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# Thermally activated barrier crossing and stochastic resonance of a flexible polymer chain in a piecewise linear bistable potential

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We study the stochastic resonance of a flexible polymer chain crossing over a piecewise linear bistable potential. The dependence of signal to noise ratio SNR on noise intensity $D$, coupling constant $k$, and polymer length $N$ is studied via two-state approximation. We find that the response of signal to the background noise strength is significant at optimum values of $D_{opt}$, $k_{opt}$, and $N_{opt}$ which suggests a means of manipulating proteins or vesicles. Furthermore, the thermally activated barrier crossing rate $r_k$ for the flexible polymer chain is studied. We find that the crossing rate $r_k$ exhibits an optimal value at an optimal coupling constant $k_{opt}$; $k_{opt}$ decreases with $N$. As the chain length $N$ increases, the escape rate for the center of mass $r_k$ monotonously decreases. On the other hand, the crossing rate for the portion of polymer segment $r_s$ increases and saturates to a constant rate as $N$ steps up.

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## I. INTRODUCTION

Understanding the physics of thermally activated barrier crossing for systems consisting of one or more than one degree of freedom [1–8] is ubiquitous in many scientific disciplines. It has diverse physical applications and serves as a tool to understand stochastic paradigms such as stochastic resonance (SR) and thermal ratchets. Furthermore, for bistable systems, applying fields such as an external load or nonuniform temperature breaks their symmetry along the reaction coordinate which may result in a unidirectional motion of particles. In the last few decades several model systems, which are far from equilibrium, have been proposed [9,10]. Especially when the external load (force) varies in time, coordination of the noise with time varying force may lead to the phenomenon of SR [11,12] as long as the system is exposed to weak sinusoidal signals.

The phenomenon of SR is of interest these days because of its significant practical applications in a wide range of fields. SR depicts the phenomenon that systems, by utilizing the thermal background noise, enhance their performance when they are subjected to a small periodic signal. Since the pioneering work of Benzi *et al.* [11], the idea of stochastic resonance has been broadened and implemented in many model systems [12–21]. Recently the appearance of entropic stochastic resonance for a Brownian particle in a confined system has been reported in [22]. Unlike conventional energetic potential, the effective potential of the confined systems may have an entropic nature due to the constrained regions. For tiny-scaled biological systems that frequently exist in a highly confined geometry, the entropic contribution to the effective potential is unavoidable and plays an important role in noise-induced resonant effects.

Often biological and soft matter systems such as polymers and membranes are complex and consist of several components. Their flexibility and connectivity lead to a fascinating dynamics under certain time varying external fields and noisy environment. The resonance behavior of these systems relies not only on the strength of the background temperature, but also on their size, flexibility, and shape of the potential. Thus, the interplay between the shape of the potential, flexibility, and size of polymer (protein) plays a crucial role in the enhancement of signal to noise ratio SNR or spectral amplification $\eta$ as reported in [15–17,23].

Earlier, Lindner *et al.* considered linearly coupled damped bistable oscillators [15]. The dependence of SNR on the coupling strength $k$, number of oscillators $N$, and noise intensity $D$ was envisioned numerically. It has been shown that the SNR of the oscillators depicts a global maximum ($\mathrm{SNR}_{max}$) at certain $D$ and $k_{opt}$ for a given $N$. Later, utilizing $\Phi_4$ field theory, Marchesoni *et al.* [16] independently checked the numerical results of Lindner *et al.* [15] in large-$N$ limit. Recently, Dikshtein *et al.* [17] considered a polymer in a symmetric bistable potential where the two end points of the polymer are restricted by motionless pining points in the perpendicular direction to the symmetric potential. It has been shown that the SNR is enhanced for wider (less deep) potential. More recently we studied the SR for a flexible polymer surmounting a bistable potential. Our analysis indicated that, due to the flexibility that can enhance crossing rate and change chain conformations at the barrier, the power amplification exhibits an optimal value at optimal chain lengths $N_{opt}$ and elastic constants $k_{opt}$ as well as at optimal noise strengths $D$ [23].

The study of thermally activated escape rate of polymer has been also the subject of many studies (see, for example, [8]). Since polymer is a flexible and an extended object with a finite length, its rate or SNR relies on its coupling constant, chain length, shape of the potential, and initial conformation along the reaction coordinate in a complicated manner. Thus, more studies are needed to understand its complex dynamics. Most of the previous studies considered the center-of-mass motion. However, in this paper we examine not only the crossing rate for the center-of-mass motion $r_k$ but also the rate for a portion of the polymer segment $r_s$. We find that $r_k < r_s$.

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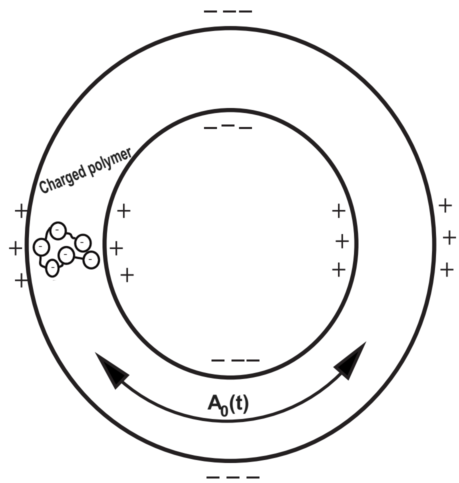

FIG. 1. Schematic for initially coiled polymer chain in a locally charged channel. The fluidic channel is subjected to an external periodic red force $A_0(t)$ (ac field).

The aim of this paper is to explore the crossing rate and stochastic resonance of a flexible polymer chain in a piecewise linear bistable potential as a function of $k$, $N$, and $D$ by considering initially coiled chain conformation. First we explore the escape rate of the chain as a function of the model parameters. We show that $r_k$ monotonously decreases with $N$; the rate $r_s$ increases and saturates to a constant value when $N$ steps up. Since the cooperation between the monomers increases with $k$, the rate increases as $k$ goes up. At certain $k_{opt}$, $r_k$ attains an optimal value, and further increases in $k$ result in a lower rate as rigid polymer crosses the barrier at the expense of higher thermal kicks.

In this paper, utilizing two-state approximation, the dependence of SNR on $D$, $k$, and $N$ is examined. For globular polymer chain we show that the response of signal to the background noise strength is significant at optimum values of $D_{opt}$ and $N_{opt}$, which suggests a means of manipulating (such as efficient separation methods) not only biopolymers, but also proteins (vesicles) of different sizes. For the chain with a finite coupling constant $k$, the SNR exhibits an optimal value at an optimal $k_{opt}$. The signal to noise ratio for the center-of-mass motion $\text{SNR}_k$ exhibits an optimal value at an optimum $N_{opt}$. On the other hand, the $\text{SNR}_s$ for the polymer segment monotonously increases with $N$. In addition, considering temperature-dependent coupling constant (entropic chain) where the elastic constant is given by $k=3D/l^2$, we further confirm that SNR for entropic chain shows a broader and a higher peak than a chain with temperature-independent coupling constant. Here, $l$ designates the Kuhn segment length.

At this point we stress that even though the model and its numerical approach are completely different from our previous work [23], the results of this work agree with that of the previous work at least qualitatively. One can note that the dynamics of such a system can be realized experimentally. One makes negatively charged coiled polymer chain, then puts the polymer within positively and negatively charged fluidic channel as shown in Fig. 1. The fluidic channel is subjected to an external periodic force (ac field). Since the polymer is negatively charged, it encounters a difficulty of crossing through the negatively charged part of the channel. Assisted by the thermal background kicks along with its conformational change, the polymer ultimately overcomes the barrier. The presence of time varying force may further enhance the rate of crossing. One can sort or manipulate polymer of specific coupling constant or chain length by tuning the angular frequency.

The rest of the paper is organized as follows. In Sec. II, we present the model. In Sec. III, we study the dependence of the crossing rate on the model parameters. In Sec. IV, we discuss how the SNR for the flexible chain behaves as a function of the model parameters. Section V deals with summary and conclusion.

## II. MODEL

Let us now consider a flexible polymer chain of size $N$ which undergoes a Brownian motion in one-dimensional piecewise linear bistable potential as shown in Fig. 1. Considering only nearest-neighbor interaction between the polymer segments (the bead-spring model), the Langevin equation that governs the dynamics of the $N$ beads $(n=1,2,3,\ldots,N)$ in a highly viscous medium under the influence of external potential $U(x)$ is given by

$$\gamma\frac{dx_n}{dt}=-k(2x_n-x_{n-1}-x_{n+1})-\frac{\partial U(x_n)}{\partial x_n}+\xi_n(t), \tag{1}$$

where $k$ is the spring (elastic) constant of the chain while $\gamma$ denotes the friction coefficient. $\xi_{n(t)}$ is assumed to be Gaussian white noise satisfying

$$\langle\xi_n(t)\rangle=0, \quad \langle\xi_n(t)\xi_n(t+\tau)\rangle=2D\gamma\delta(\tau), \tag{2}$$

with $D=k_BT$ as the strength of the thermal noise. The external potential that each bead experiences is considered to be a piecewise linear potential,

$$U(x)=\begin{cases} U_0\left[\dfrac{-x}{L_0}-1\right], & \text{if } x\le -L_0\\ U_0\left[\dfrac{x}{L_0}+1\right], & \text{if } -L_0\le x\le 0\\ U_0\left[\dfrac{-x}{L_0}+1\right], & \text{if } 0\le x\le L_0\\ U_0\left[\dfrac{x}{L_0}-1\right], & \text{if } x\ge L_0, \end{cases} \tag{3}$$

where $U_0$ and $2L_0$ denote the barrier height and the width of the piecewise linear bistable potential, respectively. If one considers only the center-of-mass motion, the second term in Eq. (1) vanishes. For a globular polymer chain, where the coupling (spring) constant $k$ is infinity, the Langevin equation [Eq. (1)] for the center-of-mass takes a simple form

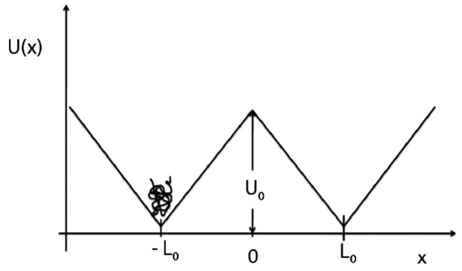

FIG. 2. Schematic for initially coiled polymer chain in a piecewise linear bistable potential. The potential wells and the barrier top are located at $x = \pm L_0$ and $x=0$, respectively. Due to the thermal background kicks, the polymer ultimately crosses the barrier assisted by its conformational change along the reaction coordinate.

$$N\gamma \frac{dx_{cm}}{dt} = \begin{cases} N\dfrac{U_0}{L_0} + \xi(t), & \text{if } x \le -L_0 \\ -N\dfrac{U_0}{L_0} + \xi(t), & \text{if } -L_0 < x \le 0 \\ N\dfrac{U_0}{L_0} + \xi(t), & \text{if } 0 < x \le L_0 \\ -N\dfrac{U_0}{L_0} + \xi(t), & \text{if } x > L_0. \end{cases} \tag{4}$$

## III. POLYMER ESCAPE RATE

We consider a polymer which has initially coiled conformation along the piecewise linear bistable potential as shown in Fig. 2. Due to the thermal background kicks, the polymer presumably crosses the barrier. The crossing rate of the chain strictly relies on the chain length, coupling constant, barrier height, and noise strength. For a compact polymer ($k \to \infty$), the monomers feel the same force along the reaction coordinate [see Eq. (4)] and due to the lack of chain conformational change at the top of the barrier, its escape rate is considerably lower than a polymer of finite $k$ value. On the other hand, the jumping rate also depends on the choice of coordinate system. The rate for the center-of-mass motion is a decreasing function of $N$ while the escape rate for the portion of polymer segment increases with $N$. The thermally activated rate strictly relies on the chain initial conformation along the piecewise linear bistable potential for the case where the microscopic relaxation time of the polymer is significant compared to the crossing time. In this case, initially stretched polymer crosses the barrier faster than the coiled chain. This is because coiled polymer first stretches before crossing the barrier. The degree of stretching depends on the relaxation time of the polymer which itself relies on the chain length, coupling constant, and the thermal background kicks. For short polymer chain surmounting a potential barrier that is large compared to $D$, $NU_B \gg D$, the chain crossing time is considerably larger than its relaxation time, and hence the crossing time may be independent of chain initial conformation. The activated barrier crossing considered in this work is strictly applicable only to the case where the crossing time is much larger than any microscopic relaxation times of the polymer.

Before we discuss how the flexible polymer chain in the double-well potential behaves, let us first calculate the crossing rate for a globular polymer chain. The problem of surmounting a piecewise linear bistable potential for a single Brownian particle in high friction limit was addressed in [25]. Following the same approach, the mean first passage time $\tau$ for the compact polymer crossing over a high potential barrier is given by

$$\tau = \frac{\gamma}{D}\left(\frac{DL_0}{NU_0}\right)^2 e^{NU_0/D}, \tag{5}$$

while the crossing rate

$$r_k = \frac{D}{\gamma}\left(\frac{NU_0}{DL_0}\right)^2 e^{-NU_0/D} \tag{6}$$

is the inverse of $\tau$. The dependence of the crossing rate $r_k$ or equivalently the mean first passage time on the potential height $U_0$, width of the potential $2L_0$, and chain length $N$ can be analyzed by exploiting Eq. (6). When $U_0$ increases, the polymer encounters a difficulty of jumping the piecewise linear bistable potential and as a result $r_k$ declines. When $N$ increases, $r_k$ decreases as large polymer crosses the potential barrier at the expense of higher thermal kicks. On the other hand, as $L_0$ steps up, the mean first passage time for the polymer to reach the other side of the well increases, which implies that $r_k$ monotonously decreases.

For the chain with a finite coupling constant, we analyze the crossing rate via numerical simulation. We introduce dimensionless parameters $\bar{x}=x/L_0$, $\tau=\gamma L^2/U_0$, $\bar{k}=kL^2/U_0$, and $\bar{t}=t/\tau$. Hereafter all the quantities are rescaled (dimensionless) so the overbars will be dropped. The behavior of the system is analyzed by integrating the Langevin equation (1) (employing Brownian dynamics simulation). In the simulation, coiled polymer chain with $N$ monomers is initially situated in one of the potential wells. Then the trajectories for the center of mass of the polymer or the portion of polymer segment are simulated by considering different time steps $\Delta t$ and time length $t_{max}$. In order to ensure the numerical accuracy, up to $5 \times 10^5$ ensemble averages have been obtained.

Let us now vary the rescaled spring constant $k$ of the chain. Figure 3 plots the dependence of $r_k$ on the rescaled $k$ for parameter choice $N=10$, $N=20$, $N=25$, and $D=0.5$. For small $k$, since the monomers become noninteracting (noncooperative), $r_k$ tends to be smaller. When coupling strength between the monomers $k$ further increases, the tendency for interconnected monomers to assist each other increases; as a result $r_k$ steps up. At certain optimal $k_{opt}$, $r_k$ attains an optimum value. Further increase in $k$ results in a lower crossing rate as larger thermal energy is required to drive the rigid chain across the reaction coordinate. The same figure depicts that $k_{opt}$ is a decreasing function of $N$. The coupling constant $k_{opt}$ relies on rescaled noise strength $D$ in a manner $k = 3DL^2/l^2$. The crossing rate for this entropic chain has been analyzed and compared with the chain of a finite $k$. The numerical analysis shows that the rate for entropic chain is considerably higher; further details will be reported elsewhere.

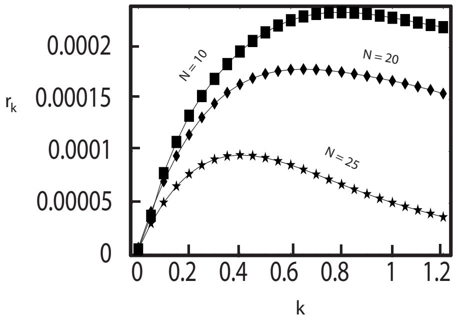

FIG. 3. Polymer crossing rate $r_k$ as a function of coupling constant $k$ for different chain lengths $N$ and noise strength $D=0.5$. The simulation results are obtained directly by integrating Eq. (1). The figure exhibits that the rate increases as $N$ declines and attains an optimal value at an optimal elastic constant $k_{opt}$. The optimal coupling constant shifts to the right as $N$ decreases.

Figure 4(a) depicts the plot of $r_k$ as a function of $N$ for parameter choice $D=0.25$, $D=0.6$, and $k=0.5$. The crossing rate for the center-of-mass motion monotonously decreases with $N$. On the contrary, the rate of the polymer segment $r_s$ increases and saturates to a constant value as $N$ and $D$ step up as shown in Fig. 4(b).

## IV. STOCHASTIC RESONANCE

In the presence of time varying signal, the interplay between noise, sinusoidal driving force together with chain flexibility, and chain length in the bistable system may lead the system into stochastic resonance provided the random tracks are adjusted in an optimal way to the recurring external force. Next we study the dependence of the SR on the model parameters employing two-state approximations without considering a continuous diffusion dynamics. In the presence of a periodic signal $A_0\cos(\Omega t)$, the Langevin equation that governs the dynamics of the system is given by

$$\gamma\frac{dx_n}{dt} = -k(2x_n - x_{n-1} - x_{n+1}) - \frac{\partial U(x_n)}{\partial x_n} + A_0\cos(\Omega t) + \xi_n(t), \tag{7}$$

where $A_0$ and $\Omega$ are the amplitude and angular frequency, respectively.

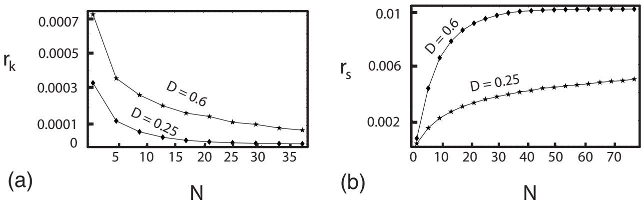

FIG. 4. (a) Dimensionless rate $r_k$ versus $N$. (b) The escape rate for polymer segment $r_s$ versus $N$. The data are obtained numerically for different rescaled noise strengths $D$ and coupling constant $k=0.5$.

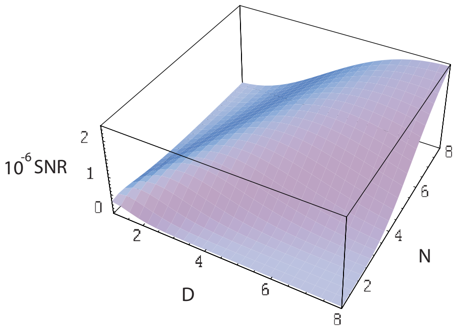

FIG. 5. (Color online) The dependence of SNR (for compact polymer chain) on $N$ and $D$ for parameter choice $A_0=0.05$. The SNR is obtained via Eqs. (6) and (10).

Employing two-state model approach [12,24], two discrete states $x(t)=\pm L_0$ are considered. Let us denote $n_+$ and $n_-$ to be the probability to find the polymer segment in the right ($L_0$) and in the left ($-L_0$) sides of the potential wells, respectively. In the presence of time varying signal, the master equation that governs the time evolution of $n_\pm$ is given by

$$\dot{n}_\pm(t) = -W_\pm(t)n_\pm + W_\mp(t)n_\mp, \tag{8}$$

where $W_+(t)$ and $W_-(t)$ correspond to the time-dependent transition probability toward the right ($L_0$) and the left ($-L_0$) sides of the potential wells. The time-dependent rate [12,24] takes a simple form

$$W_\pm = r_k \exp\left[\pm\frac{L_0 N}{U_0 D}A_0\cos(\Omega t)\right], \tag{9}$$

where $r_k$ is the Kramers rate for the polymer in the absence of periodic force $A_0=0$. We consider the case where $N \gg D$. For sufficiently small amplitude, one finds the signal to noise ratio

$$\mathrm{SNR} = \pi r_k\left(\frac{A_0 N L_0}{U_0 D}\right)^2. \tag{10}$$

Before we explore how the SNR for globular polymer behaves as a function of $N$, we introduce additional dimensionless parameter: $\bar{A}_0=A_0L/U_0$. From now on for convenience the overbar will be dropped. Figure 5 depicts the plot for the SNR for a globular polymer chain versus $D$ and $N$ for fixed values of the driving frequency and potential width. The SNR exhibits nonmonotonous noise strength dependence revealing a peak at an optimal noise strength $D_{opt}$. $D_{opt}$ steps up as $N$ inclines. This is because longer polymer crosses the barrier at the expense of higher thermal excitation. The same figure exhibits that the SNR peaks at optimum chain length $N_{opt}$. This suggests a means of manipulating not only biopolymers, but also proteins (vesicles) of different sizes. One can note that since compact polymer lacks the flexibility to conform to the piecewise linear bistable potential, the peak of the SNR is less than that of a flexible polymer chain.

For the chain with a finite coupling constant $k$, the resonance behavior of the system is examined numerically. Figure 6 shows the plot for the $\mathrm{SNR}_k$ as a function of $k$ for different values of $N$. Other parameters are fixed as $D=0.25$ and $A=0.1$. For small $k$, the monomers tend to be noninteracting; as a result the SNR becomes very small. The

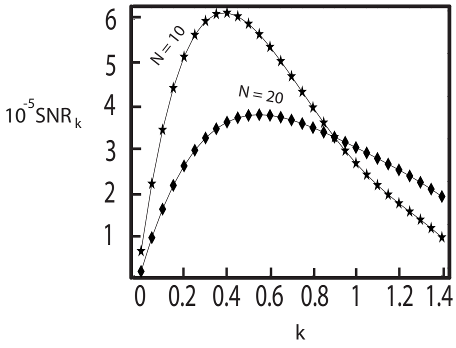

FIG. 6. The dependence of SNR$_k$ as a function of coupling constant $k$ for different chain lengths $N$, for noise strength $D=0.25$, and amplitude $A_0=0.1$. The simulation results are obtained directly by integrating Eq. (1). The figure exhibits that the SNR$_k$ increases as $N$ declines and attains an optimal value at an optimal elastic constant $k_{opt}$. Unlike the corresponding rate, the optimal coupling constant shifts to the left as $N$ decreases.

SNR peaks at an optimal chain length $k_{opt}$, and further increase in $k$ leads again to a smaller SNR as the rigid polymer is not flexible enough to adjust itself with the time varying force. The optimal spring constant $k_{opt}$ increases as $N$ increases.

Figure 7(a) plots the rate SNR$_k$ versus $N$. We observe an increase in the signal to noise ratio when the number of monomers increases. The SNR peaks at an optimal chain length $N_{opt}$ and declines again as the chain length increases. On the contrary, SNR$_s$ monotonously increases with $N$ [see Fig. 7(b)]. It is worth noting that since the flexible polymer chain responds in more cooperative and coherent manner to the time varying force, it exhibits a higher resonance peak than a globular polymer.

Finally, we emphasize that even though the model and its numerical approach are completely different from our previous work [23], the results agree with that of the previous work at least qualitatively. For instance, similar to this work, in our previous work we found that the response of signal to the background noise strength is significant at optimum values of $D_{opt}$, $K_{opt}$, and $N_{opt}$. Our previous work [23] dealt with the study of SR for a flexible polymer chain on Kramer's potential. Depending on the chain length $N$ and spring constant $k$, the chain takes either coiled or stretched conformation at the top of the barrier. When the chain is in either coiled or stretched state, the resonance is much larger than globular state revealing the intrinsic flexibility of the chain facilitating faster crossing. In the globular limit $k \rightarrow \infty$, the resonance becomes small as the compact polymer lacks the flexibility to conform to the driving force. Furthermore, we showed that the power amplification peaks at an optimal chain length and elastic constant as well as at an optimal noise strength.

## V. SUMMARY AND CONCLUSION

In summary, in this work we explore the crossing rate and stochastic resonance of a flexible polymer chain in a piecewise linear bistable potential. We investigate the chain's escape rate as a function of different model parameters. $r_k$ monotonously decreases with $N$ while the rate $r_s$ increases and saturates to a constant rate when $N$ steps up. Due to the lack of cooperation between the monomers, the rate is considerably small for a smaller $k$. The crossing rate increases as $k$ goes up. At certain $k_{opt}$, $r_k$ attains an optimal value. Further increase in $k$ results in a lower rate as rigid polymer crosses the barrier at the expense of higher thermal kicks.

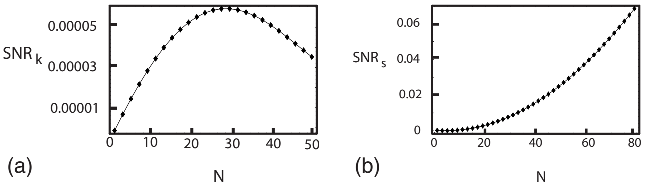

FIG. 7. (a) SNR$_k$ versus $N$. (b) SNR$_s$ for polymer segment as a function of $N$. The data are obtained numerically for noise strength $D=0.5$, amplitude $A_0=0.1$, and coupling constant $k=0.5$.

Employing two-state approximation, the dependence of SNR as a function of model parameters is studied. For a globular polymer chain we show that the response of signal to the background noise strength is significant at optimum values of $D_{opt}$ and $N_{opt}$, which suggests a means of manipulating proteins (vesicles) of different sizes. On the other hand, for the chain with a finite coupling constant $k$, the SNR exhibits an optimal value at an optimal $k_{opt}$. The signal to noise ratio for the center of mass SNR$_k$ exhibits an optimal value at an optimum $N_{opt}$. The SNR for the polymer segment SNR$_s$ monotonously increases with $N$.

In conclusion, in this work, by introducing a different model system than the previous work [23], we recapture the previous results at least qualitatively. Not only we assess the resonance property of the system, but we also further explore the barrier crossing rate by varying different model parameters. Since polymers are interconnected and flexible systems, they exhibit interesting cooperative dynamics when they are exposed to time varying external fields and noises. Understanding their dynamics is crucial not only for novel means of manipulating proteins such as DNA or RNA molecules in a nanofluidic or microfluidic channels, but also for understanding how such systems self-organize their flexible degrees of freedom. Thus, this theoretical study not only is crucial for the fundamental understanding of polymer physics, but also provides a basic paradigm in which to understand the self-organization and cooperativity induced by the chain flexibility and fluctuations.

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