODUCTION

The dynamical response of soft matter such as polymers and membranes to external forces and confinements is a ubiquitous problem occurring in biological situations. It encompasses various situations such as polymer transport across membranes, DNA electrophoresis, and cell or vesicle transport in narrow channels. Many studies on polymer problems have been reported in the context of entropic barrier and entropic trapping arising from inhomogeneous environments [1–4]. It is well known from these reports that the entropic effect due to the conformational flexibility of macromolecules affects their dynamical properties.

Consider a fluid membrane subject to an external force or a confinement. In order to understand some aspects of its dynamical response, we consider the Kramers problem of barrier crossing applied to the membrane. When viewed in two dimension, the membrane can be regarded as a semiflexible ring polymer characterized by a bending modulus. In this paper, we consider the Kramers problem where we seek the rate of a semiflexible polymer crossing the barrier of a bistable potential acting on each segment. For simplicity, we neglect the excluded volume effect between segments.

Recently there have been a number of studies on the barrier-crossing of flexible polymers [5–7]. Based upon the multidimensional Kramers theory formulated by Langer [8], they [5,7] considered the effects of chain flexibility and collective modes on the efficiency in the crossing. For a chain spring constant smaller and chain length larger than critical values, the chain undergoes coil-to-stretch transition, thereby enhancing the crossing rate. On the other hand, the work of Sebastian and Paul [6] considered the limit of very long chains, where they found there emerges another kind of mode, namely, kink motion, which facilitates the efficient barrier crossing. The work here extends the earlier work [7] to a semiflexible ring chain of infinite length for application to membrane dynamics.

In Sec. II we define our semiflexible polymer model and briefly describe the N-dimensional Kramers rate theory [8]. Using the method of functional integral, we calculate the requisite partition functions and the transition states in Sec. III. In Sec. IV, the barrier escaping rate of the semiflexible ring polymer is calculated. Concluding remarks are given in Sec. V.

II. MODEL

We consider a long and semiflexible ring chain consisting of N identical beads with the following Hamiltonian:

$$H_0 = \frac{\kappa}{2} \sum_{n=1}^{N} (\bar{r}_{n+1} - 2\bar{r}_n + \bar{r}_{n-1})^2,$$

where $\bar{r}_n$ denotes the position of the $n$th bead and the bending modulus $\kappa$ is related to temperature $T$ and persistence length $l_p$ of the chain as $\kappa = (k_B T l_p)^{1/3}$, where $l$ is the spacing between the beads. Note that the next-nearest interactions between the beads of the chain are considered to describe the internal stiffness or semiflexibility of the chain. This model is different from the typical bead-spring model of flexible chain in which only the nearest neighbor coupling such as $(\bar{r}_{n+1} - \bar{r}_n)^2$ is considered [7,9].

Now let us suppose that the above semiflexible chain is initially trapped in the left well of a one-dimensional bistable potential.

$$H_1 = \sum_{n=1}^{N} V(x_n),$$

$$V(x_n) = \frac{1}{2} \omega_a^2 a^2 x_n^2 - \frac{1}{2} \omega_B^2 a^2 x_n^4 + \frac{\omega_B}{4a^2} x_n^5,$$

where $V(\pm a) = 0$ and the barrier height is $V_0 = V(0) = \frac{1}{2} \omega_B a^2$. Hence, two local wells at $\pm a$ are separated by the
formations of the chain in the configuration space between the beads. The activation energy of each bead; here we neglect the hydrodynamic interaction between the beads. It is easy to see that the dynamics along the direction is relevant to the escape process of the chain while the chain undergoes free diffusion along the y and z directions. Hence, we restrict our analysis to the x direction with

\[ H(\{\bar{x}_n\}) = H_0 + H_1. \]  

(2.4)

To obtain the thermally activated crossing or escape rate of the whole chain over the barrier, we assume the escape process to be a Brownian motion occurring in the 3N-dimensional configuration space of the segments given in the above Hamiltonian. This assumption is valid in the limit of overdamping where the momenta of the beads have already relaxed on the time scale of their spatial diffusion of interest to us. It is easy to see that the dynamics along the x direction is relevant to the escape process of the chain while the chain undergoes free diffusion along the y and z directions. Hence, we restrict our analysis to the x direction with

\[ H(\{x_n\}) = \frac{K}{2} \sum_{n=1}^{N} (x_{n+1} - 2x_n + x_{n-1})^2 + \sum_{n=1}^{N} V(x_n). \]  

(2.5)

It is straightforward to show that there are two stable con-
formations of the chain in the configuration space \{x_n\}. These represent the states with all beads being localized near +a or −a denoted as \{x_n\}_+ and \{x_n\}_-, respectively. We want to obtain the escape from the saddle point \{x_n\}_+ to \{x_n\}_-. The activation energy of this process is determined by the path crossing a saddle point in the configuration space satisfying \( \delta H|_{\{x_n\}_+}=0 \) and involving only one unstable mode. We call this saddle point \{x_n\}_a a transition state. If the transition state of the chain is well defined and the barrier crossing is much slower than any internal relaxations in the chain, then the escape rate \( R \) is given by applying the N-dimensional Kramers rate theory in the overdamped limit formulated by Langer [8]

\[ R = \frac{\omega_x}{2\pi\gamma} \frac{Z_\omega}{Z} \sqrt{2\pi k_B T e^{-\beta\Delta H}}, \]  

(2.6)

where \( \omega_x \) is the frequency of the unstable mode at the saddle point and \( \beta^{-1} = k_B T \). The term \( \gamma \) is the damping constant for each bead; here we neglect the hydrodynamic interaction between the beads. The activation energy \( \Delta H \) and the partition function associated with the fluctuation of the chain near the transition state (initial state), \( Z_\omega(Z_-) \), can be written as

\[ \Delta H = H(\{x_n\}_+)-H(\{x_n\}_-). \]  

(2.7)

\[ Z_- = \int_{\text{well}} d^N\{x_n\} e^{-\beta[H(\{x_n\}_+)-H(\{x_n\}_-)]}, \]  

(2.8)

\[ Z_\omega = \int_{\text{saddle}} d^{N-1}\{x_n\} e^{-\beta[H(\{x_n\}_+)-H(\{x_n\}_-)]}. \]  

(2.9)

For the partition function at the saddle point \( Z_\omega \), the contribution of the unstable mode is implicitly omitted. It is important to note that the escape rate Eq. (2.6) is determined only by the local properties near the well and the saddle point.

In the next sections, we identify the well defined transition states, calculate the partition functions and finally obtain the barrier crossing rates of our semiflexible ring polymer using the functional integral method.

III. TRANSITION STATES

Our N-bead chain under the bistable potential Eq. (2.3) can be regarded as a continuous string for sufficiently large N and for not-too-weak coupling between the beads so as to remain close to each other. In order to take the continuous limit, let us define a continuous variable \( s = n/N \) with \( 0 \leq s \leq 1 \). Replacing \( x_n \) with \( x(s) \), \( \Sigma_n^N ds \), and \( x_n + 1 - x_n \) with \( dx/Nds \), we have an energy functional from Eq. (2.5) such as

\[ H(x(s)) = N \int_0^1 ds h(x(s),\dot{x}(s),\ddot{x}(s)), \]  

(3.1)

where

\[ h(x(s),\dot{x}(s),\ddot{x}(s)) = \frac{K}{2N^2} \ddot{x}(s)^2 + V(x(s)). \]  

(3.2)

Here \( \dot{x} = dx/ds \) and \( \ddot{x} = d^2x/ds^2 \).

The stationary path satisfying \( \delta H = 0 \) is determined by the Euler–Lagrange equation

\[ \frac{d^2}{ds^2} \left( \frac{\partial h}{\partial \dot{x}} \right) - \frac{d}{ds} \left( \frac{\partial h}{\partial \ddot{x}} \right) + \frac{\partial h}{\partial x} = 0, \]  

(3.3)

where results in the following differential equation for the stationary configuration denoted as \( \bar{x}(s) \):

\[ \frac{\kappa}{N^2} \frac{d^4\bar{x}}{ds^4} - \omega_x^2 \bar{x} + \frac{\omega_\theta^2}{a^2} \bar{x}^3 = 0. \]  

(3.4)

The solution is subject to the periodic boundary condition \( x(s+1) = x(s) \). It can be easily shown that three trivial real solutions of \( \bar{x}(s) = 0, \pm a \) are the only solutions if \( (2\pi)^4 \kappa > N^4 \omega_x^2 \). Hence, in either case of sufficiently stiff or short chain determined by the above inequality, the configuration \( \bar{x}(s) = 0 \) is the only transition state of the chain crossing the barrier from the left stable state, \( \bar{x}(s) = -a \), to the right stable one, \( \bar{x}(s) = a \).

Once the stationary solutions for \( x \) are obtained, the fluctuations at the well and the saddle points are to be investigated for the purpose of calculating the partition functions in Eqs. (2.8) and (2.9) by expansion.
The eigenfunctions \( \psi_j(s) \) of \( H^{(2)} \) satisfying the periodic boundary condition are

\[
\psi_j(s) = A_j \cos 2\pi js + B_j \sin 2\pi js, \quad j = 0, 1, 2, \ldots, N - 1,
\]

where \( A_0 = 1 \) and \( B_j = \pm \sqrt{2 - A_j^2} \) by normalization condition.

At \( \bar{x}(s) = \pm a \), the trivial solutions of the Euler–Lagrange equation (3.4), we have

\[
H^{(2)} \psi_j(s) = \epsilon_j \psi_j(s),
\]

\[
\epsilon_j = \omega_j^2 + \kappa \left( \frac{2\pi j}{N} \right)^4,
\]

where \( \omega_j^2 = 2\omega_B^2 \) are the curvatures of the potential at the wells. The positivity of the eigenvalues \( \epsilon_j \) for all \( j \) confirms that stationary solutions \( \bar{x}(s) = \pm a \) are the stable states as expected before [5,7].

At \( \bar{x}(s) = 0 \), another trivial solution of the Euler-Lagrange equation, we have

\[
H^{(2)} \psi_j(s) = \epsilon_j' \psi_j(s),
\]

\[
\epsilon_j' = -\omega_B^2 + \kappa \left( \frac{2\pi j}{N} \right)^4.
\]

Since the lowest eigenvalue \( \epsilon_0' = -\omega_B^2 \) is always negative, \( \bar{x}(s) = 0 \) is indeed the saddle point with only one unstable eigenmode \( \psi_0(s) \) only if \( \epsilon_1' = -\omega_B^2 + \kappa(2\pi/N)^4 > 0 \) as mentioned in the above.

But, in case of \( \epsilon_i' < 0 \), \( \bar{x}(s) = 0 \) has at least two unstable modes, \( \psi_0(s) \) and \( \psi_2(s) \). Hence, it is necessary to find a new saddle point configuration satisfying Eq. (3.4) and having only one unstable mode. Considering that the three trivial stationary solutions of the Euler-Lagrange equation are the only solutions where \( (2\pi)^4\kappa > N^4\omega_B^2 \), that is \( \epsilon_1' > 0 \), the new saddle point configuration with only one unstable mode will be the stationary solution when \( \epsilon_1' < 0 \) and \( \epsilon_j' > 2 > 0 \). To obtain the stationary solutions for \( \epsilon_i' > 0 \), let us define new parameters \( \delta = \epsilon_i' / \omega_B^2 \) and \( \eta(s) = \bar{x}(s) / a \). Then the differential equation (3.4) is rewritten as

\[
1 + \delta \frac{d^4 \eta}{(2\pi)^4 ds^4} - \eta + \eta^3 = 0,
\]

(3.11)

Due to the complexity of the above differential equation, we restrict \( \delta \) to be negative and \( |\delta| \ll 1 \). Since \( \eta(s; \delta) \) will be small in this limit, we expand \( \eta(s; \delta) \) about \( \delta = 0 \) as

\[
\eta(s) = \sqrt{|\delta|} \sum_{n=0}^{\infty} \frac{\delta^n}{n!} \eta^{(n)}(s),
\]

(3.12)

\[
\eta^{(n)}(s) = \left[ \frac{\partial^n \eta}{\partial \delta^n} \right]_{\delta=0}. \quad (3.13)
\]

Note that \( \eta \) is expanded with the leading order of \( \sqrt{|\delta|} \) to equate the Eq. (3.11) order by order consistently. For instance, considering only the zeroth and the first orders, Eq. (3.11) is decomposed as

\[
1 + \delta \frac{d^4 \eta^{(0)}}{(2\pi)^4 ds^4} - \eta^{(0)} = 0,
\]

(3.14)

\[
1 + \delta \frac{d^4 \eta^{(1)}}{(2\pi)^4 ds^4} - \eta^{(0)} = -\eta^{(0)} + \eta^{(3)} = 0.
\]

(3.15)

These equations with the periodic boundary conditions, \( \eta^{(s+1)} = \eta^{(s)}(s) \), are easily solved as

\[
\eta^{(0)} = a_1 \cos 2\pi s + a_2 \sin 2\pi s,
\]

(3.16)

\[
\eta^{(1)} = b_1(a_1, a_2) \cos 6\pi s + b_2(a_1, a_2) \sin 6\pi s,
\]

(3.17)

where \( b_1(a_1, a_2) \) are constant functions of \( a_1 \) and \( a_2 \) and \( a_1^2 + a_2^2 = 4/3 \) from the boundary condition for \( \eta^{(1)} \).

Hence, a new solution of the Euler-Lagrange equation (3.4) denoted by \( \bar{x}(s) \) is, in the limit of sufficiently small and negative \( \delta \),

\[
\frac{\bar{x}_s(s)}{a} = \pm \sqrt{|\delta|} \eta^{(0)}(s) = \pm \sqrt{\frac{2}{3}} |\delta| \psi_1(s),
\]

(3.18)

and also the eigenvalue equation for \( H^{(2)} \) can be written as

\[
\omega_B^2 \left[ 1 + \delta \frac{d^4}{(2\pi)^4 ds^4} + (2\pi)^4 \kappa \right] \psi_j = \epsilon_j' \psi_j.
\]

(3.19)

Treating the last term of the left-hand side as a perturbation, since \( \delta \) is small enough,

\[
\Delta \epsilon_j' = 2|\delta| \omega_B^2 \int_0^1 ds \psi_j^2 \psi_j^3 = \omega_B^2 |\delta|(2 + \delta_j),
\]

(3.20)
\[ \tilde{e}_j^i = e_j^i + \Delta e_j^i \]
\[ = \omega_B^2[(j^4 - 1) + |\delta|(2j^4 + \delta_{j,1})], \]
where we have used the form \( e_j^i = -\omega_B^2[1 - (1 - |\delta|)j^2] \) and \( \delta_{j,1} \) is the Kronecker delta.

This result implies that the slightly stretched chain state (3.18) represents the new saddle point with only one unstable eigenvector \( \tilde{q}_0 \), since the lowest eigenvalue \( \tilde{\omega}_0^2 = -(1 - 2|\delta|)\omega_B^2 = -\omega_B^2 \) is always negative and all the others \( \tilde{e}_j^{i>1} \) are positive. It is also worthwhile to point out that the eigenvalue of the lowest mode is smaller but those of all the higher modes are larger at this stretched state than the corresponding values at the compact state, \( \bar{x}(s) = 0 \).

In this section we have obtained the transition states \( \bar{x}_s(s) = 0 \) for \( (2\pi)^4\kappa > N^4\omega_B^2 \) and \( \bar{x}_s(s) = \pm a\sqrt{2} |\delta|/3\tilde{\psi}_1(s) \) for \( (2\pi)^4\kappa < N^4\omega_B^2 \). These results imply that a sufficiently stiff and not-so-long \( (i.e., \kappa > \kappa_c \) or \( N < N_c \)) polymer crosses the barrier keeping its compact conformation and, on the other hand, a not-so-stiff or sufficiently long \( (i.e., \kappa < \kappa_c \) or \( N > N_c \)) polymer crosses the barrier stretching its conformation. The critical values for the conformational transition, called compact-stretch transition, are defined as \( \kappa_c = \omega_B^2(N/2\pi) \) and \( N_c = 2\pi(\kappa/\omega_B^2)^{1/4} \). Using these transition states, we calculate the barrier-crossing rates in the next section.

IV. BARRIER-CROSSING RATES

As described in Sec. II, to calculate the escape rate (2.6) we first evaluate the net activation energy \( \Delta H \) in Eq. (2.7), and partition functions \( Z_- \) and \( Z_+ \) given by Eqs. (2.8) and (2.9), respectively. Note that the frequency \( \omega_o \) of the unstable mode at the saddle point is \( \omega_B \) for the compact conformation and \( \tilde{\omega}_B \) for the stretched conformation.

A. \( \kappa > \kappa_c \) or \( N < N_c \)

The activation energy is \( \Delta H = NV = N\omega_B^2d^2/4 \) in this regime, since \( \bar{x}_s = 0 \). To obtain the partition functions, it is necessary to evaluate the energy fluctuations near the left well and the saddle point, hence, for \( \{\bar{x}_n\}_- = -a \) and \( \{\bar{x}_n\}_+ = 0 \), respectively. Up to the second order, the energy fluctuations are

\[ H(\{x_n\}) - H(\{\bar{x}_n\}_-) = H[-a + \delta x(s)] - H[-a] \]
\[ = N \int_0^1 ds \delta x(s)H_{[a]}^{(2)} \delta x(s) = \Delta H_- , \]

\[ H(\{x_n\}) - H(\{\bar{x}_n\}_+ ) = H[\delta x(s)] - H[0] \]
\[ = N \int_0^1 ds \delta x(s)H_{[0]}^{(2)} \delta x(s) = \Delta H_+ . \]

The partition functions in Eqs. (2.8) and (2.9) are now written as the functional integrals

\[ Z_- = \int_{\text{well}} D[\delta x(s)] e^{-\beta\Delta H_-} , \]
\[ Z_+ = \int_{\text{saddle}} D[\delta x(s)] e^{-\beta\Delta H_+} , \]

where the prime (') in \( Z_+ \) means that the unstable mode \( \psi_0 \) is excluded.

Expressing \( \delta x(s) \) in terms of the eigenmode \( \psi_j(s) \) of the operator \( H^{(2)} \) as

\[ \delta x(s) = \sum_{j=0}^{N-1} X_j \psi_j(s) , \]

the energy fluctuations are

\[ \Delta H_- = \frac{N}{2} \sum_{j=1}^{N-1} e_j^2 X_j^2 , \]
\[ \Delta H_+ = \frac{N}{2} \sum_{j=1}^{N-1} e_j^* X_j^2 . \]

The partition functions are then obtained as

\[ Z_- = \prod_{j=0}^{N-1} \sqrt{2\frac{2\pi k_B T}{\epsilon_j}} \]
\[ = (2\pi k_B T)^{N/2} \prod_{j=0}^{N-1} \left[ \omega_+^2 + \kappa \left( \frac{2\pi j}{N} \right)^4 \right]^{-1/2} , \]

\[ Z_+ = \prod_{j=1}^{N-1} \sqrt{2\frac{2\pi k_B T}{\epsilon_j}} \]
\[ = (2\pi k_B T)^{(N-1)/2} \prod_{j=1}^{N-1} \left[ -\omega_+^2 + \kappa \left( \frac{2\pi j}{N} \right)^4 \right]^{-1/2} , \]

and the barrier-crossing rate in Eq. (2.6) for the sufficiently stiff \( (\kappa > \kappa_c) \) or not-so-long polymer \( (N < N_c) \) is

\[ R_h = R_0 \prod_{j=1}^{N-1} \sqrt{\left[ j^4 + \frac{\omega_B^2}{\kappa} \left( \frac{N}{2\pi} \right)^4 \right] / \left[ j^4 - \frac{\omega_B^2}{\kappa} \kappa \left( \frac{N}{2\pi} \right)^4 \right]} , \]

where

\[ R_0 = \frac{\omega_B^2 \omega_-}{2\pi^2} e^{-\beta N V} , \]

which is the rate for the infinitely stiff chain \( (\kappa \rightarrow \infty) \).

It is important to note that \( R_h/R_0 \) for all finite \( \kappa \) also increases as the size of the chain \( N \) increases. \( R_h/R_0 \) can be simplified in the case of \( N \gg 1 \) as
The rate (4.10) or (4.12) apparently diverges when \( \omega_0^2 = \kappa(2 \pi/N)^4 \) or, equivalently, when \( \varepsilon_1 = 0 \), i.e., at the compact-stretch transition. This is a consequence of the second-order expansion in Eq. (3.5), which treats the barrier as harmonic; on such a harmonic barrier the chain can be infinitely extended and have negatively infinite free energy [5]. To circumvent this difficulty, we have to consider the next order contribution, which is the fourth. This anharmonic correction regularizes the singularity, yielding a finite rate

\[
R = R_\delta f(\delta \sqrt{N \beta \omega_0^2 a^2}),
\]

as shown in the figures. Note that \( \delta = \varepsilon_1/\omega_0^2 = (\kappa/N) - 1 = (N_c/N)^4 - 1 \) and the function

\[
f(x) = x \sqrt{\frac{6}{\pi}} \exp \left( \frac{x^2}{12} \right) K_{1/4} \left( \frac{x^2}{12} \right)
\]

with \( K \) being the modified Bessel function of the second kind, falls to zero as \( \sqrt{x} \) when \( x \) approaches zero. Away from the transition or for large values of \( \delta \), this function increases to 1 to retain the above results of rate (4.12).

### B. \( \kappa < \kappa_c \), or \( N > N_c \)

In this regime, the corresponding activation energy is calculated using the transition solution \( \bar{x},(s) \) in Eq. (3.18) as

\[
\Delta H = H(\bar{x},) - H(-a) = NV\gamma_{\gamma} - \frac{1}{2} N \omega_B^2 \bar{a}^2 \delta^2.
\]

It implies that the conformational change of the chain to the stretched state at the barrier top, which is energetically more favorable, lowers the activation energy, leading to an increase of the rate. It is, however, worthwhile to point out that we restrict ourselves to an activation energy great enough to overcome the thermal energy \( k_B T \) for the Kramers rate to be valid.

The energy fluctuation near the saddle point in this regime is

\[
\Delta H_s = \frac{N}{2} \sum_{j=1}^{N-1} \varepsilon_j X_j^2,
\]

where \( \varepsilon_j \) is given in Eq. (3.22). The partition function \( Z_s \) is then obtained as

\[
Z_s = \prod_{j=1}^{N-1} \sqrt{\frac{2 \pi k_B T}{\varepsilon_j}} \left( -\omega_B^2 + \kappa \frac{2 \pi j}{N} \right)^{-1/2}
\]

and hence the barrier-crossing rate for the sufficiently long or not-so-stiff polymer is

\[
R_b = \frac{4}{\sqrt{2}} \bar{R}_0 \prod_{j=1}^{N-1} \sqrt{j^4 + (\omega_B^2/\kappa)(N/2 \pi)^4 - (\omega_B^2/\kappa)(N/2 \pi)^4}.
\]

where

\[
\bar{R}_0 = \frac{\omega_B \omega_0}{2 \pi \gamma} e^{-\beta N[V\gamma_{\gamma} - (\omega_B a^2 \delta^2)/6]}.
\]

Note that \( \sqrt{2} \) in \( R_b \) came from \( Z_s \) in Eq. (4.17) and the factor 4 denotes the degeneracy of the transition states in Eq. (3.18). In the limit of \( N \gg 1 \), the rate becomes

\[
R_b \approx 2 \sqrt{2} \left( \frac{\omega_B^2}{\omega_0^2} \right)^{1/4} \sqrt{\frac{\sin^2[(N/2)(\omega_B^2/4\kappa)^{1/4}] + \sinh^2[(N/2)(\omega_B^2/4\kappa)^{1/4}]}{\sin[(N/2)(\omega_B^2/\kappa)]^{1/4}} \sinh[(N/2)(\omega_B^2/\kappa)]^{1/4}}.
\]

The apparent divergence of the rate due to harmonic approximation as in the sufficiently stiff chain also disappears if the anharmonic terms are considered. The anharmonic correction again modifies the rate \( R \) as \( R_\delta f(\delta \sqrt{N \beta \omega_0^2 a^2})/(2\sqrt{2}) \) and yields a finite rate at the transition point \( \delta = 0 \).

Figure 1 depicts the rates of the chain with respect to chain length \( N \) for two different bending rigidities \( \kappa \). Sharp peaks appear in the harmonic approximation at critical chain lengths \( N_c \), signaling the compact-stretch transition as mentioned before, which, with the anharmonic correction, are regularized to be finite. It is shown that above the transition \( (N > N_c) \) the rate dramatically increases beyond \( R_0 \). Figure 2 depicts the rates of the chain with respect to bending rigidity \( \kappa \) for two values of chain length. Also for the flexibility above the transition \( (\kappa < \kappa_c) \) the rate is much enhanced compared to \( R_0 \).

In this subsection we have only considered the limit of a
slightly negative \( \delta \), since it can be treated analytically. For an arbitrary \( \delta < 0 \) it can be analyzed numerically within the same formalism as long as the activation energy is larger than the thermal energy and a similar result is expected [7].

V. CONCLUDING REMARKS

In this paper we have calculated the rate of thermally activated escape of a semiflexible polymer ring through an external bistable potential barrier using multidimensional Kramers rate theory. For this purpose, we have obtained the stationary points of the energy functional in the continuous limit and energy fluctuations near these points to calculate the requisite partition functions via the functional integral formalism.

For a sufficiently stiff or not-so-long case, i.e., \( \kappa > \kappa_c \) or \( N < N_c \), our semiflexible ring keeps its compact conformation even at the barrier top while crossing the barrier. The escape rate of the ring increases with the activation energy unchanged, as the ring is more flexible or longer.

On the other hand, for a sufficiently large or not-so-stiff case, i.e., \( N > N_c \) or \( \kappa < \kappa_c \), the compact and homogeneous conformation of the ring changes to a new stretched conformation at the barrier top. This conformational transition significantly lowers the activation energy and therefore enhances the escape rate beyond those of the compact ring. The rate enhancement is significant for a longer or more flexible ring due to the chain flexibility. But the larger contribution to the enhancement comes from the lowered activation energy due to conformational transition. We may say that the conformational fluctuation and adjustment in response to a background facilitate soft matter barrier-crossing. This could be a pervasive mechanism of soft matter escaping from a low free energy region to a higher one, but the details will be different depending upon the situations.

Recently, an experimental result on the passage of DNA molecules driven by an electric field through a microfabricated channel has been reported [10]. In this experiment, the longer DNA were found to escape the barrier faster than shorter ones, overcoming the barrier by stretching its monomers. The operating mechanism is similar to ours in a sense that the stretched conformation overcomes the barrier more easily than the coiled one, although the experimental situation is not identical to our case. Nevertheless, the Kramers problem we deal with here provides a convenient paradigm for understanding the generic features of the soft matter dynamics in various situations.

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