

## Opening of a weak link in a semiflexible ring polymer

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The dynamics of contact formation between different parts of a long chain molecule is of considerable interest in biology. The related processes of opening of a loop or closing to form a loop also are of considerable interest and have attracted the attention of experimentalists/theorists. For closing, results are available in the completely flexible limit. However, this limit is not realized in many cases. Recently, there have been investigations for the semiflexible case too. We develop an approach, which leads to an easy description of the dynamics, incorporating semiflexibility rigorously into account. With this approach, the dynamics of a semiflexible polymer ring formed by a weak bond between the two ends can be modeled as the escape of a particle over a barrier in a multidimensional potential energy surface. We then calculate the rate of opening using a multidimensional transition state theory. Effects of friction on the rate are also taken into account using the standard coupling to a bath of harmonic oscillators. We find that for shorter chains (i.e., semiflexible), the rate of opening is strongly length dependent and is well described by the equation  $A(L/l_p)^\nu \exp(Bl_p/L)$ , with  $L$  as the length, and  $l_p$  as the persistence length,  $A, B$  as the constants, and  $\nu \approx 1.2$ .

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### I. INTRODUCTION

The dynamics of contact and subsequent loop formation between the two ends of a long chain polymer has been the subject of several theoretical and experimental [1–4] investigations. Loop formation and loop opening occur in important biological processes like gene regulation, protein folding [4], and DNA replication [5]. The dynamics of loop formation and its importance in the replication of DNA has recently been reviewed by Jun and Bechhoefer [5]. In the flexible limit, there is no energy barrier to contact formation and loop closing occurs as a result of just diffusive motion among the chain conformations. The two ends have to execute a random search to find each other. A mean first passage time approach due to Szabo, Schulten, and Schulten (SSS) [6] gives the length dependence of the closure time in three dimensions,  $\tau$  as  $\sim L^{3/2}$ . A method to calculate the survival probability based on a closure approximation was proposed by Wilemski and Fixman [7]. Using their approach, Doi [8] found a closure time  $\tau \sim L^2$ . These results have been compared with numerical simulations [9,10].

In comparison, loop formation in the semiflexible case, where the length  $L$  of the molecule is comparable to the persistence length  $l_p$ , has been paid relatively little attention, though it is of great significance as many of the interesting biological processes happen in the semiflexible limit. Ring closure probabilities for wormlike chains were calculated by Yamakawa and Stockmayer [11]. The effect of twists on loop formation in DNA was studied by Shimada and Yamakawa [12]. Liverpool and Edwards [13] estimated loop formation probability for a semiflexible chain. The dynamics of loop formation for the semiflexible chains was studied experimentally by Libchaber *et al.* [1]. Motivated by this experiment, the theory for chain closure between the two ends of a semiflexible polymer was considered by Dua and Cherayil [14]. They used a model recently suggested by Harnau, Winkler, and Reineker [15]. The model relaxes the local constraint  $|\mathbf{u}(s)|=1$  obeyed by the tangent vector for all values of the

contour length variable  $s$  to  $\langle |\mathbf{u}(s)| \rangle = 1$ , where  $\langle \dots \rangle$  refer to the equilibrium average over conformations of the chain. Dua and Cherayil [14] calculate the closure time  $\tau$  numerically and find that  $\tau \sim L^\nu$  where  $\nu$  is in the range 2.2–2.4.

End to end distribution functions for semiflexible polymers have been the subject of a large number of papers. Recently, Chirikjian and Wang [16] have obtained partial differential equations for the probability distribution function of stiff chains. For the problem of ring closure, an approach similar to that of SSS was used for a semiflexible case in a recent paper by Lapidus *et al.* [4]. Several approximate expressions are available for this static distribution function [12,15,17]. Lapidus *et al.* fitted numerical data from simulations for the equilibrium distributions  $P_{eq}(r, L)$  to analytical expressions. The  $P_{eq}(r, L)$  so obtained was used to calculate the rate, assuming a one dimensional model [6]. The results were found to be in excellent agreement with molecular dynamics simulations. It is also of great interest that a good approximation for the radial distribution function, valid in the limit of large bending rigidity and for end to end distance close to zero, has been obtained by Wilhem and Frey [18].

Thirumalai [19] has proposed a simple approach to the calculation of diffusion limited rates of forming loops of semiflexible chains and used it to estimate the time required for loop formation. Jun *et al.* [5,20] have used Kramers theory to calculate  $\tau_{kr}$  for semiflexible polymers. They find  $\tau_{kr} \sim G_0(L)^{-1}$ , where  $G_0(L)$  is the equilibrium probability for the end to end distance of a semiflexible polymer being equal to zero. Chen *et al.* [21] included bending energy in the calculation of the rate and found that there is a particular length at which  $\tau$  is a minimum.

In this paper, we consider the opposite process: Once a loop is formed, what is the dynamics of it breaking open? This question does not seem to have been addressed in the literature. There have been a few studies on breaking problems involving linear chains. Sebastian and Puthur [22,23] have used a multidimensional transition state theory to cal-

culate the breaking rates of linear polymer chains under tension. Sain and Wortis [24] have studied the escape of one end of a long chain molecule from a potential well under the influence of pulling at the other end. The thermodynamics of reversible cyclization of semiflexible polymers has been considered by Cherayil and Dua [25], but the effect of semiflexibility of the chain on opening was not included explicitly. Vologodski *et al.* [26] have presented simulation results for loop formation and loop dissociation for DNA molecules. They assume the loop to be formed if the ends of the polymer come within a particular distance. We develop a “semi-classical” type of approach to the opening process. The same kind of analysis can be used for loop formation too and this shall form the subject of a future paper. Our strategy is the following: rigorous treatment of semiflexible polymers is a difficult problem because of the inextensibility constraint  $|\mathbf{u}(s)|=1$ . When this constraint is incorporated, the partition function of a semiflexible polymer can be written as a functional integral over all possible random paths on the surface of a unit sphere. Each path on the unit sphere corresponds to a conformation of the polymer in space. In particular, the minimum energy configuration of closed polymer loop in which the two ends join smoothly (one which has no tangent discontinuities) is represented by a great circle. Unlike such a loop, a rodlike polymer bent to bring the two ends close will not have the tangents joining smoothly. However, interestingly, the minimum energy conformation for such a ring polymer in which the two ends are kept close to one another, can be obtained from the great circle, by considering fluctuations about the great circle, which allow the ring to change shape and even break [see Eq. (41)]. For this purpose, we use an approximate expression for energy obtained by performing an expansion about the great circle and keeping terms up to second order in fluctuations. Using this expansion, we have found the minimum energy required to bring the two ends of a rigid polymer close to one another. Our calculation is approximate and a more precise calculation, which leads to an exact solution to the energy of a stiff polymer for which the ends coincide, was given by Yamakawa and Stockmayer [11]. However, our result for the energy is close to that obtained by them. Another approximation scheme for the minimum energy of a bent rod has been suggested by Kulic and Schiessel [27], but this does not suggest a simple description for the dynamics of looping. The reasons for adopting the approximate approach are: (a) it gives energies very close to that obtained in Ref. [11] and (b) it is far easier to do the dynamics using this approach.

Our approach to the dynamics is as follows: Once the two ends have been brought together, they can separate from each other by motion in any one of the three directions in space. We find that two of these directions are unstable as motion along them can decrease the bending energy. Motion in the third direction, leads to an increase in bending energy and is stable. Thus the system is unstable in two directions but can be made stable by joining the two ends with a bond, which one can represent using harmonic/Morse potentials. One can now write the total energy as the sum of the bending energy and the potential energies of the bonds. We analyze the resultant potential energy surface to show the existence of (1) the loop, (2) the rod, and (3) a saddle point as one goes

from loop to the rod. We introduce friction into the dynamics using the usual approach of coupling to a heat bath of harmonic oscillators and calculate the rate of breaking of the bond represented by the Morse potential. We find that the rate of opening is strongly length dependent for short chains. For very long chains, our analysis gives a pre-exponential factor  $\approx L^{-2}$ . However, in view of the fact that our approximations, while sensible for short semiflexible chains are not expected to be valid for long flexible chains and therefore, this result is not expected to be correct. For such loops, one can easily calculate the open  $\rightleftharpoons$  closed equilibrium constant. This, in combination, with the closing rate calculated using the approach of SSS, leads to rates for opening (see Sec. V B).

The organization of the paper is as follows: In Sec. II we give a brief description of the standard model that is used for a stiff polymer and the modifications needed to account for possibility of bond formation between the two ends. In Sec. III we give a simple analysis of the ring opening problem, approximating the ring as a circle and using a Morse potential interaction between the two ends. In Sec. IV we analyze the circular ring conformation and deviations from it due to fluctuations. The energy of the ring is expanded as a series, up to second order in the fluctuations. This expansion and transition state theory (TST) are used to calculate the rate of breaking in Sec. V. The effects of friction are included using a system plus reservoir model. Section VI contains the results of the model applied to a polypeptide loop. The summary and concluding remarks are given in Sec. VII.

## II. MODEL FOR A STIFF POLYMER RING

In the usual model for stiff polymers the chain is a continuous and inextensible rod, which can be bent with expenditure of energy. The position along the chain may be specified by the arc length  $s$ . The position vector of a point at an arc length  $s$  away from one end of the chain, at the time  $t$  is denoted by  $\mathbf{r} \equiv \mathbf{r}(s, t)$  [28]. The kinetic energy  $T$  and the elastic energy of bending  $E_{bend}$  of the chain are then given by

$$T = \frac{1}{2} \int_0^L \rho \left[ \frac{\partial \mathbf{r}(s)}{\partial t} \right]^2 ds \quad (1)$$

and

$$E_{bend} = \frac{\kappa}{2} \int_0^L \left[ \frac{\partial^2 \mathbf{r}(s)}{\partial s^2} \right]^2 ds. \quad (2)$$

$\partial^2 \mathbf{r} / \partial s^2 = \partial \mathbf{u}(s) / \partial s$  is the curvature at  $s$  and  $\mathbf{u}(s)$  is the tangent vector at the point  $s$  on the polymer.  $\kappa$  is the rigidity modulus and  $L$  is the total contour length. Since stiff chains are represented by differentiable curves, we have the restriction

$$|\mathbf{u}(s)| = 1. \quad (3)$$

Integrating out the momentum part, one can write the conformational partition function as

$$Z = \int D\mathbf{r}(s) \exp \left\{ -\frac{\beta\kappa}{2} \int_0^L \left[ \frac{\partial \mathbf{u}(s)}{\partial s} \right]^2 ds \right\}. \quad (4)$$

Here the path integral is over all the configurations of the chain with the constraint given by Eq. (3). Incorporating this constraint has been the problem in dealing with semiflexible polymers. This path integral can be written as an integral over  $\mathbf{u}(s)$  as well. Since the magnitude of  $\mathbf{u}(s)$  is unity, the paths lie on the surface of a unit sphere. Thus we can write  $Z$  also as

$$Z = \int D\mathbf{u}(s) \exp \left\{ -\frac{\beta\kappa}{2} \int_0^L \left[ \frac{\partial \mathbf{u}(s)}{\partial s} \right]^2 ds \right\}. \quad (5)$$

Now Eq. (5) is the partition function for a chain with free ends. We assume that there is an interaction  $V(\mathbf{R})$  between the two end points of the polymer, which are separated by the end-to-end vector  $\mathbf{R}$ . Then the total energy is

$$E_{total} = E_{bend} + V(\mathbf{R}). \quad (6)$$

$\mathbf{R}$  is defined by

$$\mathbf{R} = \mathbf{r}(0) - \mathbf{r}(L) = - \int_0^L \mathbf{u}(s) ds. \quad (7)$$

The partition function may then be written as

$$Z_{loop} = \int D\mathbf{u}(s) \exp \left( -\beta \left\{ \frac{\kappa}{2} \int_0^L \left[ \frac{\partial \mathbf{u}(s)}{\partial s} \right]^2 ds + V(\mathbf{R}) \right\} \right). \quad (8)$$

The tangent vector may be written in terms of the angle coordinates  $\theta$  and  $\phi$  of spherical polar coordinates as

$$\mathbf{u}(s) = \mathbf{i} \sin \theta(s) \cos \phi(s) + \mathbf{j} \sin \theta(s) \sin \phi(s) + \mathbf{k} \cos \theta(s). \quad (9)$$

The bending energy can be written in terms of the angles  $\theta$  and  $\phi$  as

$$E_{bend} = \frac{\kappa}{2} \int_0^L ds \left\{ \left[ \frac{d\theta(s)}{ds} \right]^2 + \sin^2 \theta(s) \left[ \frac{d\phi(s)}{ds} \right]^2 \right\}. \quad (10)$$

Now one can rewrite the partition function as a path integral over  $\theta(s)$  and  $\phi(s)$ :

$$Z_{loop} = \int D\theta(s) \int D\phi(s) \exp \{ -\beta E_{total}[\theta(s), \phi(s)] \}. \quad (11)$$

If  $V(\mathbf{R})$  was equal to zero, this would just be the path integral for a particle on the surface of a sphere. Even in this case, no closed form analytical expression exists [28–30]. But for a closed ring with sufficiently large stiffness, only paths close to a circular conformation are important. So, it should be possible to evaluate the path integral using a “semiclassical” type of approach where one expands energy as a function of deviation from the perfect circular conformation.

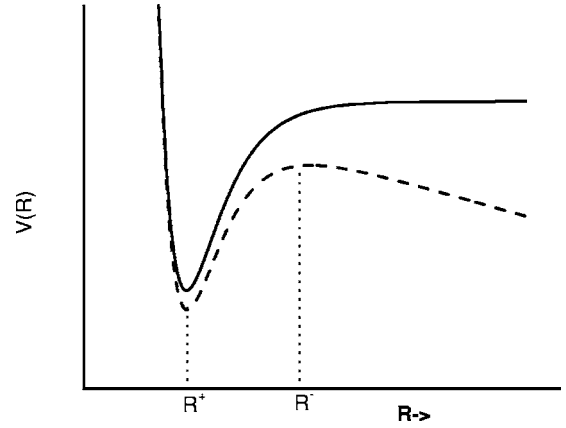


FIG. 1. The Morse potential  $V(R)$  (full line) and the function  $V(R) - 4\pi^2\kappa R/L^2$  (dashed line) plotted against  $R$ . The two extrema  $R^+$  and  $R^-$  are shown.

### III. SIMPLE ANALYSIS

The simplest description of the loop is to approximate it by a circle of radius  $r$  [31]. Since  $L$  is the length of the polymer and  $R$  is the distance between the two ends, the radius  $r$  of the circle is

$$r = \frac{L+R}{2\pi}. \quad (12)$$

The bending energy is  $E_{bend} = 2\pi^2\kappa L/(L+R)^2$  and, hence, the total energy is

$$E_{total} = \frac{2\pi^2\kappa L}{(L+R)^2} + V(R).$$

As  $R$  is very small compared to the total contour length  $L$ , a binomial expansion of the first term as a series in  $R/L$  gives

$$E_{total} \cong \frac{2\pi^2\kappa}{L} - \frac{4\pi^2\kappa R}{L^2} + V(R). \quad (13)$$

Finding the extrema by putting  $\partial E_{total}/\partial R = 0$  leads to

$$\frac{4\pi^2\kappa}{L^2} = V'(R). \quad (14)$$

We take  $V(R)$  as the Morse potential, given by

$$V(R) = D_e \{1 - \exp[-a(R-b)]\}^2, \quad (15)$$

where  $D_e$ ,  $a$ , and  $b$  are parameters of the potential. The minimum of the potential is at  $R=b$ . Now solving Eq. (14) for  $R$  one gets

$$R^\pm = b + \frac{1}{a} \ln \frac{2}{1 \pm \sqrt{1-F}}. \quad (16)$$

Here  $R^+$  corresponds to the equilibrium and  $R^-$  corresponds to the transition state for the opening. From now on, we will use the notation  $R^\alpha$  with  $\alpha=+$  or  $-$ . A plot of the Morse potential is given in Fig. 1. It has a minimum at  $R=b$ . On adding the term  $-4\pi^2\kappa R/L^2$  to it [see Eq. (13)] it gets modified to the dashed line, which has a minimum at  $R^+$  and a maximum at  $R^-$ . Defining

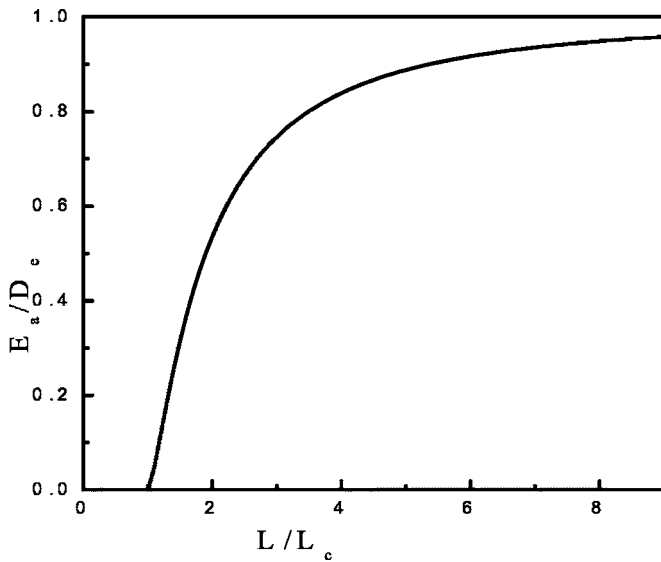


FIG. 2. The plot of  $E_a/D_e$  vs  $L/L_c$ . Activation energy is zero for  $L=L_c$ . For lengths close to  $L_c$  it goes as  $(1-L_c^2/L^2)^{3/2}$  and for  $L \gg L_c$  it becomes practically independent of length.

$$F = \frac{8\pi^2\kappa}{D_e a L^2}, \quad (17)$$

the barrier height  $E_a = E(R^-) - E(R^+)$  can be written as

$$E_a = D_e \left[ \sqrt{1-F} - \frac{F}{2} \ln \left( \frac{1 + \sqrt{1-F}}{1 - \sqrt{1-F}} \right) \right]. \quad (18)$$

It is clear that at a length

$$L_c = \sqrt{\frac{8\pi^2\kappa}{D_e a}} \quad (19)$$

the activation energy is zero—that is, the loop is no longer a minimum. A more rigorous analysis is given in Sec. IV and a plot of activation energy versus the length of the polymer is given in Fig. 2.

#### IV. SEMICLASSICAL EXPANSION—AN APPROXIMATE EXPRESSION FOR THE ENERGY OF THE BENT CHAIN

In this section we give a more rigorous, semiclassical type of analysis. We first consider a ring polymer, in which these two ends are joined smoothly—that is, tangents to the closed curve are continuous at every point on the curve. The most important path that contributes to the path integral for such a ring polymer is a great circle on the unit sphere. We perform an expansion of the energy of the polymer, as a function of fluctuations about the great circle correct up to second order. *We use this approximate form for  $E_{bend}$  in all our further calculations.* As our calculations involve breaking of the ring, the fluctuations are chosen to include those that will lead to a net end-to-end separation [see Eqs. (24) and (25)].

The definition of the tangent vector  $\mathbf{u}(s) = \partial \mathbf{r}(s) / \partial s$  may be inverted to obtain

$$\mathbf{r}(s) = \mathbf{r}_{cm} - \frac{1}{L} \int_0^L ds \int_0^s ds_1 \mathbf{u}(s_1) + \int_0^s ds_1 \mathbf{u}(s_1). \quad (20)$$

In the above,  $\mathbf{r}_{cm}$  denotes the center of mass of the molecule, which we shall take to be at the origin. We take the great circle to lie in the  $XY$  plane of a Cartesian coordinate system and imagine it to start at  $[\theta(0), \phi(0)] = (\pi/2, 0)$  and to come back to the same point, after going around the origin in the  $XY$  plane. Then any point on the great circle may be specified by the angle coordinates  $[\theta(s), \phi(s)] = (\pi/2, 2\pi s/L)$ . With this choice, using Eq. (20), the great circle corresponds to a circular ring polymer with position in three dimensional space given by

$$\mathbf{r}_{GC}(s) = \frac{L}{2\pi} \left[ \mathbf{i} \sin\left(\frac{2\pi s}{L}\right) - \mathbf{j} \cos\left(\frac{2\pi s}{L}\right) \right]. \quad (21)$$

This curve represents one end of the polymer lying in the  $XY$  plane starting at  $-L/2\pi$  on the negative  $Y$  axis, going around the  $Z$  axis along a circle of radius  $L/2\pi$ , coming back to the same point after traversing a circle of radius  $L/2\pi$ . We now wish to consider the fluctuations about this path which can be easily done by letting

$$[\theta(s), \phi(s)] = \left[ \frac{\pi}{2} + \delta\theta(s), \frac{2\pi s}{L} + \delta\phi(s) \right], \quad (22)$$

where  $[\delta\theta(s), \delta\phi(s)]$  represent the deviations from the extremum path on the unit sphere expressed in terms of angles.

Expanding the bending energy of Eq. (10) correct up to second order in the fluctuations  $\delta\theta(s)$  and  $\delta\phi(s)$  gives

$$E_{bend} = \frac{\kappa}{2} \int_0^L ds \left\{ \left[ \frac{d\delta\theta(s)}{ds} \right]^2 + \left[ \frac{2\pi}{L} + \frac{d\delta\phi(s)}{ds} \right]^2 - \left( \frac{2\pi}{L} \right)^2 \delta\theta^2(s) \right\}. \quad (23)$$

In our approach, the *bending energy* near the breaking point will be described by this expression and this should be a valid approximation, if the deviation from the circular conformation is small. It is convenient to describe the fluctuations using the Fourier expansions

$$\delta\theta(s) = \sum_{n=0}^{\infty} \delta\theta_n \cos\left(\frac{n\pi s}{L}\right) \quad (24)$$

and

$$\delta\phi(s) = \sum_{n=0}^{\infty} \delta\phi_n \cos\left(\frac{n\pi s}{L}\right). \quad (25)$$

In terms of these modes, the bending energy is

$$E_{bend} = \frac{\kappa}{4L} \left\{ 8\pi^2 - 8\pi^2 \delta\theta_0^2 + \sum_{n=1}^{\infty} (n^2 - 4) \pi^2 \delta\theta_n^2 + \sum_{n=1}^{\infty} n^2 \pi^2 \delta\phi_n^2 - 16\pi \sum_{n \text{ odd}} \delta\phi_n \right\}. \quad (26)$$

This may also be written as

$$E_{bend} = \frac{\kappa}{4L} \left\{ -8\pi^2 \delta\theta_0^2 + \pi^2 \sum_{n=1}^{\infty} (n^2 - 4) \delta\theta_n^2 + \sum_{n, \text{odd}} n^2 \pi^2 \left( \delta\phi_n - \frac{8}{n^2 \pi} \right)^2 + \sum_{n, \text{even}} n^2 \pi^2 \delta\phi_n^2 \right\}. \quad (27)$$

Equation (27) is very crucial in our approach and we make use of this expression in all further analysis.

We also derive the expression for the end-to-end vector  $\mathbf{R}$ , by expanding the components of  $\mathbf{u}(s)$  as a Taylor series up to first order, which gives

$$\mathbf{R} = L \left( \mathbf{i} \sum_{n, \text{odd}} a_n \delta\phi_n - \mathbf{j} \frac{1}{2} \delta\phi_2 + \mathbf{k} \delta\theta_0 \right) \quad (28)$$

with

$$a_n = \frac{-4}{(n^2 - 4)\pi}, \text{ if } n \text{ is odd} = 0, \text{ if } n \text{ is even.} \quad (29)$$

Thus we have  $R_x = L \sum_{n, \text{odd}} a_n \delta\phi_n$ ,  $R_y = -(L/2) \delta\phi_2$ , and  $R_z = L \delta\theta_0$ .

The closed ring corresponds to all  $\delta\theta_n$  and  $\delta\phi_n$  equal to zero. Putting all  $\delta\theta_n = 0$ ,  $\delta\phi_n = 8/\pi n^2$  for odd  $n$ , and  $\delta\phi_n = 0$  for even  $n$  gives  $E_{bend} = 0$ . This corresponds to the straight rod configuration. Interestingly, even though our expression for  $\mathbf{R}$  of Eq. (28) is correct only up to first order, using these values ( $\delta\theta_n, \delta\phi_n$ ) gives  $R_x = L$ , which is the value for the straight rod. From Eq. (27), it is obvious that if the odd  $\delta\phi_n$  values are displaced from zero to take up positive values, the energy can be decreased. This of course means that by such displacements the chain becomes less curved.

Equation (27) for  $E_{bend}$  implies that the mode  $\delta\theta_0$  is unstable, while the modes  $\delta\theta_2$  and  $\delta\phi_0$  are marginally stable (the coefficient of the square of these in  $E_{bend}$  is zero). This means that in the evaluation of the partition function within the harmonic approximation, if one integrates over these modes from  $-\infty$  to  $\infty$ , one gets divergences which are unphysical. The origin of the divergence can be understood by looking at the nature of these modes. The modes  $\delta\phi_0$  and  $\delta\theta_2$  correspond to rotations of the ring polymer as a whole. Taking  $[\delta\theta(s), \delta\phi(s)] = [\delta\theta_2 \cos(2\pi s/L), 0]$  and substituting this into the expression for  $\mathbf{r}(s)$ , we find

$$\mathbf{r}(s) = \frac{L}{2\pi} \left[ \mathbf{i} \sin\left(\frac{2\pi s}{L}\right) - \mathbf{j} \cos\left(\frac{2\pi s}{L}\right) - \mathbf{k} \delta\theta_2 \sin\left(\frac{2\pi s}{L}\right) \right]. \quad (30)$$

This  $\mathbf{r}$  corresponds to infinitesimal rotation of the circular polymer loop about the  $X$  axis. Similarly,  $\delta\phi_0$  corresponds to rotation of the polymer loop about the  $Z$  axis, and a fluctuation of the form  $\delta\theta(s) = \delta\theta_2 \sin(2\pi s/L)$  corresponds to rotation about the  $Y$  axis. When one calculates the partition function by integrating over all the modes, one can remove these rotational degrees of freedom by inserting the product of delta functions  $\delta(\delta\phi_0) \delta(\delta\theta_2) \delta(\delta\theta_{2s})$  into the functional integral and take the rotational degrees of freedom into account by explicitly putting in the factor  $8\pi^2$ . Thus we have

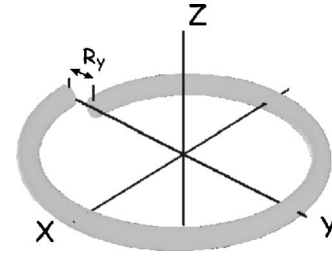


FIG. 3. The effect of changing  $\delta\phi_2$  on the smoothly closed ring. Note that this leads to a separation  $R_y$  in the  $Y$  direction. This increases the curvature of the ring and, hence, causes an increase in the energy.

$$Z_{loop} = 8\pi^2 \int D\theta(s) \int D\phi(s) \exp[-\beta E_{total}(\theta(s), \phi(s))] \times \delta(\delta\phi_0) \delta(\delta\theta_2) \delta(\delta\theta_{2s}). \quad (31)$$

The inclusion of the product of delta functions gets rid of the problem with integration over the three rotational modes. However, there are more modes with problems (possible divergences).

From Eq. (28), it follows that changes in  $\delta\phi_n$  (with  $n$  odd),  $\delta\phi_2$  and  $\delta\theta_0$  will bring about changes in  $R_x$ ,  $R_y$ , and  $R_z$ , respectively. For the ring, all the  $\delta\phi_n$ s and  $\delta\theta_n$ s are equal to zero, so that  $R_x = R_y = R_z = 0$ . From the expression for energy in Eq. (27), it is clear that  $\delta\phi_n$  (with  $n$  odd) can be increased from zero to cause a decrease in the total energy. Similarly, any change in  $\delta\theta_0$  from the value zero would also lower the energy. Thus,  $R_x$  and  $R_z$  are unstable directions. In contrast, any change in  $\delta\phi_2$  would increase the energy (Fig. 3) and thus  $R_y$  is stable. The instabilities in the  $R_x$  and  $R_z$  directions are easy to understand. Increasing  $R_x$  simply unbends the rod, lowering the energy. If one kept everything else fixed and let only  $R_z$  to change, then the loop will be transformed into a helix. The helix that results is less curved than the loop and, hence, its energy is lower. Thus, this path of opening is loop  $\rightarrow$  helix  $\rightarrow$  straight rod. We stress that these results are obtained using the simplest possible model, which has not taken the torsional contributions to the energy into account.

The two different opening up pathways may be prevented by the formation of a bond, which causes the additional contribution  $V(\mathbf{R})$  to the energy of the system. We take

$$V(\mathbf{R}) = V_M(R_x) + \frac{1}{2} k_y R_y^2 + \frac{1}{2} k_z R_z^2, \quad (32)$$

where  $k_y$  and  $k_z$  are the force constants in the  $Y$  and  $Z$  directions. The contribution of  $\delta\theta_0$  to  $E_{bend}$  is  $-(2\kappa/L)\pi^2 \delta\theta_0^2$ . Using Eq. (28), this may be written as  $-(\kappa/L^3)\pi^2 R_z^2$  and, hence,  $R_z$  may be made stable by having  $k_z > (4\kappa/L^3)\pi^2$ .

The breaking occurs by increasing the value of  $R_x$  which may be prevented by  $V_M(R_x)$ . For this, the potential  $V_M(R_x)$  should be such that it creates a minimum near  $R_x = 0$ . Further, it has to allow the dissociation when  $R_x$  increases. Therefore, we take

$$V_M(R_x) = D_e(1 - e^{-a(R_x-b)})^2. \quad (33)$$

With these choices, the breaking occurs as a result of the increase in  $R_x$  and is seen to involve only  $\delta\phi_n$  ( $n$  odd) modes only. Thus, the relevant potential energy surface for the breaking is given by

$$E[\delta\phi] = \frac{\kappa}{4L} \left\{ 8\pi^2 + \sum_{n \text{ odd}} n^2 \pi^2 \delta\phi_n^2 - 16\pi \sum_{n \text{ odd}} \delta\phi_n \right\} + V_M(R_x). \quad (34)$$

The dynamics takes place on a multidimensional surface generated by this  $E[\delta\phi]$  considered as a function of  $\delta\phi_n$ , with  $n=1, 3, 5, \dots$ .

### A. The bending energy for making contact

We have mentioned in Sec. I that a perfect circle is the minimum energy configuration only if the two ends are joined and the tangents join continuously. One can now ask: what is the minimum energy configuration for a fixed value of  $R_x$  without imposing any constraints on the two tangent vectors? The configuration can be obtained and its energy calculated, by extremizing  $\phi$  dependent part of the bending energy,  $(\kappa/4L)\sum_{n \text{ odd}}\{n^2 \pi^2 \delta\phi_n^2 - 16\pi \delta\phi\}$ , subject to the constraint

$$R_x = L \sum_{n \text{ odd}} a_n \delta\phi_n. \quad (35)$$

Doing this by the method of Lagrangian multipliers, we get

$$\delta\phi_n^e = -\frac{2\lambda L^2 a_n}{\kappa n^2 \pi^2} + \frac{8}{n^2 \pi}, \quad (36)$$

where  $\lambda$  is the Lagrangian multiplier. It is found by using Eq. (36) in Eq. (35) which gives

$$R_x = -\frac{2L^3 \lambda}{\kappa \pi^2} \sum_{n \text{ odd}} \frac{a_n^2}{n^2} + \frac{8L}{\pi} \sum_{n \text{ odd}} \frac{a_n}{n^2}. \quad (37)$$

Using  $\sum_{n \text{ odd}} (a_n/n^2) = \pi/8$  and  $\sum_{n \text{ odd}} (a_n^2/n^2) = 3/16$  leads to

$$\lambda = \frac{8\kappa\pi^2(L - R_x)}{3L^3}. \quad (38)$$

Substituting Eq. (38) into Eq. (36) one obtains the minimum energy configuration for a given  $R_x$  as

$$\delta\phi_n^e = \frac{8}{n^2 \pi} - \frac{16a_n(L - R_x)}{3n^2 L}. \quad (39)$$

The corresponding bending energy is

$$E_{min}(R_x) = \frac{4\kappa\pi^2}{3L^3} (L - R_x)^2. \quad (40)$$

Putting  $R_x=0$ , we get the minimum energy for bringing the two ends together, without any constraints on the tangents. It is

$$E_{min}(0) = \frac{4\kappa\pi^2}{3L} = 13.195 \frac{\kappa}{L}. \quad (41)$$

This value is to be compared with the exact value  $14.054\kappa/L$  obtained by Yamakawa and Stockmayer [11]. This shows that though in Eq. (34) we have retained only up to second order terms it gives a very good value for the minimum energy and thus justifies its use in our calculations below. Also, one can find the angle the tangents at the end would make (see Fig. 1 on p. 2845 of Ref. [11]) between each other. This angle  $\theta$  is found to be 60 deg in our approach, compared to the value of 81.6 deg found by Yamakawa and Stockmayer. Kulic and Schiessel [27] have used a ‘‘circle-line’’ approximation to estimate this angle and find it to be 77.5 deg, which is better than our result. However, the energy that they get is  $15.699\kappa/L$ , which is poorer.

### B. The potential energy surface for loop opening

We now find the extrema on the potential energy surface given by Eq. (34). Putting  $\partial E[\delta\phi_n]/\partial \delta\phi_n = 0$  gives

$$\frac{\kappa}{4L} (2n^2 \pi^2 \delta\phi_n - 16\pi) + V'_M(R_x) \frac{\partial R_x}{\partial \delta\phi_n} = 0. \quad (42)$$

As  $\partial R_x/\partial \delta\phi_n = La_n$ , we may solve this to get the value of  $\delta\phi_n$  at the extrema, which we denote as  $\delta\phi_n^\alpha$  ( $\alpha=+$  or  $-$ ):

$$\delta\phi_n^\alpha = \frac{8}{n^2 \pi} - \frac{2L^2 V'_M(R_x) a_n}{\kappa n^2 \pi^2}. \quad (43)$$

This may be used to calculate the value of  $R_x$  at the extrema as

$$R_x = \frac{8L}{\pi} \sum_{n, \text{ odd}} \frac{a_n}{n^2} - \frac{2L^3 V'_M(R_x)}{\kappa \pi^2} \sum_{n, \text{ odd}} \frac{a_n^2}{n^2}.$$

With the sums done as before this can be written as

$$V'_M(R_x) + \frac{8\pi^2 \kappa}{3L^3} (R_x - L) = 0. \quad (44)$$

As  $R_x$  becomes large, the derivative of the Morse potential vanishes. Therefore, the above equation has the obvious solution  $R_x=L$  [assuming  $V'_M(L)=0$ ], which is the straight rod. In addition, Eq. (44) has two more solutions. For  $R_x \ll L$  we write Eq. (44) as

$$\frac{8\pi^2 \kappa}{3L^2} = V'_M(R_x). \quad (45)$$

Equation (45) should be compared with the result of the simple analysis Eq. (14). It is seen that the factor of  $4\pi^2$  of the simple analysis is replaced by  $8\pi^2/3$  in the more rigorous analysis. Equations (45) and (40) mean that one has

effectively a potential energy  $E(R_x) = E_{min}(R_x) + V_M(R_x)$ , for  $R_x \ll L$ . Solving Eq. (45), we get the two solutions

$$R_x^\pm = b + \frac{1}{a} \ln \left( \frac{2}{1 \pm \sqrt{1 - F_1}} \right) \quad (46)$$

with

$$F_1 = \frac{16\pi^2 \kappa}{3D_e a L^2} = \left( \frac{L_c}{L} \right)^2 \quad (47)$$

and

$$L_c = \sqrt{\frac{16\pi^2 \kappa}{3D_e a}} \quad (48)$$

in this case [cf. Eq. (19)]. Each value of  $R_x^\alpha$  on substitution into the right hand side of Eq. (43) leads to  $\delta\phi_n^\alpha$ , corresponding to either the equilibrium ( $\alpha=+$ ) or the saddle ( $\alpha=-$ ). The activation energy is  $E(R_x^-) - E(R_x^+)$  and is given by,

$$E_a = D_e \left[ \sqrt{1 - F_1} - \frac{F_1}{2} \ln \left( \frac{1 + \sqrt{1 - F_1}}{1 - \sqrt{1 - F_1}} \right) \right]. \quad (49)$$

Equation (49) has the same behavior as Eq. (18) but with the critical length changed. Hence, Eq. (49) gives the dependence of the activation energy of opening on the length  $L$ . For lengths close to  $L_c$ ,  $E_a \sim (1 - L_c^2/L^2)^{3/2}$  and for  $L \gg L_c$ , it behaves as  $D_e - (c_1 + c_2 \ln L)/L^2$ , where  $c_1$  and  $c_2$  are constants (see Fig. 2). These results are for a bond described by the Morse potential and are not universal.

To form a closed loop with even the tangents joining smoothly [i.e.,  $\mathbf{u}(0) = \mathbf{u}(L)$  and  $\mathbf{R} = \mathbf{0}$ ], one has to have all the  $\delta\phi_n = 0$ . From Eq. (43), it is clear that no value of  $V_M'(R_x)$  would make this happen. Thus, with a Morse potential interaction, one would never have the two ends joining smoothly and, hence, the ring would never be a perfect circle. This is because the rigidity that would make such smooth joining happen is not included in the Morse potential.

## V. THE RATE OF BREAKING

### A. The TST rate in the absence of damping

In this section, we calculate the rate of breaking using the classical transition state theory [32]. We have already found the extrema on the potential energy hypersurface and have identified the initial state (the ring) and the saddle point over which the system has to go for the breaking to happen. We use the harmonic approximation for the fluctuations about each of the extrema and use standard transition state theory to calculate the rate. The relevant potential energy is  $E_{bend} + V(\mathbf{R})$ , which gives the multidimensional potential energy surface as a function of  $\delta\phi_n$  and  $\delta\theta_n$  coordinates. The kinetic energy of the ring given in Eq. (1) can be evaluated in terms of angular velocities  $\delta\dot{\theta}_n$  and  $\delta\dot{\phi}_n$ . For this, we Taylor expand  $\mathbf{u}(s)$  as a series in the fluctuations and retain the first order term, to get

$$\mathbf{u}(s) = \mathbf{i} \cos \left( \frac{2\pi s}{L} \right) + \mathbf{j} \sin \left( \frac{2\pi s}{L} \right) + \delta\mathbf{u}(s) \quad (50)$$

with

$$\delta\mathbf{u}(s) = -\mathbf{i} \sin \left( \frac{2\pi s}{L} \right) \delta\phi(s) + \mathbf{k} \cos \left( \frac{2\pi s}{L} \right) \delta\phi(s) - \mathbf{i} \delta\theta(s). \quad (51)$$

Then using the expansions of Eqs. (24) and (25), with  $\delta\theta_n$  and  $\delta\phi_n$  time dependent, we get the following expression for the kinetic energy, correct up to second order in  $\delta\dot{\theta}_n$  and  $\delta\dot{\phi}_n$ :

$$T = \frac{\rho L^3}{2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (\delta\dot{\phi}_n \delta\dot{\phi}_m T_{nm}^\phi + \delta\dot{\theta}_n \delta\dot{\theta}_m T_{nm}^\theta). \quad (52)$$

Consistent with our calculation of potential energy, we have used the ring geometry to evaluate the expression for the kinetic energy. The calculation has been done in the center of mass frame to avoid translational degrees of freedom. The structures of the matrices  $\mathbf{T}^\phi$  and  $\mathbf{T}^\theta$  are interesting.  $\mathbf{T}^\phi$  has no coupling between the even and the odd modes.  $\mathbf{T}^\theta$  is diagonal for even modes except for  $n$  or  $m=0$ . The expressions for matrix elements are given in Appendix A. Since breaking is caused by odd  $\delta\phi_n$  modes, the relevant part of the kinetic energy is

$$T_{odd}^\phi = \frac{\rho L^3}{2} \sum_{n,m \text{ odd}} \delta\dot{\phi}_n \delta\dot{\phi}_m T_{nm}^\phi. \quad (53)$$

We now make the harmonic approximation for motion around the  $\alpha$ th extremum by expanding  $E[\delta\phi]$  of Eq. (34) about  $\delta\phi_n^{(\alpha)}$  and keeping only terms up to second order in the fluctuations. Introducing  $y_n = \delta\phi_n - \delta\phi_n^\alpha$ , the Hamiltonian may be written as

$$H^\alpha = \frac{\rho L^3}{2} \sum_{n \text{ odd}} T_{mn}^\phi \dot{y}_n \dot{y}_m + E_0^\alpha + \sum_{n \text{ odd}} \frac{\kappa n^2 \pi^2}{4L} y_n^2 + \frac{1}{2} k^\alpha L^2 \left( \sum_{n \text{ odd}} a_n y_n \right)^2, \quad (54)$$

where

$$k^\alpha = \left[ \frac{\partial^2 V_M(R_x)}{\partial R_x^2} \right]_{R_x=R_x^\alpha}. \quad (55)$$

Expressions for  $k^\alpha$  are

$$k^+ = a^2 D_e (1 + \sqrt{1 - F_1} - F_1) \quad (56)$$

and

$$k^- = -a^2 D_e (-1 + \sqrt{1 - F_1} + F_1). \quad (57)$$

$E_0^\alpha$  is the potential energy at the  $\alpha$ th extremum and it makes no contribution to the dynamics. We now introduce  $\eta_n = \sqrt{\rho L^3} y_n$  and write  $H^\alpha$  as

$$H^\alpha = E_0^{(\alpha)} + \frac{1}{2} \sum_{m,n} \left( T_{mn}^\phi \dot{\eta}_n \dot{\eta}_m + \frac{1}{\rho L} V_{mn}^\alpha \eta_n \eta_m \right) \quad (58)$$

with

$$V_{mn}^\alpha = \frac{\kappa n^2 \pi^2}{2L^3} \delta_{mn} + k^\alpha a_n a_m. \quad (59)$$

The frequencies of the normal modes for vibration around ath extremum obey

$$|\mathbf{D}^\alpha(\omega^2)| = 0, \quad (60)$$

where the matrix

$$\mathbf{D}^\alpha(\omega^2) = \rho L \omega^2 \mathbf{T}^\phi - \mathbf{V}^\alpha. \quad (61)$$

Note that  $\mathbf{D}^\alpha(\omega^2)$  is a matrix containing contributions only from the odd  $n$  modes.  $\mathbf{T}^\phi$  and  $\mathbf{V}^\alpha$  are matrices which have  $T_{mn}^\phi$  and  $V_{mn}^\alpha$  as their  $mn$ th matrix element. As the motion around the equilibrium ( $\alpha=+$ ) is stable, the equation  $|\mathbf{D}^+(\omega^2)|=0$  has  $N(\rightarrow\infty)$  real positive solutions for  $\omega$ , which we denote by  $\omega_1^+, \omega_2^+, \omega_3^+, \dots, \omega_N^+$ . At the saddle (i.e.,  $\alpha=-$ ), one direction is unstable. Therefore, one solution of  $|\mathbf{D}^-(\omega^2)|=0$  will have  $\omega^2 = -\Omega^2$  with  $\Omega$  real. We shall denote this value as  $\omega_1^- = -i\Omega$ . The symbols  $\omega_2^-, \omega_3^-, \dots, \omega_N^-$  stand for the frequencies of the stable modes. Transition state theory [32,33] gives the rate as

$$\Gamma = \frac{1}{2\pi} \frac{\prod_{i=1}^N \omega_i^+}{\prod_{i=2}^N \omega_i^-} \exp(-E_d/k_B T). \quad (62)$$

This may also be written as

$$\begin{aligned} \Gamma &= \frac{\Omega}{2\pi} \left| \frac{\prod_{i=1}^N \omega_i^+}{\prod_{i=1}^N \omega_i^-} \right| \exp(-E_d/k_B T) \\ &= \frac{\Omega}{2\pi} \left| \frac{\det \mathbf{D}^+(\omega^2)}{\det \mathbf{D}^-(\omega^2)} \right|_{\omega^2=0}^{1/2} \exp(-E_d/k_B T) \end{aligned} \quad (63)$$

$$= \frac{\Omega}{2\pi} D_r \exp(-E_d/k_B T), \quad (64)$$

where  $D_r$  is the ratio of determinants

$$D_r = \left| \frac{\det \mathbf{V}^+}{\det \mathbf{V}^-} \right|^{1/2}. \quad (65)$$

This ratio can be calculated exactly (see Appendix B) and one gets

$$\Gamma = \frac{\Omega}{2\pi} \left| \frac{8\kappa\pi^2 + 3L^3 k^+}{8\kappa\pi^2 + 3L^3 k^-} \right|^{1/2} \exp(-E_d/k_B T). \quad (66)$$

The value of  $\Omega$  may be obtained by solving the equation (see Appendix B and the next section)

$$\left[ 1 + \frac{k^-}{\mu} S_1(\Omega) \right] [16\Omega^2 S_3(\Omega) - 1] = 16 \frac{k^-}{\mu} \Omega^2 S_2(\Omega)^2, \quad (67)$$

where  $S_1$ ,  $S_2$ , and  $S_3$  are obtained from the sums  $S'_1$ ,  $S'_2$  and  $S'_3$  (which are defined in Appendix B), respectively, by putting the friction coefficient  $\gamma=0$ . Analytical solution of Eq. (67) is possible with MATHEMATICA, but the result is rather complex and so we have not used them. It is easy to solve the equation numerically.

## B. Damped dynamics through the system plus reservoir model

The calculations in the previous section were done in the undamped limit. However, polymer dynamics is damped and introduction of damping modifies the results. A simple way to incorporate damping into the dynamics is to use the ‘‘system-plus-reservoir model’’ [34], which couples the system with a collection of harmonic oscillators so as to reproduce the effects of friction. The coupling can be used to go over smoothly from the undamped to the overdamped limit. The Hamiltonian for the semiflexible polymer with such a coupling is

$$\begin{aligned} H &= \int_0^L ds \left( \frac{\rho}{2} \dot{\mathbf{r}}^2(s) \right. \\ &\quad \left. + \frac{1}{2} \sum_{\beta} m_{\beta} \left[ \dot{\mathbf{x}}_{\beta}^2(s) + \omega_{\beta}^2 \left[ \mathbf{x}_{\beta}(s) - \frac{c_{\beta}}{m_{\beta} \omega_{\beta}^2} \mathbf{r}(s) \right]^2 \right] \right) \\ &\quad + E[\mathbf{r}(s)], \end{aligned} \quad (68)$$

where  $E[\mathbf{r}(s)] = E_{total}$  as given by Eqs. (6) and (2).  $\mathbf{x}_{\beta}(s)$  with  $\beta=1, 2, \dots, N$  denote position vectors of a collection of harmonic oscillators coupled linearly to  $\mathbf{r}(s)$ . The masses  $m_{\beta}$ , frequencies  $\omega_{\beta}$  and coupling constants  $c_{\beta}$  are chosen such that  $\mathbf{r}(s)$  obeys the Langevin equation

$$\rho \ddot{\mathbf{r}} + \rho \gamma \dot{\mathbf{r}} + \frac{\delta E}{\delta \mathbf{r}(s)} = \zeta(s, t), \quad (69)$$

where  $\zeta(s, t)$  is the noise obeying  $\langle \zeta(s, t) \rangle = 0$ ,  $\langle \zeta(s, t) \zeta(s', t') \rangle = 2k_B T \rho \gamma \delta(t-t') \delta(s-s')$ . This requires that one should have  $J(\omega)$  defined by

$$J(\omega) = \sum_{\beta} \frac{c_{\beta}^2}{m_{\beta} \omega_{\beta}} \delta(\omega - \omega_{\beta}) \quad (70)$$

equal to

$$J(\omega) = \rho \gamma \omega. \quad (71)$$

The Hamiltonian in Eq. (68) can be written in terms of  $\delta\phi_n$  and  $\delta\theta_n$ s. For this purpose, we first write  $\mathbf{u}(s)$  in terms of  $\delta\phi_n$  and  $\delta\theta_n$ s as

$$\mathbf{u}(s) = \mathbf{u}_c(s) + \sum_n (\mathbf{u}_n^\phi \delta\phi_n + \mathbf{u}_n^\theta \delta\theta_n). \quad (72)$$

In the above

$$\mathbf{u}_c(s) = \cos(2\pi s/L) \mathbf{i} + \sin(2\pi s/L) \mathbf{j}, \quad (73)$$



$$\mathbf{u}_n^\phi(s) = -\sin(2\pi s/L)\cos(n\pi s/L)\mathbf{i} + \cos(2\pi s/L)\cos(n\pi s/L)\mathbf{j} \quad (74)$$

and

$$\mathbf{u}_n^\theta(s) = -\cos(n\pi s/L)\mathbf{k}. \quad (75)$$

Using this in Eq. (20) we get

$$\mathbf{r}(s) = \mathbf{r}_c(s) + \sum_n \mathbf{r}_n(s) \quad (76)$$

with

$$\mathbf{r}_n(s) = \mathbf{r}_n^\phi(s)\delta\phi_n + \mathbf{r}_n^\theta(s)\delta\theta_n. \quad (77)$$

$\mathbf{r}_c(s)$ ,  $\mathbf{r}_n^\phi(s)$ , and  $\mathbf{r}_n^\theta(s)$  are given by

$$\mathbf{r}_c(s) = \int_0^s \mathbf{u}_c(s_1)ds_1 - \frac{1}{L} \int_0^L ds \int_0^s ds_1 \mathbf{u}_c(s_1)ds_1, \quad (78)$$

$$\mathbf{r}_n^\phi(s) = \int_0^s \mathbf{u}_n^\phi(s_1)ds_1 - \frac{1}{L} \int_0^L ds \int_0^s ds_1 \mathbf{u}_n^\phi(s_1)ds_1, \quad (79)$$

and

$$\mathbf{r}_n^\theta(s) = \int_0^s \mathbf{u}_n^\theta(s_1)ds_1 - \frac{1}{L} \int_0^L ds \int_0^s ds_1 \mathbf{u}_n^\theta(s_1)ds_1. \quad (80)$$

Equation (77) can be put into the Hamiltonian of Eq. (68) to get

$$\begin{aligned} H = & \frac{\rho L^3}{2} \sum_{n,m} (T_{mn}^\phi \delta\dot{\phi}_n \delta\dot{\phi}_m + T_{mn}^\theta \delta\dot{\theta}_n \delta\dot{\theta}_m) + E[\mathbf{r}(s)] \\ & + \int_0^L ds \sum_\beta \frac{m_\beta}{2} \left[ \dot{\mathbf{x}}_\beta(s)^2 + \omega_\beta^2 \left( \mathbf{x}_\beta(s) \right. \right. \\ & \left. \left. - \frac{c_\beta}{m_\beta \omega_\beta^2} \left\{ \mathbf{r}_c(s) + \sum_n [\mathbf{r}_n^\phi(s)\delta\phi_n + \mathbf{r}_n^\theta(s)\delta\theta_n] \right\} \right)^2 \right]. \end{aligned} \quad (81)$$

In the above,  $\mathbf{r}_c(s)$  is independent of time and has no contribution to the dynamics, so the term involving it may be absorbed into the definition of  $\mathbf{x}_\beta(s)$ . Hence Eq. (81) can be rewritten as

$$\begin{aligned} H = & \frac{\rho L^3}{2} \sum_{n,m} (T_{mn}^\phi \delta\dot{\phi}_n \delta\dot{\phi}_m + T_{mn}^\theta \delta\dot{\theta}_n \delta\dot{\theta}_m) + E[\mathbf{r}(s)] \\ & + \int_0^L ds \sum_\beta \frac{m_\beta}{2} \left[ \dot{\mathbf{x}}_\beta(s)^2 + \omega_\beta^2 \left( \mathbf{x}_\beta(s) \right. \right. \\ & \left. \left. - \frac{c_\beta}{m_\beta \omega_\beta^2} \left\{ \sum_n [\mathbf{r}_n^\phi(s)\delta\phi_n + \mathbf{r}_n^\theta(s)\delta\theta_n] \right\} \right)^2 \right]. \end{aligned} \quad (82)$$

The equations of motion that result from this Hamiltonian are

$$\begin{aligned} \sum_n \rho L^3 T_{mn}^\phi \delta\ddot{\phi}_n + \sum_{\beta,n} \frac{c_\beta^2}{m_\beta \omega_\beta^2} L^3 T_{mn}^\phi \delta\phi_n + \frac{\partial E}{\partial \delta\phi_n} \\ = \sum_\beta c_\beta \int_0^L \mathbf{x}_\beta(s) \cdot \mathbf{r}_m^\phi(s) ds, \end{aligned} \quad (83)$$

$$\begin{aligned} \sum_n \rho L^3 T_{mn}^\theta \delta\ddot{\theta}_n + \sum_{\beta,n} \frac{c_\beta^2}{m_\beta \omega_\beta^2} L^3 T_{mn}^\theta \delta\theta_n + \frac{\partial E}{\partial \delta\theta_n} \\ = \sum_\beta c_\beta \int_0^L \mathbf{x}_\beta(s) \cdot \mathbf{r}_m^\theta(s) ds \end{aligned} \quad (84)$$

and

$$m_\beta \ddot{\mathbf{x}}_\beta(s) + m_\beta \omega_\beta^2 \mathbf{x}_\beta(s) = c_\beta \left( \sum_n \mathbf{r}_n^\phi \delta\phi_n + \sum_n \mathbf{r}_n^\theta \delta\theta_n \right). \quad (85)$$

Now it is convenient to define

$$x_{n\beta}^\phi = \int_0^L \mathbf{r}_n^\phi \cdot \mathbf{x}_\beta(s) ds, \quad (86)$$

and

$$x_{n\beta}^\theta = \int_0^L \mathbf{r}_n^\theta \cdot \mathbf{x}_\beta(s) ds. \quad (87)$$

In terms of these the above equations may be rewritten as

$$\sum_n \rho L^3 T_{mn}^\phi \delta\ddot{\phi}_n + \sum_{\beta,n} \frac{c_\beta^2}{m_\beta \omega_\beta^2} L^3 T_{mn}^\phi \delta\phi_n + \frac{\partial E}{\partial \delta\phi_n} = \sum_\beta c_\beta x_{m\beta}^\phi, \quad (88)$$

$$m_\beta \ddot{x}_{m\beta}^\phi + m_\beta \omega_\beta^2 x_{m\beta}^\phi = c_\beta \sum_n L^3 T_{mn}^\phi \delta\phi_n, \quad (89)$$

$$\sum_n \rho L^3 T_{mn}^\theta \delta\ddot{\theta}_n + \sum_{\beta,n} \frac{c_\beta^2}{m_\beta \omega_\beta^2} L^3 T_{mn}^\theta \delta\theta_n + \frac{\partial E}{\partial \delta\theta_n} = \sum_\beta c_\beta x_{m\beta}^\theta \quad (90)$$

and

$$m_\beta \ddot{x}_{m\beta}^\theta + m_\beta \omega_\beta^2 x_{m\beta}^\theta = c_\beta \sum_n L^3 T_{mn}^\theta \delta\theta_n. \quad (91)$$

For motion around each extremum, we approximate the exact  $E = E_{\text{bend}} + V(\mathbf{R})$  by expanding  $V(\mathbf{R})$  up to the quadratic term. We find that the equations for  $\delta\theta_n$  and  $\delta\phi_n$  decouple. As breaking involves only odd  $\delta\phi_n$ , we confine our attention to these modes alone. Putting  $\delta\phi_n(t) = \delta\phi_n^0 e^{i\omega t}$ , for  $n=1, 3, \dots, 2N+1$  (with  $N \rightarrow \infty$ ) and  $x_{n\beta}(t) = x_{n\beta}^0 e^{i\omega t}$  we find that  $\omega^2$  satisfies the equation

$$\det \mathcal{D}^\alpha(\omega^2) = 0. \quad (92)$$

$\mathcal{D}^\alpha(\omega^2)$  is an  $(N+N\mathcal{N}) \times (N+N\mathcal{N})$  matrix given by

$$\mathcal{D}^\alpha(\omega^2) = \left[ \begin{array}{c|cccc} -\rho\omega^2 L^3 \mathbf{T} + \sum_{\beta} \frac{L^3 c_{\beta}^2}{m_{\beta} \omega_{\beta}^2} \mathbf{T} + L^2 \mathbf{V}^\alpha & \mathbf{C}_1 & \mathbf{C}_2 & \dots & \mathbf{C}_N \\ \hline \mathbf{C}_1 L^3 \mathbf{T} & \mathbf{D}_1(\omega^2) & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{C}_2 L^3 \mathbf{T} & \mathbf{0} & \mathbf{D}_2(\omega^2) & \dots & \dots \\ \vdots & \dots & \dots & \dots & \dots \\ \mathbf{C}_N L^3 \mathbf{T} & \dots & \dots & \mathbf{0} & \mathbf{D}_N(\omega^2) \end{array} \right]. \quad (93)$$

$\mathbf{T}$  and  $\mathbf{V}$  are  $N \times N$  kinetic energy and potential energy matrices, which determine the contribution of odd  $\delta\phi_n$  modes and  $\mathbf{D}_{\beta} = m_{\beta}(\omega^2 - \omega_{\beta}^2) \mathbf{I}_N$ .  $\mathbf{C}_{\beta}$  is an  $N \times N$  diagonal matrix given by  $-c_{\beta} \mathbf{I}_N$ . Using the partitioning as shown by the lines in the matrix form Eq. (93), we can rewrite Eq. (92) as

$$\det \left[ \begin{array}{c} -\rho L^3 \omega^2 \mathbf{T} + \sum_{\beta} \frac{c_{\beta}^2}{m_{\beta} \omega_{\beta}^2} L^3 \mathbf{T} + L^2 \mathbf{V}^\alpha \\ -L^3 \left( \sum_{\beta} \mathbf{C}_{\beta} \mathbf{D}_{\beta}^{-1} \mathbf{C}_{\beta} \right) \mathbf{T} \end{array} \right] = 0. \quad (94)$$

This may be simplified to

$$\det \left\{ -\rho L \omega^2 \mathbf{T} + \mathbf{V}^\alpha + \left[ \sum_{\beta} \frac{c_{\beta}^2}{m_{\beta} \omega_{\beta}^2} - \frac{c_{\beta}^2}{m_{\beta}(-\omega^2 + \omega_{\beta}^2)} \right] L \mathbf{T} \right\} = 0. \quad (95)$$

In particular, for the unstable mode, one can put  $\omega^2 = -\Omega_f^2$  and get

$$\det(\rho L \Omega_f^2 \mathbf{T} + \mathbf{V}^\alpha + \rho L \gamma \Omega_f) = 0. \quad (96)$$

It is shown in Appendix B that this can be rewritten as

$$\left[ 1 + \frac{k^-}{\rho L} S_1'(\Omega_f) \right] [16(\Omega_f^2 + \gamma \Omega_f) S_3'(\Omega_f) - 1] = \frac{16k^-}{\rho L} (\Omega_f^2 + \gamma \Omega_f) S_2'(\Omega_f)^2. \quad (97)$$

Definitions of  $S_1'$ ,  $S_2'$ , and  $S_3'$  are given in Appendix B.

The rate in presence of damping is given by

$$\Gamma_f = \frac{\Omega_f}{2\pi} \left| \frac{\prod_{i=1}^N \omega_i^+}{\prod_{i=1}^N \omega_i^-} \right| \exp(-E_d/kT),$$

where  $(\omega^{\pm})^2$  are the solutions of  $\det \mathcal{D}^\alpha(\omega^2) = 0$ . Therefore we can write

$$\Gamma_f = \frac{\Omega_f}{2\pi} \sqrt{\left| \frac{\det \mathcal{D}^+(\omega^2)}{\det \mathcal{D}^-(\omega^2)} \right|_{\omega=0}} \exp(-E_d/kT).$$

Now we evaluate  $\det \mathcal{D}^\alpha(\omega^2)$ . The partition technique gives

$$\det \mathcal{D}^\alpha(\omega^2) = \det \left[ -\rho L \omega^2 \mathbf{T} + \mathbf{V}^\alpha + \left( \sum_{\beta} \frac{c_{\beta}^2}{m_{\beta} \omega_{\beta}^2} - \frac{c_{\beta}^2}{m_{\beta}(-\omega^2 + \omega_{\beta}^2)} \right) L \mathbf{T} \right] \prod_{\beta} \det \mathbf{D}_{\beta}(\omega^2). \quad (98)$$

Thus

$$\left( \prod_n \omega_i^{\alpha} \right)^2 = \det \mathcal{D}^\alpha(\omega^2) \Big|_{\omega^2=0}. \quad (99)$$

Since  $\det \mathbf{D}_{\beta}(0)$  is independent of the equilibrium and transition state, the ratio of determinants is

$$\left| \frac{\det \mathcal{D}^+(\omega^2)}{\det \mathcal{D}^-(\omega^2)} \right|_{\omega=0} = \left| \frac{\det \mathbf{V}^+}{\det \mathbf{V}^-} \right| = D_r^2. \quad (100)$$

The first equality above implies that friction does not affect the ratio of the two determinants. We have used Eq. (65) to get the second equality. Hence, the rate in presence of friction is given by

$$\Gamma_f = \frac{\Omega_f}{2\pi} D_r \exp(-E_d/k_B T). \quad (101)$$

Equation (97) can be solved numerically to obtain  $\Omega_f$ , and hence the rate can be evaluated.

Equation (101) was derived using expansions around the closed circular shaped ring. One therefore expects that the result is valid only for  $L$  being a few times the persistence length and if  $L$  is much larger than the persistence length, the approach is not expected to lead to correct results. This is seen from an analysis of  $L \rightarrow \infty$  limits of the rate expression. In this limit, one easily finds that  $\Gamma \sim L^{-1/2}$  in the absence of friction while if friction is included,  $\Gamma \sim L^{-2}$ . However, in view of the approximations that have been made, neither of these can be expected to be correct, as our approach assumes small amplitude fluctuations, which is valid only in the semi-flexible limit.  $L \rightarrow \infty$  corresponds to the fully flexible limit, and results in this limit may be obtained by a different method. The equilibrium constant  $K_{eq}$  for closed  $\rightleftharpoons$  open is given by

$$K_{eq} = \frac{Z_{open}}{Z_{close}} = \frac{\Gamma_{opening}}{\Gamma_{closing}}. \quad (102)$$

In the above,  $Z_{open}$  and  $Z_{closed}$  are partition functions for the open and closed states.  $\Gamma_{opening}$  and  $\Gamma_{closing}$  are the rates of opening and closing. In the fully flexible limit, the partition functions are calculated below. The end-to-end distribution function is  $p(\mathbf{R}) = (3/2\pi Ll)^{3/2} \exp(-3\mathbf{R}^2/2Ll)$ , where  $l$  is the Kuhn length. Note that the Kuhn length  $l$  is related to the persistence length by the relation  $l = 2l_p$  [30]. The partition function for the open state may be calculated as

$$Z_{open} = \int d\mathbf{R} p(\mathbf{R}) = 1. \quad (103)$$

For the loop, the two ends are held together by a potential well of depth  $D_e$ . Approximating the potential within the well to be harmonic, having the form

$$V_{truncated}(\mathbf{R}) = -D_e + \frac{k_t}{2} \mathbf{R}^2, \text{ for } |\mathbf{R}| < R_c \\ = 0, \text{ otherwise.} \quad (104)$$

$R_c$  is chosen such that  $D_e = (k_t/2)R_c^2$ . Then, one gets

$$Z_{closed} = \int_{|\mathbf{R}| < R_c} d\mathbf{R} p(\mathbf{R}) \exp\left(\beta D_e - \frac{\beta k_t}{2} \mathbf{R}^2\right). \quad (105)$$

One makes little error by extending the integration over the entire space to get

$$Z_{closed} = \frac{\exp(\beta D_e)}{(1 + \beta k_t L l / 3)^{3/2}} \approx \exp(\beta D_e) \left(\frac{3}{\beta k_t L l}\right)^{3/2}. \quad (106)$$

The rate of closing, if one follows the analysis of SSS {see Eq. (6) of Ref. [4]} is given by

$$\Gamma_{closing} = \frac{4\pi D a}{(2\pi L l / 3)^{3/2}}, \quad (107)$$

where  $a$  (in their notation) is the distance that the two ends have to approach for closing. We shall take  $a$  to be equal to  $R_c$ . Then, the rate of opening is given by

$$\Gamma_{opening} = \left(\frac{2\beta^3 k_t^3}{\pi}\right)^{1/2} R_c D \exp(-\beta D_e). \quad (108)$$

This result does not depend on the length  $L$  of the polymer. It gives an approximate expression for the opening rate in the flexible limit for three dimensions.

## VI. RESULTS AND NUMERICAL CALCULATIONS

There have been several experimental investigations into loop formation. In comparison, studies of ring opening have been a few. The only theoretical investigation of ring opening seems to be the work of Dua and Cherayil [25], but their study has no dependence of the rate constant  $k_r$  [see their Eq. (27)] on the length of the chain. Our analysis in the previous sections shows that the opening is assisted by the rigidity of

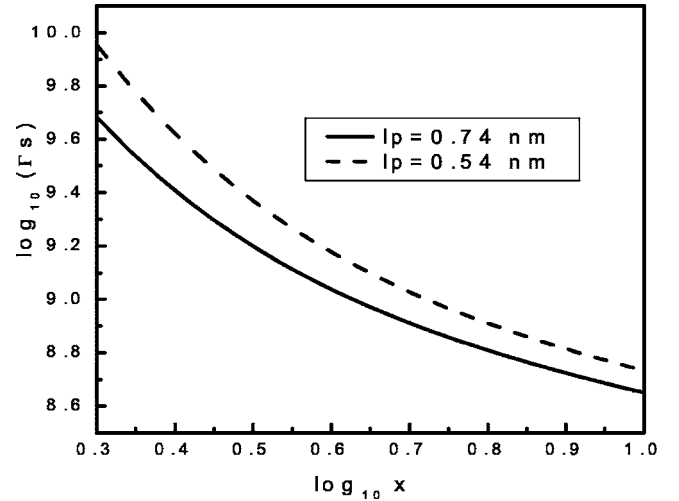


FIG. 4. The logarithm of rate of opening vs logarithm of length (as number of persistence lengths  $x = L/l_p$ ) for a hydrogen bond in a polypeptide ring with no effects of friction. We have modeled the hydrogen bond as Morse potential.

the chain. As a consequence, the activation energy for breaking depends on the length  $L$  of the chain.

Experimental measurements on closing and opening are available for DNA hairpins [1] and proteins [4]. DNA hairpin closing and opening involve formation/breaking of several hydrogen bonds and consequently are multistep processes. Therefore, our analysis above cannot be directly applied to them. Lapidus *et al.* [4] have studied the dynamics of short peptide chains using fluorescence intensity measurements. We follow their work and consider such a polypeptide and assume that it forms a loop involving the two ends, perhaps due to the hydrogen bonding. We take the bond to be weak, having  $D_e = 5$  kcal/mole,  $a = 2.5$  Å<sup>-1</sup> and  $b = 2.5$  Å. The length of the peptide unit is taken to be 0.38 nm. Calculations were done with two bending rigidities corresponding to persistence lengths of 0.54 and 0.74 nm, respectively. (Ala-Gly-Gln)<sub>n</sub> chains, considered in Ref. [4] have linear density  $\rho = 3.995 \times 10^{-16}$  kg/m and we use this in our calculations. The critical length at which the activation energy is zero may be calculated using Eq. (48) and is roughly one peptide unit (0.96 and 1.12 units) for both cases. As this is quite short, the number is only of theoretical interest. Following Lapidus *et al.* [4] we take the friction coefficient to be 50 ps<sup>-1</sup>. With these choices, the rates obtained in the calculations including friction are quite comparable to the measurements [4].

We have performed calculations, neglecting frictional effects and these are given in Fig. 4. For short chains, the rates show a strong dependence on the length  $L$ . Figure 5 gives results of calculations including friction. With  $\gamma = 50$  ps<sup>-1</sup>, friction is found to lower the rate by roughly a factor of 10. To have a simple formula for the rate, we fitted the calculated results with the formula  $Ae^{Bx}x^{-\nu}$  with  $A$ ,  $B$ , and  $\nu$  as parameters.  $x$  is the number of persistence lengths in the chain, being defined by  $x = L/l_p$ . This was found to fit the calculated rate quite well for short chains. (See Fig. 5 where the full curve shows the numerical results while the dashed curve

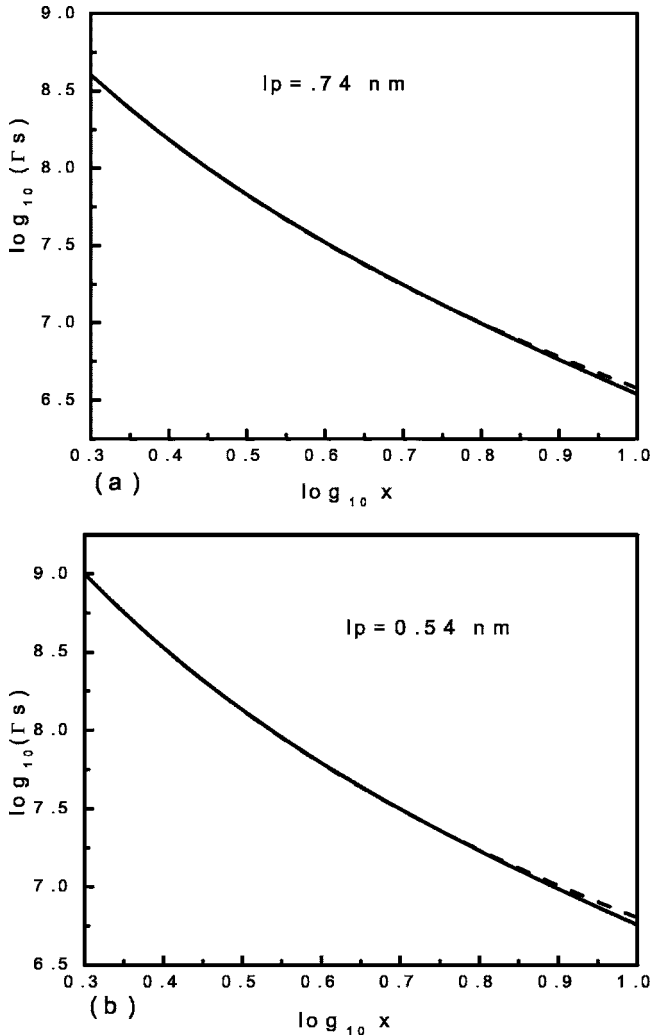


FIG. 5. (a) The logarithm of rate of opening vs logarithm of length for a polypeptide with friction included for persistence lengths  $l_p=0.74$  nm.  $\gamma$  is taken as  $50$  ps $^{-1}$ . For short chains, the rate fits with the expression  $A \exp(B/x)/x^\nu$  (dashed line) where  $x=L/l_p$ . (b) Same curves for  $l_p=0.54$  nm.

shows the fitting.) The parameters obtained were:

$$l_p=0.54 \text{ nm: } A = 3.963 \times 10^7 \text{ s}^{-1}, B = 8.033, \text{ and } \nu = 1.141,$$

$$l_p=0.74 \text{ nm: } A = 3.8202 \times 10^7 \text{ s}^{-1}, B = 6.464, \\ \text{and } \nu = 1.228.$$

The positive exponential in the fit is sensible since the activation energy for breaking is roughly  $D_e - \kappa/L$  [as is obvious from Eq. (49)]. The prefactor has a power law behavior.

Libchaber *et al.* have measured rates of opening of DNA hairpin loops. These involve hydrogen bonds between five base pairs (13 bonds in all) and, hence, opening has to involve successive bond breaking, which is not considered in our analysis. Possibly because of this, the data of Libchaber *et al.* do not show a length dependence consistent with our analysis.

## VII. SUMMARY AND CONCLUSIONS

We have considered the dynamics of opening of loop in a semiflexible ring polymer. The loop is formed by a weak bond between the ends of the polymer. The bending rigidity of the polymer is properly included in the analysis. We start with a model where the unit tangent vector to the curve representing the polymer executes Brownian motion on the surface of a sphere of unit radius. We argue that in the limit of high rigidity, the most important path contributing to the partition function for a loop of the polymer is a great circle on the unit sphere. Therefore, even for fluctuations around the loop, the great circle is a good starting point. So we expanded the energy of the polymer in terms of fluctuations about the great circle, and used this expansion correct up to second order, to describe the breaking process. We used this approach to calculate the energy required to bring the two ends together. It was found to be  $13.195\kappa/L$ , very close to the exact value of  $14.054\kappa/L$  found by Yamakawa and Stockmayer [11], thus verifying the utility of our approach. The opening of the ring can occur by moving of the two ends apart in one of the three possible directions. We found that motion in the  $X$  and  $Z$  directions be unstable while that in the  $Y$  direction is stable. The  $X$  direction is the most unstable. To make the ring stable, one has to form a bond between the two ends that would convert all the motions into stable ones. We introduced Morse/harmonic terms into the Hamiltonian which would do this and thus form a ring. The resultant multidimensional potential energy surface has three extrema corresponding to the ring, the rod, and the saddle between the two. Using these, we calculated the rate of opening. Friction can be included easily by the usual approach of coupling to a collection of harmonic oscillators.

We have used expansions around a closed circular ring. So one expects that the result is valid only for  $L$  being a few times persistence length. It was found that the pre-exponential factor obeys a power law in the  $L \rightarrow \infty$  limit. Physically, for a flexible loop, one expects the rate to be independent of length. Our result that it obeys a power law is likely to be an artifact of the approximations that we have made in derivation which are valid only in the short chain limit and are not valid in the long chain limit. In the long chain limit, the molecule is fully flexible and the result in this limit may be obtained from the equilibrium constant for open  $\rightleftharpoons$  closed and the rate of closing, which may be calculated using the approach of SSS. Such calculation does lead to a length independent opening rate in three dimensions.

Numerical calculations were done for polypeptide rings. The calculations show that in the semiflexible range, the rate of opening is highly length dependent. The rate fits with the curve  $A \exp(B/x)/x^\nu$  with  $x=L/l_p$ . The exponential accounts for the bending energy which assists the breaking. The prefactor seems to obey a power law.

In conclusion, we have developed an approach to analyze the dynamics of breaking of semiflexible polymer loops. Using this, we have calculated the opening rates of a semiflexible ring formed by a weak bond between the ends of the polymer. Closing rates also can be calculated and will be presented elsewhere.

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### APPENDIX A: THE KINETIC ENERGY

The kinetic energy may be calculated using Eq. (1). The position vector of the point  $s$  in the center of mass frame is given by

$$\mathbf{r}_{cm}(s) = \mathbf{r}(s) - \mathbf{r}_{cm} = \int_0^s \mathbf{u}(s_1) ds_1 - \frac{1}{L} \int_0^L \int_0^s \mathbf{u}(s_1) ds_1. \quad (\text{A1})$$

By considering the ring in the center of mass frame, we have removed the translational part and the remaining is the kinetic energy for rotations and vibrations. Using the tangent vector expansion Eq. (51) and the Fourier expansions Eqs. (24) and (25) one can evaluate the integral Eq. (1) to obtain the result Eq. (52). The resultant matrix elements are given below. For both  $n$  and  $m$  odd

$$T_{nm}^\phi = t_n \delta_{nm} - 16t_n t_m, \quad (\text{A2})$$

$$t_n = \frac{(4+n^2)}{2(-4+n^2)^2 \pi^2}. \quad (\text{A3})$$

For  $n, m$  even and  $\neq 2$  or  $0$

$$T_{nm}^\phi = t_n \delta_{nm}. \quad (\text{A4})$$

The other matrix elements are

$$T_{22}^\phi = \frac{(-3+4\pi^2)}{192\pi^2} \quad (\text{A5})$$

and

$$T_{m2}^\phi = -\frac{[1+(-1)^m](4+m^2)}{4(-4+m^2)^2 \pi^2} = T_{2m}^\phi. \quad (\text{A6})$$

$\delta\phi_0$  corresponds to rotation about the  $Z$  axis. The matrix element corresponding to it is evaluated to be

$$T_{00}^\phi = \frac{1}{4\pi^2} \quad (\text{A7})$$

and the corresponding kinetic energy is  $(\rho L^3/8\pi^2)\delta\dot{\phi}_0^2$ , which is precisely the rotational kinetic energy of the ring about the  $Z$  axis.

The kinetic energy matrix corresponding to the  $\theta$  modes has the following form. For  $n, m \neq 0$

$$T_{nm}^\theta = q_n \delta_{mn} - d_n d_m, \quad (\text{A8})$$

where

$$q_n = \frac{1}{2n^2 \pi^2} \quad (\text{A9})$$

and

$$d_n = \frac{[-1+(-1)^n]}{n^2 \pi^2}. \quad (\text{A10})$$

For the zeroth mode

$$T_{00}^\theta = \frac{1}{12} \quad (\text{A11})$$

and

$$T_{0n}^\theta = -\frac{[1+(-1)^n]}{2n^2 \pi^2} = T_{n0}^\theta. \quad (\text{A12})$$

$q_n = -4d_n$  for odd  $n$ .  $\delta\theta_2$  corresponds to rotation about  $X$  axis, and from Eq. (A8) the corresponding kinetic energy is  $(\rho L^3/8\pi^2)\delta\dot{\theta}_2^2$ , which is again the kinetic energy of the ring for rotation about the  $X$  axis. From these matrices, one can see that there is no coupling between  $\delta\phi_n$  and  $\delta\theta_n$  modes as well as between odd and even  $\delta\phi_n$  modes.

### APPENDIX B: THE NORMAL MODE ANALYSIS

#### 1. The unstable mode

The equations of motion Eqs. (88) and (89) for odd  $n$  reads

$$\begin{aligned} \rho L^3 \sum_n T_{mn}^\phi \delta\ddot{\phi}_n + \sum_{n,\beta} \frac{c_\beta^2}{m_\beta \omega_\beta^2} L^3 T_{mn}^\phi \delta\phi_n + \sum_n L^2 V_{mn}^\alpha \delta\phi_n \\ = \sum_\beta c_\beta x_{m\beta} \end{aligned} \quad (\text{B1})$$

and

$$m_\beta \ddot{x}_{m\beta} + m_\beta \omega_\beta^2 x_{m\beta} = c_\beta \sum_n T_{mn}^\phi L^3 \delta\phi_n. \quad (\text{B2})$$

Putting  $\delta\phi_n(t) = \delta\phi_n^0 e^{i\omega t}$  and  $x_{n\beta}(t) = x_{n\beta}^0 e^{i\omega t}$  we get

$$\begin{aligned} -\rho L^3 \omega^2 \sum_n T_{mn}^\phi \delta\phi_n^0 + \sum_{n,\beta} \frac{c_\beta^2}{m_\beta \omega_\beta^2} L^3 T_{mn}^\phi \delta\phi_n^0 + \sum_n L^2 V_{mn}^\alpha \delta\phi_n^0 \\ = \sum_\beta c_\beta x_{m\beta}^0 \end{aligned} \quad (\text{B3})$$

and

$$-m_\beta \omega^2 x_{m\beta}^0 + m_\beta \omega_\beta^2 x_{m\beta}^0 = c_\beta \sum_n L^3 T_{mn}^\phi \delta\phi_n^0. \quad (\text{B4})$$

Solving Eq. (B4) for  $x_{n\beta}^0$  and substituting back to Eq. (B3) one gets

$$\begin{aligned} -\rho L^3 \omega^2 \sum_n T_{mn}^\phi \delta\phi_n^0 + L^3 \sum_{n,\beta} \frac{c_\beta^2}{m_\beta} \left[ \frac{1}{\omega_\beta^2} - \frac{1}{(-\omega^2 + \omega_\beta^2)} \right] T_{mn}^\phi \delta\phi_n^0 \\ + \sum_n L^2 V_{mn}^\alpha \delta\phi_n^0 = 0, \end{aligned} \quad (\text{B5})$$

which can be written using Eq. (71) for the unstable mode  $-\omega^2 = \Omega_f^2$  as [34]

$$\rho L \Omega_f^2 \sum_n T_{mn}^\phi \delta \phi_n^0 + \rho L \gamma \Omega_f \sum_n T_{mn}^\phi \delta \phi_n^0 + \sum_n V_{mn}^- \delta \phi_n^0 = 0, \quad (\text{B6})$$

i.e.,

$$\rho L (\Omega_f^2 + \gamma \Omega_f) \sum_n (t_n \delta_{mn} - 16 t_n t_m) \delta \phi_n^0 + \sum_n \left( \frac{\kappa n^2 \pi^2}{2L^3} \delta_{mn} + k^- a_n a_m \right) \delta \phi_n^0 = 0. \quad (\text{B7})$$

Letting  $\sum_n t_n \delta \phi_n^0 = C_1$  and  $\sum_n a_n \delta \phi_n^0 = R_1$  and solving for  $\delta \phi_n^0$  we get

$$\delta \phi_n^0 = \frac{16(\Omega_f^2 + \gamma \Omega_f) t_n C_1}{B_n} - \frac{k^- a_n R_1}{\rho L B_n}, \quad (\text{B8})$$

where

$$B_n = (\Omega_f^2 + \gamma \Omega_f) t_n + \frac{\kappa n^2 \pi^2}{2\rho L^4}. \quad (\text{B9})$$

Multiplying Eq. (B8) by  $a_n$  and summing over we get

$$R_1 = 16(\Omega_f^2 + \gamma \Omega_f) S_2'(\Omega_f) C_1 - \frac{k^-}{\rho L} S_1'(\Omega_f) R_1, \quad (\text{B10})$$

where

$$S_1'(\Omega_f) = \sum_n \frac{a_n^2}{(\Omega_f^2 + \Omega_f \gamma) t_n + \frac{\kappa n^2 \pi^2}{2\rho L^4}}, \quad (\text{B11})$$

$$S_2'(\Omega_f) = \sum_n \frac{a_n t_n}{(\Omega_f^2 + \Omega_f \gamma) t_n + \frac{\kappa n^2 \pi^2}{2\rho L^4}}. \quad (\text{B12})$$

Similarly, multiplying by  $t_n$  and summing over odd  $n$  gives

$$C_1 = 16(\Omega_f^2 + \gamma \Omega_f) S_3'(\Omega_f) C_1 - \frac{k^-}{\rho L} S_2'(\Omega_f) R_1, \quad (\text{B13})$$

where

$$S_3'(\Omega_f) = \sum_n \frac{t_n^2}{(\Omega_f^2 + \Omega_f \gamma) t_n + \frac{\kappa n^2 \pi^2}{2\rho L^4}}. \quad (\text{B14})$$

From Eqs. (B13) and (B10), one can derive

$$\left[ 1 + \frac{k^-}{\rho L} S_1'(\Omega_f) \right] [16(\Omega_f^2 + \gamma \Omega_f) S_3'(\Omega_f) - 1] = \frac{16k^-}{\rho L} [\Omega_f^2 + \gamma \Omega_f] S_2'(\Omega_f)^2, \quad (\text{B15})$$

which can be solved for  $\Omega_f$ .

## 2. The ratio of determinants

The ratio of determinants can be evaluated in the following way [35]. The potential energy matrix can be written as

$$\mathbf{V}^\alpha = \mathbf{V}_0 + \mathbf{V}_1^{(\alpha)}, \quad (\text{B16})$$

where  $(\mathbf{V}_0)_{mn} = (\kappa n^2 \pi^2 / 2L^3) \delta_{mn}$  is a diagonal matrix and  $(\mathbf{V}_1^\alpha)_{mn} = k^\alpha a_n a_m$  is a singular matrix. Now consider the identity

$$\begin{aligned} \ln \det \mathbf{V} &= \text{Tr} \ln \mathbf{V} \\ &= \text{Tr} \ln (\mathbf{V}_0 + \mathbf{V}_1) \\ &= \text{Tr} \ln \mathbf{V}_0 + \text{Tr} \ln (1 + \mathbf{V}_0^{-1} \mathbf{V}_1). \end{aligned} \quad (\text{B17})$$

As  $\mathbf{V}_0$  is a diagonal matrix, calculation of its trace is simple. Now

$$\begin{aligned} \text{Tr} \ln (1 + \mathbf{V}_0^{-1} \mathbf{V}_1) &= \text{Tr} \sum_{m=0}^{\infty} \frac{(-1)^{m+1}}{m} (\mathbf{V}_0^{-1} \mathbf{V}_1)^m \\ &= \sum_{m=0}^{\infty} \frac{(-1)^{m+1}}{m} \text{Tr} (\mathbf{V}_0^{-1} \mathbf{V}_1)^m. \end{aligned} \quad (\text{B18})$$

But

$$\text{Tr} (\mathbf{V}_0^{-1} \mathbf{V}_1)^m = \left( \frac{2k^\alpha L^3}{\kappa \pi^2} \sum_n \frac{a_n^2}{n^2} \right)^m = \left( \frac{3L^3 k^\alpha}{8\kappa \pi^2} \right)^m. \quad (\text{B19})$$

The sum in Eq. (B19) is evaluated using MATHEMATICA. Thus,

$$\text{Tr} \ln (1 + \mathbf{V}_0^{-1} \mathbf{V}_1) = \ln \left( 1 + \frac{3L^3 k^\alpha}{8\kappa \pi^2} \right). \quad (\text{B20})$$

Hence,

$$\ln \det \mathbf{V}^+ - \ln \det \mathbf{V}^- = \ln \left( \frac{1 + \frac{3L^3 k^+}{8\pi \kappa^2}}{1 + \frac{3L^3 k^-}{8\pi \kappa^2}} \right) \quad (\text{B21})$$

which leads to Eq. (66).

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